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Control of Methane Chlorination with Molecular Chlorine Gas using Zeolite Catalysts: Effects of Si/Al Ratio and Framework Type

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Highlights

- CH₄ chlorination with Cl₂ is investigated using zeolites with various Si/Al ratios.
- Aluminum in the zeolite framework is a catalytic site for selective production of CH₃Cl.
- CH₃Cl yield increased in proportional to the amount of aluminum in zeolites.
- CH₃Cl yield can be achieved to above 20% at GHSV of 2,400 cm³ g_{cat}^{-1} h⁻¹ at 350°C.

Abstract

CH₄ chlorination with Cl₂ gas is used for the production of chlorinated products via C-H bond activation in CH₄. Due to the high reactivity of Cl₂, this reaction can occur spontaneously under UV irradiation or with mild thermal energy even in the absence of a catalyst via a free radical-mediated chain reaction mechanism

that undesirably causes excessive chlorination of the CH₄ and is thus non-selective. In this work, CH₄ chlorination is investigated using HY and MFI zeolites with various Si/Al ratios, by which the reaction is catalytically controlled for selective production of the mono-chlorinated product (CH₃Cl). Depending on the framework type, Si/Al ratio of the zeolites, and reaction conditions, different degrees of CH₄ conversion, CH₃Cl selectivity, and hence CH₃Cl yield were achieved, by which systematic relationships between the catalyst properties and performance were discovered. A high aluminum content facilitated the production of CH₃Cl with up to ~20% yield at a high gas hourly space velocity of 2,400 cm³g_{cat}⁻¹h⁻¹ with a CH₄/Cl₂ ratio of 1 at 350°C. HY zeolites generally furnished a slightly higher CH₃Cl yield than MFI zeolites, which can be attributed to the larger micropores of the HY zeolites that support facile molecular diffusion. With various flow rates and ratios of CH₄ and Cl₂, the CH₄ conversion and CH₃Cl selectivity changed simultaneously, with a trade-off relationship. Unfortunately, all zeolite catalysts suffered from framework dealumination due to the HCl produced during the reaction, but it was less pronounced for the zeolites having a low aluminum content. The results shed light on the detailed roles of zeolites as solid-acid catalysts in enhancing CH₃Cl production during electrophilic CH₄ chlorination.

Keywords

Methane, Chlorine, Electrophilic Chlorination, Zeolite, Acid Catalyst, Methyl Chloride

1. Introduction

Methane (CH₄) is one of the most abundant naturally occurring hydrocarbons, having high chemical energy due to the high bond dissociation energy of the four C-H bonds [1-4]. The recent evolution of shale gas in the last few decades has triggered an explosive expansion of the CH₄ industry, not only in the field of clean natural gas fuel, but also in the field of CH₄ utilization [1-4]. Although CH₄ can be very conveniently used as a fuel source in many vehicles and domestic heating systems, existing storage and transportation technologies limit the use of CH₄, thus engendering the need for energy-efficient conversion of CH₄ to value-added chemicals for further use.

There are numerous chemical approaches for the conversion of CH₄ to value-added chemicals in the presence of catalysts. For example, CH₄ can be used as the building block for production of benzene via dehydrogenative aromatization on Mo-supported zeolite catalysts [5–7]. Oxidative coupling of CH₄ to multicarbon containing hydrocarbons [2–3, 8–10] and partial oxidation of CH₄ to oxygenated hydrocarbons such as alcohols have also been reported [10–13]. In addition, CH₄ can be used for the production of valuable hydrogen gas via the well-known steam methane reforming (SMR) process, which accounts for the largest portion of industrially produced H₂ gas [2–3,14]. Most of the aforementioned conversion technologies are practically mature in terms of the energy balance and carbon yield [1].

The dissociation energy of the C-H bond in the CH₄ molecule is ~405 kJ mol⁻¹, making it the most stable C-H bond among those of saturated hydrocarbons [3,15]. Therefore, most CH₄ conversion technologies require high energy input for successful activation of the C-H bond in CH₄. As one of the energy-efficient alternative routes, the halogenation of CH₄ with various halogenating agents such as molecular halogens or hydrogen halides is promising [1–2, 15–18]. Due to the high reactivity of halogenating agents, the high energy input for C-H bond activation can be offset, and hence, the overall energy input for the reaction process can be reduced. Halogenation using hydrogen halides involves the partial oxidation of CH₄ and hence additional oxygen is necessary [18–20]. The oxy-halogenation process usually results in the formation of various byproducts, and the combustion of CH₄ with O₂ occurs as a side-reaction. In contrast, CH₄ halogenation with molecular halogen is an energy-efficient process that only produces halogenated products [1,21–22]. Depending on the halogen molecules, the reaction follows very different reaction kinetics and thermodynamics with different product distributions due to the differences in the reactivity of the halogen molecules [23].

Among the various halogen molecules, chlorine (Cl₂) and bromine (Br₂) molecules are reasonably acceptable halogenating agents due to the moderately high and controllable reactivity compared to that of fluorine (F₂) or iodine (I₂) molecules. CH₄ bromination is more easily controlled due to the milder reactivity of Br₂ than Cl₂, but the reaction rate is too slow as compared to that of chlorination [4,15,20]. CH₄ chlorination is thermodynamically more spontaneous than bromination, and hence the overall reaction rate is much faster, but it is difficult to control the reaction. Indeed, even upon irradiation with UV light or the input of mild thermal energy, Cl₂ molecules can be dissociated into two chlorine radicals (having much higher reactivity) that activate the C-H bond in the CH₄ molecule to form a methyl radical. The reaction involving methyl radicals continues successively via chain reaction and thus the reaction is too fast and difficult to control. The problem with this reaction is over-chlorination to polychlorinated methane products such as CH₂Cl₂, CHCl₃, and CCl₄. There is always a thermodynamic product distribution [1,21], and radical-mediated chain chlorination cannot be completely excluded from the overall reaction process.

A few studies on CH₄ chlorination have been reported, most of which are focused on control of the reaction process by using catalysts to achieve selective production of CH₃Cl with a high product yield, where CH₃Cl can be used as an important intermediate chemical in many commercial conversion processes [1,24-25]. Olah et al. reported electrophilic chlorination of CH₄ using supported metal nanoparticles, nanoporous metal oxides, and zeolite materials [11,26-28]. They indicated that super-acid catalysts in the solid phase can be used for electrophilic chlorination and Cl₂ polarization, where the acid catalyst is important for production of the mono-chlorinated product with high yield. They proposed an electrophilic chlorination pathway for the selective production of CH₃Cl via a chloride ion-mediated heterolytic cleavage mechanism. Since then, very few studies on CH₄ chlorination have been reported, most of which focused only on enhancing the catalytic performance during CH₄ chlorination, mostly from the technical point of view. In particular, the

distinct role of catalysts in controlling CH₄ chlorination by shifting the radical-mediated pathway to the ionmediated alternative has not yet been elucidated or investigated in depth.

Therefore, the major importance of the present work is to elucidate the catalytic roles for increasing the CH₃Cl yield. In order to investigate the catalytic control in CH₄ chlorination, we selected the HY and MFI zeolite catalysts with different Si/Al ratios as the catalyst candidates. Using the constructed catalyst set, we investigate the effects of the catalyst properties on the CH₃Cl productivity and framework stability under various reaction conditions with different flow rates and ratios of CH₄ and Cl₂. The results demonstrate a systematic relationship between the catalytic properties and the CH₃Cl yield, and allow us to suggest optimized reaction conditions for enhancing the CH₃Cl yield. The results shed light on the detailed roles of zeolites as solid-acid catalysts in enhancing CH₃Cl production during CH₄ chlorination, and provide scientific inspiration for the design of heterogeneous catalysts for electrophilic chlorination of CH₄.

2. Experimental

2.1. Catalyst Preparation

All the zeolite materials used in this work were commercially available from Zeolyst International and Tosoh Corporation, which provided HY zeolites with different Si/Al ratios (CBV600 (Si/Al = 2.6), CBV720 (Si/Al = 15), 390HUA (Si/Al = 250)) and MFI zeolites with different Si/Al ratios (CBV3024E (Si/Al = 15), CBV8014 (Si/Al = 40), CBV28014 (Si/Al = 140)). All the zeolite samples were pre-calcined at 550°C to form H⁺-exchanged zeolites before further use as the catalyst. The resultant zeolite samples are denoted as HY(2.6), HY(15), HY(250), MFI(15), MFI(40), and MFI(140), wherein the number in the parentheses indicates the Si/Al ratios in the zeolites.

2.2. Characterization

X-ray diffraction (XRD) patterns were taken with a Rigaku MiniFlex 600 with CuK α radiation (λ = 0.1541 nm) at 40kV, 15mA (600W), where the measurement was performed under ambient condition at the step size of 0.02° in the range of 2 θ from 5 to 40°. Scanning electron microscope (SEM) images were obtained using a Hitachi Technologies S-4700 microscope with secondary election image resolution at low voltage (3 kV) in a gentle-beam mode without a metal coating. NH₃ temperature-programmed desorption (TPD) measurements were carried out with a BEL-CAT (BEL JAPAN INC). Prior to the TPD measurement, zeolite samples in a H⁺-form were pre-treated by a He stream for 1 h at 400°C in a quartz cell, cooled down to 100°C and adsorption of NH₃ was done with 5%NH₃/He flow for 1 h. After purging the cell with He for 30 min, TPD process was performed by increasing the temperature of cell from 50°C to 750°C with ramping rate of 10°C min⁻¹ under He flow. The solid state magic angle spinning (MAS) ²⁷Al nuclear magnetic resonance (NMR) spectra were obtained using ECZ400R (JEOL) operated at 400 MHz for ²⁷Al (spinning rate = 10kHz).

CH₄ chlorination was carried out in a continuous flow fixed-bed microreactor (Inconel) by referring to the published work [29]. The reaction was investigated at atmospheric pressure at 350°C, and the gas flow rates were controlled by using a mass flow controller (LineTech). Based on the preliminary tests using the zeolite catalysts at different reaction temperatures, maximum CH₃Cl yield was obtained at 350°C. Accordingly, the CH₄ chlorination reaction was investigated only at 350°C with control of relative flow rates of CH₄ and Cl₂. The temperature of the reactor was monitored with a thermocouple located inside the catalyst bed. In a typical reaction process, 0.5 g of catalyst was modified as a 100 mesh sieve that was placed in a fixed-bed inside the microreactor. The catalyst was pretreated by purging with N₂ (50 cm³ min⁻¹) while increasing the temperature to 350°C. After the reaction temperature reached the desired temperature, the mixture of CH₄ and Cl₂ was introduced into the reactor with variation of the respective flow rates. The CH₄ flow rate was controlled at 10 and 50 cm³ min⁻¹, while the Cl₂ flow rate was controlled at 10 and 25 cm³ min⁻¹. The reaction process was monitored with a gas chromatograph that was connected to the outlet of the reactor, equipped with a flame-ionization detector (FID), by using a capillary column (HP-Plot/Q, 30 m length, 0.53 mm diameter, 40 µm thickness). The gas exhausts were ventilated by passing through a scrubber. The CH4 conversion (X_{CH4}), Cl₂ conversion (X_{Cl2}), Product selectivity ($S_{Product}$), and CH₃Cl yield (Y_{CH3Cl}) were calculated by using the following equations $(1) \sim (4)$, respectively:

$$\begin{aligned} X_{CH4}(\%) &= \frac{CH_{4_{in}} - CH_{4_{out}}}{CH_{4_{in}}} \times 100 \quad (1) \\ X_{Cl2}(\%) &= \frac{CH_3 Cl_{out} + CH_2 Cl_{2_{in}} \times 2 + CHCl_{3_{out}} \times 3}{Cl_{2_{in}}} \times 100 \quad (2) \\ S_{Product}(\%) &= \frac{Product_{out}}{CH_{4_{in}} - CH_{4_{out}}} \times 100 \quad (3) \\ Y_{CH3Cl}(\%) &= \frac{X_{CH4} \times S_{CH3Cl}}{100} \quad (4) \end{aligned}$$

where CH_{4in} , CH_{4out} , Cl_{2in} , and $Product_{out}$ represent the molar flow rate of CH₄ fed into the reactor, the molar flow rate of CH₄ escaping from the reactor, the molar flow rate of Cl₂ fed into the reactor, and the molar flow rate of chlorinated product escaping the reactor, respectively.

3. Results and Discussion

3.1. Catalyst Characterization

The crystalline structures of the zeolite catalysts with different Si/Al ratios and framework types were characterized by powder XRD, as shown in Figure 1. Figure 1A shows the XRD patterns of the HY zeolites with different Si/Al ratios in the H⁺-form. The XRD patterns of all the zeolites corresponded to the typical Faujasite (FAU)-type crystalline structure [JCPDS card no. 33-1270]. The XRD peak intensity and broadness differed for the three HY zeolite samples. The least intense and the broadest peaks were observed for HY(2.6) zeolite. As the Si/Al ratio of the HY zeolites increased, the XRD peaks became significantly sharper, indicating enhanced crystallinity. Figure 1B shows the XRD patterns of the MFI zeolites with different Si/Al ratios in the H⁺-form, which also confirm the high crystallinity of the MFI zeolite framework [JCPDS card no.

00-044-0002]. The XRD patterns of all the zeolite samples were typical of the MFI structure with the same peak positions. Similar to the HY zeolites with different Si/Al ratios, the XRD peaks of the MFI zeolites became much sharper with an increase in the Si/Al ratio in the framework due to the enhanced crystallinity.

Figure 2(A–C) shows the SEM images of the HY zeolite samples with Si/Al ratios of 2.6, 15, and 250, respectively. The SEM images showed fully crystalline morphologies without distinguishable amorphous phases. The overall morphologies of the HY zeolites with different Si/Al ratios were very similar, where crystals with a bipyramidal morphology were observed for all HY zeolite samples, along with crystals with irregular morphologies. Figure 2(D–F) presents the SEM images of the MFI zeolite samples with Si/Al ratios of 15, 40, and 140, respectively, showing fully crystalline phases without detectable amorphous phases. Compared with the HY zeolites, the MFI zeolites formed more irregularly shaped crystals and were aggregated into micron-scale particles. The acidic properties of the HY and MFI zeolites were also characterized by using NH₃ TPD (Fig. 3), which confirmed that the zeolites possess acidic properties whose quantity and strength are different. Among all the HY and MFI zeolites with different Si/Al ratios, HY(2.6) zeolite had the largest number of acidic sites due to the largest quantity of aluminum in the zeolite framework, whereas HY(250) zeolite showed the least intense NH₃ peaks and thus the absolute amount of acidic sites is the lowest. In addition, the total number of acidic sites calculated by NH₃ TPD quite fit well with the total number of aluminums in the zeolite framework, indicating that most of the framework aluminums are sufficiently acidic.

3.2. Effect of Si/Al Ratio and Framework Type on CH₄ Chlorination

Figure 4 shows the results of the CH₄ chlorination reaction using the HY and MFI zeolites under CH₄/Cl₂/N₂ flow rates of 10/10/50 cm³ min⁻¹, where the effect of the Si/Al ratio and framework type on the catalytic performance was investigated. The GHSV under these conditions was 2,400 cm³ g_{cat⁻¹} h⁻¹, excluding the balance N₂ gas. The graphs show the reaction profiles, where the conversion of CH₄ and Cl₂, selectivity of CH₃Cl, CH₂Cl₂ and CHCl₃, and CH₃Cl yield were monitored according to the reaction time. Note that the CH₃Cl yield plotted in Figure 4 was obtained by calculation of the CH₄ conversion and CH₃Cl selectivity. In our reaction studies, CCl₄ was not produced. The reaction profiles show that the CH₄ conversion and CH₃Cl selectivity, and hence the CH₃Cl yield, changed depending on the catalysts. Although it seems that there were no significant differences among the catalysts, in fact, there are quite systematic differences in the catalytic performance.

The catalytic performance for each catalyst in Figure 4 was compared on the basis of the average CH₄ conversion, Cl₂ conversion, CH₃Cl selectivity, CH₂Cl₂ selectivity, CHCl₃ selectivity, and CH₃Cl yield, as summarized in Table 1. The CH₄ conversion achieved with the series of HY zeolites was generally in the range of 36.4–40.9% depending on the Si/Al ratio, with a CH₃Cl selectivity of 47.1–49.3%. The calculated CH₃Cl yield was in the range of 17.5–19.2%, where the CH₃Cl yield decreased as the Si/Al ratio of the HY zeolites increased. HY(2.6) gave the highest CH₃Cl yield (19.2%), whereas HY(15) and HY(250) give 18.7% and 17.5% yield, respectively. In contrast, the series of MFI zeolites had slightly lower catalytic activity than

the HY zeolites, where the CH_4 conversion was in the range of 33.0–38.7% for the former. The average CH_3Cl selectivity of the MFI zeolites was in the range of 43.8–50.1%. Overall, the calculated CH_3Cl yield was in the range of 14.8–18.0%, which is lower than that of the HY zeolites.

The catalytic performance of the HY and MFI zeolites was compared with previously published results [27]. Olah et al. reported that various zeolite catalysts can be used for electrophilic CH₄ chlorination, most of which produce a CH₃Cl yield of ~25%. Although the CH₃Cl yield achieved in the present work was ~20%, the significant differences in the reaction conditions should be taken into account. The GHSV used in this work is four-times larger (i.e., 2,400 cm³ $g_{cat}^{-1} h^{-1}$) than that in the previously published work (i.e., 600 cm³ g_{cat}^{-1} h⁻¹). Notably, the reaction temperature used herein is 350°C, which is lower than that (400°C) used in the literature study. Under these circumstances, though the overall CH₃Cl yield is lower than the yield reported previously, it is noteworthy that the productivity for CH₃Cl is much larger due to the larger GHSV. It is also remarkable that the overall CH₃Cl yield achieved in this work is higher than that obtained from the radicalmediated blank reaction in the absence of catalysts (Fig. S1(A) and Table S1 in the Supporting Information). The radical-mediated chain reaction produced 14.8% of CH₃Cl yield under the same reaction condition without the catalysts, but the zeolite catalysts in this work produced ~20% of CH₃Cl yield. This should be attributed to the increase in CH₃Cl selectivity by zeolite catalysts inducing the electrophilic ionic-reaction pathway. In fact, according to the literature published elsewhere [21], the spontaneous CH₄ chlorination via radical-mediated pathway affords limited selectivity for CH₃Cl. Under the same molar ratio of CH₄ and Cl₂, the thermodynamic selectivity for CH₃Cl was ~39% [21]. However, in the present work, the zeolite catalysts afforded CH₃Cl selectivity close to 50% without compromising the CH₄ conversion. Consequently, the CH₃Cl yield can be increased as compared to the radical-mediated reaction pathway.

The CH₃Cl productivity based on the absolute weight of the catalysts and designated time for all zeolite catalysts is calculated in Table 1. The CH₃Cl productivity achieved with all the zeolite catalysts was around 7.27–9.44 mmol_{CH3Cl} g_{cat⁻¹} h^{-1} , which is about twice as large as that in the aforementioned published work [27], wherein the calculated productivity was around 2.46 mmol_{CH3Cl} g_{cat⁻¹} h^{-1} . The CH₃Cl productivity differed marginally for the zeolite catalysts (Table 1), with similar catalytic performance based on the catalyst weight. However, when the CH₃Cl yield was correlated with the number of aluminum sites in the zeolite framework, systematic relationships were observed. Based on the assumption that the aluminum sites in the zeolite framework contribute to CH₄ chlorination, the CH₃Cl yield was plotted versus the total amount of aluminum in the zeolite framework (Fig. 5). The graph shows a meaningful relationship between the CH₃Cl yield increased (Fig. 5(A)). In the case of the MFI zeolites, it was also observed that the CH₃Cl yield increased moderately with an increase in the total amount of aluminum (Fig. 5(B)). From these correlations, it is possible to conclude that the increased CH₃Cl yield may be affected by the total number aluminum sites in the zeolite framework.

Comparison of catalytic performance of the HY(15) and MFI(15) zeolite catalysts with a given Si/Al ratio of 15 allowed deduction of the effect of the framework type. There were no significant differences between the performance of the catalysts, but from a strict point of view, HY(15) produced more CH₃Cl with slightly higher productivity. The fact that HY(15) zeolite produced a slightly higher yield of CH₃Cl than MFI(15) zeolite (18.7% vs. 17.0%) suggests that the number of aluminum sites is not the only influential factor, but the zeolite framework also affects the catalytic reaction. This may be attributed to the difference in the pore sizes of the HY and MFI zeolites. HY zeolite has 12-membered-ring micropores, and is classified as a large-pore zeolite, whereas MFI zeolite has 10-membered-ring micropores, and is classified as a medium-pore zeolite. The larger micropores are more readily accessible to reactants and products, and therefore HY(15) may produce a higher CH₃Cl yield in a given reaction time.

3.3. Effect of CH4/Cl2 Ratio on CH4 Chlorination with HY zeolites Having Various Si/Al Ratios

According to our preliminary reaction studies using the zeolite catalysts, maximum CH₃Cl yield was obtained at 350°C. Beyond this temperature, the CH₃Cl yield achieved by zeolite catalysts was not in a big difference with the value obtained by the radical-mediated reaction process. Indeed, it was also reported that the zeolite catalysts show catalyzed the electrophilic monochlorination favorably at 300–350°C [27]. It is also reported that the product distribution is less relevant to the reaction temperature but strongly affected by the flow rates of CH₄ and Cl₂ [21]. Accordingly, CH₄ chlorination in the presence of the HY zeolites with various Si/Al ratios was further evaluated under different flow rates of CH₄ and Cl₂ at a given reaction temperature of 350°C. CH₄ chlorination in the presence of excess Cl₂ was evaluated by using CH₄/Cl₂/N₂ flow rates of 10/25/50 cm³ min⁻¹, where the Cl₂ concentration was 2.5 times higher than the CH₄ concentration. Due to the highly excessive concentration of reactive Cl₂, greater CH₄ conversion can be achieved (Fig. S2 and Table S2). The CH₄ conversion over all HY zeolite catalysts increased by more than 50% with compromising decrease of CH₃Cl selectivity to around 30%. The calculated yield of CH₃Cl was ~20%, which is very similar to that obtained with CH₄/Cl₂/N₂ flow rates of 10/10/50 cm³ min⁻¹. The results indicate that no significant improvement in the average CH₃Cl yield was obtained under the different reaction conditions. From the practical point of view, as long as the CH₃Cl yield and productivity are the same, excess Cl₂ is not advantageous due to the problem of handling residual Cl₂ gas after the reaction. However, the CH₃Cl yield increased from 17.5% to 18.0 and 20.3% as the aluminum content in the zeolite framework increased from HY(250) to HY(15) and HY(2.6), respectively, under the different reaction conditions.

For comparison, the use of excess CH₄ was also investigated with CH₄/Cl₂/N₂ flow rates of 50/25/50 cm³ min⁻¹ by using the series of HY zeolites (Fig. S3 and Table S3). As expected, the CH₄ conversion decreased under these reaction conditions. The CH₄ conversion achieved with all the HY zeolites was in the range of 22.1–23.8%, whilst the CH₃Cl selectivity increased to 62.5–72.5% due to the excessive concentration of CH₄. The calculated CH₃Cl yield was in the range of 13.8–16.1%, which is the lowest range of CH₃Cl yields among all the reaction conditions investigated in this work. The reactivity of CH₄ is much lower than

that of Cl₂, and hence the use of excess CH₄ may not be useful for increasing the CH₃Cl yield. However, under this fast GHSV condition, HY zeolites afforded very high CH₃Cl productivity of $33.9-38.3 \text{ mmol}_{CH3Cl} \text{ g}_{cat}^{-1}$ h⁻¹ that was about four-times higher than the productivity (8.60–9.44 mmol}_{CH3Cl} g_{cat}⁻¹ h⁻¹) achieved under slow GHSV condition. The high CH₃Cl productivity using zeolite catalysts under fast GHSV condition is highly meaningful for practical mass production of CH₃Cl.

3.4. Zeolite Catalysts After the Reaction

CH₄ chlorination always produces hydrogen chloride (HCl) as a byproduct that is detrimental to the aluminum in the zeolite framework. Collapse of the framework of zeolite catalysts after the reaction due to the dealumination by HCl has also been reported [27]. In the present work, the stability of the framework of the zeolite catalysts was examined comprehensively by using XRD and solid-state MAS ²⁷Al NMR (Fig. S4-S6). Comparison of the XRD patterns of the HY and MFI zeolite catalysts before and after the reaction shows that the peak intensities decreased appreciably after the catalytic reaction (Fig. S4). In general, highly siliceous zeolites with high Si/Al ratios show much better framework stability, where the crystallinity of the initial framework is maintained after the reaction. The HY(2.6) and HY(15) zeolites showed serious framework collapse after the reaction as compared to HY(250) zeolite having the lowest aluminum content. Similarly, the highly siliceous MFI(140) zeolite catalyst also showed the best framework stability after the reaction (Fig. S4). The framework collapse can be attributed to dealumination of the zeolite framework by HCl.

The solid-state MAS ²⁷Al NMR analysis also provided in-depth information about the environment of aluminum before and after the reaction (Fig. S5-S6). For the fresh zeolite catalysts, an intense NMR peak was observed at ~55 ppm, which corresponds to aluminum coordinated tetrahedrally inside the crystalline framework. No other peaks were observed for the zeolites. However, the intensity of the peak at ~55 ppm decreased after the reaction and another peak appeared at ~0 ppm, corresponding to the aluminum species octahedrally coordinated outside the zeolite framework. The presence of the new peak corresponding to the extra-framework aluminum species provides direct evidence of framework dealumination during the reaction. As suggested above, the framework dealumination was more pronounced for the zeolites having a high aluminum content than those having a low aluminum content. In general, the dealumination was much more extensive for the HY zeolites than the MFI zeolites, indicating that the aluminum in the HY zeolites was less stable than that in the MFI zeolites.

Despite the dealumination of the framework, it is noteworthy that the catalytic performance of each zeolite catalyst was maintained quite sustainably without notable deactivation (Fig. 4). When the Si/Al ratios of the zeolite catalysts before and after the reactions were analyzed by ICP, almost no changes in the Si/Al ratios were observed. This indicates that the extra-framework aluminum species were still trapped in the zeolite catalysts, plausibly as the AlCl₃ phase due to the presence of Cl₂ in the reaction, and this aluminum phase could maintain the reaction without notable changes relative to the initial catalytic performance. During the chlorination process, this aluminum phase may play as the Lewis acid sites anchored on the external

surface of zeolite framework. That might be the reason of sustainable catalytic performance during the whole reaction process, though coordination environment of aluminum was changed. Indeed, when the pure AlCl₃ was tested in the same reaction, it afforded the CH₃Cl yield higher than the radical-mediated reaction pathway (Fig. S1 and Table S1). This can be the evidence that the pseudo-AlCl₃ phase formed by the dealumination of the zeolite framework could be catalytically active as the Lewis acid sites for this reaction. In contrast, when pure SiO₂ was used in the absence of any heteroatoms, the reaction results were very similar to the non-catalytic radical-mediated CH₄ chlorination (Fig. S1 and Table S1). This indicated that the purely siliceous framework of SiO₂ did not possess catalytic sites that could polarize Cl₂ molecule for inducing the electrophilic chlorination.

The microporous framework of zeolite catalysts was also useful for giving higher catalytic activity with higher CH₃Cl yield than Al₂O₃ catalyst without ordered microporous structure (Fig. S1 and Table S1). Al₂O₃ catalyst exhibited higher CH₃Cl yield than that achieved from the radical-mediated reaction pathway, indicating that this catalyst could promote the electrophilic ion-mediated reaction process. However, the CH₃Cl yield (16.5%) obtained by Al₂O₃ catalyst is lower than the best zeolite catalyst (i.e., HY(2.6)) giving CH₃Cl yield of 19.2%. Such a difference might be attributed to the ordered microporous structure of the zeolite that could construct the confined reaction space, wherein the CH₄ chlorination can occur more rapidly via electrophilic activation on the acid sites inside the zeolite micropores.

4. Conclusions

The catalytic contribution of HY and MFI zeolites with various Si/Al ratios on the production of CH₃Cl under various reaction conditions was demonstrated. Although non-catalytic radical-mediated CH4 chlorination is thermodynamically favorable, the present results demonstrate that zeolites can contribute to CH₄ chlorination catalytically via electrophilic ion-mediated reaction pathway. The comparative reaction studies using the series of HY and MFI zeolites with various Si/Al ratios revealed some important findings: (1) Zeolites are useful catalysts for electrophilic CH₄ chlorination for selective production of CH₃Cl, which afforded higher CH₃Cl yield than the radical-mediated non-catalytic reaction pathway. The data show that the CH₃Cl yield can be controlled according to the zeolite catalyst; providing evidence that the zeolite catalysts exert control over electrophilic CH₄ chlorination. (2) The aluminum sites in the zeolite framework are important for increasing the CH₃Cl productivity, plausibly because the aluminum species in the zeolite framework are charge localized sites that can polarize Cl₂ molecules and thereby facilitate electrophilic chlorination. (3) The yield of CH₃Cl was maximized at an optimum flow rate and relative ratio of CH₄/Cl₂, where CH₄/Cl₂/N₂ flow rates of 10/10/50 and 10/25/50 cm³ min⁻¹ produced CH₃Cl yields similarly with ~20%. However, because the latter condition utilizes excess Cl₂, the former is more meaningful. (4) HCl produced during the reaction adversely affects the crystallinity of the framework of zeolite catalysts via dealumination of intra-framework aluminum. Significant dealumination occurred to generate octahedrally coordinated extraframework species, but the highly siliceous zeolite catalysts having a high Si/Al ratio show better durability

toward framework dealumination by HCl. In addition, the extra-framework aluminums look remained as AlCl₃ with the zeolite catalysts, which might be the reason for maintaining the catalytic performance.

Author Contributions:

K. Na initiated and conceptualized the research. S. Kwon carried out preparation of catalysts and reaction studies. H.-J Chae participated in the preparation of manuscript with K. Na.

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7. Figures and Tables



Figure 1. X-ray diffraction (XRD) patterns of (A) HY and (B) MFI zeolites with various Si/Al ratios. The numbers in parentheses indicate the Si/Al ratio of the zeolites.



Figure 2. Scanning electron microscope (SEM) images of (A–C) HY and (D–F) MFI zeolites with various Si/Al ratios. The numbers in parentheses indicate the Si/Al ratio of the zeolites.



Figure 3. NH₃ temperature-programmed desorption (TPD) profiles of (A) HY and (B) MFI zeolites with various Si/Al ratios. The numbers in parentheses indicate the Si/Al ratio of the zeolites. The red, blue, and green peaks are desorption peaks deconvoluted from the original TPD profile (black). Each NH₃ TPD profiles are normalized by the amount of total acid sites, and thus the zeolites with low Si/Al ratios show intensive peaks whereas the zeolites with high Si/Al ratios show less intensive peaks.



Figure 4. Results of CH₄ chlorination reaction with HY and MFI zeolites having various Si/Al ratios. The numbers in parentheses indicate the Si/Al ratio of the zeolites. The CH₄ conversion (X_{CH4}), Cl₂ conversion (X_{Cl2}), product selectivity ($S_{product}$), and calculated CH₃Cl yield (Y_{CH3Cl}) are designated in red, green, blue and brown, respectively. The product selectivity is also separately shown as filled triangle, unfilled square and filled square for CH₃Cl, CH₂Cl₂ and CHCl₃, respectively. The reactions were carried out with CH₄/Cl₂/N₂ flow rates of 10/10/50 cm³ min⁻¹ at ambient pressure at 350°C.



Figure 5. Correlation between CH₃Cl yield (*Y*_{CH3Cl}) and total amount of aluminum in (A) HY and (B) MFI zeolites.

Table 1. Summary of reactions showing average CH₄ conversion (X_{CH4}), Cl₂ conversion (X_{Cl2}), product selectivity for CH₃Cl (S_{CH3Cl}), CH₂Cl₂ (S_{CH2Cl2}) and CHCl₃ (S_{CHCl3}), and calculated CH₃Cl yield (Y_{CH3Cl}) obtained from the results shown in Fig. 4. CH₃Cl productivity was also given as catalyst weight-based (mmol_{CH3Cl} g_{cat}⁻¹ h⁻¹) and mole-based (mmol_{CH3Cl} mmol_{Al}⁻¹ h⁻¹) units.

	X_{CH4}	X_{Cl2}	S_{CH3Cl}	S_{CH2Cl2}	S_{CHCl3}	Y_{CH3Cl}	CH ₃ Cl Productivity Weight-based	Mole-based
	(70)	(70)	(70)	(70)	(70)	(70)	$(\text{mmol}_{\text{CH3Cl}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1})$	$(\text{mmol}_{\text{CH3Cl}} \text{ mmol}_{\text{Al}}^{-1} \text{h}^{-1})$
HY(2.6)	40.9 ± 0.3	70.3 ±	47.1 ±	33.2 ±	19.7 ± 0.3	19.2 ±	9.44	1.48
	0.5	1.0	0.5	0.2	0.5	0.7		
HY(15)	37.9 ±	64.9 ±	49.3 ±	32.5 ±	16.3 ±	18.7 ±	9.19	8.28
	0.5	2.8	1.1	1.1	1.9	0.2		
HY(250)	36.4 ±	62.7 ±	48.1 ±	31.5 ±	20.4 ±	17.5 ±	8.60	129.21
	0.2	0.6	0.3	0.2	0.4	0.06		
MFI(15)	38.8 ±	71.2 ±	43.6 ±	39.3 ±	17.1 ±	16.9 ±	8.30	7.48
	0.5	3.1	0.8	0.3	1.0	0.1		
MFI(40)	36.0 ±	62.0 ±	49.8 ±	37.9 ±	12.3 ±	17.9 ±	8.80	21.15
	1.0	4.7	1.5	1.1	2.6	0.2		
MFI(140)	32.4 ±	62.1 ±	44.7 ±	35.1 ±	20.2 ±	14.8 ±	7.27	109.22
	0.5	3.3	0.9	0.2	1.1	0.08		