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Atomic-scale mechanisms of dehydration processes in Earth's near-surface environments: High-resolution solid-state NMR study of temperature-induced structural transitions in amorphous/crystalline oxide nanoparticles and zeolites

A dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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서울대학교 대학원
지구환경과학부

김 현 나
Abstract

Atomic-scale mechanisms of dehydration processes in Earth's near-surface environments: High-resolution solid-state NMR study of temperature-induced structural transitions in amorphous/crystalline oxide nanoparticles and zeolites

Kim, Hyun Na
School of Earth and Environmental Sciences
The Graduate School
Seoul National University

Nano-scale earth materials are ubiquitous in diverse Earth's environments. Nanoparticles can be produced through diverse geochemical processes, such as weathering of silicates and chemical reactions in acid mine drainage, and through biological processes involving microorganisms. In spite of the abundance in nanoparticles in the Earth, the effect of nanoparticles on the global and geological processes is not fully understood, yet.

This dissertation is for a systematic exploration of temperature-induced changes in atomic structure of prototypical oxide nanoparticles and zeolites—a model system for natural earth
materials—using high-resolution solid-state nuclear magnetic resonance (NMR) spectroscopies with varying temperature and/or particle. The main objective of the dissertation includes exploration to how the oxide nanoparticles or zeolites affect the temperature-induced geochemical reactions such as dehydration, phase transition, and amorphization.

The structural changes in diverse hydroxyl group and water molecules on the surface of amorphous silica nanoparticles upon dehydration were obtained using fast magic-angle spinning (MAS) and 2D HetCor (heteronuclear correlation) NMR spectroscopy. The atomic-scale dehydration model for amorphous silica nanoparticles was proposed in this dissertation. The results demonstrate that the particle size of nanoparticles plays an important role in controlling the hydrogen contents, and thus overall hydrogen bond strength of hydroxyl groups and atomic structure of silanols can control dehydroxylation of amorphous silica nanoparticles. Similar dehydration models can be applied to understand the nature of hydrogen bonding between water and natural amorphous silica including amorphous opal.

The nature of temperature-induced phase transitions in alumina nanoparticles was explored using high-resolution solid-state $^{27}$Al 2D triple-quantum (3Q) MAS and 1D MAS NMR spectroscopies. The transition temperature from metastable disordered phase to stable ordered phase in alumina apparently increases as the particle size
increases, indicating a larger energy penalty for phase transitions into α-Al₂O₃ in larger alumina nanoparticles. The mechanistic details of phase transitions among alumina polymorphs provide insights into the nature of the phase transition mechanisms for other oxide nanoparticles in the earth’s surface environment.

The temperature-induced amorphization mechanism and Al-Si ordering behavior in dehydrated zeolites were investigated using $^{17}$O 2D 3QMAS NMR spectroscopy. The results demonstrated that both extent of topological disorder and chemical disorder in Na-zeolite A are affected by temperature induced amorphization. The observed structural changes in Na-zeolite A and its polymorphs with increasing temperature can provide an improved understanding of order-disorder transition mechanism of diverse aluminosilicates.

The kinetics of oxygen isotope exchange between crystalline clinoenstatite (MgSiO₃) and water under hydrothermal environments was explored using high-resolution solid-state $^{17}$O 2D 3QMAS NMR spectroscopies. The results suggest that crystallographically distinct oxygen site affect the isotope exchange reaction rate between magnesium silicate and aqueous fluid.

The structural information and mechanistic details obtained from the current study provide insights into the structure of hydrous species and dehydration mechanisms in crystalline and amorphous silicates in diverse geological settings, highlighting usually unknown effects of particle size on the dehydration processes.
Keywords: nanoparticles, dehydration, NMR, earth materials, phase transition

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Chapter 1. Introduction

Understanding the atomic- and nano-scale structures of earth materials is essential to comprehending the geochemical/geophysical processes in the earth’s surface and interior. For instance, in the earth’s interior, the variation in atomic-scale disorder and coordination in silicate melts affects the macroscale properties including activity coefficient of silica and viscosity in the system (Lee, 2005). The small amount of water content and speciation of hydrous component in silicate melts also lead the non-linear changes in diffusivity, viscosity, and heat capacity (Bjorn and Pascal, 2005 and references therein). Finally, these properties affect geological processes, such as generation, migration, and dynamics of magma (Lee et al., 2005). In the earth’s surface, the local structure of oxides affects the kinetics of geochemical reactions such as weathering, mineral dissolution, and isotope fractionation (Lee and Stebbins, 2003; Phillips et al., 2000). The structure and chemical bonding environment within a single crystal would affect the reactivity of each site as well as on macroscopic reactivity (Lee and Stebbins, 2003). Therefore, probing of microscale configuration and site specific reactivity is necessary to understand and predict the macroscopic properties of earth materials and diverse geological processes.

The nanoparticles, particles with diameters of 1 to 100 nm, are common in diverse geological environments, because the low temperature on the surface of earth is suitable environment for
formation of nanoparticles (Banfield and Zhang, 2001) through geochemical, biological and mechanical processes. For example, amorphous and opalline silica, hydrous aluminosilicates, oxides, and hydroxides can be produced by geochemical processes such as weathering, dissolution, and precipitation of solution (Banfield and Zhang, 2001 and references therein). Nanoparticles may also exist in the earth’s interior as well as on the surface. For instance, the phase transitions such as olivine-spinel transition at the depth of 440 km may produce the composites of nanoparticles. Chemical reactions between silicates and metals may also generate nanoparticles in core-mantle boundary (Banfield and Zhang, 2001).

The physical and chemical properties of nanoparticles are different from those of bulk materials because of their large surface area resulting from the small particle size. The macroscale properties of oxides nanoparticles such as compressibility, phase stability are known to be varied depending on particles size (Navrotsky, 2004). Therefore, probing and understanding of the effect of particle size on geochemical processes including dehydration and phase transition could provide an insight to understand geological processes in the earth.

This thesis is composed of 7 chapters including this introduction (chapter 1) and appendix. The chapter 2 demonstrates a summary of the principles of NMR spectroscopy, briefly. In chapter 3, the atomic structure and dehydration mechanism of amorphous silica are investigated using $^{29}$Si and $^1$H solid-state MAS NMR spectroscopy.
The atomic scale dehydration model is established, showing that both atomic structure of hydroxyl group and particle size affect the dehydration temperature of amorphous silica nanoparticles. In chapter 4, the oxygen environments in hydroxyl group and siloxane structure in amorphous silica-gel were observed using $^{17}$O NMR spectroscopy. In chapter 5, the effect of particle size on phase transitions in metastable alumina nanoparticles is studied with high-resolution solid-state $^{27}$Al NMR spectroscopy. The crystallographically distinct Al sites in alumina polymorphs are resolved in $^{27}$Al 3QMAS NMR spectra for alumina nanoparticles for the first time. The results showed that the transition temperature for $\gamma$, $\delta$, $\theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ apparently increases as the particle size increases, indicating a larger energy penalty for phase transitions into $\alpha$-$\text{Al}_2\text{O}_3$ in larger alumina nanoparticles. The effect of particle size on the dehydration or phase transition temperature in nanoparticles implies that the presence of nanoparticles in Earth’s surface and interior could lead an inhomogeneity in temperatures for geochemical reaction. In chapter 6, temperature-induced amorphization mechanism of Na-zeolite A is investigated in atomic-scales using $^{17}$O NMR spectroscopy. In addition to that, the dependence of crystallographic oxygen site on kinetics of oxygen isotope exchange between magnesium silicates and water is described in chapter 7. Finally, in the appendix, abstract of paper published in domestic journals and presented in domestic/international conferences are presented.
References


Chapter 2. Methods

2.1. Principles of solid-state NMR

Nuclear magnetic resonance (NMR) spectroscopy is one of the best methods to elucidate the atomic structure of amorphous and crystalline materials, providing the short range order information around specific atom through the interaction between magnetic moment of atomic nuclei and magnetic field. The Zeeman interaction ($H_z$) of nuclear magnetic dipole moment $\mu = \gamma \hbar I$, where $I$ is the nuclear spin, $\gamma$ is the gyromagnetic ratio of the nucleus) is dominant interaction, and there are 4 types of interactions behave as perturbations: chemical shift anisotropy, dipolar interaction, scalar coupling, quadrupolar interaction. Depending on their respective strength, compared to Zeeman interaction which is in the range of tens to several hundreds of MHz, the 4 types of interactions will induce spectral modifications that will be accounted for by first order development (e.g., chemical shift anisotropy, scalar and dipolar couplings) or both first and second order developments (e.g., quadrupolar couplings). The chemical shift anisotropy, dipolar coupling, scalar coupling, and quadrupolar interaction provide the information about coordination number (and bond angle, distance), spatial distance between atoms, chemical bond between atoms, and geometry, respectively.
2.2. Magic angle spinning

Magic angle spinning (MAS) is the most fundamental technique to improve the resolution of solid-state NMR experiments. By spinning the sample at the magic angle \( \theta_m \) (54.74°, where \( \cos^2 \theta_m = 1/3 \)) with respect to the direction of the magnetic field, the normally broad lines become narrower, increasing the resolution for better identification and analysis of the spectrum. The MAS technique eliminates the chemical shift anisotropy, heteronuclear dipolar coupling, and homonuclear dipolar coupling (e.g., \(^1\text{H}-^1\text{H}\) dipolar coupling).

2.3. Two dimensional pulse sequences used in this study

2D Heteronuclear correlation (HetCor) experiment

The HetCor experiment provide the information about spatial correlation between two nuclei [i.e., "X" (e.g., \(^{29}\text{Si}, ^{13}\text{C}\)] and "H"] through the X-H dipolar interaction. This is carried out with the cross-polarization experiment which uses the through space residual dipolar interaction. The HetCor experiments also reduce the spin lattice relaxation time and increase the sensitivity of spin “X”.

2D triple-quantum magic-angle spinning (3QMAS) experiment

The 3QMAS experiment provides the high-resolution spectra for half-integer quadrupolar nuclei while spinning the sample at the magic angle. It can be used to distinguish isotropic chemical shift from isotropic quadrupolar shifts, as well as to obtain the quadrupolar coupling parameters of individual atomic sites.
Abstract

Detailed knowledge of the atomic structure of hydrous species on surface of amorphous silica and the effect of temperature and particle size on their atomic configurations are essential to understand the nature of fluids-amorphous silicates interactions and the dehydration processes in the amorphous oxides. Here, we report the $^{29}$Si, $^1$H MAS, and $^1$H-$^{29}$Si heteronuclear correlation (HetCor) NMR spectra of 7 nm and 14 nm amorphous silica nanoparticles—a model system for natural amorphous silica—where previously unknown details of changes in their atomic structures with varying dehydration temperature and particle size are revealed. Diverse hydroxyl groups with varying atomic configurations and molecular water apparently show distinct dehydration trends. The dehydration (i.e., removal of water) of amorphous silica nanoparticles mostly results in the increase of isolated silanol by removing water molecules from hydrogen-bonded silanols associated water molecules. With further increase in dehydration temperature, the intensity of isolated silanol peak decreases above ~873 K, suggesting that the condensation of isolated
silanol may occur mainly above ~873 K. The entire dehydration (and
dehydroxylation) process completes at ~1473 K. Both the water (i.e.,
physisorbed water and hydrogen-bonded water) and hydrogen-
bonded silanol species show a dramatic change in the slope of
intensity variation at ~873 K, indicating that most of silanols is
hydrogen-bonded to water rather than to other silanols. The fraction of
hydrogen-bonded proton species is also much smaller in 14 nm
amorphous silica nanoparticles than in 7 nm amorphous silica
nanoparticles mainly due to the presences of larger fractions of water
and hydrogen-bonded silanol species. $^{29}$Si NMR results show that with
increasing dehydration temperature, the fraction of $Q^4$ species
apparently increases at the expense of $Q^2$ and $Q^3$ species. The fractions
of $Q^2$ and $Q^3$ structures in 7 nm amorphous silica nanoparticles are
larger than those in 14 nm amorphous silica nanoparticles. Dehydration of 7 nm amorphous silica nanoparticles occurs at a lower
temperature than that of 14 nm amorphous silica nanoparticles. $^{29}$Si
MAS NMR results show that a possible simultaneous dehydroxylation
can also occur with removal of the hydrogen bonded silanol in the
7nm silica nanoparticles. The energy penalty of dehydroxylation
estimated from $^{29}$Si MAS NMR spectra varies with $Q$ species and is
smaller in 7 nm than in 14 nm amorphous silica nanoparticles. These
results demonstrate that the particle size of nanoparticles plays an
important role in controlling the hydrogen contents, and thus overall
hydrogen bond strength of hydroxyl groups and atomic structure of
silanols can control dehydroxylation of amorphous silica nanoparticles.
The structural information and mechanistic details obtained from the current study provide insights into the structure of hydrous species and dehydration mechanisms in crystalline and amorphous silicates in diverse geological settings, highlighting usually unknown effects of particle size on the dehydration processes.

3.1. Introduction

Understanding the nature of hydrous species (e.g., H$_2$O and OH) in hydrous amorphous silica and silicates and their dehydration mechanism are essential to comprehending silicates-fluid interactions in the earth’s system as H$_2$O and SiO$_2$ are among the most fundamental components in the hydrosphere and lithosphere. The water and hydrogen contents of silicates vary with temperature, pressure, composition, and particle size, and their dehydration process is prevalent from the surface to deep earth’s mantle. These hydrous species exist on the surface of silica with varying hydrogen bond strengths and atomic configurations. However, the detailed atomic structure of hydroxyl groups and water contents in amorphous silicates with varying temperature and particle size is not fully understood. This is due mainly to the difficulty in quantitatively resolving distinct hydrous species using conventional x-ray scattering and/or vibrational spectroscopy. The objective of this study is to investigate the atomic structure of hydrous species in amorphous silica nanoparticles—a model system for hydrous amorphous silicates in the earth—with increasing dehydration temperature. We also attempt to
reveal dehydration processes in silicates with emphasis on the effect of local atomic configurations and particle size on the dehydration mechanisms using high resolution solid-state nuclear magnetic resonance (NMR).

In earth’s surface environments, water and hydroxyl groups are stored in hydrous/anhydrous minerals. Dehydration of those materials has been known as a primary mechanism of diagenesis of sediments including natural amorphous silica (e.g., opal-A) and clay minerals (Brown et al., 2003; Mizutani, 1977). In particular, water content decreases with increasing degree of diagenesis from opal-A (3.0~15.3 wt%), opal-CT (1.0~8.9 wt%) to chert (0.3~1.3 wt%) (Day and Jones, 2008; Jones and Renaut, 2007). In the subduction zone, the dehydration of hydrous silicates can release water into earth’s mantle (e.g., Kono et al., 2007; Rupke et al., 2004; Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1995). The dehydration of crystalline hydrous minerals has been suggested to be one of the origins of intermediate-depth seismicity in subduction zone (e.g., Hacker et al., 2003). The atomic structure and dehydration mechanism of hydrous components in hydrous phases as well as nominally anhydrous mineral (NAM) provided improved prospects for estimating the water content in the mantle (Bell and Rossman, 1992; Hirschmann et al., 2005; Kohn, 2006; Rossman, 2005).

Temperature-induced dehydration of nanoparticles has significant geochemical implications because oxide nanoparticles are ubiquitous in diverse geological environments (see Banfield and
Zhang, 2001; Foissner et al., 2009; Hochella et al., 2008 and references therein). The nm-scale hydrous amorphous silica layers were found on the surface of basaltic glasses (Ka’u desert, Hawaii) (Chemtob et al., 2010), and on naturally weathered feldspar in the Jurassic Navajo Sandstone at Black Mesa, Arizona (Zhu et al., 2006). Additionally, silica-rich deposit (~91 wt.% SiO₂) found at Home Plate, Mars by the Spirit rover may indicate a potential hydrothermal alteration (and aqueous conditions) of the volcanic rocks on the surface of Mars (Squyres et al., 2008). Mechanically, ultrafine nanoparticles can also be produced by grinding within fault planes, resulting in a significant reduction in the friction of these fault planes (Han et al., 2007). The physical and chemical properties of nanoparticles are different from those of bulk materials because of their large surface area resulting from the small particle size. The large surface areas of oxide nanoparticles generally have surface-bonded hydrous species (i.e., hydroxyl groups and water) (Navrotsky, 2004). The effect of particle size of amorphous silica thus includes the significant changes in the atomic structures of water and hydroxyl groups. This can affect the hydrogen content and water retaining capacity of nanoparticles. It should also be noted that the stability of amorphous particles has been shown to be dependent on the particle size (Navrotsky, 2004). Despite these important geochemical and chemical implications, the effects of temperature and particle size on dehydration of amorphous silica nanoparticles remain to be explored.

Amorphous silica nanoparticles—SiO₂ particles with large
surface areas and diameters of the order of nanometers—are among the most important industrial materials and they also have fundamental physical interests. Taking into consideration significant fraction of water and hydroxyl groups in the particles at room temperature, they can serve as an excellent model system for diverse hydrous amorphous silicates including opal-A and hydrous silicate melts.

Given these importance and implications, attempts have been made in the past to elucidate the atomic structures of hydroxyl groups and water in amorphous silica nanoparticles using various spectroscopic methods. In particular, infrared spectroscopy (IR), a representative method to identify unique vibrational modes of H₂O and hydroxyl groups, has been used to probe the hydrogen environments of amorphous silica, including fumed silica (Glinka et al., 2000; Leonardelli et al., 1992; McFarlan and Morrow, 1991; Morrow and McFarlan, 1991; Young, 1957), silica gel (Zhdanov et al., 1987), colloidal silica (Muster et al., 2001), and diatomite (Yuan et al., 2004). These previous studies managed to partially distinguish several OH vibrational modes such as isolated silanol groups on the surface of the silica, hydrogen-bonded silanols on the surface, adsorbed water molecules, and hydroxyl groups located inside the silica (Glinka et al., 2000; Yuan et al., 2004). However, generally, those features were not fully resolved, characterized with a large degree of overlaps among those IR signals. This led to difficulties in quantifying the hydroxyl group content unless careful calibration was carried out. In the IR
spectra of amorphous silica nanoparticles studied here broad peaks ranging from 2900 to 3700 cm$^{-1}$ were observed without any explicit provision of hydroxyl groups in the particles. The Raman and X-ray scattering for the silica nanoparticles provided the qualitative changes in the network structure of amorphous silica (Uchino et al., 2004). Achieving good resolution and quantification of these diverse hydrous species is essential to forming an improved understanding of the nature of fluid-silicate interactions and dehydration mechanisms.

High-resolution solid-state NMR spectroscopy yields information that is element specific and allows the determination of short-range structures around elements of interest in diverse amorphous/disordered silicates (e.g., Allwardt et al., 2005; Brow, 2000; Cody et al., 2005; Eckert, 1992; Hacker et al., 2003; Hazen and Sverjensky, 2010; Kirkpatrick et al., 1986; Kohn et al., 1998; Lee, 2005, 2010; Lee et al., 2008; Lee and Stebbins, 1999, 2009; Maekawa et al., 1996; Massiot et al., 2002; Oglesby and Stebbins, 2000; Phillips and Kirkpatrick, 1994; Phillips et al., 1992; Schmidt et al., 2001; Stebbins, 1988, 1995; Stebbins et al., 2008; Stebbins et al., 1992; Xue and Kanzaki, 2008; Xue, 2009; Xue et al., 1991; Yarger et al., 1995 and references therein). In particular, solid-state $^1$H MAS NMR is a powerful tool that can resolve the peaks of physisorbed water, hydrogen-bonded water, hydrogen-bonded silanol, and isolated silanol with varying hydrogen bond strengths. This is possible because peak position (chemical shift) is sensitive to hydrogen bonding strength (Xue and Kanzaki, 2004, 2009 and references therein). $^1$H MAS NMR has thus been used to
study the atomic structure of amorphous silica (DoremieuxMorin et al., 1996; Hartmeyer et al., 2007; Hu et al., 2005; Liu and Maciel, 1996a), hydrous silicate glasses (Cody et al., 2005; Eckert et al., 1988; Malfait and Xue, 2010; Xue and Kanzaki, 2008; Xue, 2009; Xue and Kanzaki, 2004, 2006, 2007, 2009; Zeng et al., 1999a), surface modification of silica particles including dehydration (Bronnimann et al., 1988), rehydration (DelaCaillerie et al., 1997a; Turov et al., 1999), difference in $^1$H chemical shift between bulk and surface silanol species for silica (Xue and Kanzaki, 2004) and other chemical reactions on amorphous oxides (Brus, 2002). The 2D NMR techniques utilizing $^1$H–$^{29}$Si heteronuclear through-space correlation [e.g., cross polarization (CP) or heteronuclear correlation (HetCor) NMR] and $^1$H–$^1$H homonuclear correlation [e.g., double quantum (DQ) MAS NMR] have been used to resolve the atomic environments of hydroxyl and water species in diverse hydrous silicates (Angeli et al., 2006; Phillips et al., 2007; Trebosc et al., 2005; Xue and Kanzaki, 2007, 2009). We note that these previous $^1$H NMR studies focused on dehydration behavior at relatively low temperature up to ~923 K (Liu and Maciel, 1996a). As the dehydration processes of diverse oxides in the earth’s interior occurs at much higher temperatures, an extension of these earlier investigations is clearly required.

$^{29}$Si MAS NMR has been used to obtain structural information on Si atom environments in amorphous silica and diverse silicates including amorphous silica nanoparticles (Leonardelli et al., 1992; Liu and Maciel, 1996a), silica gel (Cannas et al., 2004; Leonardelli et al.,
15 (Adams et al., 1991; Brown et al., 2003; Chemtob et al., 2012) and silicate glasses (Kirkpatrick et al., 1986; Kummerlen et al., 1992; Lee and Stebbins, 1999; Oglesby and Stebbins, 2000; Pierce et al., 2010; Schmidt et al., 2000; Zeng et al., 2000). The Si environment can be conveniently described using $Q^n$ notation which refers to tetrahedral Si groups with $n$ number of bridging oxygen atoms. For instance, the $Q^2$, $Q^3$, and $Q^4$ species in silica nanoparticles refer to geminal silanol $[\equiv \text{Si(OH)}_2]$, single silanol $[\equiv \text{SiOH}]$, and siloxane structures, respectively (Engelhardt and Michel, 1987). Previous calculations and experimental studies have shown that the kinetics of fluid-silicate interactions are dependent on topological variations in silicates including $Q$ species (Pelmenschikov et al., 2000). Thus, $^{29}\text{Si}$ MAS NMR study of amorphous silica nanoparticles with increasing temperature will specifically address the temperature-induced changes in $Q$ speciation, allowing us to determine the $Q$ species–dependent dehydration mechanism in silicates. As far as we know, the dehydration of silanols and subsequent structural changes in silanols with increasing temperature using $^{29}\text{Si}$ MAS NMR have not been investigated thus far for any silicate. This may be partly attributed to the long collection time (relatively long spin-relaxation time) required for such experiments. The $^{1}\text{H}$–$^{29}\text{Si}$ CP MAS NMR studies with significantly short relaxation delays (e.g., 0.6–6 s) have been used to probe the nature of surface $Q^n$ species in heated silica gel (Chuang et al., 1993; Chuang and Maciel, 1996; Liu and Maciel, 1996a). We note that estimation of $Q^n$ species can be better probed with a single pulse MAS NMR study, particularly at
high temperatures. The dehydration (i.e., removal of water) and dehydroxylation (i.e., condensation of silanol) can be separately probed by utilizing $^1$H NMR and $^{29}$Si MAS NMR, respectively, thus, the combined view of dehydration mechanisms (both dehydration and dehydroxylation processes) can also be established.

Dehydration mechanisms have been proposed on the basis of the above mentioned studies of the atomic structure of water and silanol groups in amorphous silica. It has been suggested that water is first desorbed from silanols and subsequently these silanol groups dehydroxylated (Glinka et al., 2000; Liu and Maciel, 1996a; Yuan et al., 2004; Zhuravlev, 2000). While the dehydration of amorphous silica continuously occurs with increasing temperatures up to 1473 K, quantitative structural changes of water and hydroxyl groups at high temperatures above 923 K and relevant dehydration mechanisms need to be constrained by incorporating both atomic structure of hydrogen species (probed by $^1$H NMR) and temperature-induced changes in $Q$ speciation (probed by $^{29}$Si NMR). We also note that the study about an effect of particle size on dehydration of amorphous silica nanoparticles is necessary, because the high surface area of nanoparticles may induce significant changes in water retention capacity and dehydration rate of silicates.

Here, we explore the nature (atomic configurations and their fractions) of hydrogen species and water of 7 and 14 nm amorphous silica nanoparticles with increasing temperatures up to 1473 K using high-resolution solid-state NMR with an aim to better understand the
relevant geochemical processes (e.g., dehydration, diagenesis, alterations in the surfaces of amorphous and crystalline earth materials. We report $^1$H MAS NMR spectra of amorphous silica that allow us investigate the effect of temperature and particle size on the hydrogen contents, hydrogen bond strength, and the evolution of hydroxyl groups in amorphous silica. We also report $^{29}$Si MAS NMR spectra for amorphous silica nanoparticles with varying dehydration temperature and particle size, which provide insights into $Q$ species–dependent dehydration mechanisms and energy penalty of dehydroxylation. Taking into consideration the data from these NMR results and $^1$H–$^{29}$Si heteronuclear correlation (HetCor) NMR spectra for untreated and dehydrated amorphous silica nanoparticles at high temperature, we propose an atomic-scale dehydration model for amorphous silica nanoparticles.

3.2. Experimental Methods

3.2.1. Sample Preparation

Two types of nonporous amorphous silica nanoparticles, S5130 and S5505 (fumed silica from Sigma Aldrich), with surface areas of $390 \pm 40 \, \text{m}^2/\text{g}$ and $200 \pm 25 \, \text{m}^2/\text{g}$, respectively, were used. The TEM images of silica nanoparticles show that diameter of both amorphous silica nanoparticles varies from less than 10 nm to more than 20 nm (see appendix A1). The particle size of the S5130 sample is mostly less than 10 nm but a fraction of larger particles of ~20 nm is also observed. The particle size of the S5505 particles mostly ranges between 10 to 20
nm and some particles larger than 20 nm can also be found. The shape of the particles in both samples is mostly spherical. The average diameters of S5130 and S5505 particles calculated with spherical approximations \(d = 6/(S_0 \times \rho)\), where \(d\) is average particle diameter, \(S_0\) is specific surface area, \(\rho\) is density of the materials] are 7 and 14 nm and we refer to the S5130 and S5505 as 7 and 14 nm amorphous silica nanoparticles, respectively. The particle size of the amorphous silica nanoparticles increases with increasing dehydration temperature (for TEM images of nanoparticles with varying dehydration temperature, see appendix A1). A previous Brunauer-Emmett-Teller (BET) study of 7 nm amorphous silica nanoparticles (identical to the samples used in the current study) showed that the particle size of the amorphous silica nanoparticles after heat treatment at 1273 K and 1373 K for 2 h is ~13 and 24 nm, respectively (Uchino et al., 2004). The X-ray diffraction (XRD) pattern for amorphous silica nanoparticles dehydrated at 1273 K, showed no evidence of crystalline phases. The samples referred to “untreated” silica nanoparticles were used as received from the supplier. Amorphous silica nanoparticles were heated for 2 h at varying temperatures ranging from 573 to 1473 K in a vertical tube furnace to dehydrate silanols and water. The \(^{1}H\) NMR spectra for amorphous silica nanoparticles after dehydration for 30 min is not significantly different from those after dehydration for 2 h and 6 h at 573 K and 1173 K (not shown here). Thus, we chose a 2 h dehydration duration in the current study. Vacuum-treated samples were also prepared by dehydration under vacuum for 6 h at 20 Torr (2.7 kPa) at
room temperature because a further decrease in the fraction of physiorbed water in the nanoparticles was observed beyond a dehydration duration of 2 h (e.g., up to 6 h), consistent with the previous study of the dehydration of fumed silica (Liu and Maciel, 1996a). The dehydrated samples were moved to a glove box (operated with an Ar environment) where all the sample handling (including sample packing into the NMR rotors) was done. Then the $^1$H MAS NMR spectra for the samples were collected within ~5 min. While the nanoparticles were heated at varying dehydration temperatures, the NMR spectra were collected at ambient conditions.

### 3.2.2. NMR Spectroscopy

**$^1$H MAS NMR Spectroscopy.** $^1$H MAS NMR spectra for silica nanoparticles were collected on a Varian NMR system (9.4 T) at Larmor frequency of 400.1 MHz (4 mm double-resonance Doty probe) with spinning speed of 15 kHz and Bruker Avance II 500 (11.4 T) at a Larmor frequency of 500.13 MHz (2.5 mm double-resonance Bruker probe) with spinning speed of 25 kHz, respectively. A single-pulse sequence with a 30-degree pulse (0.67 μs) and delay time of 1 s was used. Delay times between pulses were varied from 1–60 s for the both untreated and dehydrated samples at 1173 K studied here, and were found not to affect the peak shape or intensity, indicating that the proton spins are fully relaxed. Tetramethylsilane (TMS) was used as the external chemical shift reference. We found that a weak and broad $^1$H background signal attributed to the rotor and probe was observed
in both $^1$H MAS NMR spectra collected in Varian NMR system (9.4 T) and Bruker Avance II 500 (11.4 T) spectroscopy; to subtract this background signal, the $^1$H MAS NMR spectrum for an empty rotor was also measured under identical experimental conditions and was subtracted from all $^1$H MAS NMR spectra presented here (see 3.1 below). To quantify the number of proton spins in a sample, the $^1$H MAS NMR spectra for 36.3 mg of silicone rubber (polydimethylsiloxane, [-Si(CH$_3$)$_2$-O-]$_n$) were also collected under identical experimental conditions using identical rotor. The samples are filled up in the rotors, indicating similar filling factor. The hydrogen ($^1$H proton) density in amorphous silica nanoparticles was calculated by comparing the peak area in the $^1$H MAS NMR spectra of amorphous silica nanoparticles with silicone rubber (a spin-counting standard) for a unit sample. We note that the spinning-induced dehydration could occur depending on spinning speed as well as rotor and designs of NMR rotor caps (see appendix A6 for detailed discussion on the effect of spinning speed and the types of rotors used in the study). Spinning-induced dehydration, however, was not observed for amorphous silica nanoparticles at $^1$H NMR experiment with Doty 4mm probe with spinning speeds up to 15 kHz. We thus mainly report the $^1$H NMR spectra collected with the Doty 4mm probe (up to spinning speed of 15 kHz) in the current study.

$^{29}$Si MAS and $^1$H-$^{29}$Si HetCor NMR Spectroscopy. $^{29}$Si MAS NMR spectra for amorphous silica nanoparticles were collected on a Bruker Avance 400 WB (9.4 T) at a Larmor frequency of 79.55 MHz (4-mm
triple-resonance Bruker probe) and a spinning speed of 11 kHz. A single-pulse sequence with an approximately 90-degree pulse (4 μs) and delay time of 120 s were used. We explored the effect of relaxation delays on fractions of Q species. The spectra for the both untreated and dehydrated samples at 1173 K were collected using the 90-degree pulse (with relaxation delay of 120 s) and the 30-degree pulse (120 s and 3600 s, not shown here). While there are uncertainties in fractions of Q species, they do not change significantly with varying relaxation delay time, suggesting no T1 relaxation effect on quantification of Si species. We, thus, used the 90-degree pulse for a better signal-to-noise (S/N) ratio. TMS was used as the external reference. The 29Si MAS NMR spectra were apodized with a Gaussian weighting function (line width of approximately 300 Hz), which led to an improved S/N ratio without any modifications of the spectra. The number of scans was ~2000–3000 for each spectrum.

The 1H–29Si HetCor spectra for the 7 nm amorphous silica nanoparticles were collected on a Varian NMR system (9.4 T) at a Larmor frequency of 79.55 MHz (4 mm double-resonance Doty probe). Whereas the experiment with a short contact time would be beneficial to probe spatial proximity between Si and H, but the signal intensity for the spectrum significantly decreases with decreasing contact time., in order to increase CP efficiency, particularly for dehydrated amorphous silica nanoparticles above 773 K, ramped pulse with 7 ms contact time was used: we also collected 1H–29Si HetCor spectra for untreated amorphous silica nanoparticles with shorter contract time of
3 ms that does not show clear spectral differences (not shown here). FSLG (frequency-switched Lee-Goldburg) decoupling was used during the $t_1$ period (for $f_1$ dimension) to suppress the proton homonuclear dipolar interaction, followed by Lee-Goldburg CP (Lee and Goldburg, 1965). The rf field strengths of $^1$H and $^{29}$Si are 60 and 50 kHz, respectively, with a 10 kHz spinning speed for the Hartmann-Hahn condition.

3.3. Results and Discussion

3.3.1. Temperature-induced changes in hydrogen environments in hydrous amorphous silica: Insights from $^1$H MAS NMR

Figure 3.1 shows $^1$H MAS NMR spectra for 7 and 14 nm amorphous silica nanoparticles where diverse peaks corresponding to hydroxyl groups and water molecules with varying hydrogen bond strengths are partially resolved. A detailed justification of the peak assignment for each peak in the $^1$H MAS NMR spectra of the amorphous silica nanoparticles is given in an appendix. On the basis of previous $^1$H MAS NMR studies for diverse hydrous oxides (see Table 3.1), the sharp resonance peak at $\sim$3.5 ppm was assigned to physisorbed water with varying degrees of hydrogen bond strength (DelaCaillerie et al., 1997a; Liu and Maciel, 1996b) (Figure 3.1A in appendix). The peak position of physisorbed water shifts to a lower frequency (a more negative chemical shift) with decreasing water content and hydrogen bond strength (Eckert et al., 1988; Xue, 2009). Thus the different peak positions of physisorbed water imply that the
Figure 3.1. (A) $^1$H MAS NMR spectra for untreated 7 and 14 nm amorphous silica nanoparticles at 9.4 T ($\nu_r=15$ kHz). (B) $^1$H MAS NMR spectra with background signal for 7 nm amorphous silica nanoparticles at 9.4 T ($\nu_r=15$ kHz). (C) $^1$H MAS NMR spectra at 11.7 T with 25 kHz spinning speed shown spinning sideband for 7 nm amorphous silica nanoparticles. The asterisk (*) denotes the spinning sideband. (D) Comparison of $^1$H MAS NMR spectra between untreated and vacuum treatment for 7 nm amorphous silica nanoparticles at 9.4 T ($\nu_r=15$ kHz).
hydrogen bond strength for the 7 nm amorphous silica nanoparticles is stronger than that for 14 nm amorphous silica nanoparticles. As already discussed, the \(^1\)H NMR spectra shown here are background subtracted (Figure 3.1B). Taking into consideration the physisorbed water peak characterized with the Lorentzian line shape in the spectrum, the physisorbed water peak at ~3.5 ppm partially overlaps with the broad peak at 3-8 ppm. Figure 3.1C shows the spinning sideband patterns in the \(^1\)H MAS NMR spectra for 7 nm amorphous silica nanoparticles at 11.7 T with a spinning speed of 25 kHz, where spinning sidebands only for the sharp peak at ~3.5 ppm were observed (see appendix 3.A.7).

As shown in Figure 3.1D, the intensities of the broad peak at 3–8 ppm and sharp peak at ~3.5 ppm decreased after dehydration under vacuum at room temperature. As evidenced by the \(^{29}\)Si MAS NMR spectrum for 7 nm amorphous silica nanoparticles dehydrated under vacuum, this decrease is not due to dehydroxylation but mainly due to a decrease in physisorbed (~3.5 ppm) and hydrogen-bonded water (3-8 ppm) upon dehydration under vacuum. Although the broad peak at 3–8 ppm was assigned only to hydrogen-bonded silanol in the previous studies (Bronnimann et al., 1988; Liu and Maciel, 1996a), the current results indicate that it consists of both hydrogen-bonded water and hydrogen-bonded silanol. These two contributions are not well-distinguished in the \(^1\)H MAS NMR spectra for amorphous silica (Bronnimann et al., 1988; Kohn et al., 1989; Liu and Maciel, 1996a; Paris et al., 2007): the \(^1\)H MAS NMR spectra for makatite
[\text{Na}_2\text{Si}_4\text{O}_8(\text{OH}_2)\cdot4\text{H}_2\text{O}] \text{ show only a single proton peak, although both hydroxyl and molecular water are expected in the structure (Almond et al., 1997). We also found that the peak positions for physisorbed water (sharp peak at \sim3.5 \text{ ppm}) and hydrogen-bonded proton species (broad peak at 3–8 \text{ ppm}) shift to slightly lower frequencies with increasing spinning speed (see appendix A5). These results demonstrate that peak positions for hydrogen-bonded proton species, such as physisorbed, hydrogen-bonded water and hydrogen-bonded silanol, are dependent on spinning speed.}

Small but distinct proton peaks at 1.2 ppm and 1.9 ppm are observed in the $^1$H MAS NMR spectra. In a previous $^1$H NMR study of fumed silica, the 1.9 ppm peak was assigned to a water-inaccessible silanol group because of its presence in samples humidified with a saturated solution of NaOH in water at 25°C (Liu and Maciel, 1996a). In a recent NMR study of precipitated silica synthesized from aqueous solution, the 1.9 ppm peak was attributed to a water-accessible isolated silanol while a peak at 1.1 ppm was attributed to water-inaccessible isolated silanol (Hartmeyer et al., 2007). The \sim1.2 \pm 0.1 \text{ ppm peak was assigned to internal isolated silanols or free OH in opal-CT (Paris et al., 2007), hydrous Ca-Na silicate glass (Xue, 2009), and zeolites (Clarke et al., 1993; Hunger et al., 1996). In the current NMR study of amorphous silica nanoparticles, the peak at 1.9 ppm most likely corresponds to water-accessible isolated silanol, on the basis of previous peak assignments (see Table 3.1) and rehydration experiments on dehydrated samples, which showed a decrease in intensity for the}
peak at 1.9 ppm after exposure to an open atmosphere at room temperature (for further details, see appendix A5). Our preliminary study of H/D exchange between amorphous silica and D₂O also suggests that isolated silanol site (peak at 1.9 ppm) is indeed water accessible.

Based on this assignment of 1.9 ppm peak and the known relationship between hydrogen bond strength and chemical shift, we suggest that both 1.2 and 1.9 ppm peaks are likely due to isolated silanols each in a distinct atomic environment, such as internal-isolated silanol (1.2 ppm) inside the nanoparticle and a surface (and/or internal)-isolated silanol (1.9 ppm peak). The 1.2 ppm peak may arise from a Si-H species or a methyl radical due to carbon contamination (Stesmans et al., 2005) as it is easily removed after heating at 573 K. Table 3.1 also summarizes results of peak assignments for the ¹H MAS NMR spectra for amorphous silica nanoparticles.

The peak area in the ¹H MAS NMR spectra is quantitatively proportional to proton spin density (and thus hydrogen content) in a sample. By comparing the peak area of silicone rubber, a spin-counting standard for ¹H MAS NMR spectra (DelaCaillerie et al., 1997a; Liu and Maciel, 1996a, b), the hydrogen densities of the hydroxyl groups (excluding hydrogen in water) in a unit surface area can be estimated. Assuming that the broad peak at 3-8 ppm mostly consists of hydrogen-bonded silanol, the hydrogen densities of hydroxyl groups in a unit surface area would be 2.4 ± 0.8 OH/nm² for 7 nm amorphous silica nanoparticles and 3.5 ± 1.0 OH/nm² for 14 nm amorphous silica.
Table 3.1. $^1$H MAS NMR chemical shift for hydrogen species in amorphous silica

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak position (ppm)</th>
<th>Proton species</th>
<th>$B_0$ (T)</th>
<th>Spin rate (kHz)</th>
<th>Ref.*</th>
</tr>
</thead>
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<td>Amorphous silica nanoparticles</td>
<td>1.2 (T)</td>
<td>Internal-isolated silanol</td>
<td>9.4</td>
<td>15</td>
<td>Current study</td>
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<tr>
<td></td>
<td>1.9 (T)</td>
<td>Water-accessible isolated silanol</td>
<td></td>
<td></td>
<td>study</td>
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<tr>
<td></td>
<td>~2.3 (T)</td>
<td>Weakly hydrogen-bonded silanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4-3.7†</td>
<td>Physisorbed water (sharp peak)</td>
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<tr>
<td></td>
<td>3.8 (T)</td>
<td>Hydrogen-bonded water &amp; Hydrogen-bonded silanol</td>
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</tr>
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<td>Water-inaccessible isolated silanol</td>
<td>8.4</td>
<td>12</td>
<td>(1)</td>
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<tr>
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<td>3.0 (T)</td>
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<td>~3.5†</td>
<td>Physisorbed water (sharp peak)</td>
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<td>Water-inaccessible, &quot;internal&quot; silanol</td>
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<td>(3)</td>
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<td>Hydrogen-bonded silanol to other silanol</td>
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<td>4.5 (T)</td>
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<td>Isolated silanol</td>
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<td>3</td>
<td>(4)</td>
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<td>Peak</td>
<td>Description</td>
<td>Peak</td>
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<td></td>
</tr>
<tr>
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<td>Physisorbed water</td>
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<td>(5)</td>
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</tr>
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<td>H$_2$O hydrogen-bonded to bridging oxygen atoms</td>
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*(1) Liu and Maciel (1996a); (2) DelaCaillerie et al. (1997); (3) Hartmeyer et al. (2007); (4) Bronnimann et al. (1988); (5) Brus (2002); (6) Kohn et al. (1989); (7) Cody et al. (2005).† The peak position for water molecule varies depending on water content.
nanoparticles. These values are comparable to a previously reported hydroxyl group density for amorphous silica nanoparticles (2.8 ± 0.3 ± 0.4 OH/nm² for 14 nm amorphous silica nanoparticles. The detailed procedure used to calculate the density of the hydroxyl groups from ¹H and ²⁹Si NMR results is shown in appendix A4.

Figure 3.2 shows ¹H MAS NMR spectra for 7 and 14 nm amorphous silica nanoparticles with increasing dehydration temperature from room temperature up to 1473 K. The atomic environments of the hydrogen apparently change and the total signal intensity decreases with increasing OH/nm², Cab-O-Sil with surface area of 325 m²/g), where the broad peak at 3-8 ppm was assigned to mostly hydrogen-bonded silanol (Liu and Maciel, 1996b). However, the value reported in both the current and previous studies may overestimate the total fraction of hydroxyl groups because the broad peak at 3-8 ppm consists of both hydrogen-bonded water and hydrogen-bonded silanol. The hydroxyl group contents can also be estimated by combining results from both ²⁹Si and ¹H NMR, which yields values of 1.5 ± 0.4 OH/nm² for 7 nm amorphous silica nanoparticles and 1.9 dehydration temperature. Diverse hydroxyl groups with varying atomic configurations and molecular water apparently show distinct dehydration trends. For broad peak at 3-8 ppm (i.e., both hydrogen-bonded silanols and hydrogen-bonded water), peak intensity and hydrogen bond strength significantly decrease with increasing dehydration temperature. The latter is evidenced from a shift in a position of broad peak at 3-8 ppm.
A similar trend has been described for a fumed silica (Cab-O-Sil with surface area of 325 m$^2$/g) with increasing temperature up to 923 K (650 °C) (Liu and Maciel, 1996b). The peak position of physisorbed water also shifts to lower frequency with increasing dehydration temperature up to 873 K, indicating a decrease in hydrogen bond strength. The trend of temperature-induced changes in peak position for physisorbed water in $^1$H MAS NMR spectra also indicates that above ~573 K, an initial decrease in $^1$H signal of physisorbed water upon dehydration is likely due to the removal of water (Dinh et al., 2000). The signal intensity for isolated silanol apparently increases with increasing dehydration temperature and reaches its maximum value at ~873 K, when most of the water (i.e., physisorbed and hydrogen-bonded water) and hydrogen-bonded silanols are removed. These observations indicate that removal of water results in the formation of isolated silanol at the expense of hydrogen-bonded silanols. While $^1$H MAS NMR results show a decrease of hydrogen bonded silanol in amorphous silica, $^1$H NMR data alone cannot confirm whether dehydroxylation occurs below ~873 K or not because protons in hydrogen bonded silanol and hydrogen bonded water in 3-8 ppm cannot be quantitatively resolved in $^1$H NMR spectrum. The $^{29}$Si NMR results present a slight decrease of $Q^2$ and $Q^3$ species below 873 K, indicating a slight and simultaneous dehydroxylation with removal of the hydrogen bonded silanol, especially for 7 nm amorphous silica nanoparticles (see section 3.2). With further increase in dehydration temperature, the intensity of the isolated silanol peak decreases,
Figure 3.2. $^1$H MAS NMR spectra at 9.4 T with increasing dehydration temperature from room temperature up to 1473 K for (A) 7 nm amorphous silica nanoparticles, and (B) 14 nm amorphous silica nanoparticles (normalized to sample weight).
suggesting that the dehydroxylation (i.e., condensation of isolated silanol) may occur mainly above ~873 K. The entire dehydration (and dehydroxylation) process completes at ~1473 K.

A small feature at ~2.3 ppm is also observed in the $^1$H MAS NMR spectra at intermediate dehydration temperatures such as 573 K and 773 K. ... In the current study, on the basis of the several previous assignment for silica nanoparticles (DelaCaillerie et al., 1997a; Liu and Maciel, 1996a), the peak at ~2.3 ppm can be assigned to weakly hydrogen-bonded silanol. We note that the current peak assignment can be regarded as one of the possible suggestions primarily because its peak position matches with that of the molecular water with low water contents (from extrapolation of the peak position-water content trend) (for further discussion, see appendix A2). We also note that for amorphous silica nanoparticles dehydrated at 973 K, a small peak at ~2.3 ppm is observed in addition to the isolated silanol peak at 1.9 ppm after exposing the sample to an open atmosphere for longer than 800 min (see appendix A5). This result implies that the presence of the ~2.3 ppm peak in the $^1$H MAS NMR spectra for amorphous silica dehydrated above 873 K would be molecular water resulted from rehydration of the nanoparticles during sample handling and/or NMR experiments.

The $^1$H MAS NMR spectra are calibrated taking into consideration intensity of silicone rubber, demonstrating the differences in proton environments between 7 and 14 nm particles.
with increasing dehydration temperature. The difference in hydrogen environments between these two particles dramatically decreases above ~873 K when most of the water (i.e., physisorbed and hydrogen-bonded water) is removed. For example, the proton spin density (hydrogen content) in the 7 nm amorphous silica nanoparticles at room temperature is ~3.4 times larger than that in 14 nm amorphous silica nanoparticles, whereas the difference decreases significantly above 873 K. The proton environments and peak intensity for 7 and 14 nm amorphous silica nanoparticles do not show remarkable difference above 1173 K. These results indicate that the large difference in proton density between the two nanoparticles at low temperature is mainly due to the presence of physisorbed, hydrogen-bonded water and hydrogen-bonded silanol species, while the fraction of isolated silanol peak intensity is not drastically different for each type of particle.

To analyze the change in each proton species during dehydration, the $^1$H MAS NMR spectra are fitted with several Gaussian and Lorentzian functions representing proton species in the nanoparticles based on their peak shapes: physisorbed water (~3.5 ppm) and isolated silanol (1.9 ppm) are fitted with single Lorentzian and Gaussian function, respectively. The broad peak at 3-8 ppm is fitted with three Gaussian functions with distinct peak position to describe changes in hydrogen bond strength (i.e., relatively different hydrogen-bonded silanols). Here, the position of each Gaussian peak for 3-8 ppm peak is set to be invariant upon fitting. The weakly hydrogen-bonded silanol peak at ~2.3 ppm was also fitted with a single Gaussian function (Figure 3.3).
Figure 3.3. Fitting of $^1$H MAS NMR spectra for (A) 7 nm and (B) 14 nm amorphous silica nanoparticles (normalized to the height of the spectra).
The peak position and width for each proton species except physisorbed water are fixed for robust fitting results. The peak position for physisorbed water moves to lower frequency with increasing dehydration temperature as previously discussed. The peak width for water at room temperature is slightly larger than its width above 573 K, possibly due to a decrease in spin interaction between proton in water and other oxygens in hydroxyl groups and other water molecules. Detailed information of the fitting parameters for $^1$H MAS NMR spectra is given in Table 3.2. We note that the potential uncertainties in fitting of $^1$H spectra may affect the proton speciation results within error ranges (within 10~15%). The error range was estimated from the uncertainty in NMR processing condition, slight difference between experimental and fitted spectra, and possible artifacts resulting from fixed fitting parameters. Figures 3.4A and 3.4B present the variation in proton species including water and silanol intensity with dehydration temperature for 7 and 14 nm amorphous silica nanoparticles, respectively, where the sharp resonance at ~3.5 ppm (physisorbed water), broad peak at 3-8 ppm (hydrogen-bonded water and hydrogen-bonded silanol), peak at ~2.3 ppm (weakly hydrogen-bonded silanol) and peak at 1.9 ppm (isolated silanol) are shown. The dehydration of water and silanols, particularly isolated silanol, shows nonlinear temperature dependence; below 873 K, removal of hydrogen-bonded silanol and water leads to the formation of isolated silanol, whereas, at high temperatures (above ~873 K), the isolated silanol is further dehydrated, forming Si-O-Si siloxane. Both
Table 3.2. Fitting parameters and results for $^1$H MAS NMR spectra for amorphous silica nanoparticles.

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<th>Temp. (K)</th>
<th>Intensity (H atom/g $\times 10^{-23}$)</th>
<th>Intensity (H atom/g $\times 10^{-23}$)</th>
<th>Intensity (H atom/g $\times 10^{-23}$)</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>FWHM (ppm)</th>
<th>Intensity (H atom/g $\times 10^{-23}$)</th>
<th>Intensity (H atom/g $\times 10^{-23}$)</th>
<th>Intensity (H atom/g $\times 10^{-23}$)</th>
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† Hydrogen bonded water and silanol is fitted with three Gaussian functions ($\delta_{\text{iso}}$ is 5.2, 4.2, and 3.0 ppm for H-
bonded water and silanol (1), (2), and (3), respectively.; FWHM is 2.3 ppm).
†† Physisorbed water is fitted with Lorentzian function.
††† Weakly H-bonded silanol is fitted with single Gaussian function (δ_{iso} is 2.3 ppm; FWHM is 0.4 ppm)
†††† Isolated silanol is fitted with Gaussian function (δ_{iso} is 1.9 ppm; FWHM is 0.3 ppm)
* At higher temperature (above 673 K) the 2.3 ppm peak can be assigned to either weakly hydrogen-bonded silanol or molecular water with low water contents.
Figure 3.4. Variation of the quantity of proton species for amorphous silica nanoparticles with increasing dehydration temperature for (A) 7 nm and (B) 14 nm amorphous silica nanoparticles. The red, blue, black and purple lines refer to the intensity of physisorbed molecular water (sharp peak at ~3.5 ppm), hydrogen-bonded water and hydrogen-bonded silanol (broad peak at 3-8 ppm), isolated silanol (peak at 1.9 ppm) and weakly hydrogen-bonded silanol (peak at 2.3 ppm), respectively.
the water and hydrogen-bonded silanol species show a dramatic change in the slope of intensity variation at ~873 K, indicating that silanol is hydrogen-bonded to water rather than to other silanols. The hydrogen bond strength for hydrogen-bonded species in broad peak at 3-8 ppm is also much smaller in 14 nm amorphous silica nanoparticles than in 7 nm amorphous silica nanoparticles. These results demonstrate that the particle size of nanoparticles plays an important role in controlling the hydrogen contents, atomic configurations around oxygen, and thus overall hydrogen bond strength of hydroxyl groups. The detailed dehydration pathways for amorphous silica nanoparticles will be discussed later (section 3.6). We note that the proton content of each species was normalized to the mass of the amorphous silica nanoparticles. The reason that we provide the $^1\text{H}$ NMR data normalized to mass is just to show the mass conserved proton NMR spectrum for the sample (with varying temperature). The spectra normalized to surface area would emphasize an effect of particle size on the silica surface but the surface area varies with temperature.

3.3.2. Temperature-induced changes in $Q$ species in hydrous amorphous silica: Insights from $^{29}\text{Si MAS NMR}$

Figure 3.5 shows the $^{29}\text{Si MAS NMR}$ spectra and the fitting results for 7 and 14 nm amorphous silica nanoparticles with increasing dehydration temperature from 298 K to 1473 K. Three partially resolved peaks correspond to $Q^2$ ($\sim$91 ppm), $Q^3$ ($\sim$101 ppm), and $Q^4$
(~-110 ppm) species (Cannas et al., 2004; Engelhardt and Michel, 1987; Liu and Maciel, 1996a).

The $Q^2$, $Q^3$, and $Q^4$ species are due to Si sites with geminal silanol [(Si-O)$_2$≡Si=(OH)$_2$], single silanol [(Si-O)$_3$≡Si=OH], and siloxane [(SiO)$_4$Si] clusters, respectively. The $^{29}$Si MAS NMR spectra show that the fractions of $Q^2$ and $Q^3$ structures in 7 nm amorphous silica nanoparticles are larger than those in 14 nm amorphous silica nanoparticles (see below for further discussion). With increasing dehydration temperature, the fraction of $Q^4$ species apparently increases at the expense of $Q^2$ and $Q^3$ species. Though the results can be obscured by the overlap among peaks, the $Q^4$ peak position slightly moves to lower frequencies with increasing temperature. The observed change in peak position may be due to increase in mean Si-O-Si bond angle with the dehydration process (Mauri et al., 2000; Smith and Blackwell, 1983; Xue and Kanzaki, 1998) or/and an effect of next-nearest-neighbor on $Q$ species (Kim et al., 2010; Maekawa et al., 1991).

The $^{29}$Si MAS NMR spectra were fitted with several constraints concerning peak position and width for semi-quantitative insights into the changes in $Q$ species with varying temperature: note that we fitted the spectra with fixed peak width and position at -91.4 and -101.6 ppm for $Q^2$ and $Q^3$ species, respectively. The FWHM (Full Width at Half Maximum) is set to 9.6 ppm for both $Q^2$ and $Q^3$ species, and 11.1 ppm for $Q^4$ species, based on results of several trial fittings. The peak position of $Q^4$ species apparently shifts with increasing temperature and was gradually changes from -110.2 ppm at room temperature to -
Figure 3.5. $^{29}$Si MAS NMR spectra and fitting results at 9.4 T with increasing temperature from room temperature up to 1473 K for (A) 7 nm amorphous silica nanoparticles, and (B) 14 nm amorphous silica nanoparticles (normalized to the height of the spectra).
111.4 ppm up to 1473 K. Detailed information of the fitting parameters for $^{29}$Si MAS NMR spectra is given in Table 3. We also checked the effect of peak position for $Q^4$ species on general fitting results, which shows that the changes in fractions of $Q^3$ and $Q^4$ range ~3% to 7% of total Si environments depending on the peak position of $Q^4$ species (thus introducing systematic artifacts for the other fit parameters). We thus note that the fits can be rather non-unique due to the peak overlap. Additionally, the effect of next nearest neighbor on the peak positions has been reported in previous study (Kim et al., 2010), where ~ 0.5 ppm can contribute to changes in the $Q$ species peak position.

The $^{29}$Si MAS NMR spectra for 7 and 14 nm amorphous silica nanoparticles with varying dehydration temperature are fitted with three Gaussian functions, corresponding to $Q^2$, $Q^3$, and $Q^4$ species, respectively. The fitting results indicate that the fractions of $Q^2$, $Q^3$, and $Q^4$ are 5 ± 2%, 29 ± 5%, and 66 ± 7% for 7 nm amorphous silica nanoparticles, and 5 ± 3%, 28 ± 5%, and 67 ± 7% for 14 nm amorphous silica nanoparticles, respectively. The difference in the fractions of the $Q^2$, $Q^3$, and $Q^4$ species between the 7 and 14 nm amorphous silica nanoparticles is not significant taking into consideration the difference in their surface areas: the percentage of surface atom is estimated to be ~16.9 and 8.7 vol. % of 7 and 14 nm amorphous silica nanoparticles with an assumption that a top surface layer of tetrahedron would consist of surface fraction. This suggests that $Q^2$ and $Q^3$ species may exist not only on the surface of the particles but also inside amorphous silica nanoparticles (below the top surface layer).
Figure 3.6 presents the variation in $Q$ species fraction for 7 and 14 nm amorphous silica nanoparticles with varying dehydration temperature. For 14 nm amorphous particles, while the changes in the fractions of $Q$ species are not significant up to 1173 K, significant changes are observed above 1173 K. For 7 nm amorphous silica nanoparticles, a slight decrease of $Q^2$ and $Q^3$ species below ~873 K indicates that possible dehydroxylation can occur below ~873 K. Dehydration is apparently completed at ~1473 K, with $Q^4$ species being the only Si atom environment present in the amorphous silica nanoparticles. Dehydration of 7 nm amorphous silica nanoparticles occurs at a lower temperature than that of 14 nm amorphous silica nanoparticles, again indicating the effect of particle size (i.e., surface area) of the amorphous oxides on the dehydration process.

3.3.3. Structure of amorphous silica with varying temperature: Insights from $^1$H-$^{29}$Si HetCor NMR

Figure 3.7 shows the $^1$H-$^{29}$Si HetCor spectra and projections in $^1$H and $^{29}$Si dimension for 7 nm amorphous silica nanoparticles before and after dehydration under vacuum 3.7C) and 973 K (Figure 3.7D), where the correlations between the proton environments (e.g., water, silanol) and silicon environments (e.g., $Q^2$, $Q^3$, $Q^4$) through dipolar coupling are partially resolved. In the case of untreated amorphous silica nanoparticles, the physisorbed water peak at ~3.5 ppm is correlated to $Q^2$, $Q^3$, and $Q^4$ correlated to $Q^2$ and $Q^3$ structures. The isolated silanol (peak at 1.9 ppm) structures, and the broad peak at 3–8
Table 3.3. Fitting parameters and results for $^{29}$Si MAS NMR spectra for amorphous silica nanoparticles.

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<th>$Q^2$</th>
<th>$Q^3$</th>
<th>$Q^4$</th>
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</tbody>
</table>

$\delta_{iso}$ is set to -91.4 and -101.6 ppm for $Q^2$ and $Q^3$ species, respectively. The FWHM is fixed to 9.6 ppm for both $Q^2$ and $Q^3$ species, and 11.1 ppm for $Q^4$ species.
Figure 3.6. Population of Si atom species for 7 and 14 nm amorphous silica nanoparticles with increasing dehydration temperature.
ppm is correlated to $Q^2$ and $Q^3$ structures. The isolated silanol (peak at 1.9 ppm) shows a proximity to the $Q^3$ structure. The peak at 1.2 ppm in the $^1$H dimension is not observed (taking into consideration its low signal intensity in the $^1$H MAS NMR spectrum). After dehydration under vacuum, the intensities of both the sharp peak at ~3.5 ppm and broad peak at 3-8 ppm in the $^1$H dimension decreases, consistent with the trend shown in the $^1$H MAS NMR spectrum (Figure 3.1). The peak at ~1.9 ppm (isolated silanol) shows the correlation with both $Q^2$ and $Q^3$ structures, indicating that the proximity between $Q^2$, $Q^3$, and water decreases after dehydration under vacuum. For amorphous silica nanoparticles dehydrated at 773 K, the intensity of the broad peak at 3-8 ppm in the $^1$H dimension decreases significantly as also shown in the $^1$H MAS NMR spectrum. For amorphous silica nanoparticles dehydrated at 973 K, the isolated silanol peak at 1.9 ppm shows correlation mainly to the $Q^3$ structure and minor but measurable interactions with $Q^2$ and $Q^4$. Note that correlation in the HetCor spectrum shows the spatial proximity (i.e., through-space) between atoms but does not show atomic correlations through chemical bonds.

### 3.3.4. Comparison of $^1$H and $^{29}$Si NMR results

The detailed proton speciation in the amorphous silica nanoparticles can also be established by comparing the results from both $^1$H NMR and $^{29}$Si MAS NMR, allowing us to constrain the dehydration (removal of water) and dehydroxylation (condensation of silanol) processes microscopically.
Figure 3.7. $^{1}$H-$^{29}$Si HetCor spectra and projections in $^{1}$H and $^{29}$Si dimension at 9.4 T for 7 nm amorphous silica nanoparticles before and after dehydration under vacuum at 20 Torr (2.7 kPa) at room temperature for 6 h (9A and 9B, respectively) and after dehydration at 773 K (9C) and 973 K (9D) for 2h. Contour lines are drawn with 15 lines in logarithmic scale with a spacing factor of 1.2. The labels $is$, $hs$, $hw$ and $pw$ refer to isolated silanol, hydrogen-bonded silanol, hydrogen-bonded water, and physisorbed water, respectively.
Figure 3.8 presents the variation of proton species retrieved from $^{1}$H and $^{29}$Si MAS NMR results. Because the $^{29}$Si MAS NMR results provide the relative changes in the fractions of silanol groups (e.g., geminal silanol, single silanol), in order to estimate the absolute hydroxyl density, the fraction needs to be calibrated with $^{1}$H MAS NMR results. Thus, the variation of hydrogen density retrieved from $^{29}$Si MAS NMR results (sum of protons in single and geminal silanol = $2 \times Q^2$ fraction + $1 \times Q^3$ fraction) are scaled to match the variation of isolated silanol intensity in the $^{1}$H MAS NMR spectra at ~873 K, where the water molecules are mostly removed. The relative changes in the Si–OH content predicted from $^{29}$Si MAS NMR for both 7 and 14 nm nanoparticles are consistent with the trend observed from the $^{1}$H NMR, and the match is even better when considering only the hydroxyl groups at high temperature. Alternatively, one of the reviewers kindly pointed out that the quantitative hydroxyl group density in amorphous silica can be directly calculated based on the $^{29}$Si NMR results (i.e., fraction of $Q$ species) with following equation (Eq. 3.1):

$$2[Q^2] + [Q^3] = NBO/T = 2[H_2O]/(1-[H_2O])$$

where $[H_2O]$ is the mole fraction of water existing as hydroxyl group in amorphous silica, and NBO/T is the ratio of non-bridging oxygens per Si. The estimated hydroxyl fractions for 7 and 14 nm amorphous silica nanoparticles from $^{29}$Si NMR are ~8.9 OH/nm$^2$ and ~14.7 OH/nm$^2$ respectively, and are much larger than those estimated from the proton spin counting (see section 3.4). Indeed, previous study also showed that hydroxyl group density in amorphous silica nanoparticles can be
overestimated if calculated from $^{29}\text{Si}$ NMR result with equations similar to Eq.1 above (Humbert, 1995; Leonardelli et al., 1992). The $Q^2$ and $Q^3$ intensity in the $^{29}\text{Si}$ MAS NMR spectra for the amorphous silica nanoparticles can be overestimated due to the presence of $Q^4$ species with a chemical shift range similar to $Q^2$ and $Q^3$ (Humbert, 1995). That said, the density of hydroxyl group in the current study is consistent with the estimated hydroxyl group densities from previous studies (DelaCaillerie et al., 1997b; Liu and Maciel, 1996a; Morrow and McFarlan, 1991; Zhuravlev, 1987) (see discussion in section 3.1 above). Additionally, detailed $^{1}\text{H}-^{29}\text{Si}$ CP MAS NMR experiments for the similar nanoparticles at ambient temperature confirmed that the current peak assignment as well as relative fractions $Q$ species are correct (Liu and Maciel 1996). While we are not certain about the intuitive origin for the discrepancy in the estimated Si-OH fraction, according to Eq. 1, in order to yield the fraction of hydroxyl group from $^{1}\text{H}$ MAS NMR spectrum for 7 nm amorphous silica nanoparticles, the fractions of $Q^2$ and $Q^3$ should be $\sim3$ and $\sim5\%$, respectively, which is significantly smaller than the current value ($Q^2+Q^3 = 36\%$) in the $^{29}\text{Si}$ MAS NMR spectra (Figure 3.6). We were not able to find possible sources of uncertainty and potential errors associated with $^{29}\text{Si}$ NMR spectra that may affect the estimated NMR intensity from 36% to 8% (e.g., effect of delay time, artifacts of NMR fitting procedure). Currently, taking into consideration the fact that hydroxyl group contents from $^{1}\text{H}$ NMR and spin counting analysis are consistent with those from previous estimations, we treat $^{29}\text{Si}$ MAS NMR results rather semi-qualitatively. The reason for the discrepancy remains
Figure 3.8. Variation of proton species retrieved from $^1$H and $^{29}$Si MAS NMR results for (A) 7 nm and (B) 14 nm amorphous silica nanoparticles. The black line refers the intensity of total proton including all types of water and hydroxyl group. The blue line refers the intensity of isolated silanol (peak at 1.9 ppm) in amorphous silica nanoparticles retrieved from $^1$H MAS NMR result. The red line refers the relative changes in proton intensity of total sianol (sum of protons in single and geminal silanol) in amorphous silica nanoparticles retrieved from $^{29}$Si MAS NMR spectra.
3.3.5. Effect of atomic structure and topology in amorphous silica on its dehydration

The change in hydrogen environments of adsorbed water and silanols in amorphous silica nanoparticles were elucidated from $^1$H MAS NMR spectra. In addition, $^{29}$Si MAS NMR results provide additional details of dehydroxylation processes, forming a Si-O-Si bond from Si-OH. Previous ab initio calculations of crystalline silicates have shown that hydrolysis of silicate networks depends on the detailed connectivity of $Q$ species, lattice topology, and thus medium-range structures (Pelmenschikov et al., 2000). The dehydroxylation kinetics and processes can also be affected by the $Q$ species involved in the processes. As shown in Eqs. 2 through 4 below, each $Q$ species may undergo distinct dehydroxylation processes, yielding insights into the $Q$ species-dependent dehydroxylations:

$$Q^2 + Q^2 \rightarrow Q^3 + Q^3 \ + H_2O$$  \hspace{1cm} (3.2)
$$Q^2 + Q^3 \rightarrow Q^3 + Q^4 \ + H_2O$$  \hspace{1cm} (3.3)
$$Q^3 + Q^3 \rightarrow Q^4 + Q^4 \ + H_2O$$  \hspace{1cm} (3.4)

Figure 3.9A shows the changes in the $Q^n$ fraction at each temperature with respect to the total change in the $Q^n$ fraction [i.e., $(Q^n$ at each temperature–$Q^n$ at 298 K)/(Q$n$ at 1473 K–$Q^n$ at 298 K)]. The normalized change in $Q^n$ shows the effect of atomic structure of silanol and particle size on dehydroxylation of amorphous silica nanoparticles.
Figure 3.9. (A) The relations between normalized degree of dehydroxylation and temperature (K). (B) Ln(normalized degree of dehydroxylation) vs. 1/temperature (K).
Thus, as particle size increases, hydroxylation becomes more difficult. While the choice of dehydration duration of ~2 h (particularly at high temperature) can be somewhat arbitrary, the structure and the hydrogen contents in the nanoparticles with varying temperature can yield insights into the relative difficulty (i.e., energy penalty) for dehydroxylation. Here, we used the fractions of hydroxyl groups in the nanoparticles (heated for 2h) to obtain the energy penalty for the removal of water from the nanoparticles. We thus note that the below discussion of energy penalty is only for a semi-quantitative effect of particle size on the relative difficulty of dehydroxylation. Figure 3.9B presents the effect of temperature on each $Q$-species $[\ln (\text{normalized changes in } Q^n \text{ fraction}) \text{ vs. } 1/T (\text{K}^{-1})]$ for both 7 and 14 nm amorphous silica nanoparticles. Note that the slopes of the plots correspond to the energy penalty of dehydration for condensation of $Q^2$ and $Q^3$ species. The relative energy penalty of dehydroxylation for each $Q$ species from $^{29}$Si NMR is useful to estimate the effect of topological arrangement of $Q$ species on energy penalty of dehydroxylation. The energy penalties for condensation of $Q^2$ are smaller than that of $Q^3$ species for both 7 nm and 14 nm amorphous silica nanoparticles. Depending on particle size, the energy penalties decreases with decreasing particle size. These results indicate that both particle size and atomicstructure of silanol can control dehydroxylation of amorphous silica nanoparticles. Though speculative, the higher dehydroxylation temperature for the 14 nm particles may be due to a higher fraction of internal silanols, which would require significant network rearrangement for silanol to condensate into siloxane. Note that the pronounced effect of particles size (e.g., 7 and 14
nm) on dehydration mechanism is due to the fundamental difference between their structures (i.e., hydrogen and Si environments) with varying particle size as carefully shown in Figures 3.4 and 3.6. In particular, fractions of $Q$ species and hydrous species (e.g., OH and $\text{H}_2\text{O}$ groups with varying hydrogen bond strength) depend on particle size, and each structural unit has apparently distinct energy penalty for dehydroxylation.

### 3.3.6. Atomic-scale dehydration mechanisms for amorphous silica nanoparticles and their geochemical implications

Several dehydration mechanisms for amorphous silica, including silica gel, amorphous silica nanoparticles, and diatomite, have been proposed using NMR spectroscopy (Bronnimann et al., 1988; Dinh et al., 2000; Liu and Maciel, 1996a) and vibrational spectroscopies such as IR (McFarlan and Morrow, 1991; Young, 1957; Yuan et al., 2004) and Raman (Uchino et al., 2004; Yuan et al., 2004). Further extensive study of the structural changes of water and hydroxyl groups and an effect of particle size on dehydration of amorphous silica nanoparticles is necessary, because the high surface area of nanoparticles may induce significant changes in the water retention capacity and dehydration rate of silicates. Here, we have shown that the NMR results provide previously unknown details of temperature-induced dehydration and dehydroxylation processes in hydrous amorphous silica. The experimental data also have shown the presence of Si in $Q^2$, $Q^3$ and $Q^4$ species (from $^{29}\text{Si}$ MAS NMR results), and diverse hydroxyl groups with varying atomic configurations.
and molecular water exist in untreated amorphous silica nanoparticles (from $^1$H MAS NMR results). There are several types of distinct proximities among water, hydroxyl groups, anhydrous oxygen, including (1) water-water, (2) water-hydroxyl group, (3) water-surface oxygen, (4) hydroxyl group-hydroxyl group, and (5) hydroxyl group-surface oxygen. In the following proposed model, we take into consideration all the available configurations with diverse aforementioned proximities. We note that the relative proximities among those species need to be confirmed to validate the (currently somewhat speculative) model below. Figure 3.10 shows the atomic-scale dehydration mechanisms of amorphous silica nanoparticles on the basis of these $^1$H and $^{29}$Si MAS NMR results where the dehydration pathway generally follows the 4 distinct steps from low to high temperature. The first step involves removal of physisorbed water and hydrogen-bonded water, leading to a decrease in a fraction of silanol bonded to water, the second step follows by forming hydrogen-bonded silanol with nearby silanols. Additional successive removal of hydrogen species results in the formation of isolated silanol, the process depending on particle sizes and temperature (Figure 3.5). Finally, at temperature above ~873 K, the formation of siloxane cluster is accompanied. In detail, the dehydration of amorphous silica nanoparticles is characterized by the removal of water at low temperatures, and subsequent dehydroxylation at high temperature above ~873 K. We note that a possible simultaneous dehydroxylation can also occur below ~873 K with removal of the hydrogen bonded silanol, as shown in $^{29}$Si MAS NMR results for 7 nm amorphous silica nanoparticles.
Below ~873K most hydrogen-bonded silanols becomes isolated silanol with two distinct of isolated silanols, namely, isolated single and isolated geminal silanols, leading to a further reduction of hydrogen bonding strength (Eqs. 3.5a and b). At higher temperatures (above ~873 K), dehydroxylation of these isolated silanols is dominant, indicating that \( Q^2 \) and \( Q^3 \) species above ~873 K are isolated geminal and isolated single silanol. As temperature increases up to 1473 K the dehydroxylation of isolated geminal silanols (\( Q^2 \) species) may lead to a formation of isolated single silanols (\( Q^3 \) species) (Eq. 3.6 and 3.7) and the dehydroxylation of isolated single silanols results in a siloxane cluster (Si-O-Si) as shown below (Eq. 3.8):

\[
\equiv\text{Si-OH} [Q_3] \cdot \cdot \cdot \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} [Q_3] + \text{H}_2\text{O} \quad (3.5a)
\]

\[
=\text{Si}=(\text{OH})_2 [Q_2] \cdot \cdot \cdot \text{H}_2\text{O} \rightarrow =\text{Si}=(\text{OH})_2 [Q_2] + \text{H}_2\text{O} \quad (3.5b)
\]

\[
\equiv\text{Si-OH} [Q_3] + =\text{Si}=(\text{OH})_2 [Q_2] \rightarrow \text{Si-O-Si} [Q_4] + \equiv\text{Si-OH} [Q_3] + \text{H}_2\text{O} \quad (3.6)
\]

\[
=\text{Si}=(\text{OH})_2 [Q_2] + =\text{Si}=(\text{OH})_2 [Q_2] \rightarrow \equiv\text{Si-OH} [Q_3] + =\text{Si-OH} [Q_3] + \text{H}_2\text{O} \quad (3.7)
\]

\[
\equiv\text{Si-OH} [Q_3] + =\text{Si-OH} [Q_3] \rightarrow 2 \text{Si-O-Si} [Q_4] + \text{H}_2\text{O} \quad (3.8)
\]

Figure 3.10 shows the combined view consistent with the above schemes where both the variation in nature of hydrogen bonding, types of hydroxyl groups, and \( Q \) species-dependent dehydroxylation mechanism are illustrated. Note that the schemes shown in Eqs. 6-8 are identical to Eqs. 2-4 above but with emphasis on hydroxyl group environments.

Both dehydration and dehydroxylation in the amorphous silica nanoparticles are affected by the particle size and their detailed atomic environments (e.g., \( Q \) species, hydrogen bonding strength). The absolute
water content in amorphous silica increases with decreasing particle size
and the dehydroxylation process at higher temperature above ~873 K is
also clearly affected by the particle size as evidenced by different
enthalpies of dehydroxylation for 7 and 14 nm amorphous silica
nanoparticles as evidenced by $^{29}\text{Si MAS NMR}$ results.

The structural information and mechanistic details obtained from
the preceding experiments provide insights into the structure of hydrous
species and dehydration mechanisms in crystalline and amorphous
silicates in diverse geological settings, highlighting usually unknown
effects of particle size on the dehydration processes. First, similar
dehydratation models can be applied to understand the nature of hydrogen
bonding between water and natural amorphous silica including
amorphous opal, allowing us to obtain its water content during
diagenesis in the sedimentary basin. While the systematic relation
between water content, particle size, and its transition mechanisms in
amorphous opal need further investigation, the changes in nature of
hydrogen bonding during transition from amorphous to crystalline opal
can be experimentally probed and established (Day and Jones, 2008; Jones
and Renaut, 2007). The structural transition of opal-A with thermal aging
leads to a reduction of $Q^2$ and $Q^3$ as well as an increase of the average Si–
O–Si angle (Brown et al., 2003), which is consistent with the temperature-
induced structural changes of amorphous silica nanoparticles in the
current study. The dehydration-induced variation in the fractions of $Q^2$,
$Q^3$, and $Q^4$ species (i.e., polymerization) may also lead to changes in the
overall Si isotope composition of amorphous opal (De La Rocha et al.,
1997; Demarest et al., 2009; Hendry and Robinson, 2012; Kieffer, 1982). The on-going quantum chemical calculations of the equilibrium Si isotope fractionation of silica species provide additional constraints on the effect of the degree of polymerization on Si isotope composition in amorphous silica.

Second, water and hydroxyl groups are present in hydrous amorphous silica layers on the surface of earth materials in contact with acidic fluids (Chemtob et al., 2010; Chemtob et al., 2012; Zhu et al., 2006) as well as silica deposits on Mars (Squyres et al., 2008), indicating that hydrothermal environments formerly existed on Mars. The variation of $Q^2$ and $Q^3$ in an amorphous silica layer, following the current dehydration model, may play a role as a potential geothermometer.

Third, particle size for amorphous silica nanoparticles is an essential parameter to determine hydrogen content (i.e., water and hydroxyl content) in amorphous silica at low temperature below 873 K. The hydrogen content in 7 nm amorphous silica nanoparticles is ~3.4 times larger than that in 14 nm amorphous silica nanoparticles at room temperature, suggesting water retention capacity depends on particle size. The essential role of particle size in a dehydration model is also obvious in energetics for dehydroxylation of amorphous silica nanoparticles, as evidenced by the $^{29}$Si MAS NMR results. The lower energy penalty for dehydroxylation of 7 nm amorphous silica nanoparticles than for 14 nm amorphous silica nanoparticles implies that the dehydroxylation of amorphous silica (i.e., Si–OH + Si–OH → Si–O–Si + H$_2$O) becomes more difficult as particle size increases. The presence of nanoparticles in fault
plane is known to decrease the friction coefficient between the fault planes, softening overall seismic energy release (Han et al. 2007). While the origins of this change was not clearly demonstrated, nanoparticles formed mechanically at fault planes may contain considerable water and hydroxyl groups on their surfaces as shown in the current study. The hydration of nanoparticles and their dehydration during further slips in fault planes would be thus expected to reduce the friction between the planes. Similarly we expect that particle size would have an influence on the degree of decrease of the friction coefficient in the fault plane. While this is largely speculative, the presence of nanoparticles with smaller diameters (and thus with larger hydrogen content) in a fault plane may lead to a larger decrease in the friction coefficient, because the water retention capacity of the nanoparticles increases significantly with decreasing particle size.

Finally, similar techniques used for the current study can be effective in exploring structure of hydroxyl groups in diverse oxyhydroxides (e.g., δ-AlOOH), hydrous minerals (e.g., lawsonite, talc, aluminum hydroxide), and nominally anhydrous minerals (e.g., olivine, garnet, pyroxenes) in the earth’s deep mantle (Rossman, 1996; Sano et al., 2008; Suzuki et al., 2000; Xue and Kanzaki, 2009; Yesinowski et al., 1988). The potential NMR results allow us to understand changes in hydrogen bond strengths around proton and hydroxyl in those high pressure phases. The dehydration mechanism of the hydrous phases can be obtained using high-resolution solid-state NMR techniques studied here. The effect of particle size on the stability of these hydrous minerals and
Figure 3.10. Atomic-scale dehydration mechanisms of amorphous silica nanoparticles. Schematic diagrams for dehydration mechanisms are shown. From top to bottom, A) water adsorbed on both geminal and single silanols, B) water adsorbed on single silanols, C) water adsorbed on geminal silanols, respectively. The blue numbers refer to five types of proximities among water, hydroxyl group, and surface oxygen in amorphous silica: (1) water-water, (2) water-hydroxyl group, (3) water-surface oxygen, (4) hydroxyl group-hydroxyl group, and (5) hydroxyl group-surface oxygen.
and crystalline silicates with varying pressure and temperature and make nanoparticles in the subducting slab remains to be explored. As the detailed hydrogen environment can now be probed, the current result can shed light on opportunity to identifying hydrogen species in amorphous a link between the nature of hydrogen bonding in these earth materials and diverse key macroscopic properties.

Appendix

3.A.1. TEM image of amorphous silica nanoparticles

The HR-TEM image was obtained on a 300 kV JEM-3010(JEOL) electron microscope equipped with a Gatan digital Camera (MSC-794). The specimens for electron microscopy were prepared by dropping the amorphous silica nanoparticles diluted in ethyl-alcohol on a carbon coated film and drying for 2 days in ambient environment. Figure 3.A1 presents the TEM image of (A) 7 nm and (B) 14 nm amorphous silica nanoparticles. While the particle size is generally uniform, a small fraction of particles with diameter >20 nm are also observed (Figure 3.A1, middle and right images). Figure3.A2 shows the TEM image of 7 nm amorphous silica nanoparticles before and after heating at 873, 1073, and 1473 K where the diameter of the particles increases with increasing dehydration temperature.

3.A.2. Peak assignments

The peak assignments of the hydroxyl groups and molecular waters can be more complicated than those discussed in the manuscript. In order to
Figure 3.A1. TEM image of untreated (A) 7 nm and (B) 14 nm amorphous silica nanoparticles.
Figure 3.A2. TEM image of 7 nm amorphous silica nanoparticles before and after dehydration at 873, 1073, and 1473 K.
better constrain the peak assignments, additional experiments, including rehydration of heated amorphous silica nanoparticles (see appendix 3.A5), an analysis of spinning sideband patterns in $^1$H MAS NMR spectra (see appendix 3.A7), and an analysis of the effect of spinning speed (see appendix 3.A6), were performed. The observed proton peaks in the current $^1$H MAS NMR spectra can be assigned on the basis of the results from the additional 1D and 2D NMR experiments and the previous $^1$H NMR studies on diverse hydrous silica and silicate glasses (see Table 3.1).

3.A.2.1. Peak at 1.2 ppm

The peaks at 1.2 ppm is likely due to internal isolated silanol based on previous assignments of $^1$H NMR spectra for silica gel, precipitated silica, and opal-CT (Brus, 2002; Hartmeyer et al., 2007; Paris et al., 2007) and zeolites (Clarke et al., 1993; Hunger et al., 1996). It could also be a proton in a Si–H species or hydrocarbon such as methyl radical due to carbon contamination of the silica surface (Stesmans et al., 2005). We, however, cannot confirm the assignment with the current experimental data.

Additionally the 1.2 ppm peak has often been assigned to organic contamination of the NMR rotor (e.g., finger greases) (Kohn, 1996; Yesinowski et al., 1988; Zeng et al., 1999b). It is unlikely to be due to organic contamination of the NMR rotor in this case because the peak is observed only in the untreated (i.e., as-received) and dehydrated under vacuum amorphous silica nanoparticles; no peak is seen in the amorphous silica nanoparticles dehydrated above 573 K,
regardless of experimental conditions (e.g., choice of probe, magnetic field) or sample rehydration.

3.A.2.2. Peak at 1.9 ppm

The peak at 1.9 ppm is assigned to water accessible isolated silanol on the basis of previous peak assignments (see Table 1) and additional rehydration experiments (see A5). The peak intensity reduced with rehydration, indicating the 1.9 ppm peak is water-accessible.

3.A.2.3. Peak at ~2.3 ppm

The peak at ~2.3 ppm has been assigned to a weakly hydrogen-bonded silanol (see Table 1 and references therein). Additionally, the peak position for molecular water extrapolated from the peak position-water content trend can be approximately 2.3 ppm at dehydration temperature above ~ 673 K. In the $^1$H MAS NMR spectra for amorphous silica nanoparticles dehydrated above 973 K, the presence of the ~2.3 ppm peak could be evidence of rehydration (see A5). Its peak position shifts to lower frequency ‘reversibly’ with varying spinning speed (an increases in spinning speed from 15 to 25 to 33 kHz followed by a decrease to 25 and then to 15 kHz) (see A6), indicating it is not isolated silanol. Thus, in the current study, the peak at ~2.3 ppm is assigned to weakly hydrogen-bonded silanol at 297 K and 573 K where molecular water peak can be clearly observed at ~ 3.5 ppm. At higher temperature (above 673 K) the 2.3 ppm peak can be assigned to either weakly hydrogen-bonded silanol or molecular water with low water contents.
3.A.2.4. Sharp peak at \( \sim 3.5 \) ppm

The sharp resonance peak, whose position varied between 2.4 and 3.7 ppm depending on water content, is assigned to physisorbed water as evidenced by the irreversible dehydration during spinning (see A6), and previous studies (see Table 1). The previous NMR studies utilizing \(^1\)H and \(^2\)H NMR also have confirmed that the peak at \( \sim 3.5 \) ppm in the similar silica nanoparticles indeed corresponds to physisorbed water molecules (Kobayashi et al., 2008) with near-isotropic motion (Kinney et al., 1993; Kobayashi et al., 2008).

3.A.2.5. Broad peak at 3-8 ppm

The broad peak at 3-8 ppm is assigned to hydrogen-bonded silanol and hydrogen-bonded water on the basis of comparison of \(^1\)H and \(^{29}\)Si MAS NMR spectra for amorphous silica upon dehydration under vacuum and previous studies (see Table 1).

3.A.3. \(^1\)H MAS NMR spectra of amorphous silica nanoparticles with spinning speed of 7 kHz

Figure 3.A3 shows the \(^1\)H MAS NMR spectra for 7 nm amorphous silica nanoparticles collected at 9.4 T with spinning speed of 15 and 7 kHz. Since the peak positions for water and hydrogen-bonded silanol shift to lower frequency with increasing spinning speed, the overall shapes of the \(^1\)H MAS NMR spectra show small changes with spinning speed.
Figure 3.A3. $^1$H MAS NMR spectra at 9.4 T using Doty 4 mm probe with increasing dehydration temperature from room temperature up to 1473 K for 7 nm amorphous silica nanoparticles at spinning speed of (A) 15 kHz and (B) 7 kHz
3.A.4. Ratio of hydrogen-bonded water to hydrogen-bonded silanol in broad peak at 3–8 ppm

The hydrogen densities of the hydroxyl groups calculated by comparison of the $^1$H and $^{29}$Si MAS NMR results is rather more accurate than those calculated by fitting of the $^1$H MAS NMR spectra because of the peak overlap between hydrogen-bonded silanol and hydrogen-bonded water in broad peak at 3–8 ppm in the $^1$H MAS NMR spectra for amorphous silica nanoparticles (see section 3.1). Here, we estimated the hydrogen densities of hydroxyl groups by comparing the $^1$H and $^{29}$Si MAS NMR results for amorphous silica nanoparticles (see section 3.3.4 and Figure 3.9). Figure 3.9 shows that the Si–O–H content predicted from comparison of $^{29}$Si and $^1$H MAS NMR results is $1.5 \pm 0.4$ OH/nm$^2$ for 7 nm amorphous silica (~2.3 ppm), and hydrogen-bonded silanol (a fraction of the broad peak at 3–8 ppm) should be $1.5 \pm 0.4$ and $1.9 \pm 0.4$ OH/nm$^2$ for 7 and 14 nm amorphous silica nanoparticles, respectively. The fraction of hydrogen-bonded silanol in the broad peak at 3–8 ppm is $\sim 62 \pm 7\%$ and $\sim 45 \pm 5\%$ in the $^1$H MAS NMR spectra for untreated 7 and 14 nm amorphous silica nanoparticles, respectively. We note that the specific fraction of hydrogen-bonded silanol composing the broad peak at 3–8 ppm may depend on other parameters that control water content (e.g., particle size, humidity during storage).
Figure 3.A4. $^1$H MAS NMR spectra for untreated 7 nm amorphous silica nanoparticles under different humidity.
3.A.5. Rehydration of amorphous silica nanoparticles

3.A.5.1. Hydration of untreated (i.e., as-received) amorphous silica nanoparticles

The relative humidity of atmosphere affects the water content in the amorphous silica nanoparticles, and thus the $^1$H MAS NMR spectra. Figure 3.A4 shows the $^1$H MAS NMR spectra for untreated 7 nm amorphous silica nanoparticles in different humidity, showing that the peak position for sharp resonance at ~3.5 ppm (physisorbed molecular water) shifts reversibly depending on humidity. These results are consistent with previous studies (DelaCaillerie et al., 1997b; Liu and Maciel, 1996a). Thus, the difference in $^1$H NMR spectra for the untreated sample (without dehydration and/or heat treatment) reflects the humidity as well as the natural water retention capability of the nanoparticles with varying particle size.

3.A.5.2. Rehydration of heated (i.e., dehydrated) amorphous silica nanoparticles

In order to explore the reactivity with moisture and water accessibility of dehydrated amorphous silica nanoparticles, we performed rehydration of amorphous silica nanoparticles using $^1$H MAS NMR. Figure 3.A5 shows the $^1$H MAS NMR spectra collected at 9.4 T for rehydrated amorphous silica nanoparticles after dehydration at (A) 573 K, (B) 773 K, and (C) 973 K for 2 h. The rehydration was performed by opening the rotor cap in an open atmosphere with relative humidity of 53–55%. For amorphous silica nanoparticles dehydrated at 573 K and 773 K, the isolated silanol peak intensity at
1.9 ppm significantly decreases with increasing exposure time up to 1200 min, while the sharp peak intensity at 2.7 ppm for physisorbed water increased and its peak position shifted to higher frequency. These results indicate that the isolated silanol responsible for the peak at 1.9 ppm is indeed water-accessible and can thus be hydrated during rehydration of the sample. For amorphous silica nanoparticles dehydrated at 973 K, the isolated silanol at 1.9 ppm was a single-proton species, while the small peak at ~2.3 ppm was also observed after exposure durations of longer than 800 min. These results suggest that the peak at ~2.3 ppm in amorphous silica nanoparticles dehydrated above 973 K could result from rehydration of the sample. Note again that the isolated silanol at 1.9 ppm is the unique proton species in amorphous silica nanoparticles dehydrated above 973 K without rehydration.

3.A.6. Effect of spinning speed on $^1$H MAS NMR spectra

3.A.6.1. Effect of spinning speed on peak positions of hydrogen species in $^1$H MAS NMR spectra

Figure 3.A6 shows the $^1$H MAS NMR spectra at 11.7 T using a Bruker 2.5 mm probe for 7 nm amorphous silica nanoparticles before (298 K, Figure 3.A6-A) and after dehydration at 1173 K (Figure 3.A6-B) with varying spinning speed (an increase in spinning speed from 15 to 25 to 33 kHz followed by a decrease to 25 and then to 15 kHz). Additionally, the peak position, shape, and intensity change with varying spinning speed regardless of magnetic field (see Figure 3.A7).
Figure 3.A5. $^1$H MAS NMR spectra at 9.4 T for rehydrated amorphous silica nanoparticles in an open atmosphere (relative humidity of 53–55%) with spinning speed of 15 kHz and increasing exposure time after dehydration at (A) 573 K, (B) 773 K, and (C) 973 K.
For untreated amorphous silica nanoparticles, the resolution among the peaks for physisorbed water, hydrogen-bonded water, and hydrogen-bonded silanol in the $^1$H MAS NMR spectra are not improved with increasing spinning speed, suggesting that a relatively low spinning speed of 7 kHz and 15 kHz is sufficient to resolve the proton environments in amorphous silica nanoparticles studied here. While the peak positions for the sharp peak at ~3.5 ppm and broad peak at 3–8 ppm shift to lower frequency when spinning speed increases from 15 kHz to 33 kHz, those for the peaks at 1.9 and 1.2 ppm are largely invariant. These results indicate that the peak positions for hydrogen-bonded proton species, such as water and hydrogen-bonded silanol, are dependent on spinning speed but those for isolated (i.e., non-hydrogen bonded silanols) are not. For amorphous silica nanoparticles dehydrated at 1173 K, the peak at ~2.3 ppm and isolated silanol peak at 1.9 ppm were observed. The presence of ~2.3 ppm peak in the sample at 1173 K indicates that the sample was rehydrated during preparation (see A5 above). With increasing spinning speed (i.e., 15 → 25 → 33 kHz), the peak position at ~2.3 ppm shifts to lower frequency, while the peak at 1.9 ppm does not shift. These results suggest that the peak at ~2.3 ppm can be assigned to weakly hydrogen-bonded silanol but cannot be due to isolated silanol. Note that the peak position for isolated silanol at 1.9 ppm (dehydrated at 1173 K) is invariant upon spinning. The observed increases in peak width with increasing spinning speed can be due to changes in the structure and dynamics partly stemming from the frictional heating
Figure 3.A6. $^1$H MAS NMR spectra for 7 nm amorphous silica nanoparticles (A) before and (B) after dehydration at 1173 K measured at 11.7 T with varying spinning speed (an increase in spinning speed from 15 to 25 to 33 kHz followed by a decrease to 25 and then to 15 kHz).
**Figure 3.A7.** $^1$H MAS NMR spectra for 7 nm amorphous silica nanoparticles collected with varying spinning speed up to (A) 33 kHz and (B) 15 kHz using Bruker 2.5 mm at 11.7 T. The black lines indicate the spectra measured during increasing spinning speed; the red lines indicate the spectra measured during decreasing spinning speed.
and/or centrifugal force during magic angle spinning (Doty et al., 1998; Elbayed et al., 2005). The estimated increase in the sample temperature due to frictional heating during spinning can be ~45 K (with spinning speed of 15 kHz in the Doty 4 mm probe). Previous experimental studies have shown that this would not lead to a significant change in dynamics of physisorbed water and silanols in hydrous oxide glasses and thus amorphous silica nanoparticles: previous variable temperature static $^2$H NMR study for hydrous rhyolite glasses does not show meaningful changes in the nature of dynamics between 295 and 335 K (Eckert et al., 1987).

3.A.6.2. Spinning-induced dehydration of amorphous silica nanoparticles

We found that spinning-induced dehydration would occur in the $^1$H MAS NMR experiment for amorphous silica nanoparticles depending on different rotor and probe design and maximum spinning speed.

Effect of maximum spinning speed

Figure 3.A7 (A) and (B) show the $^1$H MAS NMR spectra collected with Bruker 2.5 mm probe at 11.7 T for amorphous silica nanoparticles with varying spinning speed up to 33 kHz (i.e., an increase in spinning speed from 7, 15, 25 to 33 kHz followed by a decrease to 25, 15, and then to 7 kHz), and 15 kHz (i.e., an increase in spinning speed from 7, 10 to 15 kHz followed by a decrease to 10 and
then to 7 kHz), respectively. For the former case (spinning up to 33 kHz, Figure 3.A7-A), while the changes in peak position and intensity in the $^1$H MAS NMR spectra collected with a spinning speed of 7 kHz before (black line) and after (red line) increasing spinning speed up to 33 kHz are negligible for the broad peak at 3–8 ppm (i.e., reversible change), the sharp peak at ~3.5 ppm shows reduced intensity and an apparent shift in peak position (i.e., irreversible change). This result indicates that spinning-induced dehydration of the hydrogen species responsible for the sharp peak at ~3.5 ppm (physisorbed water) occurs during spinning up to 33 kHz while those H species responsible for the peak at 3–8 ppm (hydrogen-bonded water and hydrogen-bonded silanol) are not significantly affected. While the spinning-induced dehydration is observed for the former case (spinning up to 33 kHz, Figure 3.A3-A), permanent dehydration due to spinning has not been observed for the latter (spinning up to 15 kHz). These results indicate that the spinning speed affect the degree of spinning-induced dehydration.

**Probe effect**

Figure 3.A8 shows the $^1$H MAS NMR spectra for amorphous silica nanoparticles with varying spinning speed up to 15 kHz (i.e., an increase in spinning speed from 7 to 10 to 15 kHz followed by a decrease to 10 and then to 7 kHz) using different probes (e.g., Bruker 2.5 mm, Bruker 4 mm, and Doty 4mm probe). We found that even at lower spinning speed (<15 kHz) a slight spinning induced dehydration
are observed upon spinning using 4mm Bruker probe (Figure A12-B), suggesting that there are indeed slight differences in sealing capability among the probes. These results confirm that rotor and probe design also affects the degree of spinning-induced dehydration of amorphous silica nanoparticles: note that the spectra presented in the text are all collected with the spinning speed of 15 kHz using 4 mm Doty probe that shows a negligible spinning-induced dehydration.

3.A.7. NMR characteristics of water molecules for amorphous silica nanoparticles

3.A.7.1. Dynamics of water molecules in amorphous silica nanoparticles

The detailed NMR characteristics [e.g., chemical shift anisotropy (CSA), dipolar coupling], dynamics and structure of silanol and physisorbed water in amorphous silica nanoparticles at room temperature have been extensively discussed and/or confirmed by previous studies (Bronnimann et al., 1988; DelaCaillerie et al., 1997b; Hartmeyer et al., 2007; Kinney et al., 1993; Kobayashi et al., 2008; Liu and Maciel, 1996a; Paris et al., 2007; Vega and Scherer, 1989). The dynamics of water molecules can affect the overall peak shape and spinning sideband patterns as indicated by the previous dephasing experiments (Bronnimann et al., 1988; Kinney et al., 1993): while diverse anisotropic nuclear spin interactions can be prevalent for physisorbed water molecule in amorphous silica nanoparticles, these interactions have not been well demonstrated due to its intrinsic
Figure 3.A8. $^1$H MAS NMR spectra for 7 nm amorphous silica nanoparticles collected using (A) Bruker 2.5 mm at 11.7 T, (B) Bruker 4 mm at 11.7 T, and (C) Doty 4 mm probe at 9.4 T with varying spinning speed up to 15 kHz. The black lines indicate the spectra measured during increasing spinning speed; the red lines indicate the spectra measured during decreasing spinning speed.
mobility at room temperature (Bronnimann et al., 1988; Kinney et al., 1993; Liu and Maciel, 1996a). Indeed, the liquid-like, near-isotropic motion of physisorbed water (i.e., molecular water) has been reported in previous $^1$H and $^2$H NMR studies for amorphous silica (Kinney et al., 1993; Kobayashi et al., 2008).

3.A.7.2. Relative magnitude of anisotropic NMR interactions for water and hydroxyl group

The analysis of the relative intensity of the spinning sideband could provide the nature of the proton environments. Magnitude of dipole coupling between the water molecules in the physisorbed water can be comparable to that involving hydroxyl groups, and can be partially revealed by observing spinning sideband patterns for the $^1$H NMR spectra. In order to estimate the relative magnitude of NMR anisotropic interactions on the spinning sideband patterns for both hydroxyl and water phases, the relative intensity for each spinning sideband component (3-8 ppm peak and 3.5 ppm peak) need to be evaluated. That said, spinning sideband patterns for the untreated amorphous silica nanoparticles with varying spinning speed provide additional insights into the magnitude of NMR spin interactions for both 3-8 ppm peak and 3.5 ppm peak. Figure 3.A9 shows the changes in spinning sideband pattern in $^1$H MAS NMR spectra (at 11.7 T) for untreated amorphous silica nanoparticles with varying spinning speed from 7 kHz up to 33 kHz. We note that the outer layer water is prevalent in untreated amorphous silica nanoparticles. $^1$H MAS NMR
spectrum with 7 kHz spinning speed shows that the spinning sidebands due both to broad peak at 3-8 ppm and sharp peak at ~ 3.5 ppm are observed. With increasing spinning speed, the intensity of spinning sideband decreases. While the spinning sidebands for broad peak at 3-8 ppm are not observed above 25 kHz, those for sharp peak at ~ 3.5 ppm are still observed above 25 kHz. The current result shows that the relative intensity of spinning sideband for broad peak at 3-8 ppm is reduced more significantly with increasing spinning speed than that for sharp peak at ~ 3.5 ppm. While we are not certain about the origin of the observed trend, it is clear that these two peaks have varying degree of anisotropy (either due to dipolar interactions, CSA) and/or dynamics mostly relevant for outer layer water. Additionally, this rather complex behavior may also be due to the presence of mobile (yet with stronger anisotropic interactions) outer layer water.

3.A.8. Estimation of fraction of surface atoms in amorphous silica nanoparticles

Assumptions

1. The surface atom consists of the top surface layer of tetrahedral
2. The height of the tetrahedron is similar with crystalline SiO$_2$ quartz, which is 2.1 Å.
3. The amorphous silica nanoparticles are spherical.

Calculation

1. Surface volume = total volume of particle - non-surface volume (bulk volume)
Figure 3.A9. $^1$H MAS NMR spectra at 11.7 T for 7 nm amorphous silica nanoparticles with varying spinning speed. The asterisk (*) denotes the spinning sideband.
1.1 Total volume of particle = \( \frac{4}{3} \pi r^3 \), where the \( r \) is the radius of particle (i.e., \( \frac{d}{2} \))

1.2 Non-surface volume = \( \frac{4}{3} \pi (r - 2.1\text{Å})^3 \)

1.3 Surface volume = \( \frac{4}{3} \pi [r^3 - (r - 2.1\text{Å})^3] \)

2. The percentage of surface atom = Surface volume/ total volume of particle

2.1. The percentage of surface atom = \( 100 \times \left[ r^3 - (r - 2.1\text{Å})^3 \right] \)

2.2. The percentage of surface atom for 7 nm silica particle

\[ = 100 \times \frac{[(3.5 \text{ nm})^3 - (3.29 \text{ nm})^3]}{(3.5 \text{ nm})^3} = 16.941\% \]

2.3 The percentage of surface atom for 14 nm silica particle

\[ = 100 \times \frac{[(7 \text{ nm})^3 - (6.79 \text{ nm})^3]}{(7 \text{ nm})^3} = 8.732\% \]

3.A.9. Dehydration of amorphous silica nanoparticles under vacuum

The comparison of the \(^1\text{H}\) and \(^{29}\text{Si}\) MAS NMR spectra for amorphous silica nanoparticles dehydrated under vacuum allows us to provide improved peak assignment of the broad peak at 3-8 ppm (due both hydrogen-bonded water and hydrogen-bonded silanol). Figure 3.A10 shows the \(^1\text{H}\) and \(^{29}\text{Si}\) MAS NMR spectra collected at 9.4 T for 7 nm amorphous silica nanoparticles before and after dehydration under vacuum at 20 Torr (0.7 kPa) for 6 h. Whereas the variation in the \(^{29}\text{Si}\) MAS NMR spectra for amorphous silica nanoparticles is negligible, the proton environments were significantly different before and after dehydration under vacuum as shown in the
Figure 3.A10. (A) $^1$H and (B) $^{29}$Si MAS NMR spectra at 9.4 T for 7 nm amorphous silica nanoparticles before and after dehydration under vacuum for 6 h.
$^1$H MAS NMR spectra: the peak intensities of both the ~3.5 and 3–8 ppm peaks in the $^1$H MAS NMR spectra significantly decreased, but those of the 1.9 and ~2.3 ppm peaks increased. The results indicate that the water species, including physisorbed water and hydrogen-bonded water, were removed upon dehydration under vacuum but silanol groups were not removed. Taking into consideration dehydration-induced conversion of types of hydroxyl groups from hydrogen bonded silanols (peak at 3-8 ppm) to isolated silanols (i.e., 1.9 and 2.3 ppm peaks) under vacuum, the increases in peak intensity at 1.9 and ~2.3 ppm under vacuum should be accompanied by the decrease in the intensity contribution of hydrogen-bonded silanol to the broad peak at 3–8 ppm. The increases in peak intensity for isolated silanols are apparently smaller than the total decrease in peak intensity at 3-8 ppm. The results thus indicate that the broad peak at 3–8 ppm consists of both hydrogen-bonded water and hydrogen-bonded silanol.

3.A.10. Ratio of hydrogen-bonded water to hydrogen-bonded silanol in broad peak at 3-8 ppm

The hydrogen densities of the hydroxyl groups calculated by comparison of the $^1$H and $^{29}$Si MAS NMR results is rather more accurate than those calculated by fitting of the $^1$H MAS NMR spectra because of the peak overlap between hydrogen-bonded silanol and hydrogen-bonded water in broad peak at 3–8 ppm in the $^1$H MAS NMR spectra for amorphous silica nanoparticles. Here, we estimated the hydrogen densities of hydroxyl groups by comparing the $^1$H and
\(^{29}\)Si MAS NMR results for amorphous silica nanoparticles. Figure 3.8 shows that the Si–O–H content predicted from comparison of \(^{29}\)Si and \(^{1}\)H MAS NMR results is \(1.5 \pm 0.4 \text{ OH/nm}^2\) for 7 nm amorphous silica nanoparticles and \(1.9 \pm 0.4 \text{ OH/nm}^2\) for 14 nm amorphous silica nanoparticles.

The ratio between hydrogen-bonded silanol and hydrogen-bonded water in the broad peak at 3–8 ppm in the \(^{1}\)H MAS NMR spectra for amorphous silica nanoparticles can be calculated based on the fitting results for \(^{1}\)H MAS NMR spectra and the hydrogen densities of hydroxyl groups in amorphous silica nanoparticles. The population of hydrogen atom in hydroxyl groups [i.e., sum of peak intensities for isolated silanol (1.2 and 1.9 ppm), weakly hydrogen-bonded silanol (~2.3 ppm), and hydrogen-bonded silanol (a fraction of the broad peak at 3–8 ppm)] should be \(1.5 \pm 0.4\) and \(1.9 \pm 0.4 \text{ OH/nm}^2\) for 7 and 14 nm amorphous silica nanoparticles, respectively. The fraction of hydrogen-bonded silanol in the broad peak at 3–8 ppm is \(\sim 62 \pm 7\%\) and \(\sim 45 \pm 5\%\) in the \(^{1}\)H MAS NMR spectra for untreated 7 and 14 nm amorphous silica nanoparticles, respectively. We note that the specific fraction of hydrogen-bonded silanol composing the broad peak at 3–8 ppm may depend on other parameters that control water content (e.g., particle size, humidity during storage).
3.A.11. Cross sections from $^1$H-$^29$Si HetCor spectra for amorphous silica nanoparticles

Figure 3.A11 shows $^1$H cross sections (F1) from $^1$H-$^29$Si HetCor spectra for amorphous silica nanoparticles at 9.4 T for 7 nm amorphous silica nanoparticles taken at the $Q^2$ (-91 ppm), $Q^2$ (-100 ppm), and $Q^4$ (-110 ppm) position with increasing dehydration temperature. Figure 3.A12 presents the $^{29}$Si cross sections (F2) from $^1$H-$^{29}$Si HetCor spectra for amorphous silica nanoparticles at 9.4 T for 7 nm amorphous silica nanoparticles taken at each $^1$H frequency with increasing dehydration temperature.

3.A.12. Fitting procedure of $^1$H MAS NMR spectra

While the simulation of $^1$H spectra has inherent uncertainties due to the overlap among peaks from water and hydrogen-bonded silanol, as reviewer #2 suggested, the sharp peak at ~3.5 ppm (i.e., physisorbed water) and broad peak at 3–8 ppm (i.e., hydrogen-bonded water and hydrogen-bonded silanol) can be resolved by considering their distinct peak shapes. We note that this resolution (and thus the quantitative estimation of peak intensity) can often be complicated, particularly for the $^1$H MAS NMR spectra of untreated 14 nm amorphous silica nanoparticles collected with a spinning speed of 15 kHz. In order to resolve these ambiguities and increase the confidence of the fitting results, we simulated the series of $^1$H MAS NMR spectra for amorphous silica nanoparticles collected with 15 kHz and 7 kHz spinning speeds. Figure 3.A13 shows the $^1$H MAS NMR spectra for 7
Figure 3.A11. $^1$H cross sections (F1) from $^1$H-$^{29}$Si HetCor spectra for amorphous silica nanoparticles at 9.4 T for 7 nm amorphous silica nanoparticles taken at the $Q^2$ (-91 ppm), $Q^2$ (-100 ppm), and $Q^4$ (-110 ppm) position with increasing dehydration temperature.
Figure 3.A12. $^{29}$Si cross sections (F2) from $^1$H-$^{29}$Si HetCor spectra for amorphous silica nanoparticles at 9.4 T for 7 nm amorphous silica nanoparticles taken at each $^1$H frequency with increasing dehydration temperature.
nm amorphous silica nanoparticles collected at 9.4 T with spinning speed of 15 and 7 kHz. Since the peak positions for water and hydrogen-bonded silanol shift to lower frequency with increasing spinning speed, the overall shapes of the $^1$H MAS NMR spectra show small changes with spinning speed. Thus, the overlapped peaks in the $^1$H MAS NMR spectrum with a 15 kHz spinning speed could be separated in that with a 7 kHz spinning speed.

Figure 3.A14 shows the simulation of $^1$H MAS NMR spectra for 14 nm amorphous silica nanoparticles collected at spinning speeds of 15 kHz and 7 kHz with the proton species in the nanoparticles represented by several Gaussian and Lorentzian functions, based on their peak shapes. Figure 3.A15 presents the variations of the proton species in 14 nm amorphous silica nanoparticles with spinning speed as obtained from $^1$H MAS NMR spectra. There was no quantitative variation in the proton species in the 14 nm amorphous silica nanoparticles with changing spinning speed, within the error range. These results indicate that the simulation of $^1$H MAS NMR spectra for amorphous silica nanoparticles is likely to be correct.
Figure 3.A13. $^1$H MAS NMR spectra at 9.4 T with increasing dehydration temperature from room temperature up to 1473 K for 7 nm amorphous silica nanoparticles at spinning speed of (A) 15 kHz and (B) 7 kHz.
Figure 3.A14. Simulation of $^1$H MAS NMR spectra for 14 nm amorphous silica nanoparticles collected at 9.4 T at (A) 15 kHz and (B) 7 kHz spinning speed.
Figure 3.A15. Variation of the quantity of proton species for 14 nm amorphous silica nanoparticles calculated from $^1$H MAS NMR spectra at (A) 15 kHz and (B) 7 kHz spinning speeds. The blue, red, purple, and black lines indicate intensities of physisorbed water (sharp peak at ~3.5 ppm), hydrogen-bonded silanol and hydrogen-bonded water (broad peak from 3 to 8 ppm), weakly hydrogen-bonded silanol (peak at 2.3 ppm), and isolated silanol (peak at 1.9 ppm), respectively.
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Chapter 4. Direct observation of oxygen environments for hydroxyl and siloxane structures in amorphous silica-gel: $^{17}$O solid-state NMR study

Abstract

The atomic structure of hydrous species including hydroxyl group and water are important to understanding silicates-fluid interactions in the earth’s system. Although probing of atomic structure of oxygen in hydrous amorphous silicate is the most direct evidence to resolve the Si-O-Si and Si-OH in amorphous silica, the limited number of $^{17}$O NMR studies for hydrous amorphous silicates and silica has been reported so far. Here, we explore the nature of hydrous species in amorphous silica gel using $^{17}$O NMR spectra as well as $^1$H and $^{29}$Si NMR spectra with increasing temperature up to 1273 K. The diverse hydrous species and organic molecules such as alkyl groups exist in as-synthesize amorphous silica gel, which significantly decreases with increasing temperature. $^1$H MAS NMR results show that the hydrogen bond strength decreases with increasing temperature and isolated silanol become a single proton environment in amorphous silica gel above 873 K. Although $^{17}$O MAS NMR experiments cannot provide the quantitative fraction of Si-OH in as-synthesized amorphous silica gel at 298 K, the significant changes in $^{17}$O MAS NMR spectra for amorphous silica gel is observed with increasing temperature. These temperature-induced changes in $^{17}$O NMR spectra are certainly due to dehydroxylation of amorphous silica.
above 673 K, particularly due to condensation of isolated silanol above 873 K. By subtracting the $^{17}$O NMR spectra for annealed amorphous silica gel at 1073 K from that at 673 K, the $^{17}$O peaks for hydrogen bonded and isolated silanol are observed for the first time. Although the S/N ratio of $^{17}$O MAS NMR spectra for amorphous silica in here is not enough to obtain precise NMR parameter for hydroxyl group with varying hydrogen bond strength, the currently undergoing $^{17}$O MAS experiments is promising to elucidate the effect of hydrogen bond strength on the NMR parameters of oxygen sites in hydroxyl group.

4.1. Introduction

The atomic structure of amorphous silica has long been investigated in many experimental and theoretical studies due to its fundamental interest as one of the simplest covalent oxides. Particularly, the understanding the nature of hydrous species (e.g., $\text{H}_2\text{O}$ and $\text{OH}$) on the surface of amorphous silica is essential to comprehending silicates-fluid interactions in the earth’s system. However, the atomic structures of hydrous species in amorphous silicates, particularly for oxygen environments, are not fully understood. The objective of this study is to investigate the atomic structure of oxygen site of hydrous species in amorphous silica gel with increasing temperature.

The hydrous species exist on the surface of silica with varying hydrogen bond strengths (e.g., physisorbed water, hydrogen-bonded water, hydrogen-bonded silanol, and isolated silanol) and atomic
configurations (e.g., single silanol, geminal silanol). Those hydrous species affects the macroscale properties of silicate melts such as phase relations, viscosity, thermal conductivity, which plays an important role in the migration of magmas.

Given these importance and implications, attempts have been made in the past to elucidate the atomic structures of hydroxyl groups and water in amorphous silica nanoparticles using various spectroscopic methods. In particular, infrared spectroscopy (IR), a representative method to identify unique vibrational modes of H$_2$O and hydroxyl groups, has been used to probe the hydrogen environments of amorphous silica. However, generally, those features in amorphous silica were not fully resolved, characterized with a large degree of overlaps among those IR signals. This led to difficulties in quantifying the hydroxyl group content unless careful calibration was carried out.

High-resolution solid-state NMR spectroscopy yields information that is element specific and allows the determination of short-range structures in amorphous silica. Thus, the structure of water and hydroxyl group has been probed using $^1$H and $^{29}$Si NMR spectroscopies, which provide the information about hydrogen bond strengths around protons and number of hydroxyl group around Si atoms, respectively. In addition to H and Si environments, probing of oxygen environments in hydrous amorphous silicates are essential to resolve the Si-O-Si and Si-OH in amorphous silica, because the oxygen plays an important role as bridges between Si atoms or Si and H atoms.
$^{17}$O NMR is one of the most effective and promising probes of O atom sites and their specific reactivities in crystalline and amorphous silicates (Lee et al., 2010; Lee and Lee, 2006; Lee and Stebbins, 2003, 2006; Lee et al., 2003; Lee and Weiss, 2008). However, the limited number of $^{17}$O NMR studies for hydrous amorphous silicates and silica has been reported because the low natural abundance of $^{17}$O isotope, which indicates the $^{17}$O isotope enriched samples are necessary to collect $^{17}$O NMR spectrum.

Previous $^{17}$O NMR study for sol-gel produced silica reported that the single $^{17}$O NMR experiment cannot provide direct quantitative information simultaneously on both the Si-OH groups and Si-O-Si structure, because their nutation frequencies are different. While the bridging oxygen is in the strong quadrupole coupling limit ($\nu_Q \gg \nu_{RF}$), the hydroxyl oxygen is in the weak quadrupole limit ($\nu_Q \ll \nu_{RF}$). Thus, the $^{17}$O nutation curve for Si-O-Si structure behaves like solid, that for Si-OH behaves like liquid (van Eck et al., 1999). For instance, a 90° pulse for hydroxyl oxygen acts as a 270° pulse for the bridging oxygen. These results indicate that the optimized experimental condition is needed to observe the Si-OH signal in $^{17}$O MAS NMR spectra.

Although a single $^{17}$O MAS NMR experiment cannot observed the both oxygen sites for Si-O-Si and Si-OH in as-synthesized amorphous silica gel, the peak for Si-OH with $C_q$ of 3~4 MHz was often observed in $^{17}$O NMR spectra for hydrous silicates glass and silica gel (Cong and Kirkpatrick, 1996; Oglesby et al., 2001; van Eck et al., 1999; Walther et al., 1990). In $^{17}$O 3QMAS NMR spectra for amorphous silica
gel, van Eck and coworkers observed small amount of hydroxyl oxygen with $C_q$ of 2.8~3.2 MHz as well as hydroxyl oxygen with $C_q$ of $<0.2$ kHz (van Eck et al., 1999). Because the hydroxyl oxygen with $C_q$ of $\sim 3$ MHz is in strong quadrupole coupling limit, it would behaves like solid. Thus, the bridging oxygen and hydroxyl oxygen with $C_q$ of $\sim 3$ MHz may be observed simultaneously in $^{17}$O MAS NMR spectrum. These results indicate that different types of hydroxyl oxygen exist and their $C_q$ are different each other. Previous quantum chemical calculation reported that the $C_q$ of hydroxyl oxygen has a trend to increase with decreasing hydrogen bond strength (Xue and Kanzaki, 1998). However, experimental study for an effect of hydrogen bond strength on the NMR parameter for oxygen site in hydroxyl group has not been reported yet.

Here, we explore the nature of hydrous species in amorphous silica gel using high-resolution multi-nuclei solid-state NMR. We report $^{17}$O MAS NMR spectra of amorphous silica gel with increasing annealing temperature up to 1373 K that allow us investigate the effect of temperature and hydrogen bond strength on the structure of hydroxyl oxygen in amorphous silica gel. We also collected the $^1$H and $^{29}$Si MAS NMR spectra for amorphous silica gel with increasing annealing temperature, which provide the complementary view to understand the atomic structure of hydroxyl group in amorphous silica gel.
4.2. Experimental Methods

4.2.1. Sample Preparation

The amorphous silica gel is synthesized by the hydrolysis of SiCl$_4$ in diethyl ether (C$_4$H$_{10}$O) solution at about 0°C using 40 % $^{17}$O-enriched water. The solution was stirred for 30 min by hand shaking and then was dried under N$_2$ flow for 3 days. The X-ray diffraction (XRD) pattern for synthesized silica gel, showed no evidence of crystalline phases. The samples were heated for 2 h at varying temperatures ranging from 673 to 1373 K (heating rate of 275 K/h) in an Ar environment. While the silica gel was heated at varying dehydration temperatures, the NMR spectra were collected at ambient conditions.

4.2.2. NMR Spectroscopy

$^1$H MAS NMR Spectroscopy. $^1$H MAS NMR spectra for amorphous silica gel were collected on a Varian NMR system (9.4 T) at Larmor frequency of 400.1 MHz (4 mm double-resonance Doty probe) with spinning speed of 14 kHz. A single-pulse sequence with a 30-degree pulse (0.67 $\mu$s) and delay time of 1 s was used. Tetramethylsilane (TMS) was used as the external chemical shift reference. We found that a weak and broad $^1$H background signal attributed to the rotor and probe was observed in both $^1$H MAS NMR spectra collected in Varian NMR system (9.4 T) spectroscopy; to subtract this background signal, the $^1$H MAS NMR spectrum for an empty rotor was also measured under identical experimental conditions and was subtracted from all
$^1$H MAS NMR spectra.

$^{29}$Si MAS NMR Spectroscopy. $^{29}$Si MAS NMR spectra for amorphous silica gel were collected on a Varian NMR system of 9.4 T at a Larmor frequency of 79.55 MHz (Doty 4 mm probe) and a spinning speed of 11 kHz. A single-pulse sequence with a 30-degree pulse (1.2 μs) and delay time of 120 s were used.

$^{17}$O MAS NMR Spectroscopy. $^{17}$O MAS NMR spectra for amorphous silica gel were collected on a Varian NMR system of 9.4 T, and Varian 600 MHz (14.1 T) spectrometers with a triple resonance 4 mm Bruker probe, and 2.5 mm Varian probe, respectively. The Larmor frequency is 54.23 and 81.35 MHz, respectively. A single-pulse sequence with a 15-degree pulse (0.2 μs) was used and delay time varies from 1 s for as-synthesize amorphous silica to 90 s for annealed samples above 873 K. The spinning speed is 14 kHz at 9.4 T and 20 kHz at 14.1 T.

4.3. Results and Discussion

4.3.1. $^1$H MAS NMR Result

Figure 4.1 shows $^1$H MAS NMR spectra for amorphous silica gel with increasing annealing temperature. In as-synthesized silica gel at 298 K, diverse peaks corresponding to hydroxyl groups and water molecules as well as organic molecules are partially resolved. On the basis of previous $^1$H MAS NMR studies for amorphous silica and chemically modified silica, the peak at ~ 4ppm was assigned to physisorbed water on the surface of amorphous silica with varying degrees of hydrogen bond strength (Bronnimann et al., 1988; Liu and
Maciel, 1996). The broad shoulder peak at ~ 7 ppm was assigned to the hydrogen-bonded water and hydrogen-bonded silanol on the basis of the comparison of ¹H and ²⁹Si MAS NMR spectra for amorphous silica nanoparticles upon dehydration under vacuum (for details, see chapter 3). The sharp resonances at 1.4 and 1.0 ppm were assigned to CH₂ and CH₃ sites of alkyl group, respectively (Pursch et al., 1997). The alkyl group may the residuals of diethyl ether (C₄H₁₀O) solution used for sample synthesis. The sharp peak at 3.8 ppm may be assigned to Si-O-CH₃, because of which chemical shift is known between 3 and 4 ppm (Camus et al., 2003).

With increasing temperature, the intensities of proton signals including both hydrous species and alkyl group in silica gel are reduced, significantly. At 673 K, the peak at ~ 3 ppm was assigned to physisorbed water molecules, because its peak gradually shifts to lower frequency with decreasing water content as a result of the removal of water molecules (DelaCaillerie et al., 1997; Kim and Lee, in review). The broad peak for hydrogen bonded silanol and small peak for isolated silanol is observed at ~ 7 ppm and 2 ppm, respectively. With increasing temperature the peak intensity for isolated silanol increases as the hydrogen bond strength of hydrogen-bonded silanol decreases (GCA reference). Although the 1.4 ppm peak for CH₂ in the alkyl group almost disappears, the peak for CH₃ in the alkyl group also observed at 1 ppm. At 873 K, the only hydrous species including water and silanol are observed, and the proton signals for organic molecules totally disappear. At 1073 K, the isolated silanol is the single
Figure 4.1. $^1$H MAS NMR spectra at 9.4 T with increasing temperature from room temperature up to 1273 K for 2 amorphous silica gel.
proton environment is amorphous silica gel. At 1273 K, there is no detectable proton atom in $^1$H MAS NMR spectrum, indicating the dehydration process of amorphous silica gel is completed.

4.3.2. $^{29}$Si MAS NMR Result

Figure 4.2 shows the $^{29}$Si MAS NMR spectra for amorphous silica gel with increasing annealing temperature from 298 K to 1473 K, where the $Q^2$ (-91 ppm), $Q^3$ (-101 ppm), and $Q^4$ (-110 ppm) species partially resolved. The $Q^2$, $Q^3$, and $Q^4$ species in pure amorphous silica refer Si sites in geminal silanol [(Si-O)$_2$=Si=(OH)$_2$], single silanol [(Si-O)$_3$≡Si−OH], and siloxane [(SiO)$_n$Si] clusters, respectively (Engelhardt and Michel, 1988). Note that the organic molecules such as alkyl group are also observed in as-synthesized amorphous silica gel, thus $Q^2$ and $Q^3$ also could refer Si sites in (Si-O)$_2$=Si=(O-R)$_2$ and (Si-O)$_3$≡Si−(O-R), respectively, where R is the organic group. The $^{29}$Si MAS NMR spectra show that the fractions of $Q^2$ and $Q^3$ structures are larger than $Q^4$ structures in as-synthesized silica gel, indicating significant fraction of silnols exist in the sample. This result is consistent with those of the previous studies for amorphous silica gel. At 673 K, the peak intensities of $Q^2$ and $Q^3$ structures significantly decrease. The atomic scale dehydration model for amorphous silica in chapter 3 presented that dehydroxylation (i.e., condensation of hydroxyl group) occurs above 873 K in pure amorphous silica nanoparticles. According to that, the reduction of $Q^2$ and $Q^3$ structures at 673 K should not be a result of dehydration, and should be due to a destabilization of organic
Figure 4.2. $^{29}$Si MAS NMR spectra for amorphous silica gel at 9.4 T with increasing temperature from room temperature up to 1473 K.
molecules on the surface of amorphous silica gel. These results are consistent with the $^1$H NMR results in chapter 5.3.1. With increasing annealing temperature from 673 K up to 1273 K, the fraction $Q^4$ structure increases gradually at the expense of $Q^2$ and $Q^3$ structures. According to the $^1$H NMR results, the temperature-induced change in $Q^n$ structures above 673 K is due to dehydroxylation, because the organic molecules disappear above that. Though the results can be obscured by the overlap among peaks, the $Q^4$ peak position slightly moves to lower frequencies with increasing temperature. The observed change in peak position suggests that the mean Si-O-Si bond angle can increase with the dehydration process (Mauri et al., 2000; Smith and Blackwell, 1983; Xue and Kanzaki, 1998). At 1273 K, the $Q^4$ structure is the single silicon structure in amorphous silica gel, indicating the end of dehydration of amorphous silica gel.

The $^{29}$Si MAS NMR spectra were fitted with several constraints concerning peak position and width for semi-quantitative insights into the changes in $Q$ species with varying temperature: note that we fitted the spectra with fixed peak width and position at -92.3, -102.2, -110.2 ppm for $Q^2$, $Q^3$, and $Q^4$ species, respectively. The FWHM (Full Width at Half Maximum) is set to 3.4 ppm for both $Q^2$ and $Q^3$ species, based on results of several trial fittings. The FWHM of $Q^4$ species is fixed at 4.8 ppm. Figure 4.3 shows the fitting results of $^{29}$Si MAS NMR spectra for amorphous silica gel with increasing temperature with three Gaussian peaks. The fitting results indicate that the fractions of $Q^2$, $Q^3$, and $Q^4$ are $8 \pm 3\%$, $49 \pm 5\%$, and $43 \pm 7\%$ for as-received amorphous
Figure 4.3. Simulation of $^{29}$Si MAS NMR spectra for amorphous silica gel with increasing temperature.
Figure 4.4. Population of Si atom species for amorphous silica gel with increasing dehydration temperature.
silica gel. Figure 4.4 presents the population of $Q^n$ structures in amorphous silica gel. With increasing temperature up to 1273 K, the fraction of $Q^2$ and $Q^3$ gradually decreases. While the reduction of $Q^2$ species occurs above 673 K, the significant reduction of $Q^3$ species is observed after annealing at 673 K. These results indicated that organic molecules such as alkyl group is generally adsorbed in $Q^3$ species rather than $Q^2$ species, because the dehydroxylation of amorphous silica nanoparticles is generally occurs above 773 K.

4.3.3. $^{17}$O MAS NMR Result

Figure 4.5 shows the $^{17}$O MAS NMR spectra for as-synthesized amorphous silica gel collected at different magnetic field (9.4 and 14.1 T), showing characteristic quadrupolar line shape of oxygen sites in amorphous silica gel. The peak width decrease apparently in $^{17}$O MAS NMR spectra collected at 14.1 T than at 9.4 T, because the contribution of quadrupolar broadening in the peak decreases as static magnetic field increases (i.e., quadrupolar broadening $\propto 1/B_0$). Although several oxygen sites including Si–OH, Si–O–C, and Si–O–Si are expected to present in as-synthesized amorphous silica gel on the basis of $^1$H and $^{29}$Si MAS NMR results, the single peak is observed at ~40 ppm in both $^{17}$O MAS NMR spectra collected at 9.4 T and 14.1 T. On the basis of previous studies, the single peak at ~40 ppm is assigned to bridging oxygen (i.e., oxygen site in Si-O-Si unit). However, other peaks for the Si–OH or Si–O–C sites are not observed well. The NMR parameters for Si-O-Si and Si-OH sites in amorphous silica studied in previous
Figure 4.5. $^{17}$O MAS NMR spectra for amorphous silica gel collected at 9.4 and 14.1 T.
studies are given in Table 4.1.

The lack of $^{17}$O peaks for Si-O-H in the $^{17}$O MAS NMR spectra for as-synthesized amorphous silica gel may originates the very short $T_1$ (~0.1 ms) and small $C_q < 200$ kHz of hydroxyl oxygen (van Eck et al., 1999). In order to observe the Si-OH in as-synthesized amorphous silica gel, the acquisition parameters are need to be optimized, because the $^{17}$O nutation curve for Si-O-Si structure behaves like solid, that for Si-OH behaves like liquid (van Eck et al., 1999). Figure 4.6 shows the $^{17}$O MAS NMR spectra for as-synthesized amorphous silica gel collected at 14.1 T with varying pulse length, showing the two $^{17}$O sites having different nutation frequency. With increasing pulse length from 1.0 to 2.9 µs, the peak at ~40 ppm for bridging oxygen decreases, whereas the peak intensity at ~15 ppm increases. Based on the previous work, the peak at ~ 15 ppm is assigned to hydroxyl oxygen, having low $C_q$ less than 200 kHz. This result is consistent with previous $^{17}$O NMR study for produced silica (van Eck et al., 1999).

Figure 4.7 presents the $^{17}$O MAS NMR spectra at 9.4 T for amorphous silica gel with increasing temperature up to 1273 K, showing the gradual variation in oxygen environments in the sample. The quadrupolar line shape and peak intensity changes significantly with increasing annealing temperature from 298 K up to 873 K. These results may originate from a removal of water and organic molecules on the surface of amorphous silica gel. Though slight, changes in peak intensity in $^{17}$O NMR spectra for amorphous silica gel are observed with increasing temperature above 873 K up to 1273 K. These changes
Table 4.1. $^{17}$O MAS NMR parameters for oxygen atoms in amorphous silica

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$C_q$ (MHz)</th>
<th>$\eta$</th>
<th>Ref*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica gel</td>
<td>Si-O-Si</td>
<td>42</td>
<td>5.3</td>
<td>0</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>Si-O-H</td>
<td>~0±20</td>
<td>&lt; 0.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si-OH</td>
<td>~20</td>
<td>2.8-3.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Amorphous silica</td>
<td>Si-O-Si</td>
<td>50</td>
<td>5.8</td>
<td>0</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>Si-O-H</td>
<td>20</td>
<td>4</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Silica gel</td>
<td>Si-O-H</td>
<td>-10</td>
<td>4.4</td>
<td>0</td>
<td>(3)</td>
</tr>
<tr>
<td>Crystalline KHSi$_2$O$_5$</td>
<td>Si-O-Si</td>
<td>51</td>
<td>4.95</td>
<td>0.1</td>
<td>(4)</td>
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<tr>
<td></td>
<td>Si-O-H</td>
<td>60</td>
<td>3.5</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Silicate cluster*</td>
<td>Si-O-H</td>
<td>10~19</td>
<td>7~8</td>
<td>0.47~0.53</td>
<td>(5)</td>
</tr>
</tbody>
</table>

*(1) Van Eck et al., 1999; (2) Walter et al., 1998; (3) Cong and Kirkpatrick, 1996; (4) Oglesby et al., 2001; (5) Xue and Kanzaki, 2001
Figure 4.6. $^{17}$O MAS NMR spectra for amorphous silica gel collected at 14.1 T with varying radio frequency pulse length.
in $^{17}$O NMR spectra above 673 K certainly originate from dehydration of hydroxyl group in amorphous silica gel, because the peaks for organic molecules are not observed in $^1$H NMR spectra above 873 K. Figure 4.8 presented the difference between $^{17}$O MAS NMR spectra for annealed amorphous silica gel at different temperature, shows the oxygen environments dehydrated with increasing temperature. The difference in $^{17}$O MAS NMR spectra between 298 K and 673 K shows the significant quadrupolar line, which would corresponding oxygen sites in hydrogen bonded Si-OH and Si-O-C. Though the signal to noise (S/N ratio) is rather low, the quadrupolar pattern at ~ 30 ppm is also observed in the differences in $^{17}$O MAS NMR spectra between 673 K and 1073 K as well as between 873 K and 1073 K. The reduced signal in $^{17}$O MAS NMR spectra with increasing temperature from 873 K to 1073 K should be assigned to oxygen site in isolated silanol(i.e., Si-OH), because isolated silanol is the single proton environments in amorphous silica gel above 873 K. These results imply that the NMR parameters for oxygen site in isolated silanol can be measured with increasing annealing temperature of amorphous silica gel. Unfortunately, the $^{17}$O MAS NMR spectra with higher S/N ratio are necessary to obtain accurate NMR parameters for oxygen site in Si-OH with varying hydrogen bond strength. Further experiments are currently undergoing to collect extremely high S/N ratio of amorphous silica gel and an analysis of correlation between Cq of oxygen site in Si-OH and hydrogen bond strength would be achieved in the near future.
Figure 4.7. $^{17}$O MAS NMR spectra for amorphous silica gel at 9.4 T with increasing temperature from room temperature up to 1473 K.
Figure 4.8. Reduced oxygen signals in $^{17}$O MAS NMR spectra for amorphous silica gel during annealing at different annealing temperatures.
References


Chapter 5. Effect of particle size on phase transitions in metastable alumina nanoparticles: A view from high-resolution solid-state $^{27}$Al NMR study


Abstract

Detailed knowledge of the atomic structures of diverse metastable/stable polymorphs in alumina nanoparticles with varying particle size is essential to understand their macroscopic properties and their phase transition behaviors. In this study, we report high-resolution solid-state $^{27}$Al 2D triple-quantum (3Q) magic-angle spinning (MAS) and 1D MAS nuclear magnetic resonance (NMR) spectra for alumina nanoparticles with varying temperature and particle size with an aim to explore the nature of phase transitions in alumina nanoparticles. Although the $^{27}$Al MAS NMR spectra of alumina nanoparticles cannot fully resolve all the crystallographically distinct Al sites for metastable aluminas such as $\gamma$, $\delta$, and $\theta$-$\text{Al}_2\text{O}_3$, the simulation of $^{27}$Al MAS NMR spectra collected at different magnetic fields following the Czjzek model allows us to obtain the quantitative fractions of alumina polymorphs in nanoparticles and the NMR characteristics of their Al sites. The $^{27}$Al 3QMAS NMR spectra resolved crystallographically distinct $[^6]$Al and $[^4]$Al sites in ($\gamma$, $\delta$)- and $\theta$-$\text{Al}_2\text{O}_3$ in the isotropic dimension for the first time. The fraction of $\theta$-$\text{Al}_2\text{O}_3$ gradually increases up to $\sim$1473 K at the expense of a decrease in ($\gamma$, $\delta$)-
Al₂O₃. The onset of formation of α-Al₂O₃ from metastable aluminas is observed above ~1493 K. Several phase transitions in alumina nanoparticles observed in the current study include, γ, δ → θ-Al₂O₃, γ, δ → α-Al₂O₃, and θ → α-Al₂O₃. Although the phase transition γ, δ → θ-Al₂O₃ occurs gradually with increasing annealing temperature from 873 K to 1473 K, the phase transitions γ, δ → α-Al₂O₃ and θ → α-Al₂O₃ occur dramatically within a narrow temperature range between 1473 K and 1573 K. The observed difference in temperature range (gradual vs. dramatic) for phase transition γ, δ → θ-Al₂O₃ and γ, δ, θ → α-Al₂O₃ originates from the different structural disorder in the metastable aluminas (i.e., γ-, δ-, θ-) and α-Al₂O₃. The effect of particle size on the phase transition (γ, δ) → θ-Al₂O₃ between 298 K and ~1473 K is not observed significantly. On the other hand, the transition temperature for γ, δ, θ → α-Al₂O₃, where the 50 % for alumina is α-Al₂O₃, apparently increases as the particle size increases (as evidenced by TEM observation), indicating a larger energy penalty for phase transitions into α-Al₂O₃ in larger alumina nanoparticles. This could be due to higher surface energy of θ-Al₂O₃ than that of α-Al₂O₃ and/or the fact that transition from θ-Al₂O₃ to α-Al₂O₃ is kinetically favored for smaller nanoparticles. The mechanistic details of phase transitions among alumina polymorphs provided in the current study yield insights into the nature of the phase transition mechanisms for other oxide nanoparticles ubiquitous in the earth’s surface environment.
5.1. Introduction

The atomic structure of alumina and the phase transition mechanism have long been investigated in many experimental and theoretical studies due to its fundamental interest as one of the simplest covalent oxides (Fitzgerald et al., 1997; Gan et al., 2009; Hagaman et al., 2010; John et al., 1983; Kryukova et al., 2000; Levin and Brandon, 1998; MacKenzie and Smith, 2002; O'Dell et al., 2007; Ollivier et al., 1997; Perander et al., 2007; Pinto et al., 2004; Repelin and Husson, 1990). Alumina also has diverse industrial uses, for example, in catalysts, adsorbents, and gate microelectronic devices (e.g., (Kresse et al., 2005). Given these important roles of alumina, the atomic structures of diverse alumina polymorphs are relatively well known (Levin and Brandon, 1998) and references therein). However, the nature of phase transitions among alumina polymorphs is not fully understood due to manifested configurational disorder and their pronounced metastability (see below for further discussion), which leads to broad ranges of transition temperatures rather than a single well-defined transition temperature between polymorphs. Additionally, the effect of particle size on phase transitions among metastable phases in nanoparticles has not been fully investigated. Because the large surface area of nanoparticles plays an essential role in controlling their phase transition behaviors, it is necessary to explore the effect of particle size on the transition temperature of alumina nanoparticles. The objective of this study is to investigate the effect of particle size on the nature of phase transitions among alumina
polymorphs including metastable phases in alumina nanoparticles.

In addition to the well-known stable $\alpha$-$\text{Al}_2\text{O}_3$ with a corundum structure, diverse metastable polymorphs have also been reported. These include $\gamma$-, $\delta$-, $\theta$-, $\kappa$-, $\chi$-, and $\eta$-$\text{Al}_2\text{O}_3$, and are often called metastable aluminas with their stability fields depending on the annealing temperature, time, and types of precursor (Levin and Brandon, 1998) and references therein). For instance, $\gamma$-$\text{AlOOH}$ (i.e., boehmite) transforms to $\alpha$-$\text{Al}_2\text{O}_3$ via $\gamma$-, $\delta$-, and $\theta$-$\text{Al}_2\text{O}_3$. The transition temperatures between $\gamma$- and $\delta$-$\text{Al}_2\text{O}_3$, between $\delta$- and $\theta$-$\text{Al}_2\text{O}_3$, and between $\theta$- and $\alpha$-$\text{Al}_2\text{O}_3$ are $\sim$ 700–800, 900–1000, and 1000–1100°C, respectively (Levin and Brandon, 1998; Santos and Santos, 1992) and references therein). Extensive studies of temperature-induced phase transitions of alumina have revealed that the temperature of the transition from metastable alumina such as $\gamma$- and $\theta$-$\text{Al}_2\text{O}_3$ into stable $\alpha$-$\text{Al}_2\text{O}_3$ varied with the particle size (Bokhimi et al., 2001; Gan et al., 2009), defects density (Liu et al., 2005), and presence of seeds (Nordahl and Messing, 2002; Rajendran, 1994).

In particular, the particle size (i.e., surface area) of alumina nanoparticles has been identified as one of the crucial factors controlling the relative stability of $\gamma$-$\text{Al}_2\text{O}_3$ and its phase transitions (McHale et al., 1997a; Navrotsky, 2001). The effect of particle size on the nature of the phase transitions among alumina polymorphs is due to an increased role of the surface energy with decreasing particle size (e.g., (Navrotsky, 2001). An alumina polymorph with lower surface energy becomes more stable than one with higher surface energy as
Figure 5.1. Crystal structure of (A) $\gamma$-Al$_2$O$_3$, (B) $\theta$-Al$_2$O$_3$, and (C) $\alpha$-Al$_2$O$_3$ with crystallographically distinctive aluminum sites.
the particle size decreases (i.e., the surface area increases). A molecular
dynamics simulation demonstrated that surface energy of $\alpha$-Al$_2$O$_3$ is
larger than that of $\gamma$-Al$_2$O$_3$, which is consistent with calorimetric data
for nanocrystalline alumina (Blonski and Garofalini, 1993; McHale et
al., 1997b). Additional differential thermal analysis for phase transition
from boehmite into $\alpha$-Al$_2$O$_3$ showed that transition temperature for $\gamma$
$\rightarrow$ $\alpha$-Al$_2$O$_3$ decreases from 1565 K to 1465 K as the crystallite size of
boehmite decreases (Bokhimi et al., 2001). The systematic,
spectroscopic study of the effect of particle size of $\gamma$-Al$_2$O$_3$
nanoparticles and other alumina polymorphs remains to be explored.

The atomic structure and phase transitions of alumina
polymorphs have been studied mainly using X-ray diffraction (XRD),
transmission electron microscopy (TEM), and solid-state nuclear
magnetic resonance (NMR) spectroscopy. XRD and TEM studies have
successfully provided the atomic structure of crystalline alumina of the
$\gamma$, $\theta$, and $\alpha$-Al$_2$O$_3$, (Figure 5.1). These studies using TEM and XRD
studies have furthered our understanding of the atomic structure and
phase transition mechanism of metastable aluminas (Gan et al., 2009;
Levin et al., 1997; Lin et al., 2004; Macedo et al., 2007a; Ollivier et al.,
1997; Yang et al., 1988). Its application to heterogeneous metastable
aluminas can, however, be limited because the XRD patterns for those
alumina phases are not well distinguished due to low crystallinity and
significant degree of disorder in the metastable aluminas, (e.g., $\gamma$- and
$\delta$-Al$_2$O$_3$). Furthermore, because the temperature ranges of stability of
each metastable alumina overlap, two or more phases can coexist in a
sample within a given temperature range. It is often difficult to obtain the quantitative fractions of alumina polymorphs using either XRD or TEM (Levin et al., 1997; Ollivier et al., 1997; Yang et al., 1988).

NMR spectroscopy providing short-range structures around a specific nuclide of interest has been particularly effective in exploring the atomic structure of disordered oxide materials. Previous $^{27}$Al magic-angle spinning (MAS) NMR studies have provided the atomic configuration of oxygen and aluminum atoms in crystalline alumina (Fitzgerald et al., 1997; John et al., 1983; MacKenzie and Smith, 2002; Mastikhin et al., 1981; O’Dell et al., 2007; Piedra et al., 1996) as well as amorphous alumina thin films (Lee et al., 2009b; Lee et al., 2010b). The atomic scale structure of quadrupolar nuclei (e.g., $^{27}$Al) in alumina can be described by structurally relevant NMR parameters such as the quadrupolar coupling constant ($C_q$), asymmetry parameter ($\eta$), and isotropic chemical shift ($\delta_{iso}$). Simulation of the 1D MAS NMR spectra with these NMR parameters allows us to obtain the quantitative fraction of each phase in a sample with heterogeneous mixtures of multiple phases (as is the case for the current nanoparticles) (Ashbrook and Duer, 2006; Ashbrook and Smith, 2006; Duer, 2004; Lee and Stebbins, 2003; Lee et al., 2003; Lee and Weiss, 2008; Phillips, 2000). To confirm the NMR characteristics of Al sites in alumina polymorphs, previous $^{27}$Al NMR studies of alumina have analyzed the spinning sideband and simultaneously simulated $^{27}$Al MAS NMR spectra $\theta$- and $\alpha$-$\text{Al}_2\text{O}_3$ collected at different magnetic fields (O’Dell et al., 2007; Pecharroman et al., 1999; Perander et al., 2007; Sabarinathan et al.,
The analysis of spinning sideband patterns in $^{27}$Al MAS NMR spectra has yielded excellent results and confirmed the NMR parameters of Al sites in $\alpha$-Al$_2$O$_3$ (Pecharroman et al., 1999; Sabarinathan et al., 2010). A simulation of the central transition peak in $^{27}$Al MAS NMR spectra measured at different magnetic fields (e.g., 8.4 T and 14.1 T) also successfully obtained the NMR parameters for Al sites in $\theta$-Al$_2$O$_3$ (O'Dell et al., 2007). A recent study also reported the simulation of $^{27}$Al MAS NMR spectra for $\gamma$-Al$_2$O$_3$ using the Czjzek model that have been effective in resolving Al sites in the disordered oxides (de Lacaille et al., 2008; Lee et al., 2009a; Massiot et al., 2002; Neuville et al., 2004).

Recent progress in 2D triple-quantum (3Q) MAS also provide much improved resolution among the different sites for quadrupolar nuclides (e.g., $^{27}$Al, $^{17}$O) (Lee, 2005; Lee et al., 2010a; Massiot et al., 1996; Neuville et al., 2004; Stebbins et al., 2000; Stebbins et al., 1999; Tangeman et al., 2004; Xue et al., 2010). $^{27}$Al 3QMAS NMR method has been used to elucidate the atomic scale structures of a single phase of crystalline and amorphous alumina (e.g., $\gamma$-Al$_2$O$_3$ or $\alpha$-Al$_2$O$_3$) as well as aluminum (oxy)hydroxides (e.g., boehmite, bayerite, gibbsite) (Chupas et al., 2001; Damodaran et al., 2002; Hagaman et al., 2010; Lee et al., 2009b; Lee et al., 2010b), and thus it may also be useful to resolve crystallographically distinct Al sites in multiple phases of alumina with varying temperature.

Here, we explore the atomic structure of alumina polymorphs and the effect of particle size on the nature of phase transitions in
alumina nanoparticles using high-resolution solid-state NMR. The NMR characteristics as well as fractions of Al sites in metastable aluminas are obtained by simulating \(^{27}\text{Al}\) MAS NMR spectra measured at different magnetic fields. We also report the first \(^{27}\text{Al}\) 3QMAS NMR spectra of resolved alumina nanoparticles resolving alumina polymorphs including (\(\gamma, \delta\))-\(\theta\)- and \(\alpha\)-\(\text{Al}_2\text{O}_3\). On the basis of the data from these NMR results, we provide an improved insight into the nature of phase transitions of alumina nanoparticles with emphasis on the effect of particle size.

5.2. Experimental Methods

5.2.1. Sample Preparation and Characterization

Three types of alumina nanoparticles, FA51, FA81, and FA100 (Cabot Co., SpectAl series) with surface areas of 55±10, 79±10, and 97±19 m\(^2\)/g, respectively, were used. The particle sizes (i.e., diameters) of the alumina nanoparticles calculated using a spherical approximation \(d = 6/S_0\rho\), where \(d\) is the average particle size, \(S_0\) is the specific surface area, and \(\rho\) is the true density of the material) are 27, 19, and 15 nm for FA51, FA81, and FA100, respectively. Here, we refer to FA51, FA81, and FA100 as 27, 19, and 15 nm alumina nanoparticles, respectively. The alumina nanoparticles were heated for 2 h at temperatures ranging from 873 to 1473 K in a vertical tube furnace. As for standard metastable alumina, the crystalline \(\gamma\)-alumina was also purchased from Sigma Aldrich (product no. 544833).
5.2.2. X-ray Diffraction Spectroscopy and Transmission Electron Microscopy

The X-ray diffraction patterns were collected on New D8 Advance (Bruker) using Cu Kα X-rays, a 2θ range of 15–75°, a step width of 0.02°, and a scan rate of 1°/min. The transmission electron microscopy (TEM) study was performed on a 300 kV JEM-2100 instrument (JEOL Ltd.) with a Gatan digital camera. The specimens for electron microscopy were prepared by suspending them in ethanol and placing a few droplets of the suspension on a carbon-coated film.

5.2.3. $^{27}$Al NMR Spectroscopy

$^{27}$Al MAS spectra were collected at various magnetic fields on Varian 400 MHz (9.4 T), Bruker 500 MHz (11.7 T), and Varian 600 MHz (14.1 T) spectrometers with a triple resonance 4 mm Bruker probe, 4 mm Doty Scientific MAS probe, and 2.5 mm Varian probe, respectively. Single-pulse acquisition with a pulse length of 0.2 μs [radio frequency tip angle of about 15° for solids] was used with a recycle delay of 1 s and spinning speeds of 15 kHz at 9.4 and 11.7 T and 20 kHz at 14.1 T. The simulation of $^{27}$Al MAS spectra was performed with the Dmfit program (Massiot et al., 2002). $^{27}$Al 3QMAS NMR spectra were collected on the Varian 400 MHz (9.4 T) spectrometer using a fast amplitude modulation- (FAM-) based shifted-echo pulse sequences (1 s relaxation delay–3.0 μs pulse for 3Q excitation–$t_1$ delay–FAM pulse train with a 0.6 μs pulse-echo delay–15 μs soft pulse for echo reconversion–$t_2$ acquisition) with a spinning speed of 15 kHz.
(Kentgens and Verhagen, 1999; Madhu et al., 1999). An AlCl₃ solution of 2 mol% was used as an external frequency standard.

5.3. Results and Discussion

5.3.1. Characterization of Alumina Nanoparticles

Figure 5.2 shows TEM images of alumina nanoparticles of several sizes with increasing annealing temperature. The as-received alumina nanoparticles are mostly spherical and aggregated. Although the particle sizes varies (from ~16 to ~50 nm for FA51, from ~14 to ~26 nm for FA81, and from ~8 to ~16 nm for FA100), the average particle sizes are similar to the calculated sizes (i.e., 27, 19, and 15 nm for FA51, FA81, and FA100, respectively). The particle size of γ, δ, and θ phases seems invariant upon annealing and drastically increases up to ~100 nm with phase transition into α-Al₂O₃ above 1473 K. This result is consistent with the result from previous electron microscopic observation [e.g., TEM and scanning electron microscope (SEM) images] (Nordahl and Messing, 2002; Wu et al., 1996).

Figure 5.3 presents the XRD patterns of as-received alumina nanoparticles and γ-Al₂O₃. The results show that the multiple phases of alumina exist in the samples: the XRD pattern for 27 nm alumina nanoparticles shows diffraction peaks for crystalline γ-, δ-, and θ-Al₂O₃, and those for 15 and 19 nm alumina nanoparticles mainly consists of γ- and δ-Al₂O₃. We note that the quantitative estimation of the fractions of alumina polymorphs in the nanoparticles using XRD is often difficult because metastable alumina phases are not well distinguished.
Figure 5.2. TEM images of (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles before and after annealing at various temperatures.
**Figure 5.3.** XRD patterns for $\gamma$-Al$_2$O$_3$ and alumina nanoparticles. Red, blue, and purple vertical lines correspond to the peak positions and intensities of $\gamma$-Al$_2$O$_3$ (JCPDS file no.00-050-0741), $\delta$-Al$_2$O$_3$ (JCPDS file no.00-016-0394), and $\theta$-Al$_2$O$_3$ (JCPDS file no.00-23-1009), respectively.
(Cava et al., 2007; Macedo et al., 2007b). Furthermore, the diffraction peak positions (i.e., \(2\theta\) values) for metastable aluminas are similar (for instance, see diffraction peaks for \(\delta\)- and \(\theta\)-\(\text{Al}_2\text{O}_3\) in Figure 5.3). Thus, we attempt to yield quantitative fraction of each alumina phase using NMR (see results and discussion below).

### 4.3.2. \(^{27}\text{Al}\) MAS NMR Spectra

Figure 5.4A shows the \(^{27}\text{Al}\) MAS NMR spectra at 11.7 T for 27, 19, and 15 nm alumina nanoparticles. The \(^{4}\text{Al}\) and \(^{6}\text{Al}\) peaks are well resolved at 0–20 and 50–80 ppm, respectively, showing unique quadrupolar peak shapes. The \(^{27}\text{Al}\) MAS NMR spectrum for 27 nm alumina nanoparticles differs from those for 15 and 19 nm alumina nanoparticles and shows an additional sharp feature at ~10 ppm that is due to \(^{6}\text{Al}\) peak for \(\theta\)-\(\text{Al}_2\text{O}_3\) (in addition to \(\gamma\)- and \(\delta\)-\(\text{Al}_2\text{O}_3\)) in the 27 nm alumina nanoparticles, as also indicated by the XRD result.

Figure 5.4B shows the \(^{27}\text{Al}\) MAS NMR spectra for 27 nm alumina nanoparticles collected at 9.4, 11.7, and 14.1 T. As the magnetic field \((B_0)\) increases, the widths of the \(^{4}\text{Al}\) and \(^{6}\text{Al}\) peaks decrease because the contribution of quadrupolar broadening in the peak decreases with static magnetic field (i.e., quadrupolar broadening \(\propto 1/B_0\)) (Ashbrook and Duer, 2006; Duer, 2004; MacKenzie and Smith, 2002). Crystallographically distinct aluminum sites in \(\gamma\)-, \(\delta\)-, and \(\theta\)-\(\text{Al}_2\text{O}_3\) are not fully resolved in the \(^{27}\text{Al}\) MAS NMR spectra even at 11.7 T, mainly due to their similar peak positions for \(^{4,6}\text{Al}\) sites and disordered structure of \(\gamma\)- and \(\delta\)-\(\text{Al}_2\text{O}_3\). In the current \(^{27}\text{Al}\) MAS NMR
results, γ- and δ- Al₂O₃ are not well distinguished from each other. The lack of resolution between γ- and δ-Al₂O₃ in alumina nanoparticles is due to their similar atomic environments and pronounced topological disorder and thus to similarities in the peak positions of γ-, δ-, and θ-Al₂O₃ (Pecharroman et al., 1999): the δ-Al₂O₃ consists of a superlattice of the γ-Al₂O₃ structure with ordered cation vacancies (Jayaram and Levi, 1989). Simulation of the central transition peaks in these ²⁷Al MAS NMR spectra collected at varying static magnetic field allows us to quantitatively discriminate crystallographically distinct Al sites in metastable alumina nanoparticles (see section 3.3. below for further information).

Figure 5.5A–C present the ²⁷Al MAS NMR spectra at 11.7 T for 27, 19, and 15 nm alumina nanoparticles, respectively, with increasing annealing temperature up to 1573 K. The spectra show subtle, gradual changes in the quadrupolar peak shapes for the [⁴]Al and [⁶]Al sites. With increasing temperature up to 1473 K, an increase in the intensity of the sharp feature at ~10 ppm, the [⁶]Al site in θ-Al₂O₃, is obvious. Though slight, changes in [⁴]Al peak shape are indeed observed with increasing temperature, which may indicate changes in the atomic environment around Al during the phase transition γ → δ → θ-Al₂O₃ (see Figure 5.5D). Above 1473 K, a new [⁶]Al peak for α-Al₂O₃ appears at ~14 ppm. The peak is partially resolved from the [⁶]Al peaks for metastable aluminas owing to its symmetric shape and distinct peak position. The peak intensity for [⁶]Al in α-Al₂O₃ increases dramatically with increasing temperature from 1473 K up to 1573 K: the peak
Figure 5.4. (A) $^{27}$Al MAS NMR spectra at 11.7 T for as-received alumina nanoparticles with varying particle size. (B) $^{27}$Al MAS NMR spectra for 27 nm alumina nanoparticles at various magnetic fields.
intensity for $[^4]$Al decreases with increasing temperature above 1473 K because the structure of $\alpha$-Al$_2$O$_3$ has only a $[^6]$Al site. Figure 5.5D compares the $[^6]$Al peaks in the $^{27}$Al MAS NMR spectra of alumina nanoparticles with varying particle size at various temperatures. The fraction of $\alpha$-Al$_2$O$_3$ in alumina nanoparticles annealed between 1473 K and 1573 K varies with the particle size. For instance, the phase transition into $\alpha$-Al$_2$O$_3$ is apparently complete at 1523 K for 15 nm nanoparticles, with $\alpha$-Al$_2$O$_3$ being the only Al site in the nanoparticles. Thus, the 15 nm alumina nanoparticles consist only of $\alpha$-Al$_2$O$_3$ after annealing at 1523 K. However, the 19 and 27 nm nanoparticles still have a significant fraction of metastable aluminas at 1523 K. The phase transition into $\alpha$-Al$_2$O$_3$ is apparently complete at ~1573 K for 27 and 19 nm alumina nanoparticles. These results indicate that transition temperature for $\theta \rightarrow \alpha$-Al$_2$O$_3$ decreases with decreasing particle size.

5.3.3. Quantification of Metastable Alumina Phases in Nanoparticles

The quantitative fraction of each alumina polymorph in nanoparticles can be estimated from the analysis of the unique quadrupolar peak shape for each Al sites with NMR parameters including $C_q$, $\eta$, and $\delta_{iso}$. The NMR parameters for $[^4,6]$Al sites in the metastable aluminas studied in previous and current studies are given in Table 4.1. Although the NMR parameters for the $[^4,6]$Al sites of $\theta$- and $\alpha$-Al$_2$O$_3$ were generally confirmed, those for $\gamma$-Al$_2$O$_3$ show a wide range of variation (Hagaman et al., 2010; Kraus et al., 1996; O'Dell et al., 2007; Pecharroman et al., 1999; Sabarinathan et al., 2010; Skibsted et al., 1991):
reported \( C_q \) values for the \(^{[6]}\)Al site in \( \gamma\)-Al\(_2\)O\(_3\) varies from 4±1 to 7.5±1 MHz (Hagaman et al., 2010; Kraus et al., 1996; Perander et al., 2007). Additionally, the NMR parameters for the \(^{[4,6]}\)Al sites in \( \delta\)-Al\(_2\)O\(_3\) have not been reported. The simultaneous simulation of \(^{27}\)Al NMR spectra collected at different magnetic fields allows us to obtain robust NMR parameters (O’Dell et al., 2007; Perander et al., 2007). In the current study, following protocols has been used to obtain NMR parameters for the Al sites in the alumina phases. First, we roughly simulated the spectra at 11.7 T using the previously reported NMR parameters for each phase (Table 4.1). Then, we adjusted the detailed NMR parameters by simulating the spectra collected at 9.4 T, 11.7, and 14.1 T simultaneously, with a constraints of intensity ratio between \(^{[4]}\)Al and \(^{[6]}\)Al for each alumina phase. Detailed information on the NMR parameters for alumina nanoparticles studied in the current study is also given in Table 4.2.

Figure 5.6 shows the \(^{27}\)Al MAS NMR spectra that were simulated simultaneously at 9.4, 11.7, and 14.1 T. The simulation of the \(^{[4]}\)Al and \(^{[6]}\)Al peaks for \((\gamma, \delta)\)-Al\(_2\)O\(_3\) in the \(^{27}\)Al MAS NMR spectrum were performed using the Czjzek model (de Lacaillerie et al., 2008; Lee et al., 2009a; Massiot et al., 2002; Neuville et al., 2004). Taking into consideration expected similarity between NMR parameters for \(^{[4,6]}\)Al sites in \((\gamma, \delta)\)-Al\(_2\)O\(_3\), we consider a single \(^{[4]}\)Al and \(^{[6]}\)Al peak for \((\gamma, \delta)\)-Al\(_2\)O\(_3\). The average \( C_q \) and \( \delta_{iso} \) for \(^{[4]}\)Al in \((\gamma, \delta)\)-Al\(_2\)O\(_3\) are 5.7±1.0 MHz and 72±3 ppm, respectively, and those for \(^{[6]}\)Al are 4.2±1.0 MHz and 14±3 ppm. We also collected the \(^{27}\)Al MAS NMR spectrum for
Figure 5.5. $^{27}$Al MAS NMR spectra at 11.7 T for (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles with increasing annealing temperature up to 1573 K. (D) Comparison of $^{15}$Al peaks in $^{27}$Al MAS NMR spectra for alumina nanoparticles with varying particle size.
standard γ-Al₂O₃ [single phase, sigma Aldrich, product no. 544833, mixture of nanorods (~ 50 nm length) and nanoparticles (~ 10 nm diameter)]. The spectrum was also simulated well with similar approach: δ_{iso} = 72.5±3.0 ppm, C_q = 5.7±1.0 MHz for the [4]Al site and δ_{iso} = 14±2 ppm, C_q = 4.7±1.0 MHz for the [6]Al site. These NMR parameters for the [4,6]Al sites in (γ, δ)-Al₂O₃ show intermediate value between those reported in previous studies of γ-Al₂O₃ (Hagaman et al., 2010; Kraus et al., 1996; O’Dell et al., 2007; Pecharroman et al., 1999; Perander et al., 2007).

We note that there is a minor but detectable difference in NMR line shape for [6]Al sites and relative peak intensity ([4]Al/[6]Al) in the standard γ-phase (sigma Aldrich, 544833) and the γ-Al₂O₃ in the mixed phases, indicating that the particle size and morphology of the particles may lead to a slight change in structural distortion and thus NMR parameters. Similar particle size effect on NMR parameters, particularly C_q, has been observed for α-alumina nanoparticles (Sabarinathan et al., 2010). Currently, the changes in these NMR parameters are relatively small (see Table 4.2) and thus are within uncertainty. Yet this potentially interesting effect of particle size remains to be explored.

The $^{27}$Al NMR parameters for θ-Al₂O₃ are δ_{iso} = 80.5 ppm, C_q = 6.0 MHz, and η_q = 0.7 for the [4]Al site and δ_{iso} = 10.5 ppm, C_q = 3.45 MHz, and η = 0.0 for the [6]Al site, respectively. These results are consistent with those from previous studies (O’Dell et al., 2007; Pecharroman et al., 1999). Note that the quadrupolar NMR parameters
Table 5.1. $^{27}$Al NMR parameters for metastable and $\alpha$ alumina

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<th>$\eta$</th>
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<td>(3)</td>
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*(1) Perander et al., 2007; (2) Kraus et al., 1996; (3) Hagaman et al., 2010; (4) O’Dell et al., 2007; (5) Pecharroman et al., 1999; (6) Sabarinathan et al., 2010 (7) Skibsted et al., 1991
Table 5.2. $^{27}$Al NMR parameters for simulation of $^{27}$Al NMR spectra. $\delta_{iso}$ is the isotropic chemical shift, $C_q$ is the quadrupolar coupling constant, $\eta$ is the asymmetry parameter. The $\Delta \delta_{iso}$ is the full width at half-maximum of the distribution of the isotropic chemical shift in the Czjzek model, which is used for simulation of the $[4]$Al and $[6]$Al peaks for $(\gamma, \delta)$-$Al_2O_3$. The $[4]$Al:$[6]$Al ratio in ideal $\gamma, \delta, \theta$- and $\alpha$-$Al_2O_3$ is 25:75, 38:62, 50:50, and 0:100, respectively (Pecharroman et al., 1999; Repelin and Husson, 1990).

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<th>Sample</th>
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<th>$\delta_{iso}$ (ppm)</th>
<th>$\Delta \delta_{iso}$ (ppm)</th>
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<th>$\eta$</th>
<th>$[n]$Al/($[4]$Al+$[6]$Al) $\times 100$ (%)</th>
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*The quadrupolar NMR parameters, such as $v_q$, $\eta$ and $\sigma$ are correlated among each other. The relations among them can be described with the following equation (de Lacaillerie et al., 2008):

$$\langle C^2_q \rangle = \left(\frac{2}{3} I(2I-1)\right)^2 \langle v^2_q (1+\eta^2/3) \rangle = \left(\frac{2}{3} I(2I-1)\right)^2 5\sigma^2$$
In Dmfit program (version released in 2011) used in the current study, therefore, $C_q$ is used as an input parameter and the $\sigma$ value is automatically adjusted depending on $C_q$ value: the estimated $\sigma$ is $\sim 380\pm 60$ kHz and $280\pm 50$ kHz for $^{41}$Al and $^{6}$Al sites in $\gamma, \delta$-$Al_2O_3$, respectively.

† The Gaussian or Lorentzian broadening factor ($\sim 300$Hz to 2000 Hz) is applied to simulate Al sites in $\gamma, \delta$-, $\theta$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$, respectively.
Figure 5.6. Simulation of $^{27}$Al MAS NMR spectra for as-received 27 nm alumina nanoparticles at 9.4, 11.7, and 14.1 T and for $\gamma$-$\text{Al}_2\text{O}_3$ at 11.7 T.
are correlated with deviation from perfect tetrahedral or octahedral symmetry (Ghose and Tsang, 1973). The current results imply that deviation from perfect cubic symmetry for Al site in $\theta$-Al$_2$O$_3$ is larger than those for $\gamma$-Al$_2$O$_3$. In contrast, as also deduced from XRD patterns, the dispersion of NMR parameters for Al sites in $\gamma$- and $\delta$-Al$_2$O$_3$ phases indicate a moderate degree of structural disorder around Al sites in $\gamma$- and $\delta$-Al$_2$O$_3$ as previously reported (Lippens and Deboer, 1964). $\theta$-Al$_2$O$_3$ shows less disordered structures as indicated by narrow dispersions in the NMR spectra and XRD patterns (Figures 5.3 and 4.5).

Figure 5.7 shows the simulated $^{27}$Al MAS NMR spectra for alumina nanoparticles with varying particle size and annealing temperature, which provides the quantitative changes in the fractions of each alumina phase in the nanoparticles (see supporting on-line materials for the complete sets of NMR spectra with varying temperature). For the NMR parameters of the $[^{6}]$Al site in $\alpha$-Al$_2$O$_3$, we follow the previously reported values (i.e., $\delta_{iso} = 15.9$ ppm, $C_q = 2.4$ MHz, and $\eta_q = 0$) (Kraus et al., 1998; O’Dell et al., 2007; Sabarinathan et al., 2010; Skibsted et al., 1991). The intensity ratio between the $[^{4}]$Al and $[^{6}]$Al sites in $\theta$-Al$_2$O$_3$ is $\sim$50±5:50±5, which is consistent with the previously reported ratio for the ideal structure of $\theta$-Al$_2$O$_3$ (O’Dell et al., 2007; Pecharroman et al., 1999). Though indirect, $[^{4}]$Al and $[^{6}]$Al ratio in the ($\gamma$, $\delta$)-Al$_2$O$_3$ may provide quantitative fraction of $\gamma$- and $\delta$-Al$_2$O$_3$. The ratios between $[^{4}]$Al and $[^{6}]$Al for ($\gamma$, $\delta$)-Al$_2$O$_3$ in 15, 19, and 27 nm alumina nanoparticles are $\sim$26±8:74±8, 30±8:70±8, and 32±8:68±8,
Figure 5.7. Simulation of $^{27}$Al MAS NMR spectra at 11.7 T for (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles with increasing annealing temperature.
respectively. These are intermediate between the values for the ideal structures of \( \gamma \)- and \( \delta \)-Al\(_2\)O\(_3\): the \([4]Al:[6]Al\) ratios in ideal \( \gamma \)- and \( \delta \)-Al\(_2\)O\(_3\) are about 25:75 and 38:62, respectively (Pecharroman et al., 1999; Repelin and Husson, 1990). The current result may indicate that the fraction of \( \gamma \)-Al\(_2\)O\(_3\) is more significant in a smaller nanoparticles, because the \([4]Al:[6]Al\) ratio in (\( \gamma \), \( \delta \))-Al\(_2\)O\(_3\) approaches the ideal ratio for \( \gamma \)-Al\(_2\)O\(_3\) as the particle size decreases from 27 nm to 15 nm. The fraction of each alumina phase in alumina nanoparticles based on NMR results in the current remains to be tested with other quantitative experimental techniques.

Figure 5.8A–C show the variations in the population of each alumina phase in 27, 19, and 15 nm alumina nanoparticles, respectively, with increasing annealing temperature up to 1573 K, which demonstrates the effect of particle size on the stability field for alumina polymorphs. The population of alumina polymorphs in as-received alumina nanoparticles varies with the particle size. The (\( \gamma \), \( \delta \))-Al\(_2\)O\(_3\): \( \theta \)-Al\(_2\)O\(_3\) ratio is approximately 99±0.5:1±0.5, 96±2:4±2, and 80±3:20±3 for the 15, 19, and 27 nm alumina nanoparticles, respectively. With increasing temperature above ~873 K, the population of \( \theta \)-Al\(_2\)O\(_3\) gradually increases up to ~1473 K at the expense of (\( \gamma \), \( \delta \))-Al\(_2\)O\(_3\). The fractions of \( \theta \)-Al\(_2\)O\(_3\) after annealing at 1473 K are ~16±5\%, 18±5\%, and 38±5\% for 15, 19, and 27 nm alumina nanoparticles, respectively, and thus a major fraction (62%–84\%) of the alumina nanoparticles exist as (\( \gamma \), \( \delta \))-Al\(_2\)O\(_3\). The error bar in the fraction of each alumina phase stems from the deviation from a perfect match between experimental and
simulated spectra (~3%), the contribution from the uncertainties in estimated NMR parameters (~3%), and possible artifacts introducing fixed value for NMR parameters upon simulations (~3%). Taking into consideration of those uncertainties, the total error bar of ±5 % is estimated. The significant fraction of (γ, δ)-Al₂O₃ in the nanoparticles at 1473 K is somewhat unexpected, considering the previously known transition temperatures for γ → δ-Al₂O (700–800°C) and δ → θ-Al₂O (900–1000°C) (Levin and Brandon, 1998 and references therein). However, the presence of γ-Al₂O₃ above 1473 K also has been reported in previously XRD studies for both nanocrystalline and bulk alumina (heating rate of 3-50 K/min) (Bokhimi et al., 2001; Gan et al., 2009). Note that kinetic broadening upon phase transition among nanoparticles may contribute to the presence of larger fractions of (γ, δ)-Al₂O₃. This effect of kinetic broadening on phase transition needs to be explored using further NMR studies with varying annealing time.

Figure 5.8D–F (enlarged plots of Figure 5.8A–C) shows the variation in the population of alumina phases between ~1400 and ~1600 K for alumina nanoparticles. Multiple phases of alumina including γ-, δ-, θ-, and α-Al₂O₃ coexist in alumina nanoparticles from ~1473 K to the temperature at which all phase transitions into α-Al₂O₃ are complete (i.e., ~1573 K for 27 and 19 nm nanoparticles and ~1523 K for 15 nm nanoparticles). With increasing temperature from ~1473 K to ~1573 K, the population of α-Al₂O₃ increases dramatically at the expense of the metastable aluminas. The transition temperature for γ, δ, θ → α-Al₂O₃ decreases with decreasing particle size. In this study, the
Figure 5.8. Variation in populations of (γ, δ)-, θ-, and α-Al₂O₃ in (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles with increasing annealing temperature up to 1573 K. (D–F) show enlarged plots of Figure 5.8A–C at temperatures of 1400 and 1600 K.
transition temperature for $\gamma$, $\delta$, $\theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ is defined by the temperature of which the 50 % of alumina nanoparticles exist in form of $\alpha$-$\text{Al}_2\text{O}_3$. Although the phase transition $\gamma$, $\delta \rightarrow \theta$-$\text{Al}_2\text{O}_3$ occurs gradually with increasing annealing temperature from 873 K to 1473 K, the phase transitions $\gamma$, $\delta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ and $\theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ occur dramatically within a narrow temperature range between 1473 K and 1573 K.

5.3.4. $^{27}$Al 3QMAS NMR Spectra

Figure 5.9A and 4.9B show the $^{27}$Al 3QMAS NMR spectra for 27 nm alumina nanoparticles before and after annealing at 1497 K for 2 h; the resolution is considerably better than that of the $^{27}$Al MAS NMR spectra. The crystallographically distinct $[6]$Al and $[4]$Al sites in ($\gamma$, $\delta$)- and $\theta$-$\text{Al}_2\text{O}_3$ as well as $\alpha$-$\text{Al}_2\text{O}_3$ are resolved in the isotropic dimension. For robust peak assignment, we calculated the expected position for the center of gravity of the $[4,6]$Al sites in $\gamma$-, $\theta$-, and $\alpha$-$\text{Al}_2\text{O}_3$ using previously reported NMR parameters shown in Table 4.1. Figure 5.9C shows the expected position of the center of gravity of the $[4,6]$Al sites for $\gamma$-, $\theta$-, and $\alpha$-$\text{Al}_2\text{O}_3$ in $^{27}$Al 3QMAS NMR spectra (Hagaman et al., 2010; Kraus et al., 1996; O’Dell et al., 2007; Pecharsky et al., 1999; Perander et al., 2007; Sabarinathan et al., 2010; Skibsted et al., 1991). On the basis of plots in figure 5.9C, the peak at -10 ppm in the isotropic dimension is assigned to the $[6]$Al site in $\alpha$-$\text{Al}_2\text{O}_3$, which appears after annealing at 1497 K (Hagaman et al., 2010; Kraus et al., 1996; O’Dell et al., 2007; Sabarinathan et al., 2010; Skibsted et al., 1991). The peaks at -8
Figure 5.9. $^{27}$Al 3QMAS NMR spectra for 27 nm alumina nanoparticles (A) as-received and (B) annealed at 1497 K for 2 h. (C) Expected center of gravity for $\gamma$-, $\delta$-, $\theta$-, and $\alpha$-Al2O3 calculated on the basis of previous works: solid square (Kraus et al., 1996); solid triangle (Perander et al., 2007); solid circle (Hagaman et al., 2010); solid diamond (O’Dell et al., 2007); open circle (Sabarinathan et al., 2010); open diamond (Skibsted et al., 1991); open square (Pecharroman et al., 1999). Red, blue, and purple symbols refer to ($\gamma$, $\delta$)-, $\theta$-, and $\alpha$-Al2O3, respectively.
ppm and -53 ppm in the isotropic dimension are assigned to the $^{[6]}$Al and $^{[4]}$Al sites in $\theta$-Al$_2$O$_3$, respectively (O'Dell et al., 2007; Pecharroman et al., 1999). These $^{[6]}$Al and $^{[4]}$Al peak intensities for $\theta$-Al$_2$O$_3$ increase after annealing at 1497 K, following the $\gamma$, $\delta \rightarrow \theta$ phase transition. The broad peaks ranging from -10 to -20 ppm and at $\sim$ -45 ppm are assigned to unresolved $^{[6]}$Al and $^{[4]}$Al sites in $\gamma$- and $\delta$-Al$_2$O$_3$, respectively as their intensities decrease significantly after annealing at 1497 K (Hagaman et al., 2010; Kraus et al., 2003; Perander et al., 2007). These results are consistent with the temperature-induced phase transition sequence of alumina (i.e., $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$-Al$_2$O$_3$).

Figure 5.10 shows the $^{27}$Al 3QMAS NMR spectra for alumina nanoparticles with varying particle size and annealing temperature; the $^{[4]}$Al and $^{[6]}$Al peaks for ($\gamma$, $\delta$)-, $\theta$-, and $\alpha$- Al$_2$O$_3$ are resolved (see supporting on-line materials for the complete sets of NMR spectra with varying temperature). The $^{[4,6]}$Al peaks for $\theta$-Al$_2$O$_3$ are observed in the $^{27}$Al 3QMAS NMR spectra for the 15 and 19 nm alumina nanoparticles as well as the 27 nm alumina nanoparticles. We note that the presence of $\theta$-Al$_2$O$_3$ is not clear in the XRD patterns for 15 nm and 19 nm alumina nanoparticles (see Figure 5.3). The discrepancy may be due to that small fraction ($\sim$3±2 %) of $\theta$-Al$_2$O$_3$ is not detected using XRD. As the annealing temperature increases to $\sim$1473 K, the peak intensities for the $^{[4,6]}$Al sites in ($\gamma$, $\delta$)-Al$_2$O$_3$ decrease, whereas those for $\theta$-Al$_2$O$_3$ increase. Above 1473 K, the $^{[6]}$Al peak for $\alpha$-Al$_2$O$_3$ is observed, indicating the onset of the $\theta \rightarrow \alpha$ phase transition. These results are consistent with those of the $^{27}$Al MAS NMR spectra.
5.3.5. Effect of Particle Size on Phase Transitions of Metastable Alumina

Several phase transitions in alumina nanoparticles observed in the current study include, (1) $\gamma, \delta \rightarrow \theta$-Al$_2$O$_3$, (2) $\gamma, \delta \rightarrow \alpha$-Al$_2$O$_3$, and (3) $\theta \rightarrow \alpha$-Al$_2$O$_3$. Although the phase transition $\gamma, \delta \rightarrow \theta$-Al$_2$O$_3$ occurs gradually within a broad temperature range between ~ 873 K and 1473 K, both phase transitions, $\gamma, \delta \rightarrow \alpha$-Al$_2$O$_3$ and $\theta \rightarrow \alpha$-Al$_2$O$_3$ occurs within narrow temperature range between ~ 1473 K and 1573 K. The different temperature range between phase transition $\gamma, \delta \rightarrow \theta$ and $\gamma, \delta, \theta \rightarrow \alpha$ may originate from the different structural disorder between the metastable aluminas (i.e., $\gamma$-, $\delta$-, $\theta$-) and $\alpha$-Al$_2$O$_3$. The configurational disorder of $\gamma$- and $\delta$-Al$_2$O$_3$ may induce a gradual $\gamma, \delta \rightarrow \theta$ phase transition from 873 K to 1473 K as has been observed for structural transitions in compressed amorphous oxides (see Lee et al., 2008).

Figure 5.11 presents the normalized variation in the $(\gamma, \delta)$-, $\theta$- and $\alpha$-Al$_2$O$_3$ population with varying particle size and annealing temperature. The normalized variations of $(\gamma, \delta)$- and $\theta$-Al$_2$O$_3$ population in 27, 19, and 15 nm nanoparticles between 298 K and ~1473 K are similar to each other, indicating that the effect of particle size on the phase transition $(\gamma, \delta) \rightarrow \theta$-Al$_2$O$_3$ is not significant. On the other hand, effect of particle size on the variation of $\alpha$-Al$_2$O$_3$ population is obvious between ~ 1473 K and ~ 1673 K. The transition temperature for $\gamma, \delta, \theta \rightarrow \alpha$-Al$_2$O$_3$, where a 50% for alumina is $\alpha$-Al$_2$O$_3$, is 1523±10, 1518±10, and 1490±10 K for 27, 19, and 15 nm alumina nanoparticles, respectively. This result indicates that the phase
Figure 5.10. $^{27}$Al 3QMAS NMR spectra for 15, 19, and 27 nm alumina nanoparticles after annealing at various temperatures.
transition $\gamma, \delta, \theta \rightarrow \alpha$-Al$_2$O$_3$ occurs at lower temperatures for smaller alumina nanoparticles. Although the transition temperature in this study may change with the annealing time because the equilibrium or steady state for phase transitions of alumina may not be reached with an annealing duration of 2 h, the current results can yield insights into the relative difficulty for phase transition $\gamma, \delta, \theta \rightarrow \alpha$-Al$_2$O$_3$. This could be due to higher surface energy of $\theta$-Al$_2$O$_3$ than that of $\alpha$-Al$_2$O$_3$ and/or it could be due to the fact that transition from $\theta$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ is kinetically favored for smaller nanoparticles. A detailed study for surface energy of $\theta$-Al$_2$O$_3$ phase remains to be explored.

In this study, we quantified the fractions of alumina polymorphs in nanoparticles and reported the NMR characteristics of their Al sites using both high-resolution 1D $^{27}$Al MAS and 3QMAS NMR. Particularly, first 2D NMR spectra for complex nanoparticles resolved crystallographically distinct $[6]$Al and $[4]$Al sites in ($\gamma, \delta$)- and $\theta$-Al$_2$O$_3$. The results show that phase transition $\gamma, \delta \rightarrow \theta$-Al$_2$O$_3$ occurs gradually with increasing annealing temperature from 873 K to 1473 K and the phase transitions $\gamma, \delta, \theta \rightarrow \alpha$-Al$_2$O$_3$ occur dramatically within a narrow temperature range between 1473 K and 1573 K. In addition to that, the results clearly demonstrate that phase transition $\gamma, \delta, \theta \rightarrow \alpha$-Al$_2$O$_3$ occurs at lower temperatures for smaller alumina nanoparticles. The current results may be helpful to account for a transition behavior in other simple and complex oxide nanoparticles. Nanoparticles with complex compositions are produced through geochemical (Banfield and Zhang, 2001; Foissner et al., 2009; Hochella et al., 2008) and
mechanical processes (Han et al., 2007) in diverse geological settings. Although the alumina nanoparticles in this study are not ubiquitous in the earth, they are the simplest compound that exhibits the complexities of diverse earth materials. In addition to Al₂O₃, other minerals including Fe₂O₃, TiO₂, and ZrO₂ also exhibit different surface energies among stable and metastable polymorphs, indicating a similar effect of particle size on their relative stability in nanoparticles (Navrotsky, 2004). The potential metastability of earth materials in nano-sized domain may induce heterogeneity of mantle (e.g., nanoscale spinel phases at the olivine-spinel transition at 400 km depth) (Banfield and Zhang, 2001). The structural information on alumina polymorphs and the mechanistic details obtained from the experiments described here provide insights into the nature of the phase transitions of other oxide nanoparticles, highlighting the effects of particle size.
Figure 5.11. Normalized variation in the (A) (γ, δ)- and θ- Al₂O₃, (B) α-Al₂O₃ population in particles of several sizes annealed at several temperatures
References
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Chapter 6. Temperature-induced amorphization of Na-zeolite A: Multi-nuclear high-resolution solid-state NMR study

Kim, H. N. & Lee, S.K. will be submitted in *American Mineralogist*

Abstract

Detailed knowledge of the atomic structure of Na-zeolite A with increasing temperature is essential to understand the mechanism of the temperature-induced amorphization of the zeolite. While the phenomenology and mechanism of the aluminosilicate frameworks in zeolite upon annealing has long been investigated well, the extent of the ordering behavior between Si and Al during temperature-induced amorphization has not been fully understood. In this study, we studied the previously unknown details of temperature-induced amorphization of Na-zeolite A, a model system of natural aluminosilicates, with an aim to confirm the presence of Al-O-Al linkages in the amorphous phase of Na-zeolite A using high-resolution $^{29}$Si, $^{27}$Al, and $^{17}$O solid-state nuclear magnetic resonance (NMR) spectroscopies. X-ray diffraction patterns confirmed that Na-zeolite A transforms to nepheline through a phase transition of Na-zeolite A → amorphous phase → low-carnegieite → nepheline with increasing annealing temperatures up to 1173 K. Based on the high-resolution solid state NMR results, we propose a three-step amorphization of Na-zeolite A with increasing temperature. The first step begins with
structural distortion around the Si and Al tetrahedrons resulting in dehydration between 773 and 873 K, as evidenced by the increased peak widths in the $^{27}$Al, $^{29}$Si and $^{17}$O MAS NMR spectra, respectively. Between 873 K and 1073 K, the amorphization of the zeolite, or loss of the long-range order period in the atomic structure, occurs with a significant increase in the topological and chemical disorder. 2D $^{17}$O 3QMAS NMR spectra show the presence of an Al-O-Al linkage in the amorphous phase of Na-zeolite A, which serves as direct evidence of the violation of the ‘Aluminum avoidance rule’. The sequential phase transition from the amorphous phase to low-carnegieite and nepheline occurred above 1073 K and was accompanied by a decrease in the Al-O-Al linkage. The observed structural changes in Na-zeolite A and its dehydrated phases with increasing temperature provides an improved understanding of the order-disorder transition mechanism of diverse alumina silicates.

6.1. Introduction

Zeolites are a group of microporous aluminosilicate minerals, which are common in a variety of sedimentary rocks including soils, deep-sea sediments, basaltic flows (Hay and Sheppard, 2001 and references therein). Zeolites have diverse industrial uses including as catalysts, adsorbents, ion exchangers, and microscale applications (Boyd et al., 1947; Breck et al., 1956; Coronas and Santamaria, 2004; Greaves et al., 2005; Greaves et al., 2003a; Kokotailo and Fyfe, 1989; Mintova and Bein, 2001). The three-dimensional networks of zeolite
consist of corner-sharing AlO$_4$ and SiO$_4$ tetrahedra as well as charge balancing cations such as Na and Ca. The zeolite network is known to collapse and transform into amorphous phase. The temperature-induced amorphization of zeolite and the accompanying structural changes have long been investigated in many experimental and theoretical studies due to the fundamental and technological interests (Bursill and Thomas, 1981; Colyer et al., 1997; Djordjevic et al., 2001; Greaves et al., 2007; Greaves et al., 2003b; Haines et al., 2009; Kosanovic et al., 2004; Kosanovic et al., 1997; Markovic et al., 2003; Markovic et al., 2006; Ohgushi et al., 2001; Peral and Iniguez, 2006; Ponyatovsky and Barkalov, 1992; Radulovic et al., 2010; Radulovic et al., 2013). While the structure of crystalline phases upon amorphization of zeolite has been explored and identified, little is known about the extent of chemical disorder between Si and Al tetrahedrons and topological variations in both crystalline and amorphous phases during amorphization. The objective of this study is thus to investigate the atomic structure and extent of chemical and topological disorder in both crystalline and amorphous phases during the temperature-induced amorphization of one of the synthetic zeolites, Na-zeolite A using multi-nuclear solid-state NMR spectroscopies.

Na-zeolite A is one of the most important zeolites with diverse applications such as molecular sieves, catalysis (Meier et al., 1988). The structure of Na-zeolite A consists of three secondary building units (SUBs) including α-cage, β-cage (sodalite cage), and double four-
membered rings (D4R) (Figure 6.1). The α-cage with a diameter of 1.14 nm is constructed of eight-membered oxygen rings. The β-cages are located at each corner of the zeolite cube and there is a single six-membered ring (S6R) at the boundary between the α-cage and β-cage. A double four-membered ring connects the two β-cages (Meier et al., 1988). The water molecules are located inside the α- and β-cage of zeolite A (Meier et al., 1988). The thermal dehydration leads to a twisting of the tetragonal prism in the aluminosilicate network (Cruciani and Gualtieri, 1999; Johnson et al., 1982). Thus, with increasing temperature, the microporous structure becomes relatively unstable and collapses into an amorphous phase as an intermediate state between zeolites at low temperature and dehydrated crystalline phases at high temperature (Dimitrijevic et al., 2004; Greaves et al., 2003b). For instance, Na-zeolite A transforms into an amorphous phase at approximately 700 - 800 °C and then transforms to low-carnegieite and nepheline with further heating (Greaves et al., 2007; Kosanovic et al., 2004; Mimura and Kanno, 1980; Stoch and Waclawska, 1994 and references therein).

Various experimental efforts have been made to elucidate the nature of temperature-induced amorphization of zeolite on the atomic scale (Bursill and Thomas, 1981; Colyer et al., 1997; Dimitrijevic et al., 2004; Djordjevic et al., 2001; Greaves et al., 2007; Greaves et al., 2003a; Greaves et al., 2003b; Greaves and Meneau, 2004; Haines et al., 2009; Lutz et al., 1985; Radulovic et al., 2010; Radulovic et al., 2013). In particular, X-ray diffraction (XRD), infrared spectroscopy (IR), and
transmission electron microscopy (TEM) have been used to probe the diverse structural changes of zeolite with varying temperatures (Bursill and Thomas, 1981; Colyer et al., 1997; Dimitrijevic et al., 2004; Djordjevic et al., 2001; Flanigen et al., 1971; Greaves et al., 2007; Markovic et al., 2003; Markovic et al., 2006; Radulovic et al., 2010; Radulovic et al., 2013). The IR spectra demonstrate the sensitive vibration bands of the primary building units of Na-zeolite A such as the single six-membered ring (S6R) and double four-membered ring (D4R) in the range of 500 ~ 650 cm⁻¹ (Djordjevic et al., 2001; Markovic et al., 2003; Markovic et al., 2006). Particularly, amorphization mechanisms of Na-zeolite A have been proposed on the basis of the above-mentioned studies of the structural distortion of building units (Djordjevic et al., 2001; Radulovic et al., 2013). It has been suggested that the dehydration of Na-zeolite A at ~ 400 °C induces the distortion of TO₄ frameworks. Further increase of the temperature above 700 °C leads to a collapse of long-range order in the zeolite (i.e., amorphization). During the amorphization, while the breaking of the O-O bond begins from the D4R structure, the S6R building units are conserved and reconnected to form low-carnegieite (Dimitrijevic et al., 2004). The oxygen linkages between Si and Al tetrahedrons are expected to be deconstrained during temperature-induced amorphization and return to regular bridging configurations once the order–disorder transition is complete (Greaves et al., 2003b). Despite these efforts, there is no evidence that the chemical order between the Si and Al tetrahedrons in the oxygen linkages are affected during
amorphization. Thus, the presence of Al-O-Al linkages that violate the Al avoidance rule should be confirmed by $^{17}$O NMR.

Achieving information regarding both topological and chemical disorder is essential to gain an improved understanding of the amorphization of zeolite. The ordering behaviors of Si-Al framework cations in crystalline aluminosilicates including zeolites, mica, anorthite, and aluminosilicate glasses have been studied for several decades (Carpenter, 1991; Cheng et al., 2000; Herrero et al., 1985; Lee and Stebbins, 1999; Murdoch et al., 1988; Phillips et al., 1992; Zhao et al., 2001). The short-range Si-Al order of framework cations can be denoted with the Al avoidance or Loewenstein’s rule, which postulates that the Al-O-Si linkage is more favorable than the Si-O-Si and Al-O-Al linkages (Loewenstein, 1954). Although the Si-Al ordering in zeolites with Si/Al ≥ 1 is likely to follow the Al avoidance rule, the aluminosilicate glasses have been known to contain some Al-O-Al linkages in their atomic structures, even with composition of Si/Al = 1 (Lee and Stebbins, 1999; Lee and Stebbins, 2000; Stebbins et al., 1999b). The extent of Si-Al disorder amorphous phase formed by the collapse of zeolite has not been extensively investigated (Greaves et al., 2007; Greaves et al., 2003b). The \textit{ab initio} study of pressure-induced amorphization in Zeolite A suggested an increase in the topological disorder in amorphous phase, not in the chemical disorder upon amorphization (Peral and Iniguez, 2006). The extent of chemical disorder in the amorphous state of zeolite could provide important constraints on the thermodynamic properties of the intermediate
amorphous phase such as configurational heat capacity and entropy (Lee and Stebbins, 1999). High-resolution solid-state NMR spectroscopy has been effective to explore the short-range structures (including Si-Al disorder) in diverse amorphous/disordered silicates (Engelhardt and Michel, 1988; Kim and Lee, 2013a; Lee, 2005; Lee and Stebbins, 1999; Lee and Stebbins, 2000; Lippmaa et al., 1980; Stebbins et al., 1986). Thus, the technique is suitable to estimate the temperature-induced changes in the extent of disorder in both amorphous and crystal phases during the amorphization of zeolite. Previous solid-state NMR studies investigated the structure of zeolites before and after phase transition (e.g., Na-zeolite A and nepheline) (Dimitrijevic et al., 2004; Radulovic et al., 2013). However, to the best of our knowledge, the atomic structures of the intermediate phases, including the amorphous and crystalline phases (e.g., dehydrated zeolite, carnegieite, and nepheline), have not been explored.

$^{29}$Si MAS NMR has been used to investigate the environment surrounding Si atoms in crystalline and amorphous silicates including zeolite, carnegieite, nepheline, and aluminosilicate glasses (Engelhardt and Michel, 1988; Kirkpatrick, 1988; Lippmaa et al., 1980; Ramdas and Klinowski, 1984; Stebbins, 1988; Stebbins et al., 1986 and see references therein). Because the number of atoms neighboring Al of tetrahedral Si can be described, the extent of the chemical disorder between Si and Al and topological disorder in Na-zeolite A, can be obtained using $^{29}$Si MAS NMR, in principle. The tetrahedral Si environment can be conventionally described using the $Q(m\text{Al})$ notation, which refers to
tetrahedral Si groups with \( m \) number of neighboring Al atoms. For instance, \( Q(0\text{Al}) \), \( Q(1\text{Al}) \), \( Q(2\text{Al}) \), \( Q(3\text{Al}) \), and \( Q(4\text{Al}) \) refer to \( \text{Si(OSi)}_4 \), \( (\text{AlO})\text{Si(OSi)}_3 \), \( (\text{AlO})_2\text{Si(OSi)}_2 \), \( (\text{AlO})_3\text{O(OSi)} \), and \( (\text{AlO})_4\text{Si} \), respectively.

The peak width and shape also provides topological information in short range order; in general, narrow peaks with full width at half maximum (FWHM) in orders of several ppm correspond to crystalline phases and very broad peaks with FWHM in orders of several tens of ppm correspond to amorphous phases in silicates (Engelhardt and Michel, 1988). A \(^{29}\text{Si}\) MAS NMR study of zeolites with increasing temperatures will address the temperature-induced changes in \( Q(m\text{Al}) \) speciation. In addition, it will also help to estimate the quantitative fraction of the amorphous phase during amorphization. \(^{27}\text{Al}\) MAS NMR has provided the atomic configuration of aluminum atoms in crystalline and amorphous aluminosilicates including zeolites (Engelhardt and Michel, 1988; Lee, 2010; Lippmaa et al., 1986 and references therein). In particular, 2D \(^{27}\text{Al}\) 3QMAS NMR successfully resolved crystallographically different aluminum sites in zeolite as well as highly crystallized \( \alpha \)-alumina and disordered \( \gamma \)-alumina (Chen et al., 2004; Hagaman et al., 2010; Kim and Lee, 2013b; Neuhoff et al., 2002a; Sabarinathan et al., 2010). Thus, 2D \(^{27}\text{Al}\) 3QMAS NMR is expected to resolve the multiple phases of aluminosilicates during the temperature-induced amorphization. We also note that the degree of topological and chemical disorder can be directly explored by probing the atomic structure around the oxygen atoms during the amorphization of zeolite using \(^{17}\text{O}\) NMR (Lee, 2005; Lee and Stebbins,
In particular, two-dimensional, solid-state $^{17}$O 3QMAS NMR is a powerful tool to reveal Si-Al ordering in crystalline and amorphous aluminosilicates by resolving the peaks of Si-O-Al, Si-O-Si, and Al-O-Al linkages (Amoureux et al., 1998; Cheng et al., 2000; Dirken et al., 1997; Ernst et al., 2004; Freude et al., 2001; Lee et al., 2010; Lee and Stebbins, 2000; Lee and Stebbins, 2009; Lee and Weiss, 2008; Lee et al., 2012; Neuhoff et al., 2002b; Pingel et al., 1998; Stebbins et al., 1997; Stebbins et al., 1999b; Zhao et al., 2001). Here, we explore the Si-Al ordering behavior in Na-zeolite A and its dehydrated phases at various temperatures using multi-nuclear solid-state NMR. We report the first 2D $^{17}$O 3QNMR spectra as well as $^{29}$Si and $^{27}$Al NMR spectra of the intermediate amorphous phases during the temperature-induced phase transition of Na-zeolite A. The multi oxygen environments including Al-O-Al, Si-O-Si, and Si-O-Al linkages were observed in amorphous phase of Na-zeolite A, indicating the violence of Al avoidance rule. Based on the NMR results, we provide an improved insight into the atomic-scale amorphization mechanism of zeolite with an emphasis on the ordering of Si-Al framework cations.

6.2. Experimental Methods

6.2.1. Sample Preparation and Characterization

Na-zeolite A (Molecular sieves 4 Å from Sigma Aldrich) was used. The samples were ground by hand for 30 min in an agate mortar. Then the ground samples were sieved by manual shaking for 1 h to separate the particles with diameters between 70 and 170 μm. Next,
the zeolites were reacted with an equal weight of 40% $^{17}$O enriched H$_2$O in sealed gold tubes at 150 °C and 0.5 kbar for 110 h in a hydrothermal reaction vessel. The $^{17}$O enriched zeolites were annealed at different temperatures under an Ar atmosphere. The annealing temperature of the samples increased by 275 K/h to the target temperatures (e.g., 773 ~ 1373 K) and further isothermal annealing was carried out for 3 hours. The temperature-induced structural changes of the annealed samples at lower temperatures could return to the initial states (i.e., before annealing) with rehydration. Thus, the annealed samples were moved to a glove box (operated with an Ar environment) where the samples were packed into NMR rotors and the NMR experiments were performed within ~ 5 min. The rehydration and related structural changes in the sample were not observed during the NMR experiments. While the samples were annealed at varying temperatures, the X-ray diffraction pattern and NMR spectra were collected at ambient conditions.

6.2.2. NMR Spectroscopy

$^{29}$Si NMR Spectroscopy. $^{29}$Si MAS NMR spectra were collected on a Varian NMR spectrometer (9.4 T) at a Larmor frequency of 79.55 MHz (4-mm Doty probe) and a spinning speed of 11 kHz. A single-pulse sequence with an approximately 30-degree pulse (1.6 μs) and delay time of 120 s was used. TMS was used as the external reference.

$^{27}$Al NMR Spectroscopy. $^{27}$Al MAS spectra were collected on a Varian
NMR (9.4 T) spectrometer with a Doty 4-mm probe. The single-pulse acquisition with a pulse length of 0.2 μs [radio frequency (rf) tip angle of about 15 ° for solids] was used with a recycle delay of 1 s and spinning speed of 15 kHz. $^{27}$Al 3QMAS NMR spectra were collected using fast amplitude modulation- (FAM-) based shifted-echo pulse sequences (1 s relaxation delay–3.0 μs pulse for 3Q excitation–$t_1$ delay–FAM pulse train with a 0.8 μs pulse-echo delay–19 μs soft pulse for echo reconversion–$t_2$ acquisition). A solution of AlCl$_3$ (2 mol%) was used as an external frequency standard.

$^{17}$O NMR Spectroscopy. $^{17}$O NMR spectra of amorphous silica gel were collected on a Varian NMR spectrometer of 9.4 T at a Larmor frequency of 54.23 MHz (Doty 4 mm probe) and a spinning speed of 15 kHz. For $^{17}$O MAS NMR spectra, a single-pulse sequence with a 15-degree pulse (0.175 μs) was utilized. A delay time of 1 s was used for zeolites evacuated at room temperature, and a delay time of 8 s was used for zeolites annealed above 873 K. $^{17}$O 3QMAS NMR spectra were collected using FAM-based shifted-echo pulse sequences (1 s relaxation delay–3.0 μs pulse for 3Q excitation–$t_1$ delay–FAM pulse train with a 0.8 μs pulse-echo delay–19 μs soft pulse for echo reconversion–$t_2$ acquisition). Tab water was used as an external frequency standard.

6.2.3. X-ray diffraction spectroscopy

The X-ray diffraction patterns were collected on a MiniFlex (Rigaku) using Cu K$_\alpha$ X-rays, a 2θ range of 5–70°, a step width of 0.02°,
and a scan rate of 1°/min.

6.3. Results and Discussion

6.3.1. Sample characterization

Figure 6.1 presents the XRD patterns of Na-zeolite A and its dehydrated phases with increasing annealing temperatures. The diffraction patterns of Na-zeolite A are observed at temperatures from 298 K to 953 K. The relative intensities of the diffraction peaks of Na-zeolite A are different below and above ~ 933 K. These results were reported in previous studies and may be due to dehydration and/or the accompanying migration of sodium ions (Breck et al., 1956; Pilter et al., 2000; Reed and Breck, 1956). At 953 K, the overall intensities of the diffraction patterns of Na-zeolite A start to decrease, indicating the initiation of the phase transition of Na-zeolite $A \rightarrow$ amorphous phase. At 973 K, sharp diffraction peaks with low intensities for the low-carnegieite phase are observed. These results suggest that the atomic structure in the long-range order of Na-zeolite A begins to collapse into an amorphous phase between ~873 K and ~953 K and the amorphous phase re-crystalizes into low-carnegieite between ~ 953 K and ~ 973 K. Considering the phase transition sequence and diffraction intensities of the crystalline phases, the fraction of amorphous phases in the sample reach a maximum value between 953 and 973 K. Further increase in the annealing temperature led to a phase transition of low-carnegieite $\rightarrow$ nepheline as seen in the diffraction patterns at 1073 K and 1173 K. Note that the dehydrated zeolite below 973 K would be re-
Figure 6.1. (A) The structure of Na-zeolite A, showing the secondary building units such as $\alpha$-cage, $\beta$-cage (sodalite cage), and double four-membered rings (D4R). The crystallographically different oxygen site also described. The water molecules located inside the $\alpha$- and $\beta$-cage...
are not shown (Meier et al., 1988). (B) XRD patterns of Na-zeolite A and dehydrated phases with increasing annealing temperatures. Red (square), purple (circle), and blue (diamond) colors correspond to the peak positions and intensities of Na-zeolite A (JCPDS file no. 04-010-2001), low-carnegieite (Thompson et al., 1993), and nepheline (JCPDS file no. 01-079-0992), respectively.
hydrated during measurements of XRD pattern (see below chapter 3.6) as we mentioned above, thus slight distortion of zeolite framework may not be detected in XRD results, here (and possibly in previous studies that the samples were not in-situ and be exposed to open atmosphere during measurement).

6.3.2. $^{29}$Si MAS NMR Results

Figure 6.2 shows the $^{29}$Si MAS NMR spectra at 9.4 T of Na-zeolite A and its dehydrated phases with increasing annealing temperatures. In the $^{29}$Si MAS NMR spectra of Na-zeolite A at 298 K (i.e., before annealing), a narrow peak corresponding to the tetrahedral Si site with four neighboring Al atoms [i.e., Q(4Al)] is observed at -88 ppm (Engelhardt and Michel, 1988; Lippmaa et al., 1981). At 873 K, the peak width for Q(4Al) species at -88 ppm slightly increases, indicating the structural distortion of the Si tetrahedron in the crystalline zeolite. At 953 K, a broad Gaussian-shaped peak ranging from -80 to -100 ppm and a narrow peak at -88 ppm is observed. While the broad peak is almost invariable at 973 K, the narrow peak at -88 ppm shifts to -82 ppm. We assign the broad peak to the Si atoms in the amorphous phase based on the analogy to that of the amorphous silicates (Kim and Lee, 2013a; Lee and Stebbins, 1999). The narrow peaks at -88 ppm and -82 ppm are assigned to the Q(4Al) environment in Na-zeolite A and low-carnegieite, respectively, based on previous studies (Stebbins et al., 1986; Thompson et al., 1993). These results are consistent with the XRD results, showing the fraction of the amorphous phase have a
Figure 6.2. $^{29}$Si MAS NMR spectra at 9.4 T of Na-zeolite A and dehydrated phases with increasing annealing temperatures up to 1173 K.
maximum value and small fraction of crystalline phase changes from Na-zeolite A into low-carnegieite at 953 ~ 973 K. At 1073 K, the spectrum shows two narrow peaks at -82 ppm and -88 ppm and one broad peak at approximately -90 ppm, indicating the Si environments in low-carnegieite, nepheline, and possibly amorphous phase. At 1173 K where the nepheline is the single phase according to XRD result, two sharp peaks at -82 ppm and -88 ppm, which are assigned to crystallographically distinct Q(4Al) sites (Si2 and Si1, respective), and a peak at -94 ppm assigned to the Q(3Al) site are also observed (Gregorkiewitz, 1984; Stebbins et al., 1986). The presence of Q(3Al) peak at 1173 K suggests that slight dealumination would occur during annealing, because the Q(3Al) peak in nepheline is observed in the presence of Si in excess than that for stoichiometric nepheline (i.e., Si/Al=1) (Stebbins et al., 1986). The slight dealumination of Na-zeolite A upon annealing has been reported in previous work (Corbin et al., 1984; Neuhoff et al., 2002b).

In order to quantify the fraction of Na-zeolite A and dehydrated phases at various annealing temperatures, the $^{29}$Si MAS NMR spectra are simulated with several Gaussian functions representing Q(mAl) species in the multi-crystalline and amorphous phase in the samples (Figure 6.3): Q(4Al) peaks in Na-zeolite A (-88 ppm) and low-carnegieite (-82 ppm) are simulated with a single Gaussian function, respectively. The Q(mAl) species in the amorphous phase are simulated with one Gaussian function with FWHM of 13.9 ppm. The two Q(4Al) peaks for Si2, Si1 tetrahedral sites and one Q(3Al)
Figure 6.3. Simulation of $^{29}$Si MAS NMR spectra at 9.4 T of Na-zeolite A and dehydrated phases with increasing annealing temperatures. Red, purple, blue, and black lines correspond to Q species in Na-zeolite A, low-carnegieite, nepheline, and amorphous phase, respectively.
peak in nepheline are simulated with three Gaussian functions at -83, -88, and -93 ppm, respectively. The ratio between Si2 and Si1 site is approximately 1.6:1 in this work, while it is known 3:1 in ideal structure of crystalline nepheline (Buerger et al., 1947). We guess that the inconsistency may due to the presence of Q(3Al) species and/or possibly remained amorphous phase in the sample even annealing at 973 K. The small broad Q(mAl) peak for amorphous peak could not be noticed well due to overlap with narrow peaks with high intensity for crystalline nepheline. The peak position and width of each Q species except the Q(4Al) species in Na-zeolite A are fixed for robust simulation results. The peak width of the Q(4Al) species in Na-zeolite A at 873 K is slightly larger than that its width at 298 K, due to an increase in the structural distortion of the Si tetrahedron, as previously discussed.

6.3.3. 27Al MAS NMR Results

Figure 6.4 shows the 27Al MAS NMR spectra at 9.4 T of Na-zeolite A and dehydrated phases with increasing annealing temperature, showing resolved [4]Al sites in multiple phases including Na-zeolite A, carnegieite, nepheline, and the amorphous phase. The 27Al spectra of Na-zeolite A at 298 K and 773 K show a narrow [4]Al peak at -62 ppm, with FWHM of 3.5 ppm and 2.9 ppm, respectively, indicating that the topological disorder decreases after annealing at 773 K. We guess that the damaged structure of Na-zeolite A from mechanical grinding in sample preparation may be healed by
**Figure 6.4.** $^{27}$Al MAS NMR spectra at 9.4 T of Na-zeolite A and dehydrated phases with increasing annealing temperatures up to 1173 K.
annealing at 773 K. At 823 K, the peak width and position suddenly varies: the FWHM significantly increases to 9.7 ppm and its position also shifts to a lower frequency. The observed change in the peak position and width may be due to an increase in topological disorder (Lippmaa et al., 1986), indicating a distortion of the frameworks in Na-zeolite A upon dehydration between 773 K and 823 K, as evidenced by XRD. The broad $^{[4]}$Al peak between 823 K and 953 K readily returns back to original narrow peak before annealing upon rehydration under an ambient atmosphere (see below chapter 3.6). At 953 K, an additional broad peak approximately ranging from 30 ppm to 80 ppm is observed, and is tentatively assigned to the amorphous phase based on XRD results and previous $^{27}$Al NMR studies for amorphous aluminosilicates (Lee and Stebbins, 2000). At 973 K, the peak width decreases with a phase transition from the amorphous phase to low-carnegieite. At 1073 K, the peak at 63 ppm is also observed and at 1037 K, two crystallographically distinct $^{[4]}$Al sites in nepheline are observed at 66 and 60 ppm (Lippmaa et al., 1986).

Figure 6.5 shows the $^{27}$Al 3QMAS NMR spectra at 9.4 T of Na-zeolite A and dehydrated phases with increasing annealing temperatures. While the $^{[4]}$Al peak of Na-zeolite A shows a linear shape with a slope of 31/17, that for the amorphous or disordered phase show a broad oval shape (Kim and Lee, 2013b; Lee and Stebbins, 2000). The $^{[4]}$Al peak at 873 K shows a broad but similar linear peak shape with Na-zeolite A before annealing, suggesting that the peak broadening is due to the slight distortion of the Al tetrahedron within
Figure 6.5. $^{27}\text{Al}$ 3QMAS NMR spectra at 9.4 T of Na-zeolite A and dehydrated phases with increasing annealing temperatures up to 1173 K. Contour lines are drawn from 3% to 98% of the relative intensity with an increment of 5%.
the zeolite structure. At 953 K and 973 K, an oval shaped $^{[4]}\text{Al}$ peak is observed, which is assigned to Al sites in the amorphous phase by the analogy with previously reported $^{27}\text{Al}$ 3QMAS NMR spectra of Na-aluminosilicate glasses (Lee and Stebbins, 2000). At 1073 K and 1173 K, crystallographically distinct $^{[4]}\text{Al}$ sites of nepheline and low-carnegieite are observed. The total isotropic projection, which is the sum over data along lines parallel to MAS dimension, is also shown in Figure 6.6, where the $^{[4]}\text{Al}$ sites in the crystalline phase and amorphous phase are resolved in the isotropic dimension. Because the isotropic dimension in 3QMAS NMR spectra is free from quadrupolar broadening, the Al sites in distorted zeolite frameworks and the amorphous phase could be distinguished in isotropic dimension. The peak width of $^{[4]}\text{Al}$ peak in Na-zeolite A slightly increases from 298 K to 873 K, and decreases with increasing annealing temperature up to 953 K. These results indicate that the increased structural distortion around Al tetrahedron at 873 K gradually decreases with amorphization. The broad peak ranging from -30 ppm to -50 ppm is observed at 933 ~973 K, which is assigned to the amorphous phase. The peak intensity for the amorphous phase is maximized at 973 K, which is consistent result with $^{29}\text{Si}$ MAS NMR and XRD results.

3.4. Comparison of $^{29}\text{Si}$ and $^{27}\text{Al}$ MAS NMR results

While the Si and Al atoms in Na-zeolite A have a tetrahedral structure, the possible difference in temperature-induced structural changes between Si and Al tetrahedrons has not been thoroughly
Figure 6.6 Isotropic projection of $^{27}$Al 3QMAS NMR spectra of Na-zeolite A and dehydrated phases with increasing annealing temperatures up to 1173 K at 9.4 T.
investigated. The detailed changes in zeolite frameworks upon annealing could be obtained by comparing the results of the $^{29}$Si NMR and $^{27}$Al NMR, allowing us to distinguish the degree of distortion of Si and Al tetrahedrons, respectively. Figure 6.7 presents the comparison of $^{29}$Si and $^{27}$Al MAS NMR spectra at 298 K and 873 K, showing the different degree of structural distortion between the Si and Al tetrahedrons. The Q(4Al) peak in the $^{29}$Si MAS NMR spectra shows a slight change in the peak position and width before and after annealing at 873 K. The peak position is identical and the FWHM changes from 1.7 ppm at 298 K and to 2.8 ppm at 873 K. The $^{[4]}$Al peak in the $^{27}$Al NMR spectra, otherwise, shows more significant changes before and after annealing at 873 K. The peak position shifts to a lower frequency and the FWHM changes from 3.5 ppm at 298 K to 9.7 ppm at 873 K. These results suggest that the temperature-induced structural distortion of the Si and Al tetrahedron in the Na-zeolite A framework are possibly different from each other: the degree of distortion around the Al tetrahedron could be more significant than that around the Si tetrahedron. Previous studies indicated that the $^{29}$Si and $^{27}$Al chemical shifts of zeolites have a linear correlation with mean Si-O-Al bond angles, which equally affect the peak position and width in the $^{29}$Si and $^{27}$Al NMR spectra (Engelhardt and Michel, 1988; Lippmaa et al., 1986; Newsam, 1987). Thus, the variation of the Si-O-Al bond angle is not the origin of the significant peak broadening in the $^{27}$Al MAS NMR spectra rather than that in $^{29}$Si MAS NMR. The peak broadening of the $^{[4]}$Al peak in the $^{27}$Al MAS NMR spectra may be emphasized because
Figure 6.7 Comparison of area-normalized $^{29}$Si and $^{27}$Al MAS NMR spectra of Na-zeolite A at 298 K and 873 K. The black and red lines refer to spectra at 298 K and 873 K, respectively.
the $^{27}$Al is a quadrupolar species. A quadrupolar coupling constant ($C_q$), one important NMR parameter affecting the peak width and shape in $^{27}$Al MAS NMR spectra, is an index of the degree of the distortion around Al tetrahedron (Engelhardt and Michel, 1988; Engelhardt and Veeman, 1993; Weller et al., 1994). Thus, a small structural variation in the zeolite framework would lead a distribution of the chemical shifts and $C_q$ for $^{14}$Al peak in $^{27}$Al NMR spectra, whereas it would only affect the distribution of the chemical shift for $^{29}$Si NMR spectra. These results suggest that $^{27}$Al MAS NMR could detect smaller variations in the structure of the zeolite framework than $^{29}$Si MAS NMR.

3.5. $^{17}$O MAS NMR Results

Figure 6.8 presents the $^{17}$O 3QMAS NMR spectra of Na-zeolite A and dehydrated phases with increasing annealing temperatures, showing the temperature-induced changes in the oxygen environments. Na-zeolite A has three crystallographically distinct O atom sites, O1, O2, and O3, with populations of 1:1:2 (Freude et al., 2001). Among the three oxygen atoms, the O1 is the bridge oxygen between the adjacent sodalite units and the O2 and O3 oxygen atoms compose the 4-membered rings and 6-membered rings in the sodalite cage (i.e., $\beta$-cage) as shown in Figure 1 (Meier et al., 1988). The environments of those O atoms are chemically similar Si-O-Al linkage with little variation in Si-O-Al angle. At 298 K, crystallographically distinct Si-O-Al sites including O1, O2, and O3 in Na-zeolite A are
Figure 6.8. $^{17}$O 3QMAS NMR spectra at 9.4 T of Na-zeolite A dehydrated phases with increasing annealing temperatures up to 1173 K. Contour lines are drawn from 8% to 98% of the relative intensity with an increment of 5%.
partially resolved in the isotropic dimension; the peaks at -25 ppm and -31 ppm were assigned to Si-O2-Al linkage and unresolved Si-O1-Al and Si-O3-Al linkages according to previous studies (Neuhoff et al., 2002b; Pingel et al., 1998). After annealing at 873 K, the three Si-O-Al sites are not resolved due to peak broadening in the MAS and isotropic dimensions, indicating an increase in the topological disorder in the short-range order around the oxygen atoms. Between 933 K and 973 K, the 17O 3QMAS NMR spectra show three types of bridging oxygens (BO, e.g., Si-O-Al, Al-O-Al, and Si-O-Si). The peaks at ~ -12 ppm, -25 ppm, and -45 ppm in the isotropic dimension correspond to Al-O-Al, Si-O-Al, and Si-O-Si linkages, respectively at 9.4 T (Lee and Stebbins, 2000; Stebbins et al., 1999a). The Si-O-Al linkage is not crystallographically distinguished in 17O 3QMAS NMR spectra due to an increased disorder between 933 and 973 K. As indicated by the change in the number of contour lines of the Al-O-Al peak, the fraction of Al-O-Al and Si-O-Si linkages has a maximum at 953 K, indicating that the degree of chemical disorder between Al and Si in the Na- zeolite A is maximized with amorphization. At 1073 K, the peak intensities of the Al-O-Al and Si-O-Si linkage are still observed though with small intensity, implying the amorphous phase exists and the disorder-order transition in the sample is not complete. At 1173 K, the Si-O-Al peak is observed, which should be assigned in oxygen sites in nepheline according to XRD results. While it has been known that crystallographically distinct six oxygen sites (from O1 to O6) exist in nepheline, those are not resolved well in 17O 3QMAS NMR spectrum.
at 9.4 T (Buerger et al., 1947).

Figure 6.9A shows the total isotropic projections of the $^{17}$O 3QMAS NMR spectra for the Na-zeolite A and its dehydrated phases, confirming that Si-O-Al was dominant, and a small but non-negligible fraction of Al-O-Al and Si-O-Si is also detected at 933 ~ 1073 K. These results indicate that the chemical order between Si and Al is affected during amorphization. Figure 6.9B presents enlarged spectra of the projections in the isotropic dimension of the $^{17}$O 3QMAS NMR spectra of Na-zeolite A and dehydrated phases in the frequency range of -15 to -45 ppm showing the changes in the structural disorder around the Si-O-Al linkage during amorphization. At 298 K, the peaks for O1 and O3 species are overlapped at -31 ppm, while the peak for O2 species is resolved at -24 ppm in isotropic dimension. With increasing temperature up to 873 K, the peaks for distinct oxygen environments are broaden and shift to higher frequency in isotropic dimension. The shift of peak position of Si-O-Al linkages in Na-zeolite A may due to a removal of H2O and/or migration of Na ions upon annealing because the $^{17}$O chemical shift of Na-zeolite A is affected by extraframework species (e.g. water molecules and cations) as well as Si-O-Al bond angle (Neuhoff et al., 2002b). From the 933 K to 1073 K, the temperature range where Al-O-Al and Si-O-Si linkages are observed, the peak width in the isotropic dimension of the Si-O-Al linkage gradually decreases on increasing the temperature from 933 K to 1073 K. These results indicate a gradual decrease in the topological disorder of the Si-O-Al linkage on increasing the temperature from 933 K to
Figure 9 Isotropic projection of $^{17}$O 3QMAS NMR spectra of Na-zeolite A and dehydrated phases with varying annealing temperatures at 9.4 T.
1073 K, which is consistent with $^{27}$Al 3QMAS NMR results.

6.3.6. Reversibility of temperature-induced phase transition of Na-zeolite A

The dehydrated zeolites without the collapse of framework are known to be readily rehydrated (i.e. reversible dehydration), whereas completely dehydrated zeolite with subsequent amorphization do not undergo rehydration (i.e. irreversible dehydration) (Alberti et al., 2001; Bish and Carey, 2001; Cruciani, 2006 and references therein). The structure of dehydrated zeolites without amorphization may be readily back to structure of hydrated zeolite unless it is in-situ experiment or quips the system controlling the atmosphere. The advantage of solid-state NMR spectroscopy in the investigation of temperature-induced structural changes of aluminosilicates as well as other materials, is the prevention of re-hydration of dehydrated samples during measurements. The combination of sample packing into NMR rotors under an Ar atmosphere in a glove box and centrifugal force during magic angle spinning successfully prevented the rehydration of the dehydrated sample (Kim and Lee, 2013a).

Figure 6.10 shows the $^{27}$Al MAS NMR spectra of dehydrated Na-zeolite A at 873 K and then, prepared in a glove box (under Ar gas) or in an open atmosphere. The spectra show obvious structural changes back to before dehydration up on sample preparation (i.e., packing into rotor) in an open atmosphere. These results indicate that the dehydrated zeolite is rehydrated by exposure to open atmosphere.
Figure 6.10. $^{27}$Al MAS NMR spectra of dehydrated Na-zeolite A at 873 K and then, prepared in a glove box (black line) or in an open atmosphere (red line).
for only few minutes, which significantly affects the experimental results. These results indicate that the distorted structure in dehydrated zeolite is the metastable state and the slight structural distortion may not be detected well without careful sample handling.

Figure 6.11 shows the changes in $^{17}$O 3QMAS NMR spectra of Na-zeolite A before and after annealing at 933 K and subsequent storing in desiccator for 7 months (the humidity was controlled below 30%). The peaks for Al-O-Al and Si-O-Si linkages shown in the spectra right after sample preparation are not observed after 7 months. The $^{17}$O 3QMAS spectrum after 7 months is almost similar with that for Na-zeolite A before annealing. The projection in isotropic dimension of $^{17}$O 3QMAS NMR show that Al-O-Al and Si-O-Si linkage disappeared for 7 months after annealing at 933 K, and the peak shape of Si-O-Al linkage also shows similar peak position though its peak width is much broader than that before annealing. These results indicate that the temperature induced amorphous and distorted structure in dehydrated Na-zeolite A at 933 K back to that before dehydration for 7 months very sluggish.

6.3.7. Temperature-induced amorphization and Si-Al ordering

The NMR results provided previously unknown details of the temperature-induced amorphization in Na-zeolite A. The experimental data also indicated the presence of Al-O-Al, Si-O-Si, and Si-O-Al linkages (from $^{17}$O NMR results), and diverse Q($m$Al) species with varying atomic configurations (from $^{29}$Si NMR results) in amorphous Na-zeolite A.
Figure 6.11. (A) $^{17}$O 3QMAS NMR spectra and (B) Isotropic projection of $^{17}$O 3QMAS NMR spectra for Na-zeolite A before and after annealing at 933 K and subsequent storing in desiccator for 7 months.
Based on the high-resolution solid-state NMR results, we observed a three-step amorphization of Na-zeolite A with increasing temperature. The first step involves the dehydration of Na-zeolite A, leading to a structural distortion around Si and Al tetrahedrons between 773 ~ 873 K, as evidenced by an increase in the peak width of $^{27}\text{Al}$ and Q(4Al) peaks in the $^{27}\text{Al}$ and $^{29}\text{Si}$ MAS NMR spectra, respectively. The structural distortion occurs over short-range order and is accompanied by slight changes in the bond angle and bond length from the perfect cubic structure of Na-zeolite A. The XRD diffraction pattern proves that long-range order in zeolite structure exists at 773 K, while disorder in the short-range order increases as evidenced by $^{27}\text{Al}$ and $^{29}\text{Si}$ NMR. In the first step, the Si-Al disorder is not observed because the dehydration and structural distortion does not accompany the bond breaking and rehydration readily occurs with an exposure in an open atmosphere for few minutes. The second step involves the collapse of zeolite frameworks with a loss of period in the long-range order (i.e., amorphization) above ~ 873 K, which increases the extent of topological and chemical disorder in the sample. The presence of an Al-O-Al linkage indicates that chemical disorder increased with amorphization, not following the Al-O-Al avoidance rule. Although the amorphous phase do not undergo a glass transition, its atomic scale structure is similar to that of NaAlSiO$_3$ glass. Although the presence of Al-O-Al and Si-O-Si linkages in amorphous phase confirm the T-O-T bond breaking, the amorphous phase could rehydrated sluggishly and back to crystalline Na-zeolite phase. Finally,
at temperatures above ~ 1073 K, crystallization from the amorphous phase to carnegieite and a phase transition from carnegieite to nepheline occurred and accompanied the decrease in both topological and chemical disorder (i.e. Al-O-Al linkage). The observed structural changes in Na-zeolite A and its dehydrated phases with increasing temperature provide an improved understanding of the order-disorder transition mechanism of diverse alumina silicates.
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Chapter 7. Kinetics oxygen site exchange between magnesium silicates and water: Implications for interaction between Mg-silicates and aqueous fluids

Abstract

Detailed knowledge of the rate and mechanisms of oxygen isotope exchange between silicates and aqueous fluids is needed for the interpretation of isotope disequilibrium processes in nature, including mineral dissolution, sorption reactions, and stable-isotope fractionation. Depending on the oxygen site in clinoenstatite, the rate of isotope exchange would vary and the high resolution $^{17}\text{O}$ NMR experiment will allow us to measure atomic site dependent kinetics of isotope exchanges between magnesium silicates and aqueous fluid. Here, we report the $^{17}\text{O}$ NMR spectra of $^{17}\text{O}$ exchanged enstatite with varying reaction time with an aim to explore the nature of oxygen isotope exchange between crystalline enstatite and water under hydrothermal environments. The high-resolution $^{17}\text{O}$ MAS and 2D 3QMAS NMR spectra resolve the different isotope exchange rate depending on crystallographically discriminated oxygen site such as Si-O-Si ad Si-O-Mg. With increasing reaction time, the intensity of $^{17}\text{O}$ spectra increases as a result of further isotope exchange between clinoenstatite and water with time. In addition to that the relative population of Si-O-Mg to Si-O-Si significantly increases with increasing reaction time from 500 h to 1000 h. These results indicate that isotope exchange rate is affected by crystallographically
7.1. Introduction

Magnesium silicates are the most abundant composition of the Earth’s mantle. Detailed knowledge of the rate and mechanisms of oxygen isotope exchange between magnesium silicates and aqueous fluids is needed for the interpretation of isotope disequilibrium processes in nature, including mineral dissolution, sorption reactions, and stable-isotope fractionation. For instance, isotopic disequilibrium provides an opportunity to investigate the temporal relationships in geologic systems.

Given these geological implications, the kinetics of oxygen isotope exchange between silicates and water has been studied extensively (Cole and Chakraborty, 2001; Cole and Ohmoto, 1986; Lasaga et al., 1994; Rimstidt and Barnes, 1980) using mass spectroscopy. Though a net rate of bulk exchange reaction has been investigated, the dependence of atomic structure of silicates on isotope exchange kinetics has not been investigated yet due to spectroscopic difficulties.

High-resolution solid-state $^{17}$O NMR spectroscopy yields element specific and information that allows the determination crystallographically distinct oxygen site in materials with quantitative information about $^{17}$O isotope (Lee and Stebbins, 2003; Lee et al., 2003; Xu and Stebbins, 1998). Recent $^{17}$O NMR study for isotope exchange between ‘Al₁₃’ polyoxocation \( \left( \text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12} \right)^{7+} \) and water.
solvent reported different rates of exchange depending on local structure of surface (Phillips et al., 2000). The atomic site dependence on the rate for oxygen exchange between fundamental earth materials and water is also necessary to understand the kinetics of the water-rock interaction systematically.

Here, we explore the nature of oxygen isotope exchange between crystalline enstatite (MgSiO$_3$) and water under hydrothermal environments. $^{17}$O MAS and 2D 3QMAS NMR spectra of $^{17}$O exchanged enstatite with varying exchange time were reported that allow us investigate the crystallographically discriminated reaction rate and mechanism of oxygen isotope exchange between magnesium silicate and aqueous fluid in atomic scale view.

7.2. Experimental Methods

7.2.1. Sample Preparation and Characterization

Clinoenstatite were synthesized by annealing MgSiO$_3$ powder (from Goodfellow, 99.9%) at 1500 °C for 2 hours. The samples were ground with hand-pressure for 30 min in agate mortar. Then, the ground samples were sieved by manual shaking for 1 h to separate the particles between 28 and 50 μm diameters. Then, the samples are reacted with an equal weights of 40% $^{17}$O enriched H$_2$O in sealed gold tubes at 350 °C, 1 kbar in a hydrothermal reaction vessel with varying reaction time.
7.2.2. NMR Spectroscopy

$^{17}$O NMR Spectroscopy. $^{17}$O NMR spectra for amorphous silica gel were collected on a Varian NMR system of 9.4 T at a Larmor frequency of 54.23 MHz (Doty 4 mm probe) and a spinning speed of 15 kHz. For $^{17}$O MAS NMR spectra, a single-pulse sequence with a 30-degree pulse (1.2 $\mu$s). $^{17}$O 3QMAS NMR spectra were collected using a fast amplitude modulation- (FAM-) based shifted-echo pulse sequences (1 s relaxation delay–3.0 $\mu$s pulse for 3Q excitation–$t_1$ delay–FAM pulse train with a 0.8 $\mu$s pulse-echo delay–19 $\mu$s soft pulse for echo reconversion–$t_2$ acquisition). The delay time was 1 s and water was used as an external frequency standard.

7.2.3. X-ray diffraction spectroscopy and Scanning Electron Microscopy

The X-ray diffraction patterns were collected on MiniFlex (Rigaku) using Cu K$_\alpha$ X-rays, a $2\theta$ range of 5–70°, a step width of 0.02°, and a scan rate of 1°/min. The scanning electron microscopy (SEM) study was performed on a JEOL SUPERPROBE instrument (JEOL Ltd.). The specimens for electron microscopy were prepared by carbon coating on the slide glass.

7.3. Results and Discussion

Figure 7.1 presents the XRD patterns of the clinoenstatite before and after hydrothermal reaction up to 500 h, where the diffraction patterns confirm that the prepared sample is crystalline.
clinoenstatite phase. The diffraction patterns for crystalline clinoenstatite do not change before and after isotope exchange reaction up to 500 h. This result indicates that a phase transition is not occurred during hydrothermal reaction between clinoenstatite and water.

Figure 7.2 presents the SEM images of clinoenstatite before and after the hydrothermal reaction for 500 h, showing the surface morphology of clinoenstatite particles with ×1000 and ×5000 magnification. The clinoenstatite particles have irregular shape with diameters between 30 μm and 70 μm. While the morphology of the sample is generally not changed in SEM images with ×500 magnification, the significant difference in surface morphology is observed with image of ×3000 magnification upon hydrothermal reaction for 500 h. Whereas lots of fractured fragments with diameters less than 3 μm are observed on the surface of clinoenstatite before hydrothermal reaction, fibrous surface without fractured fragment is observed after the hydrothermal reaction. These results suggest that chemical alteration such as dissolution-precipitation may occur on the surface of clinoenstatite due to hydrothermal reaction. We note that the chemical alteration may occur near surface of the grain and the bulk structure of the samples would not be altered as shown in XRD patterns.

Figure 7.3 presents the 17O MAS NMR spectrum for 17O isotope exchanged clinoenstatite at 9.4 T, showing diverse oxygen site including Si-O-Mg and Si-O-Si in clinoenstatite. The
Figure 7.1. XRD patterns for clinoenstatite before and after hydrothermal reaction for 72 h and 500 h (JCPDS file no. 01-075-1404).
Figure 7.2. SEM images for clinoenstatite before and after hydrothermal reaction for 1000 h with (A) ×1000 and (B)×5000 magnification.
Figure 7.3. $^{17}$O MAS NMR spectra at 9.4 T for $^{17}$O exchanged clinoenstatite with varying hydrothermal reaction time.
crystallographically distinct 6 oxygen sites (2 types of Si-O-Si and 4 types of Si-O-Mg) are exist in clinoenstatite (Morimoto et al., 1960). While the six types of oxygen environments are not fully resolved in the $^{17}$O MAS NMR spectra in this study, the narrow peak at ~ 40 ppm and broad peak at ~ 10 ppm is assigned to oxygen environments in Si-O-Mg and Si-O-Si, respectively based on the previous study (Ashbrook et al., 2007). The overall intensity and peak shape in $^{17}$O NMR spectra for $^{17}$O isotope exchanged clinoenstatite vary with increasing reaction time. In particular, the changes are dramatic with reaction time between 500 h and 1000 h. While the NMR intensity slightly increases with increasing reaction time from 250 h to 500 h, it dramatically increases with increasing reaction time from 500 h to 1000 h. The peak shape is also significantly changes with varying reaction from 500 h to 1000 h. These results suggest that the isotope exchange mechanism between clinoenstatite and water may vary depending on reaction time. Figure 7.4 shows the changes in total intensity of $^{17}$O MAS NMR spectra with varying reaction time, showing linear relation between exchanged $^{17}$O intensity in the sample and reaction time.

Figure 7.5 shows the $^{17}$O 3QMAS NMR spectra for $^{17}$O isotope exchanged clinoenstatite at 9.4 T, where the Si-O-Si and Si-O-Mg peaks are resolved well in isotropic dimension. However, crystallographically distinct Si-O-Si sites or Si-O-Mg sites are not resolved well, neither. Total isotropic projection, which is sum over data along lines parallel to MAS dimension, is also shown in Figure 7.6.
Figure 7.4. $^{17}$O MAS NMR spectra at 9.4 T for $^{17}$O exchanged clinoenstatite with varying hydrothermal reaction time.
The peak at ~ -30 ppm and -45 ppm in the isotropic dimension correspond to Si-O-Mg and Si-O-Si linkage, respectively at 9.4 T. With increasing reaction time, the absolute peak intensity of $^{17}$O spectra increases and a population between Si-O-Si and Si-O-Mg linkage also varies. While the peak intensities for Si-O-Si and Si-O-Mg linkages are rather similar after isotope exchange for 500 h, the relative peak intensity for Si-O-Mg linkages significantly increases after 1000 h. These results indicate that the oxygen isotope exchange rate is slower in Si-O-Mg linkage than Si-O-Si linkage. The peak width of Si-O-Mg and Si-O-Si linkage also varies in isotropic dimension depending on reaction time. The peak width for Si-O-Mg show significant decrease in peak width increasing reaction time from 500 h to 1000 h. These results indicate that the structural disorder exist around Si-O-Mg linkage in the clinoenstatite after 500 h reaction. provide previously unknown details of $^{17}$O isotope exchange between clinoenstatite and water. The experimental data suggest that $^{17}$O isotope exchange rate have dependence on the crytatalographically discriminated site in crysatlline clinoenstatite. Under hydrothermal condition (T=350 °C, P=1 kbar), the $^{17}$O isotope exchange rate for Si-O-Mg is slower than that for Si-O-Si. These results may due to isotope exchange occur through dissolution-precipitation mechanism on the surface of enstatite.
Figure 7.5. $^{17}$O 3QMAS NMR spectra at 9.4 T for $^{17}$O exchanged clinoenstatite with varying hydrothermal reaction time. Contour lines are drawn at 5% intervals from relative intensities of 8-98% with added lines at 5% for 250 h and 500 h and 3% for 1000 h reaction time.
Figure 7.6. Isotropic projection of $^{17}$O 3QMAS NMR spectra at 9.4 T for $^{17}$O exchanged clinoenstatite with varying hydrothermal reaction time.
References
Xu, Z., and Stebbins, J.F. (1998) Oxygen site exchange kinetics...
Appendix

A1. Abstracts Published in Korean Journal

A1.1. Effect of particle size on the atomic structure of amorphous silica nanoparticles: Solid-state NMR and quantum chemical calculations

Hyun Na Kim and Sung Keun Lee
Published in Journal of Mineralogical Society of Korea, 21, 321-329 (2008)

Abstract

Amorphous silica nanoparticles are among the most fundamental SiO₂ compounds, having implications in diverse geological processes and technological applications. Here, we explore structural details of amorphous silica nanoparticles with varying particle sizes (7 and 14 nm) using ²⁹Si and ¹H MAS NMR spectroscopy together with quantum chemical calculations to have better prospect for their size-dependent atomic structures. ²⁹Si MAS NMR spectra at 9.4 T resolve Q², Q³ and Q⁴ species at -93 ppm, -101 ppm, -110 ppm, respectively. The fractions of Q², Q³, Q⁴ species are 7 ± 1%, 27 ± 2%, and 66±2% for 7 nm amorphous silica nanoparticles and 6 ± 1%, 21 ± 2%, and 73 ± 2% for 14 nm amorphous silica nanoparticles. Whereas it has been suggested that Q² and Q³ species exist on particles surfaces, the difference in Q² + Q³ fraction in both 7 and 14 nm particles is not significant, suggesting that Q² and Q³ species could exist inside
particles. $^1$H MAS NMR spectra at 11.7 T shows diverse hydrogen environments, including physisorbed water, hydrogen bonded silanol, and non-hydrogen bonded silanol with varying hydrogen bond strength. The hydrogen contents in the 7 nm silica nanoparticles (including water and hydroxyl groups) are about 3 times of that of 14 nm particles. The larger chemical shifts for proton environments in the former suggest stronger hydrogen bond strength. The fractions of non-hydrogen bonded silanols in the 14 nm amorphous silica nanoparticles are larger than those in 7 nm amorphous silica nanoparticles. This observation suggests closer proximity among hydrogen atoms in the nanoparticles with smaller diameter. The current results with high-resolution solid-state NMR reveal previously unknown structural details in amorphous silica nanoparticles with particle size.
A1.2. $^{17}$O solid-state NMR study of the effect of organic ligands on atomic structure of amorphous silica gel: Implications for surface structure of silica and its dehydration processes in earth's crust

Hyun Na Kim and Sung Keun Lee
Published in *Journal of Mineralogical Society of Korea*, 25, 271-282 (2012)

**Abstract**

We explore the effect of removal of organic ligand on the atomic configurations around oxygen in hydroxyl groups in amorphous silica gel (synthesized through hydrolysis of SiCl$_4$ in diethylether) using high resolution $^{17}$O solid state NMR spectroscopy. $^1$H and $^{29}$Si MAS NMR spectra for amorphous silica gel showed diverse hydrogen environments including water, hydroxyl groups (e.g., hydrogen bonded silanol, isolated silanol), and organic ligands (e.g., alkyl chain) that may interact with surface hydroxyls in the amorphous silica gel, for instance, forming silica-organic ligand complex (e.g., Si-O···R). These physically and chemically adsorbed organic ligands were partly removed by ultrasonic cleaning under ethanol and distilled water for 1 hour. Whereas $^{17}$O MAS NMR spectra with short pulse length (0.175 $\mu$s) at 9.4 T and 14.1 T for as-synthesized amorphous silica gel showed the unresolved peak for Si-O-Si and Si-OH structures, the $^{17}$O MAS NMR spectra with long pulse length (2 $\mu$s)
showed the additional peak at ~0 ppm. The peak at ~0 ppm may be
due to Si-OH structure with very fast relaxation rate as coupled to
liquid water molecules or organic ligands on the surface of amorphous
silica gel. The observation of the peak at ~0 ppm in $^{17}$O MAS NMR
spectra for amorphous silica gel became more significant as the
organic ligands were removed. These results indicate that the organic
ligands on the surface of amorphous silica gel interact with oxygen
atoms in Si-OH and provide the information about atomic structure of
silanol and siloxane in amorphous silica gel. The current results could
enhance the understanding of dehydration mechanism of diverse
silicates, which is known as atomic scale origins of intermediate depth
(approximately, 70~300 km) earthquakes in subduction zone.
A2. Publication list

Journal Articles

International Journals


**Domestic Journals (Korean)**


**Conference Abstracts**

**International Conferences**

**Kim, H.N. and Lee, S.K.** Effect of particle size on phase transition among metastable alumina nanoparticles: A view from high resolution 2D solid-state $^{27}$Al NMR study, 2012 American Geophysical Union Fall meeting, San Francisco, USA, December 3-7, 2012 (poster)


**Kim, H.N. and Lee, S.K.** Atomic structure and dehydration kinetics in amorphous silica nanoparticles: Multi-nuclear solid-state NMR study, The 1st SNU-KYOKUGEN mini-symposium, Seoul,
Korea, October 20, 2008. (Oral)


**Domestic Conferences**


(Oral)


Kim, H.N. and Lee, S.K. Temperature induced changes in atomic
요약 (국문초록)

지구상에는 눈에는 보이지 않지만, 수~수십 나노미터의 입자 크기를 갖는 나노입자들이 존재하고 있다. 나노입자는 표면적이 커짐에 따라 체적(bulk)과는 다른 물리화학적 특성을 가지므로 다양한 규산염 나노입자의 물리화학적 성질에 입자크기가 미치는 영향에 대한 연구가 필요하지만, 이에 대한 체계적인 연구가 미흡한 실정이다. 고분해능 고상 핵자기공명 (nuclear magnetic resonanace, NMR) 분광분석은 특정 원자 주변환경에 대한 단거리 정보를 정량적으로 제시하는 분광분석 방법으로서, 결정질 및 비정질 시료의 원자구조 규명에 효과적이다. 따라서 본 학위논문에서는 각각에 존재하는 다양한 규산염 광물의 모델시스템으로서, 실리카와 알루미나 나노입자 및 체올라이트의 온도증가에 따른 원자환경 변화에 대해 연구하였으며, 특히 나노입자 크기가 탈수반응 반응시에 미치는 영향에 대한 고상핵자기 공명분광분석 연구를 실시하였다.

비정질 실리카 나노입자의 표면의 수산기와 물리흡착 된 물의 원자구조의 차이를 빠른 회전속도의 MAS (magic-angle spinning) NMR과 2D HetCor (heteronuclear correlation) 실험을 통해 연구하였다. 이를 바탕으로 본 연구에서는 비정질 규산염 나노입자의 탈수반응에 따른 원자환경의 변화 양상을 제시하는 원자단위의 탈수반응 메커니즘 모델을 제시하였다. 나노입자 크기는 비정질 규산염 나노입자의 물과 수산기의 양과 수소결합의 세기를 결정하며, 수산기의 원자구조와 함께 탈수반응 온도에 영향을 준다.
알루미나 나노입자의 온도 증가에 따른 상전이 메커니즘에 인자크기가 미치는 영향을 고분해능 2D \(^{27}\)Al 3Q(triple quantum) MAS NMR 분광분석을 통해 연구하였다. 본 연구에서, 알루미나에 존재하는 다양한 동질이상에 존재하는 알루미나 원자환경의 변화를 정량적으로 측정하였으며, 입자 크기가 감소함수록 안정상에서 안정상 알루미나의 상전이 온도가 뚜렷하게 작아짐을 관찰하였다.

Na-A형 제올라이트의 온도 증가에 따른 비정질화 메커니즘 및 무질서도의 변화에 대해 \(^{17}\)O 3QMAS NMR 분광분석을 통해 연구하였다. 온도 증가에 따른 제올라이트의 비정질 메커니즘 과정에서 원자사이의 결합각과 결합길이와 같은 위상적 무질서도 이외에 Si-Al 배열과 같은 화학적 무질서도가 증가함을 최초로 규명하였다. 이로부터 다양한 알루미노규산염 주구물질의 결정질-비정질 상전이 메커니즘에 대한 실마리를 제시할 것으로 기대된다.

지구 맨틀의 주 구성성분인 마그네슘 규산염 광물의 하나인 완화휘석(enstatite)과 물의 상호작용에 대한 산소 동위원소 교환반응 속도를 \(^{17}\)O 3QMAS NMR 분광분석을 통해 연구하였다. 그 결과, 연결산소와 비열결 산소와 같은 산소원자 환경의 차이에 따라 물과 마그네슘 규산염 광물 사이의 동위원소 교환반응속도의 차이를 관찰하였다.

본 학위논문의 결과는 나노 지구물질의 온도 증가에 따른 탈수반응 또는 상전이와 같은 지구화학 반응온도에 대한 나노입자 크기 및 수산기의 원자구조의 중요성을 제시한다. 이와 같이 나노입자의 크기에 따른 탈수반응 또는 상전이 온도의 변화는, 나노입자의 존재가 다양한 지구화학 반응속도 또는 반응온도에 불균질성을 가지고 올 수 있음을 의미한다. 본 학위 논문을 통하여,
보다 다양한 조성의 나노 지구물질의 온도 증가에 따른 탈수반응 메커니즘에 대한 이해를 고양시킬 것으로 기대된다.

주요어: 나노입자, 탈수반응, NMR, 지구물질, 상전이

학번: 2005-23250
감사의 글

무지에 가까운 설익음으로 시작한 어린 학생이 한 명의 연구자로 성장하기까지 많은 분들께 도움을 받았습니다. 가장 먼저 지도교수이신 이성근 교수님께 깊이 감사드립니다. 말로는 표현할 수 없는 많은 가르침을 주셨고, 존경할 수 있는 연구자의 자세를 몸소 보여주셨습니다. 또한 저에게 지구물질과학의 즐거움을 일깨워 주시고, 끝임없는 격려와 조언을 해주신 김수진 교수님께 감사의 말씀 드립니다. 제 부족한 박사논문을 보완해주시고 조언을 아끼지 않으신 이용일 교수님, 유인석 교수님, 정해명 교수님, 김영규 교수님, 김영희 교수님께도 감사를 표현합니다. 대학원 생활의 기쁨과 어려음을 함께 나눠온 이범한 선배님, 그리고 박신영, 이유수, 김효임, 김은정 후배님들에게 더할 수 없는 애정을 보냅니다. 경기도 화성의 인재육성에 기여하시며, 부족한 저에게 격려를 아끼지 않으며 연구장학금을 주신 정희준 이사장님과 관계자분들께도 깊은 감사의 마음을 전합니다. 마지막으로 사랑하는 가족들의 전폭적인 지원과 신뢰 덕분에 학위를 받을 수 있었습니다. 끝없는 사랑으로 저를 낳아주시고 길러주시 아버지 어머니께, 그리고 가족의 둔든한 버팀목으로 성장해 준 동생에게 깊은 감사의 마음 전합니다.