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공학박사 학위논문

Methane oxychlorination over CeO_2 and metal oxychloride catalysts

세리아 및 금속 산화염소화물 촉매를 통한 메탄의 산화염소화반응

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허 은

Abstract

Methane oxychlorination over CeO_2 and metal oxychloride catalysts

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Although the proportion of renewable energy resources is accelerating, fossil fuels are still expected to account for 77% of energy use in 2040. Recently, methane is in the spotlight because of its abundance in shale gas and natural gas. However, methane has a strong C–H bond. It is hard to selectively break the bond and directly transform into desirable chemicals other than CO or CO_2.

Conversion of methane into substituted derivatives and higher hydrocarbons is a most desirable goal. The conversion of CH_4 into high-value chemicals via the syngas route is the main industrial process currently in use. Since the syngas route must overcome the high thermodynamic barrier, resulting in the large energy consumption, researchers have been trying to

directly convert methane into chemical products other than CO or CO_2 via oxidative methane coupling, direct methane aromatization, or halogenation of methane. Among them, halogenation of methane has the advantage over the others due to the relatively low reaction temperature.

Chlorine (Cl) is an important element for manufacturing important industrial chemicals and consumer products. Chloride chemicals of C_2 and C_3 have been used in industry, and oxychlorination of C_2, C_3 has been investigated for a long time since it has weaker C-H bond than methane.

Here, the oxidative chlorination of methane to produce chloromethane (CH_3Cl, CM) over CeO_2 and metal oxychloride catalysts was investigated.

We focused on CeO_2 catalyst since it was reported to have higher oxidative chlorination of methane. Oxychlorination of methane was performed over CeO_2 catalyst while changing different reactant ratios. The reactions were carried out at 480℃ by changing O_2 and HCl concentrations at fixed CH_4 concentration. It was found that the ratio of O_2:HCl (1:2) is the most important parameter to obtain high CH_4 conversion and CH_3Cl selectivity. Note that excessive HCl gives rise to the formation of the increased amount of more chlorinated products, such as CH_2Cl_2 or $CHCl_3$, due to the subsequent chain reaction with HCl and excessive O_2 promoting the oxidation of methane to CO and CO_2. The optimum reactant ratio of

CH_4:O_2:HCl was 4:1.5:3, with the highest CH_3Cl yield (14.3%). Various characterization results indicated that CeO_2 catalyst was slightly sintered and had no carbon and chlorine deposition on the surface after the reaction.

Also, oxidative chlorination of methane over metal oxychloride catalysts was studied since they showed good performance on C_{2-3} oxychlorination. CeOCl, LaOCl, and EuOCl were applied to oxidative chlorination of methane in the range of 480-520℃. It was found that CeOCl showed the highest CH_4 conversion and CM yield although the CM yield was lower than CeO_2. Ni was doped on the oxychlorides catalysts to improve the activity. However, it was found that Ni doping only improved CO_2 formation rather than CM production.

From these two studies, we can conclude that CeO_2 is the best catalyst for oxidative chlorination of methane since it has high reactivity. Also, oxychloride catalysts suppress CO_x generation than CeO_2. Ni addition is not desirable since it showed CO_2 production when the support-only experiments showed no CO_2 formation.

Keywords: Oxidative chlorination, methane, CeO_2, metal oxychloride (M-OCl), chloromethane (CH_3Cl)

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Chapter 1. Introduction

1.1. Methane

The utilization of fossil fuels, such as coal, petroleum, and natural gas, has provided a large amount of energy and useful chemicals for industry and our daily lives, however, it has caused serious impacts on the environment. In addition, the depletion of fossil fuels has been accelerated due to the high dependency in energy consumption for several decades. Renewable and environmentally friendly alternative resources are under development, but it is still highly dependent on fossil fuels.

Methane is one of the most abundant and low-cost carbon-based feedstocks available (shown in Figure 1-1) [1]. Methane, which takes the most part of the natural or shale gas (shown in Figure 1-2), is regarded as an important raw material for the synthesis of chemicals or fuels in the future. Since CH_4 has the most stable structure among organic molecules, CH_4 activation is much more difficult than other hydrocarbons [2]. As the emerging number of untapped and unconventional natural gas reserves are recently found, the development of efficient and selective methane conversion processes to fuels and chemicals has become critical in the recent years [3].

To dissociate the first C-H bond of CH_4 to CH_3^*+H is the main issue associated with utilization of methane, since C-H bond activation has a large associated energy of 440 kJ/mol. From this point of view, an optimum catalyst is required to lower the energy and facilitate the bond dissociation process [4].

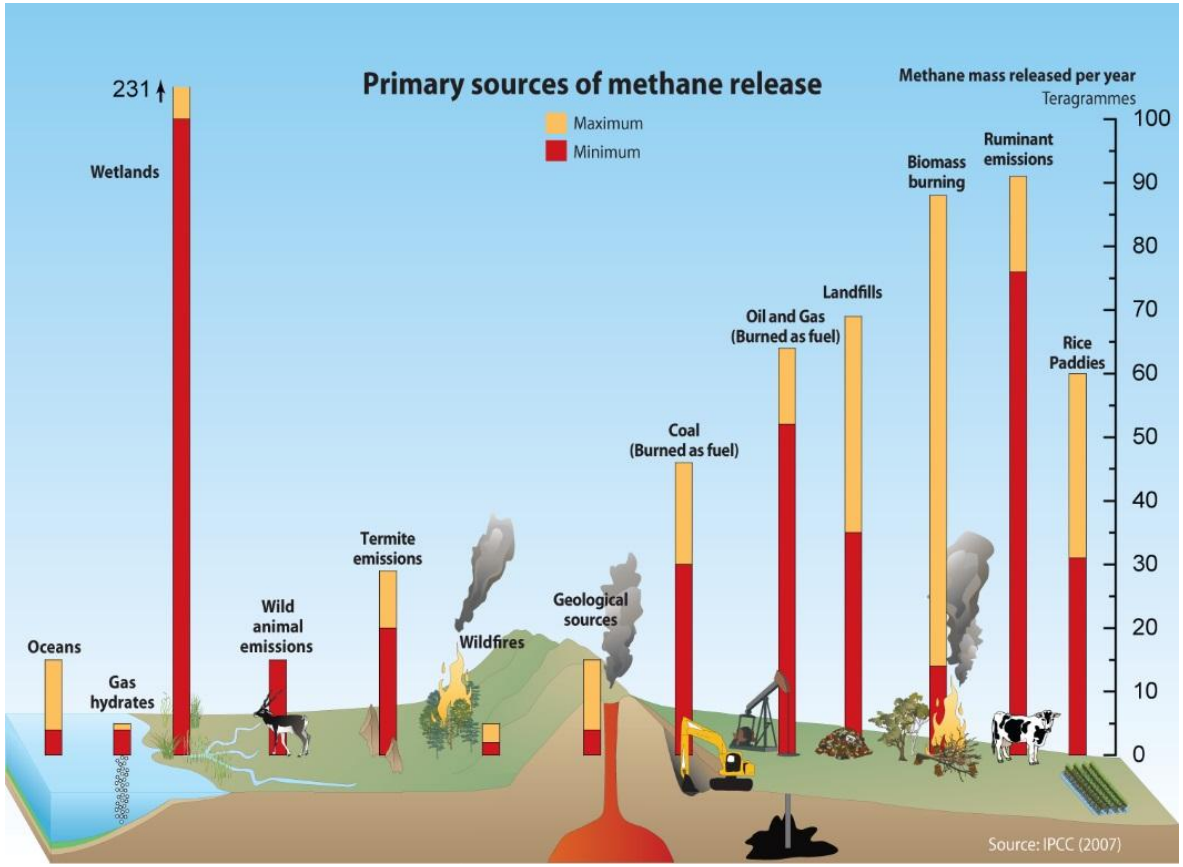

Figure 1-1. Primary sources of methane release. [5]

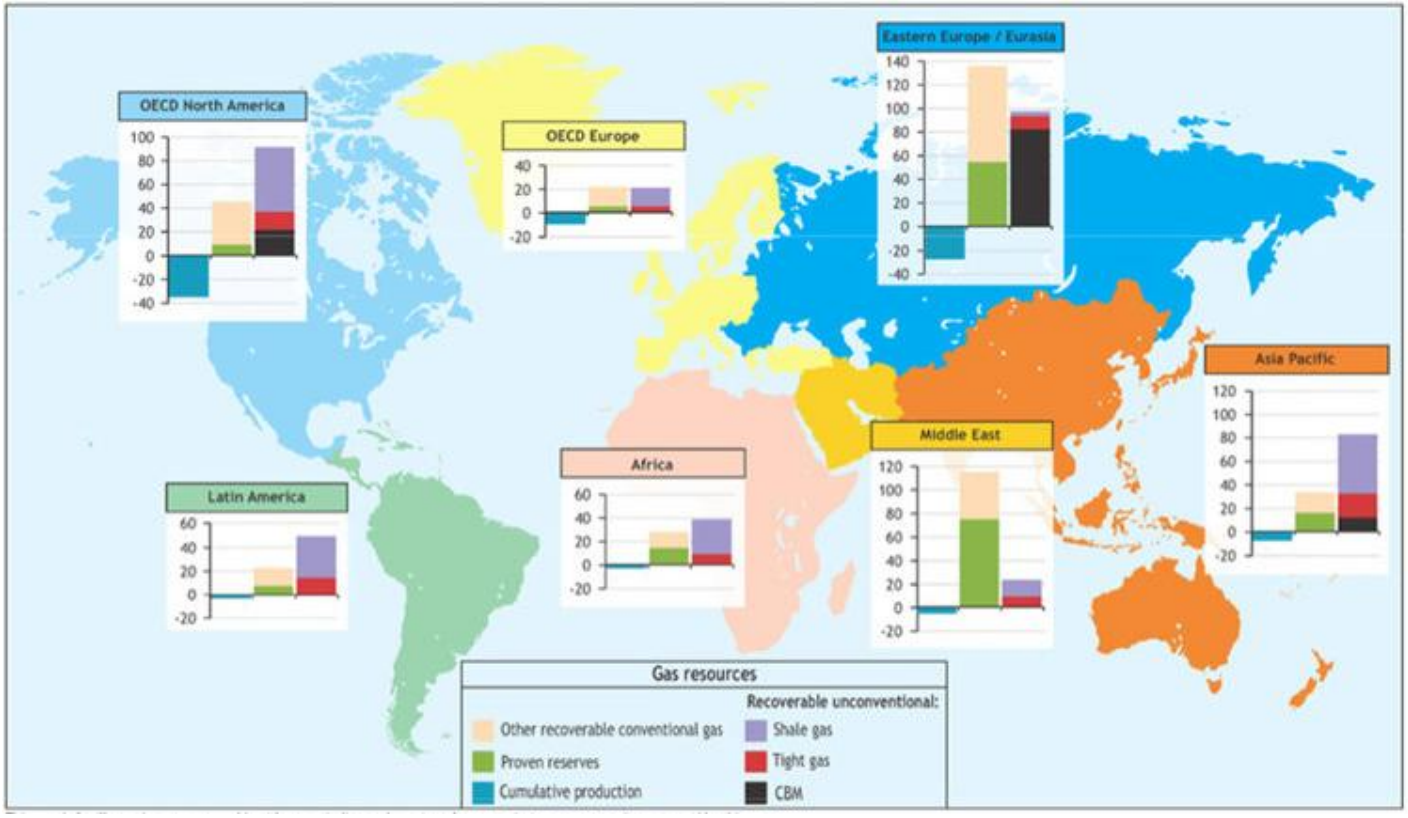

Figure 1-2. World natural gas resources, Jan. 2010 (tcm) [6]

1.2. Methane activation

Chemical processes based on methane activation are getting more economically attractive. Because most of the methane is burned for heating and electrical generation and a tiny fraction is used as a fuel in vehicles, the carbon and hydrogen contents in methane are not utilized to their full potential in the chemical industry.

Presently, in industry, methane is transformed into bulk chemicals by the both direct and indirect routes [7]. Nowadays, methane activation which converts methane into syngas (H_2+CO) at high temperature (>700℃) is popular, followed by making chemical feedstocks from the produced syngas (see Fig. 1-3 and Table 1-1). Steam reforming (SR) is promising because of its high productivity (more than 75% of hydrogen gas) and high efficiency. Also, it is easy to operate stably in various reaction conditions. However, it needs long time to reach the stable reaction condition and consumes lots of energy. Compare with SR, Partial oxidation (POX) needs short time to reach the stable reaction condition. Also, it is operated in low reaction temperature, so the energy consumption was low. On the other hand, it only produces few hydrogen gas, and is hard to control the operation. From this, many research groups tried to overcome the disadvantages by using better catalysts, however, it is still on investigation [8]. Hot spots appear often in this reaction, so that

the efficiency of POS is low. Autothermal reaction (ATR) also easily reach the reaction condition as POX. Also, in this reaction, endothermic and exothermic reaction occurs at the same time, beneficial in heat management. However, similar with POX, low hydrogen production and difficulty in reaction control are its disadvantage. Carbon dioxide reforming (CDR) is promising since it uses carbon dioxide who is the greenhouse gas as the reactant. But it produces too much CO after the reaction. Coke formation makes catalysts deactivated in a short time. Low efficiency and high energy consumption of CDR are the problems to be solved [9].

This process is energy intensive and the cost is high, so that it is needed to develop one-step process to make methane converted into useful chemicals.

One-step technologies, such as oxidative coupling of methane (OCM), selective oxidation of methane and halogenation, have been proposed. Both OCM and selective oxidation make methane react with oxygen, however, the product is easy to react and turn into other chemical, so the kinetic protection or the selective separation of the product is necessary. Studies on both OCM and selective oxidation has been investigated for a long time, and still needs more work to do [10].

Halogenation has been studied from 19th century, found out iodination is inactive, and fluorination is explosively reactive. Since it is hard to control the reaction on iodination and fluorination, bromination and

chlorination has

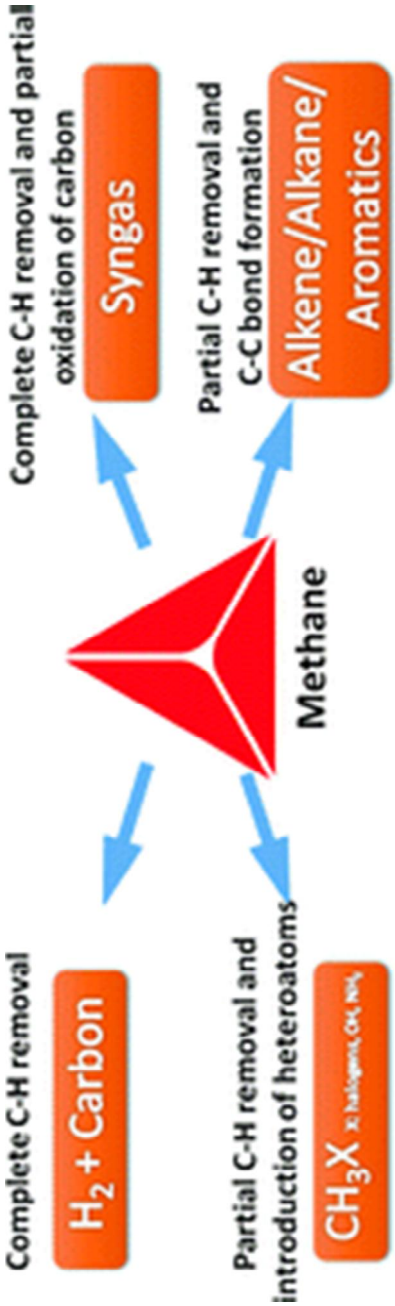

Figure 1-3. Various ways of methane activation. [7]

Table 1-1. Methane activation reactions to produce syngas

Reaction	Equation
Steam reforming	$CH_4 + H_2O = CO + 3H_2$ (endothermic)
Partial oxidation	$CH_4 + 0.5\ O_2 = CO + 2H_2$ (exothermic)
Autothermal reforming	$CH_4 + H_2O = CO + 3H_2$ $CH_4 + 0.5\ O_2 = CO + 2H_2$
Carbon dioxide reforming	$CH_4 + CO_2 = 2CO + 2H_2$ (endothermic)

been studied [11, 12]. (shown in Figure 1-4) Bromination of methane is preferred over chlorination as the former provides a higher selectivity for mono-haloalkanes and more facile halogen elimination than the latter because of the weaker C-Br bond (284.9 kJ/mol) than C-Cl bond (338 kJ/mol) [13]. However, chlorination of methane attracts more attention since chlorine is currently being used as one of the most important chemical elements in the production of numerous chemicals, either directly as component or as production intermediates (shown in Figure 1-5) [14].

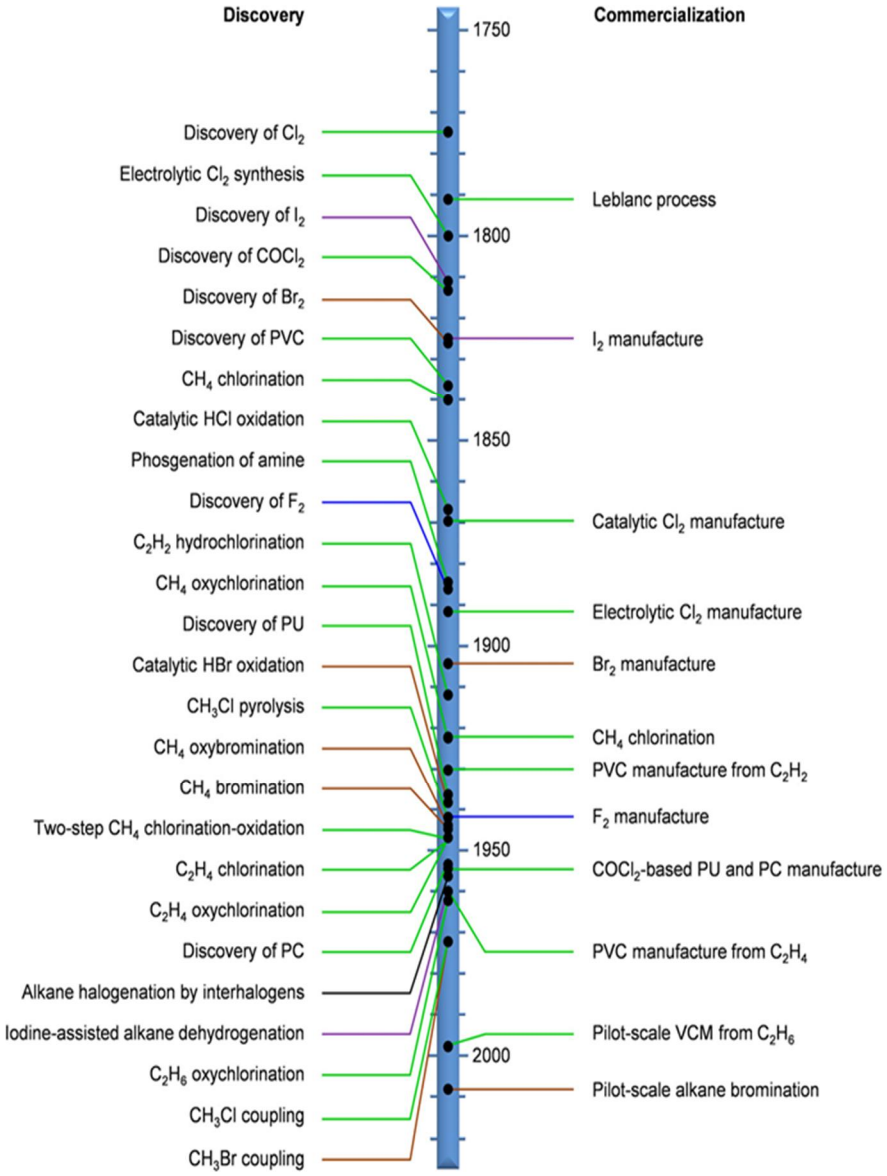

Figure 1-4. Chronological development of halogen-mediated processes (left) and their implementation in industry (right) for hydrocarbon conversion to comodities. [15]

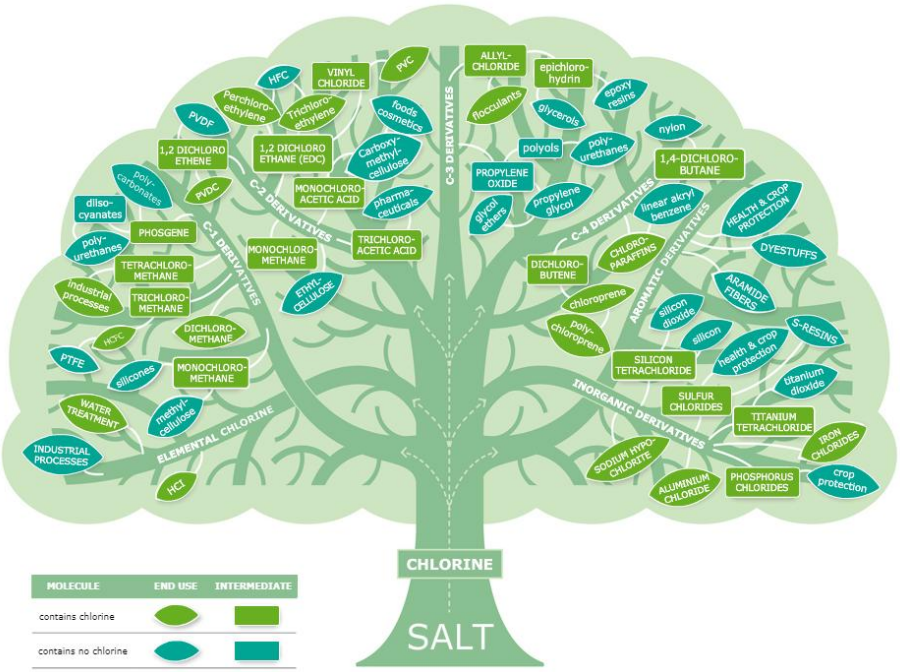

Figure 1-5. Chlorine tree. [15]

1.3. Oxychlorination of methane

Usually, halogenation of hydrocarbons produces hydrogen halide, so that it needs additional reaction to make halogen gas from hydrogen halide. Since methane has strong C-H bonding energy, C2 or C3 was introduced as the hydrocarbon reactant.

Ethylene oxychlorination was studied by various research groups, and their results are shown in the Table 1-2.

Table 1-2. Catalysts for Ethylene Oxychlorination [15]

Catalyst	Reactivity		Conditions		
	X (%)	S (%)	reactor	GHSV (h^{-1})	T (K)
$CuNaRCl_x/Al_2O_3$	99	94 (EDC)	fluidized	–	533
$CuKCl_x/MgO\text{-}SiO_2$	34	95 (EDC)	fluidized	760	633
$CuMgNaCl_x/r\text{-}Al_2O_3$	99	97 (EDC)	fixed	–	553
$CuPdNaCl_x/Al_2O_3$	97	82 (EDC)	fixed	200	547
$PdFeNaCl_x/Al_2O_3$	88	60 (VCM)	fixed	200	560
$RhFeZnLiCl_x/\alpha\text{-}Al_2O_3$	29–46	42–77 (VCM)	fluidized	–	623
LaOCl	33	87 (VCM)	fluidized	62	672
CeO_2	35	85 (EDC)	fixed	–	673
$CeO_2\text{-}ZrO_2$	60	50 (VCM)	fixed	–	673

However, oxyhalogenation of methane do not need such recycling step since it uses HX instead of X_2 (X=F, Cl, Br, and I). Moreover, it is thermodynamically more stable than halogenation [15]. Considering such economical point of view, oxyhalogenation of hydrocarbon is more favorable than halogenation in industry.

Oxychlorination is a key-process in the modern chemical industry, playing an important role for incorporation of chlorine atoms into both saturated and unsaturated hydrocarbons, such as methane, ethylene and benzene [16]. Chlorine-mediated process for the one-step conversion of light alkanes into ethylene and propylene is shown in the Figure 1-6.

In the oxychlorination reaction, methane is reacted with HCl and oxygen over a catalyst to produce mono-chloromethane and water (eq. 1):

$$CH_4 + 1/2\ O_2 + HCl = CH_3Cl + H_2O\ (\Delta H^0_{298K} = -\ 685.8\ kJ/mol)\ (eq.\ 1)$$

However, it is not easy to have the high selectivity of methyl chloride since the subsequent chain substitution can occur in the reaction condition to produce di-or tri-substituted chlorinated products.

There were previous studies about oxyhalogenation of $C_{1\text{-}3}$ alkane. Ramirez et al. studied ethane and propane oxyhalogenation over EuOCl, showing high olefin selectivity [17]. Their study found out that ethane

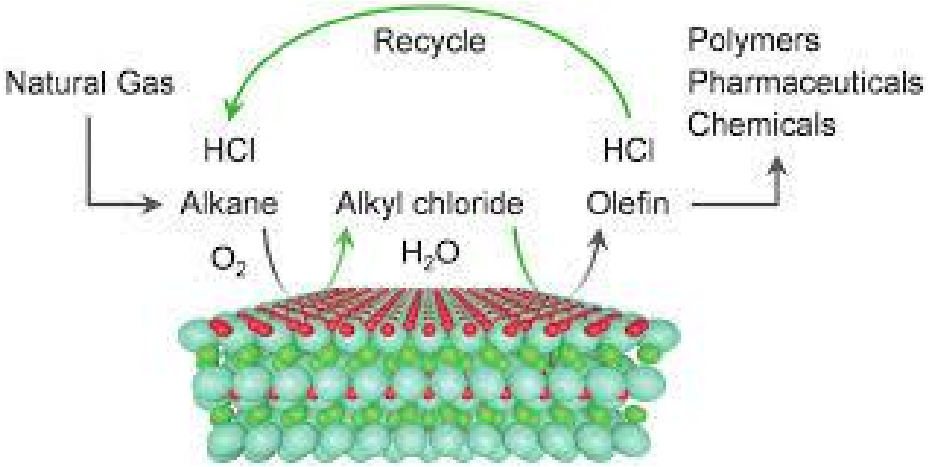

Figure 1-6 Closed-loop chlorine-mediated process for the one-step conversion of light alkanes into ethylene and propylene [18]

oxychlorination showed lower CO_x than oxybromination. They also reported that the apparent activation energy of C_2H_6 oxychlorination (128 kJ/mol) over EuOCl is lower than the oxybromination (220 kJ/mol) over EuOBr, implying that oxychlorination is better than oxybromination again. Lercher et al. used LaOCl for methane oxychlorination and found out that it turned into $LaCl_3$ which acted as the catalyst to produce methyl chloride [19]. In addition, since CeO_2 showed good performance in oxychlorination of hydrocarbon, CeOCl was also tried as catalyst for methane oxychlorination.

FeO_x/CeO_2 was also studied on oxychlorination of methane [20]. It showed the highest CM yield at 510℃ and found out Fe restrained the sintering of catalyst because of the Fe-Ce solid solution.

1.4. Objective

In this study, we investigate the catalytic performance of oxidative chlorination of methane over several metal oxychloride catalysts which showed good performance in oxidative chlorination of C_2 and C_3. Nickel, who is cheap and widely used in methane activation, was loaded on the prepared metal oxychloride catalysts to figure out whether it can promote the reactivity of the metal oxychloride catalysts for the methane oxychlorination.

As global warming has become a serious environmental problem, and greenhouse gases such as CH_4 and CO_2 are primarily responsible for it [21, 22], studies on methane oxychlorination over catalysts will be helpful both on environmental and chemical engineering aspects.

Chapter 2. Effect of reactant ratios on methane oxychlorination over CeO_2 catalyst

2.1. Introduction

Although the proportion of renewable energy resources is accelerating, fossil fuels are still expected to account for 77% of energy use in 2040 [23]. Recently, natural gas or shale gas in which methane is the major component has received attention due to its abundance on earth.[24] Methane has a strong C–H bond, so that it is hard to selectively break the bond and directly transform into desirable chemicals other than CO or CO_2. Hence, the conversion of CH_4 into high-value chemicals via the syngas route is the main industrial process currently in use [25-27]. Since the syngas route must overcome the high thermodynamic barrier, resulting in the large energy consumption, researchers have been trying to directly convert methane into products other than CO or CO_2 via oxidative methane coupling, direct methane aromatization, or halogenation of methane [3, 28]. Among them, halogenation of methane has the advantage over the others due to the relatively low reaction temperature.

In the 20th century, halogenation of methane by X_2 (X=F, Cl, Br, and

I) was examined [29-31]. Among the halogen molecules, it was found that iodine was too inactive and that fluoride was too explosively reactive to control the reaction [28]. Hence, bromine and chlorine were regarded as better candidates for halogenation [32]. Especially, chlorination of methane received more attention due to the more familiar chlorine-based processes in industry, such as the production of vinyl chloride. However, since chlorination of methane must use the dangerous Cl_2 gas and, moreover, requires the additional step of recovering the molecular Cl_2 by catalytic HCl oxidation (Deacon reaction)[33], the oxychlorination reaction is regarded as a more feasible approach that can produce chloromethane in one step using HCl and O_2.[15]. The reaction of methane oxychlorination is as follows:

$$CH_4 + 1/2\ O_2 + HCl = CH_3Cl + H_2O\ (\Delta H^0_{298K} = -\ 685.8\ kJ/mol)$$

Methane oxidative chlorination has been investigated recently over Pd(II) complexes-heteropolyacids-silica gel,[34] supported acid [29], Pt metal [29], and metal oxide catalysts [35]. Meanwhile, CeO_2 was found as the most promising catalyst among many single metal oxide candidates for methane oxychlorination because of its high CH_4 conversion and CH_3Cl selectivity [35-37]. However, the previous study fixed the reactant ratio of CH_4:O_2:HCl to 4:1:2. A question arises as to how the reactant ratios affect the activity and selectivity of methane oxychlorination over CeO_2. Therefore, this study aims at finding the optimum reactant ratio for producing more CH_3Cl with less

byproducts, such as CH_2Cl_2, CO, and CO_2, over CeO_2 catalyst.

2.2. Experimental

2.2.1. Preparation of catalysts

The CeO_2 catalyst was acquired in various ways. Some was manufactured by Sigma Aldrich, Alfa Aesar, Samchum, and TCI (Tokyo Chemical Industry Co., LTD.). Also, CeO_2 provided by Rhodia was examined. The CeO_2 catalysts were calcined at 600℃ for 6 h in a muffle furnace.

2.2.2. Characterizations

N_2 adsorption and desorption isotherms were measured at -196℃ on a Micromeritics ASAP 2010 apparatus. The average pore diameter, average pore volume, and specific surface area were calculated by using the Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods, respectively.

The powder X-ray diffraction (XRD) patterns were taken by using a Rigaku (Smart Lab) diffractometer with Cu K_α radiation (λ=0.1542nm). The voltage and current of X-ray were 40 kV and 50 mA, respectively. The patterns were collected with a scanning step size of 0.02° at a speed of 2.5°/min.

Temperature-programmed reduction (TPR) measurements were made in a flow system. 50mg catalyst was placed in a TPR cell and pretreated in Ar at 300℃ for 30 min, followed by 60-minute-long air zero treatment at the same temperature condition. The water produced by the reduction was captured in the drierite trap. The temperature of the sample was programmed to rise at a constant rate of 10℃/min and the amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD).

2.2.3. Catalyst reaction tests

The reaction system is shown in Figure 2-1.

All catalytic reactions were performed in a 3/8-inch quartz tubular reactor at a reaction temperature of 480℃. The sieved catalyst (180~250㎛, 0.1g) was located on the filter in the middle of the quartz reactor. The reaction temperature was controlled by a thermocouple placed just above the catalyst bed. To protect the thermocouple from HCl in the reactant, a narrow glass cap covered the thermocouple, which was inserted into the quartz reactor. Each reactant, such as HCl (40%, Ar balance), CH_4, and O_2 balanced with N_2, was introduced into reactor via mass flow controllers (MFC) with a gas hourly space velocity of 30,000h^{-1}. During the reaction, the effluent gas was analyzed

by gas chromatography (GC, Agilent 6890N). The GC was equipped with two detectors and two columns: thermal conductivity detector (TCD) with packed column (Carboxen 1000) and flame ionization detector (FID) with capillary column (HP-Plot Q). After the GC analysis, the effluent gas passed through the sodium carbonate trap so that the corrosive gas could be neutralized before venting out.

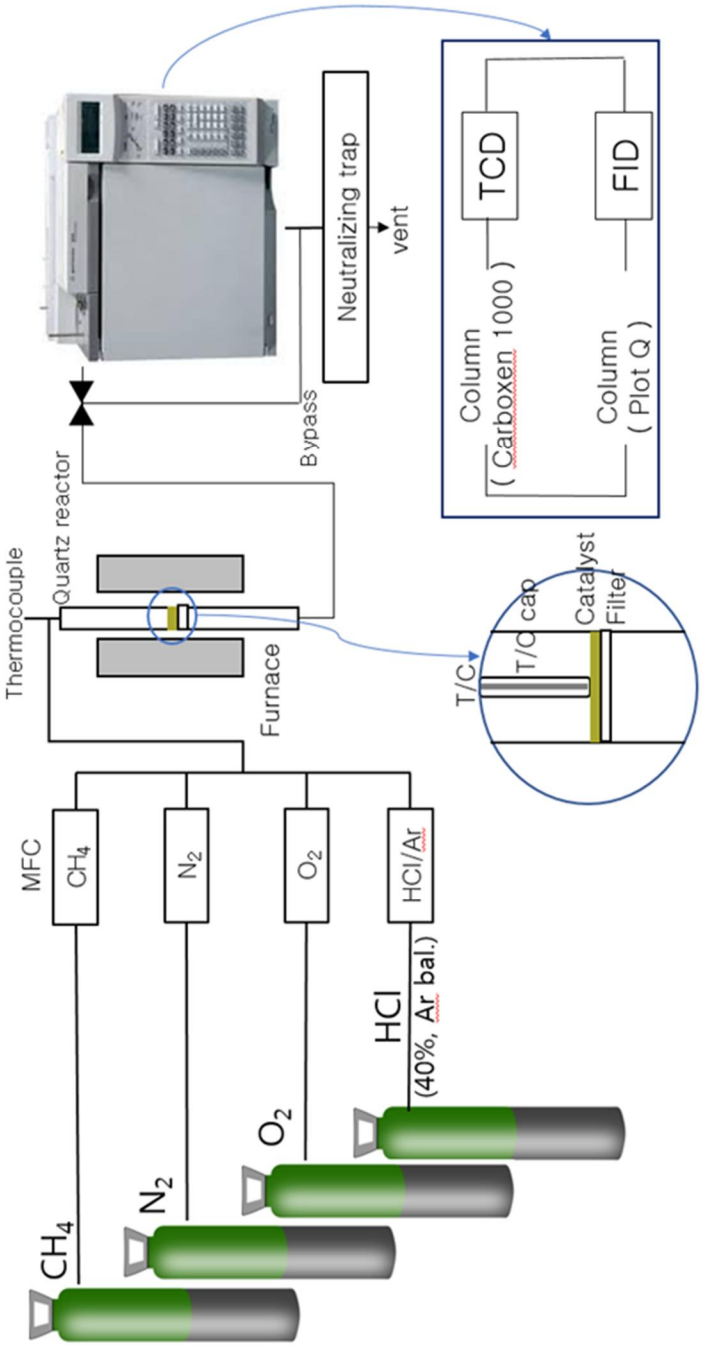

Figure 2-1. The methane oxychlorination reaction system.

2.3. Results and discussion

2.3.1 Selection of CeO_2

CeO_2 from various manufacturers were examined.

Before the reaction, CeO_2 catalysts which were calcined at 600℃ for 6hr were sieved with the particle size of 180-250 ㎛. Catalytic characterization before the reaction was performed, found out different surface area and pore size among the CeO_2 catalysts, shown in the Table 2-3. All the CeO_2 catalysts before the reaction showed light-yellow color.

During the reaction, all CeO_2 catalysts showed good performance compared with other metal oxide catalysts, such as MgO, Al_2O_3, and TiO_2. However, each catalyst showed different result. After the reaction, the CeO_2 catalysts was analyzed using BET and XRD.

Since results of each used CeO_2 catalysts from various manufacturers showed difference (shown in Table 2-4), the catalysts before the reaction was examined by temperature-programmed reduction (TPR) to figure out quantitative information on the reducibility of each CeO_2 catalysts. The TPR graph of CeO_2 catalysts from Rhodia, Sigma Aldrich, and Junsei is presented in Figure 2-2. As shown in the figure, for pure CeO_2, the peak at a temperature

of 525℃ represents surface reduction of CeO_2 [38-42]. CeO_2 from Rhodia, Sigma Aldrich, and Junsei showed H_2 consumption, however, the peak intensity of each CeO_2 catalysts sample was different.

Table 2-3. Surface area, average pore diameter, and average pore volume of CeO_2 catalysts from different manufacturers: before the reaction

Manufacturer	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
Sigma Aldrich	118.6	8.2	0.33
Alfa Aesar	105.5	8.9	0.24
Rhodia	128.7	9.2	0.30
Jungwoo	123.9	7.2	0.30
Junsei	55.4	0.7	0.10
Kanto	78.8	0.1	0.20

Table 2-4 Surface area, average pore diameter, and average pore volume of CeO_2 catalysts from different manufacturers: after the reaction

Manufacturer	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
Sigma Aldrich	54.8	0.17	10.7
Alfa Aesar	20.7	15.9	0.09
Rhodia	87.2	15.2	0.34
Jungwoo	97.0	9.4	0.34
Junsei	47.1	1.0	0.11
Kanto	62.5	0.5	0.20

Chapter 3. Methane oxychlorination over metal oxychloride catalysts

3.1. Introduction

Methane takes the most part of the natural or shale gas, so that it is regarded as an important raw material for the synthesis of chemicals or fuels in the future. Since CH_4 has the most stable structure among organic molecules, CH_4 activation is much more difficult than other hydrocarbons [2]. To dissociate the first C-H bond of CH_4 to CH_3^*+H is the main issue associated with the utilization of methane, because C-H bond activation has a large dissociation energy of 440 kJ/mol. From this point of view, an optimum catalyst is required to lower the energy barrier for methane activation and facilitate the selective bond dissociation process [4].

As the emerging number of untapped and unconventional natural gas reserves are recently found, the development of efficient and selective methane conversion processes to fuels and chemicals has become critical in the recent years [3].

Bromination of methane is preferred over chlorination as the former provides a higher selectivity for mono-haloalkanes and more facile halogen

elimination than the latter because of the weaker C-Br bond (284.9 kJ/mol) than C-Cl bond (338 kJ/mol) [13]. However, chlorination of methane attracts more attention since chlorine is currently being used as one of the most important chemical elements in the production of numerous chemicals, either directly as component or as production intermediates [14]. Usually, halogenation of alkane produces hydrogen halide, so that it needs additional reaction to recover halogen gas from hydrogen halide. However, oxyhalogenation of methane do not need such recycling step since it uses HCl instead of Cl_2. Moreover, oxyhalogenation is better than halogenation since the former enables 100% halogen atom efficiency [15]. Considering such economical point of view, oxyhalogenation of hydrocarbon is more favorable than halogenation in industry.

In the methane oxychlorination reaction, methane is reacted with HCl and oxygen over a catalyst to produce mono-chloromethane and water (eq. 1):

$$CH_4 + 1/2\ O_2 + HCl = CH_3Cl + H_2O\ (\Delta H^0_{298K} = -\ 685.8\ kJ/mol) \quad (eq.\ 1)$$

However, it is not easy to have the high selectivity of methyl chloride since the subsequent chain substitution can occur in the reaction condition to produce di- or tri-substituted chlorinated products.

There were previous studies about the oxyhalogenation of C_{1-3} alkane. Ramirez et al. studied ethane and propane oxyhalogenation over

EuOCl, which showed high olefin selectivity.[17] They found that ethane oxychlorination produced lower CO_x than oxybromination. They also reported that the apparent activation energy of C_2H_6 oxychlorination (128 kJ/mol) over EuOCl is lower than the oxybromination (220 kJ/mol) over EuOBr, implying that oxychlorination over EuOCl is a promising route to convert methane. Lercher et al. reported that LaOCl catalyst is active for methane oxychlorination [19, 20]. In addition, since CeO_2 showed good performance in the oxychlorination of hydrocarbon, CeOCl is also selected as a potential catalyst for methane oxychlorination. Hence, we applied CeOCl, EuOCl and LaOCl catalysts to the methane oxychlorination in this study.

This study aims at investigating the catalytic performance of the oxidative chlorination of methane over several metal oxychloride catalysts which showed good performance in oxidative chlorination of C_{1-3} alkane. Nickel, which is cheap and widely used in methane activation, was loaded on the prepared metal oxychloride catalysts to figure out whether it can promote the reactivity of the metal oxychloride catalysts for the methane oxychlorination.

3.2. Experimental

3.2.1 Preparation of metal oxychloride (M-OCl) catalysts

LaOCl was prepared by following the method reported by Lercher [19]. At room temperature, NH_4OH base solution was added dropwise into the $LaCl_3$ precursor solution. The mixed suspension was stirred for 1hr and then precipitated. After centrifuging the solution, obtained precipitate was washed with ethanol to remove residual base, followed by freeze drying. The sample was calcined at 550℃ for 8hr.

CeOCl was prepared by solid state reaction between CeO_2 (Sigma Aldrich) and $CeCl_3 \cdot 6H_2O$ (Junsei), following the previous literature [46]. Before powder mixture of two precursors was ground in mortar, $CeCl_3 \cdot 6H_2O$ was dried in an oven at 80℃ to remove moisture. After drying the mixture, the powder was calcined in N_2 flow (50ml/min) at 750℃ for 10hr. The obtained powder was washed with distillated water (DIW) to remove unreacted $CeCl_3$, then dried in air at 80℃.

EuOCl was prepared by treating Eu_2O_3 (Sigma Aldrich, 99.5%) at 540℃ for 4hr under HCl (40%, Ar balance) atmosphere.

Nickel was impregnated on all prepared metal oxychloride catalysts by using incipient wetness impregnation method. Each support was loaded with 5 mol% of Ni, using an aqueous solution of nickel (II) nitrate hexahydrate.

3.2.2 Characterization

3.2.2.1 BET

N_2 adsorption / desorption was performed to figure out the specific surface area of each catalysts before and after the reaction, referred as fresh and used sample. This characterization was performed in a Micromeritics ASAP 2010 apparatus. The BET surface area was obtained by using Brunauer–Emmett–Teller (BET) methods. Prior to the measurement, all samples were degassed under evacuated condition at 200 °C for 3 h.

3.2.2.2 XRD

The powder X-ray diffraction (XRD) patterns were taken from Rigaku (Smart Lab) diffractometer with Cu K_α radiation (λ=0.1542nm) under the voltage of 40kV and the current of 50 mA. The patterns were collected with a scanning step size of 0.02° at a speed of 2.5°/min.

3.2.3 Reaction system setup and condition

By using the reaction system as shown in Figure 2-1, oxidative

chlorination of methane over metal oxychloride was performed. Reactants were introduced in a 3/8-inch quartz tubular reactor via MFC (mass flow controller). On the catalyst bed (180~250㎛, 0.1g), reaction was carried out in the temperature range of 480 and 520℃ at 1 atm. The ratio of reactants was set to CH_4:O_2:HCl of 4:1:2 with the GHSV of 30,000h^{-1}. The effluent gas was analyzed by gas chromatography (GC, Agilent 6890N), equipped with two detectors and two columns: thermal conductivity detector (TCD) with packed column (Carboxen 1000) and flame ionization detector (FID) with capillary column (HP-Plot Q). The effluent gas passed through the sodium carbonate aqueous solution trap so that the corrosive gas could be neutralized before venting out.

3.3. Results and discussion

3.3.1 Metal oxychloride catalysts

In the previous work, we tested CeO_2 for methane oxidative chlorination since it showed good activity among the various metal oxide catalysts [35, 48]. Accordingly, we applied various oxychloride catalysts to the methane oxychlorination in comparison of CeO_2. The prepared oxychloride catalysts and CeO_2 were tested under the same condition.

As presented in Table 1, the increase in reaction temperature resulted in the increased CH_4 conversion under all reaction temperatures. CeOCl, LaOCl, and EuOCl showed the increase in CH_4 conversion from 6.6 to 14.3%, 1.8 to 9.3%, 1.4 to 2.9 % when the reaction temperature increased from 480 to 520℃, respectively. Methane conversion over CeO_2 was higher than those over oxychloride catalysts, especially at lower temperature (480℃). When the reaction temperature increased from 500 to 520℃, CM yield over CeOCl increased markedly from 6.2 to 9.6%, while the CM yield decreased slightly from 14.4 to 13.9% over CeO_2, because of the saturated CH_4 conversion.

In Figure 3-1, the activity results of all metal oxychlorides and CeO_2 catalysts at 520℃ were compared. As seen, CeOCl showed the highest CM selectivity (67.5%) among the metal oxychloride catalysts, even higher than CeO_2 (44.2%). In addition, we can figure out that, although CeO_2 has higher conversion (31.4%) than metal oxychloride catalysts (CeOCl=14.2%, LaOCl=9.3%, EuOCl=2.9%), CeO_2 produces more CO_x (selectivity=49.3%) than CM (44.2%) at 520℃. From this point of view, CeOCl is promising since it has higher target product selectivity with less production of CO and CO_2.

N_2 physisorption results of the catalysts before and after the reaction are shown in Table 2. The surface area of post-reaction CeOCl was decreased negligibly (29.9 to 28.8 m^2/g), although LaOCl and EuOCl showed the drastic decrease in surface area, from 31.1 to 2.9 m^2/g and 14.7 to 5.6 m^2/g,

respectively. In addition, CeO_2 demonstrated the significant decrease in BET surface area by 50% after the reaction.

XRD pattern of oxychloride catalysts and CeO_2 catalyst before and after the reaction is shown in Figure 3-2. XRD patterns of all catalysts before and after the reaction did not change too much. Both the XRD pattern of the fresh and used CeO_2 catalyst showed diffraction peaks corresponding to the cerium oxide phase with a fluorite crystal structure (JCPDS number of 43-1002). Also, fresh and used CeOCl, LaOCl and EuOCl catalysts showed same XRD patterns of theie references with JCPDS number of 52-1843, 08-0477, and 12-0163, respectively. Note that all metal oxychloride catalysts maintained their original phase after the reaction.

Table 3-1. Comparison of CeO_2 and M-OCl (M=Ce, La, and Eu) catalysts. (Reaction conditions: CH_4:O_2:HCl=4:1:2, GHSV=30,000h^{-1}, Time-on-stream=2hr, P=1atm)

Catalyst_temp.	Yield (%)					CH_4 conversion (%)
	CM	DCM	TCM	CO	CO_2	
CeOCl 480	4.9	0.5	0.0	0.8	0.3	6.6
CeOCl 500	6.8	1.1	0.0	1.1	0.2	9.2
CeOCl 520	9.6	2.0	0.0	2.1	0.5	14.2
LaOCl 480	1.2	0.1	n.d.	0.5	n.d.	1.8
LaOCl 500	3.7	0.5	0.0	3.3	n.d.	7.5
LaOCl 520	4.2	0.7	0.1	4.3	n.d.	9.3
EuOCl 480	0.8	0.0	n.d.	0.6	n.d.	1.4
EuOCl 500	0.9	0.0	n.d.	1.0	n.d.	1.9
EuOCl 520	1.1	0.1	n.d.	1.7	n.d.	2.9
CeO_2 480	9.8	2.4	0.1	1.7	1.2	15.2
CeO_2 500	14.4	2.4	n.d.	7.9	5.6	30.4
CeO_2 520	13.9	2.0	0.0	9.0	6.5	31.4

* n.d.: not detected

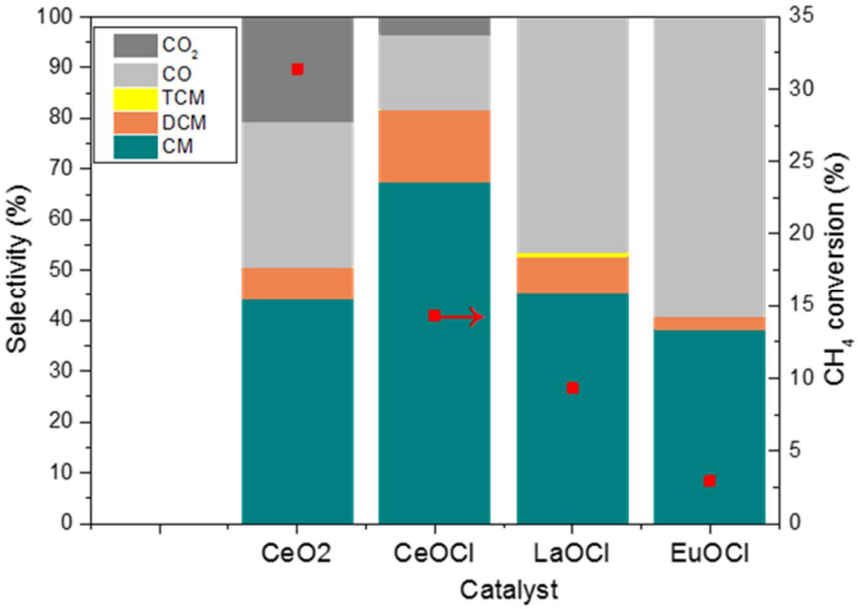

Figure 3-1. The product yield over CeO_2, CeOCl, LaOCl, and EuOCl for methane oxychlorination. (Reaction conditions: CH_4:O_2:HCl=4:1:2, GHSV=30,000h^{-1}, Time-on-stream=2hr, P=1atm, T_{RXN}=520℃)

Table 3-2 Surface area of oxychloride catalysts before and after the reaction.

Catalyst	CeOCl		LaOCl		EuOCl		CeO_2	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
Surface Area (m^2/g)	29.9	28.8	31.1	2.9	14.7	5.6	123.9	61.3

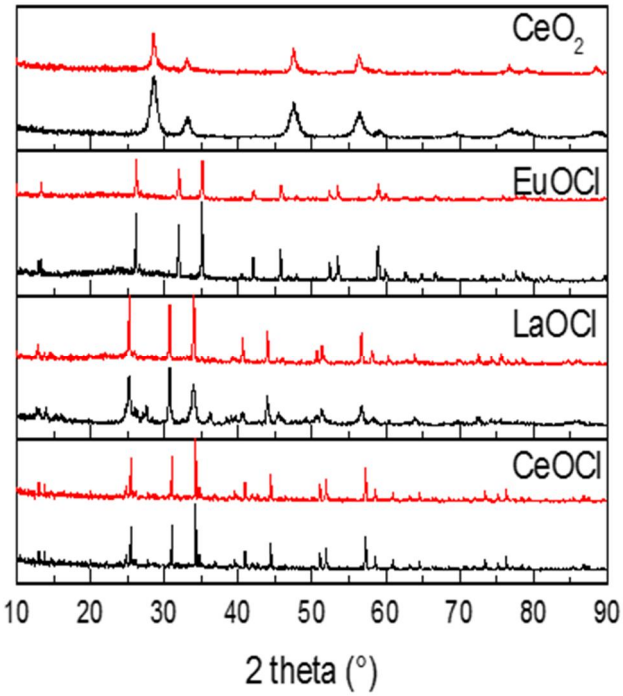

Figure 3-2. XRD pattern of fresh (black) and used (red) oxychloride catalysts. (Reaction conditions: CH_4:O_2:HCl=4:1:2, GHSV=30,000h^{-1}, Time-on-stream=2hr, P=1atm)

3.3.2 Ni supported on metal oxychloride catalysts

Many researchers examined various metals to convert methane into value-added product, and reported that noble metal like Pt, Ru, Rh, Ir and transition metals like Ni, Fe, Co are very reactive for the methane oxidation [49]. Especially, since Lercher et al. reported the promotional effect of Ni loading on LaOCl in methane oxychlorination, we impregnated Ni on the prepared metal oxychloride catalysts.

After CeOCl, LaOCl, and CeOCl catalysts were impregnated with 5 mol% of Ni, their reaction activity was examined at 520℃, which are summarized in Table 3-3. When Ni was loaded on CeOCl or LaOCl, the methane conversion decreased from 14.2 to 9.1% and 9.3 to 7.4%, respectively, although the methane conversion over Ni/EuOCl was enhanced from 2.9 to 5.0%. In the case of CO_2 formation, all the Ni-containing metal oxychloride catalysts showed higher CO_2 selectivity than non-Ni metal oxychloride catalysts. Both Ni/LaOCl and Ni/EuOCl demonstrated the enhanced CM yield, in good agreement with Lercher et al.[19] However, in case of Ni on CeOCl, Ni did not improve CM yield probably because Ni-supported CeOCl showed lower CH_4 conversion (9.1%) than CeOCl (14.2%).

Lercher et al. mentioned that doping with Ni over the parent LaOCl sample reduced the catalytic activity and a rate of methane conversion of 0.16

mmol/(h·g_{cat})[19]. Oxygen uptake was also lower on Ni/LaOCl ($1.45x10^{-3}$mmol/g_{cat}) than LaOCl ($1.49x10^{-3}$mmol/g_{cat}) according to their report. From this, we can conclude that the ability to bind and activate oxygen on the surface is weak on Ni/LaOCl catalyst, resulted in lower methane conversion than LaOCl catalyst. It will cause less methane oxidation on the Ni/LaOCl catalyst and make CH_3Cl selectivity higher than other metal oxychloride catalysts.

Table 3-3 The catalytic activity comparison between metal oxychloride catalyst and Ni-containing metal oxychloride catalyst. (Reaction conditions: CH_4:O_2:HCl=4:1:2, GHSV=30,000h^{-1}, Time-on-stream=2hr, P=1atm, Temperature=520℃)

Catalyst	Yield (%)					CH_4 conversion (%)
	CM	DCM	TCM	CO	CO_2	
CeOCl	9.6	2.0	0.0	2.1	0.5	14.2
Ni/CeOCl	6.0	0.8	0.1	1.5	0.7	9.1
LaOCl	4.2	0.7	0.1	4.3	n.d.	9.3
Ni/LaOCl	4.8	0.7	0.0	1.5	0.4	7.4
EuOCl	1.1	0.1	n.d.	1.7	n.d.	2.9
Ni/EuOCl	1.6	0.1	n.d.	2.3	0.2	5.0

* n.d.: not detected

Chapter 4. Conclusions

The oxychlorination of methane was performed with different catalysts: i) CeO_2, in order to study the effect of each reactant gas on the production of methyl chloride, which can be used for the value-added chemical production, and ii) metal oxychloride catalysts, in order to study the effect of each metal oxychloride for the higher monochloromethane yield.

This study clearly demonstrates that the oxidative chlorination of methane can be significantly affected by the reactant ratio. The best condition for the highest CM yield was CH_4:O_2:HCl=4:1.5:3. It was found that the ratio of O_2 to HCl (1:2) is the most important parameter to obtain high CH_4 conversion and CH_3Cl yield. However, HCl above the optimum ratio gives rise to the formation of CH_2Cl_2 (dichloromethane, DCM), and excessive O_2 leads to production of CO/CO_2 with remarkably higher CH_4 conversion. Too much oxygen will cause catalytic combustion, so when the reaction is carried, the oxygen concentration should be carefully adjusted.

Here, we examined oxychloride catalysts for methane oxychlorination. Among CeOCl, EuOCl, and LaOCl catalysts, CeOCl showed the best performance with high CM selectivity, and less CO and CO_2 production, compared with CeO_2 reference catalyst. LaOCl and EuOCl showed no CO_2 formation, although methane conversion was lower than CeOCl. Unlike other metal oxychloride catalysts, CeOCl catalyst did not

change structural and textural property after the reaction, indicating its excellent stability.

Bibliography

1. Peringer, E., Podkolzin, S. G., Jones, M. E., Olindo, R., and Lercher, J. A., **2006.** $LaCl_3$-based catalysts for oxidative chlorination of CH_4, *Topics in Catalysis* 38 (1), 211-220.

2. Wang, R., Ran, J., Qi, W., Niu, J., and Du, X., **2015.** A comparison of methane activation on catalysts Pt_2 and PtNi, *Computational and Theoretical Chemistry* 1073, 94-101.

3. Wang, B., Albarracín-Suazo, S., Pagán-Torres, Y., and Nikolla, E., **2017.** Advances in methane conversion processes, *Catalysis Today* 285, 147-158.

4. Carey, J. J. and Nolan, M., **2016.** Dissociative adsorption of methane on the Cu and Zn doped (111) surface of CeO_2, *Applied Catalysis B: Environmental* 197, 324-336.

5. Grid Arendal: "Primary Sources of Methane Release" (http://www.grida.no/resources/6608)

6. Business Insider: "MAP: Here's Where All Of The World's Natural Gas Lies" (http://www.businessinsider.com/map-worlds-natural-gas-2012-5?utm_source=copy-link&utm_medium=referral&utm_content=topbar&utm_term=desktop)

7. Tang, P., Zhu, Q., Wu, Z., and Ma, D., **2014.** Methane activation: the past and future, *Energy & Environmental Science* 7 (8), 2580-2591.

8. Cheephat, C., Daorattanachai, P., Devahastin, S., and Laosiripojana, N., **2018.** Partial oxidation of methane over monometallic and bimetallic Ni-, Rh-, Re-based catalysts: Effects of Re addition, co-fed reactants and catalyst support, *Applied Catalysis A: General* 563, 1-8.

9. 가스신문: "수소생산의 필요한 개질기술 소개"

(http://www.gasnews.com/news/articleView.html?idxno=85690)

10. Oyama, S. T., **1988.** Oxidative Coupling of Methane to Higher Hydrocarbons, *Catalysis Reviews* 30 (2), 249-280.

11. Weissman, M. and W. Benson, S., *Pyrolysis of methyl chloride, a pathway in the chlorine-catalyzed polymerization of methane*. (1984). Vol. 16, p 307-333.

12. Degirmenci, V., Yilmaz, A., and Uner, D., **2009.** Selective methane bromination over sulfated zirconia in SBA-15 catalysts, *Catalysis Today* 142 (1), 30-33.

13. Paunović, V., Zichittella, G., Moser, M., Amrute, A. P., and Pérez-Ramírez, J., **2016.** Catalyst design for natural-gas upgrading through oxybromination chemistry, *Nature Chemistry* 8 (8), 803-809.

14. Hammes, M., Valtchev, M., Roth, M. B., Stöwe, K., and Maier, W. F., **2013.** A search for alternative Deacon catalysts, *Applied Catalysis B: Environmental* 132-133 (Supplement C), 389-400.

15. Lin, R., Amrute, A. P., and Pérez-Ramírez, J., **2017.** Halogen-

Mediated Conversion of Hydrocarbons to Commodities, *Chemical Reviews* 117 (5), 4182-4247.

16. Li, Z., Zhou, G., Li, C., and Cheng, T., **2013.** Effect of Pr on copper-based catalysts for ethane oxychlorination, *Catalysis Communications* 40 (Supplement C), 42-46.

17. Zichittella, G., Puértolas, B., Paunović, V., Block, T., Pöttgen, R., and Pérez-Ramírez, J., **2018.** Halogen type as a selectivity switch in catalysed alkane oxyhalogenation, *Catalysis Science & Technology* 8 (8), 2231-2243.

18. Zichittella, G., Aellen, N., Paunović, V., Amrute, A., and Pérez-Ramírez, J., *Olefins from Natural Gas by Oxychlorination*. (2017). Vol. 56,

19. Peringer, E., Salzinger, M., Hutt, M., Lemonidou, A. A., and Lercher, J. A., **2009.** Modified Lanthanum Catalysts for Oxidative Chlorination of Methane, *Topics in Catalysis* 52 (9), 1220-1231.

20. Kim, J., Ryou, Y., Hwang, G., Bang, J., Jung, J., Bang, Y., and Kim, D. H., **2018.** Oxychlorination of methane over FeO_x/CeO_2 catalysts, *Korean Journal of Chemical Engineering* 35 (11), 2185-2190.

21. Guo, T., Du, J., Wu, J., and Li, J., **2016.** Palladium catalyst supported on stair-like microstructural CeO_2 provides enhanced activity and stability for low-concentration methane oxidation, *Applied Catalysis A: General* 524, 237-242.

22. Yang, H., Xie, P., Ni, L., and Flower, R. J., **2011.** Underestimation of

CH4 Emission from Freshwater Lakes in China, *Environmental Science & Technology* 45 (10), 4203-4204.

23. Administration, U. S. E. I., *International Energy Outlook 2017*. **(2017)**.

24. Hassani, A., Mosavian, M. T. H., Ahmadpour, A., and Farhadian, N., **2017.** Improvement of methane uptake inside graphene sheets using nitrogen, boron and lithium-doped structures: A hybrid molecular simulation, *Korean Journal of Chemical Engineering* 34 (3), 876-884.

25. Cho, E. H., Koo, K. Y., Lee, H. W., Park, Y.-K., Yoon, W. L., and Ko, C. H., **2017.** Preparation of egg-shell-type Ni/Ru bimetal alumina pellet catalysts: Steam methane reforming for hydrogen production, *International Journal of Hydrogen Energy* 42 (29), 18350-18357.

26. Jeon, J., Nam, S., and Ko, C. H., **2018.** Rapid evaluation of coke resistance in catalysts for methane reforming using low steam-to-carbon ratio, *Catalysis Today* 309, 140-146.

27. Świrk, K., Gálvez, M. E., Motak, M., Grzybek, T., Rønning, M., and Da Costa, P., **2018.** Syngas production from dry methane reforming over yttrium-promoted nickel-KIT-6 catalysts, *International Journal of Hydrogen Energy*, in press.

28. Horn, R. and Schlögl, R., **2015.** Methane Activation by Heterogeneous Catalysis, *catalysis letters* 145 (1), 23-39.

29. Olah, G. A., Gupta, B., Felberg, J. D., Ip, W. M., Husain, A.,

Karpeles, R., Lammertsma, K., Melhotra, A. K., and Trivedi, N. J., **1985.** Electrophilic reactions at single bonds. 20. Selective monohalogenation of methane over supported acidic or platinum metal catalysts and hydrolysis of methyl halides over .gamma.-alumina-supported metal oxide/hydroxide catalysts. A feasible path for the oxidative conversion of methane into methyl alcohol/dimethyl ether, *Journal of The American Chemical Society* 107 (24), 7097-7105.

30. McBee, E. T., Hass, H. B., Neher, C. M., and Strickland, H., **1942.** Chlorination of Methane, *Industrial & Engineering Chemistry* 34 (3), 296-300.

31. Manukyan, N. V. and Martirosyan, V. H., **2003.** Investigation of the chlorination mechanism of metal oxides by chlorine, *journal of materials processing technology* 142 (1), 145-151.

32. Taifan, W. and Baltrusaitis, J., **2016.** CH_4 conversion to value added products: Potential, limitations and extensions of a single step heterogeneous catalysis, *Applied Catalysis B: Environmental* 198, 525-547.

33. Amrute, A. P., Mondelli, C., Moser, M., Novell-Leruth, G., López, N., Rosenthal, D., Farra, R., Schuster, M. E., Teschner, D., Schmidt, T., and Pérez-Ramírez, J., **2012.** Performance, structure, and mechanism of CeO_2 in HCl oxidation to Cl_2, *Journal Of Catalysis* 286, 287-297.

34. Volkova, L. K. and Tret'yakov, V. P., **1995.** Oxychlorination of methane to methyl chloride at 300°C in the system palladium(II) complexes-heteropolyacids-silica gel, *Theoretical and Experimental Chemistry* 31 (1),

27-31.

35. He, J., Xu, T., Wang, Z., Zhang, Q., Deng, W., and Wang, Y., **2012.** Transformation of Methane to Propylene: A Two-Step Reaction Route Catalyzed by Modified CeO_2 Nanocrystals and Zeolites, *Angewandte Chemie International Edition* 51 (10), 2438-2442.

36. Scharfe, M., Lira-Parada, P. A., Paunović, V., Moser, M., Amrute, A. P., and Pérez-Ramírez, J., **2016.** Oxychlorination–Dehydrochlorination Chemistry on Bifunctional Ceria Catalysts for Intensified Vinyl Chloride Production, *Angewandte Chemie International Edition* 55 (9), 3068-3072.

37. Lambrou, P. S., Polychronopoulou, K., Petallidou, K. C., and Efstathiou, A. M., **2012.** Oxy-chlorination as an effective treatment of aged Pd/CeO_2-Al_2O_3 catalysts for Pd redispersion, *Applied Catalysis B: Environmental* 111–112, 349-359.

38. Maciel, C. G., Silva, T. d. F., Hirooka, M. I., Belgacem, M. N., and Assaf, J. M., **2012.** Effect of nature of ceria support in CuO/CeO_2 catalyst for PROX-CO reaction, *Fuel* 97, 245-252.

39. Oliveira, R. L., Bitencourt, I. G., and Passos, F. B., **2013.** Partial oxidation of methane to syngas on Rh/Al_2O_3 and Rh/Ce-ZrO_2 catalysts, *Journal of the Brazilian Chemical Society* 24, 68-75.

40. Chen, D., He, D., Lu, J., Zhong, L., Liu, F., Liu, J., Yu, J., Wan, G., He, S., and Luo, Y., *Investigation of the role of surface lattice oxygen and bulk lattice oxygen migration of cerium-based oxygen carriers: XPS and designed*

H_2-TPR characterization. (2017). Vol. 218,

41. Kang, Y., Sun, M., and Li, A., **2012.** Studies of the Catalytic Oxidation of CO Over Ag/CeO_2 Catalyst, *catalysis letters* 142 (12), 1498-1504.

42. Liu, L., Shi, J., Cao, H., Wang, R., and Liu, Z., **2017.** Fabrication of CeO_2–MO_x (M = Cu, Co, Ni) composite yolk–shell nanospheres with enhanced catalytic properties for CO oxidation, *Beilstein journal of nanotechnology* (8), 2425-2437.

43. Tamizhdurai, P., Sakthinathan, S., Chen, S.-M., Shanthi, K., Sivasanker, S., and Sangeetha, P., **2017.** Environmentally friendly synthesis of CeO_2 nanoparticles for the catalytic oxidation of benzyl alcohol to benzaldehyde and selective detection of nitrite, *Scientific Reports* 7, 46372.

44. Huang, Y., Yan, C.-F., Guo, C.-Q., and Huang, S.-L., **2015.** Enhanced Photoreduction Activity of Carbon Dioxide over Co_3O_4/CeO_2 Catalysts under Visible Light Irradiation, *international journal of photoenergy* 2015, 1-11.

45. Shi, D., Hu, R., Zhou, Q., and Li, C., **2015.** Effect of Cr-doping on $CuCl_2$-KCl-CeO_2/γ-Al_2O_3 catalysts for ethane oxychlorination, *Applied Catalysis A: General* 506, 91-99.

46. Farra, R., Girgsdies, F., Frandsen, W., Hashagen, M., Schlögl, R., and Teschner, D., **2013.** Synthesis and Catalytic Performance of CeOCl in Deacon Reaction, *catalysis letters* 143 (10), 1012-1017.

47. Scharfe, M., Lira-Parada, P. A., Amrute, A. P., Mitchell, S., and

Pérez-Ramírez, J., **2016.** Lanthanide compounds as catalysts for the one-step synthesis of vinyl chloride from ethylene, *Journal Of Catalysis* 344, 524-534.

48. Hur, E. and Kim, D. H., **2019.** Effect of reactant ratio on methane oxychlorination over CeO_2 catalyst, *Journal Of Nanoscience and Nanotechnology*, in press.

49. Singha, R. K., Shukla, A., Yadav, A., Sivakumar Konathala, L. N., and Bal, R., **2017.** Effect of metal-support interaction on activity and stability of Ni-CeO_2 catalyst for partial oxidation of methane, *Applied Catalysis B: Environmental* 202, 473-488.

국문초록

세리아 및 금속 산염소화물 촉매를 통한 메탄의 산화염소화반응

재생가능한 에너지자원의 비율이 증가되고 있지만, 화석연료는 2040년에도 여전히 총 에너지 사용량의 77%를 차지할 것으로 예상된다. 최근에는, 셰일가스나 천연가스에 다량 함유된 메탄이 각광받고 있다. 그러나, 메탄은 강한 C-H 결합을 갖는다. 선택적으로 결합을 끊고 바로 CO나 CO_2 이외의 바람직한 화합물로 전환하는 것은 어렵다.

메탄을 치환된 유도체나 탄화수소로 전환하는 것이 가장 바람직한 목표다. 메탄을 합성 가스로 전환한 후 고부가가치 화학물질로 만드는 것이 현재 널리 사용되고 있는 주요 산업 공정이다. 합성가스를 거치는 경로는 높은 열역학적 문제점을 극복해야 하여 에너지 소비량이 많아지기 때문에, 메탄의 산화커플링, 직접 메탄 방향족화 또는 메탄의 할로겐화 등의 연구가 진행되고 있다. 그 중에서도, 메탄의 할로겐화는 비교적 낮은 반응 온도로 인해 다른 반응들보다 유리하다.

염소 (Cl)는 산업적 화학물질 및 소비재를 제조하는 데 중요한 요소이다. C_2 와 C_3 의 염화물이 산업에서 사용되었고, 메탄보다 C-H 결합이 약한 C_2, C_3 의 산화염소화는 오랫동안 연구되어왔다.

이 논문에서는 CeO_2 및 금속 산화클로라이드 촉매를 사용하여 클로로 메탄 (CH_3Cl; CM)을 생성하는 메탄의 산화 염소화가 연구되었다.

CeO_2 촉매는 메탄의 산화 염소화 반응에서 다른 금속산화물 촉매보다 더 좋은 성능을 보이는 것으로 보고되었기 때문에 CeO_2 촉매에 중점을 두었다. 반응물의 비율에 따른 변화를 관찰하기 위해 CeO_2 촉매를 사용한 메탄의 산화 염소화가 수행되었다. 반응은 고정된 CH_4 농도에서 O_2 와 HCl 농도를 변화시키며 480 ℃에서 수행되었다. 높은 CH_4 전환율과 CH_3Cl 선택성을 얻기 위해서는 O_2:HCl=1:2 의 비율이 가장 중요한 매개변수라는 사실이 밝혀졌다. 과량의 HCl 은 부가적으로 생성물과 HCl 사이의 연쇄 반응으로 인해 CH_2Cl_2 또는 $CHCl_3$ 과 같은 더 많은 양의 염소화 된 생성물의 형성을 야기한다. 과량의 산소는 산화를 촉진하여 CO 및 CO_2 를 생성하는 것을 보였다. CH_4 : O_2 : HCl 의 최적 반응물 비율은 4 : 1.5 : 3 이었고, 이때 가장 높은 CH_3Cl 수율 (14.3 %)을 보였다. 다양한 특성 분석 결과, CeO_2 촉매가 약간 소결되었고 반응 후에 표면에 탄소와 염소 침착이 없음을 알 수 있었다.

또한, 금속 산화염화물 촉매를 사용한 메탄의 산화염소화 반응이 진행되었다. 이 촉매는 C_{2-3} 산화염소화에서 양호한 성능을 나타내었다. CeOCl, LaOCl 및 EuOCl 을 촉매로 사용하여 480-520℃의 반응온도범위내에서 메탄의 산화 염소화를 수행하였다. CeOCl 은 비록 CM 수율이 CeO_2 보다 낮았지만, 금속 산화염화물 촉매 중 가장 높은 CH_4 전환율과 CM 수율을 나타내었다. 활성을 향상시키기 위해 금속 산화염화물 촉매에 Ni 를 담지했다. 그러나,

Ni 담지는 CM 생성보다는 CO_2 형성만을 향상시킨다는 것이 발견되었다.

이 두 연구에서 우리는 CeO_2 가 높은 반응성을 가지기 때문에 메탄의 산화 염소화를 위한 최상의 촉매라고 결론 내릴 수 있다. 또한, 산화염화물 촉매는 CeO_2 보다 CO_x 생성을 억제하여 니켈 첨가는 메탄 활성화가 저하된다.

주요어: 산화염소화 반응, 메탄, 세리아, 금속 산염화물, 클로로메탄

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Abbreviations and Acronyms

ATR	Autothermal reforming
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CDR	Carbon dioxide reforming
CM	Chloromethane (CH_3Cl)
DCM	Dichloromethane (CH_2Cl_2)
EOC	Ethane oxidative chlorination
FID	Flame ionization detector
MFC	Mass flow controller
MOC	Methane oxidative chlorination
OCM	Oxidative coupling of methane
POX	Partial oxidation
SR	Steam reforming
TCD	Thermal conductivity detector
TCM	Trichloromethane (chloroform, $CHCl_3$)
TPR	Temperature Programmed Reduction
XRD	X–ray diffraction

감사의 글

중국유학동안, 세상은 넓고 인재는 많다는 것을 몸소 체험하고 한국으로 돌아온 지 올해로 꼭 10년이 되었습니다. 그 중 6년을 서울대에서 보내며 많은 사람들과 인연을 맺을 수 있었고, 값진 교훈을 얻을 수 있었습니다. 이렇게 학위를 마치는 시점에서, 서면으로나마 그분들께 감사함을 전하고 싶습니다.

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더불어 제 학위심사의 심사위원으로서 따스한 격려와 냉철한 조언을 아끼지 않으셨던 이종민 교수님, 이원보 교수님, 김지만 교수님, 박영권 교수님께도 감사의 말씀을 전하고 싶습니다. 교수님들의 심사평을 통해 연구자의 시각과 사고에 대해 더욱 고찰해보게 되었습니다.

제가 서울대로 오기 전 석사과정을 보낸 KIST의 많은 박사님들께도 감사드립니다. 그분들의 지도하에 제가 연구란 무엇인지 좀 더 생각해보고 기초를 닦을 수 있었습니다.

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허 은