

[Review Paper]

Propene Production from Ethene and Methane Using Silver- and Proton-exchanged Zeolite Catalysts

Koji INAZU, Toru KOYAMA, Akimitsu MIYAJI, and Toshihide BABA*

Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, G1-14 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, JAPAN

(Received November 26, 2007)

Two new methods for the catalytic synthesis of propene using solid acid catalysts are presented. The first approach is a new method for the activation of methane, involving conversion of methane to propene over silver-exchanged zeolite in the presence of ethene. In the second method, ethene conversion proceeds directly and selectively over proton-exchanged zeolite under the control of a molecular sieving effect.

The heterolytic dissociation of methane over silver cationic clusters (Ag_n^+) in Ag^+ -exchanged zeolites, leading to the formation of silver hydride ($\text{Ag}_n\text{-H}$) and $\text{CH}_3^{\delta+}$ species, which reacts with ethene to form propene around 673 K. Using ^{13}C -labeled methane as a reactant, propene is shown to be a primary product from methane and ethene. Thus, a significant proportion of propene was singly ^{13}C -labeled ($^{13}\text{CC}_2\text{H}_6$).

Under these reaction conditions, H^+ -exchanged zeolites, such as H-ZSM-5 do not catalyze the methane conversion, only ethene being converted into higher hydrocarbons, such as propene. Ethene is selectively converted to propene over SAPO-34 at 723 K with a yield of 52.2% and selectivity of 73.3% at ethene conversion of 71.2%. The high and selective propene yields achieved over SAPO-34 can be attributed to a shape selectivity effect of the small-pore SAPO-34.

KeywordsMethane activation, Propene production, Silver-exchanged zeolite catalyst, Ethene conversion,
Proton-exchanged zeolite catalyst**1. Introduction**

Ethene (C_2H_4) and propene (C_3H_6) are indispensable in petrochemical industries, and the demand for propene in particular has grown rapidly due primarily to the high growth in direct propene use¹⁾. Both chemicals are produced mainly through the cracking of naphtha, especially in European and East Asian countries. In these processes, the co-production of propene by steam cracking is determined largely by the feeding conditions, and the yield of propene is relatively low in terms of fluid catalytic cracking (FCC) units. In the USA and Canada, ethene is produced by the dehydrogenation of ethane (C_2H_6), a component of natural gas.

Methane (CH_4), the most inert of the hydrocarbons, constitutes an abundant yet low-value fossil feedstock, and has been extremely difficult to activate for conversion to industrial raw materials. However, as a principal component of natural gas, methane is being considered as a potential resource for energy and chemical production¹⁾. Basic and applied research on topics

ranging from synthetic gas production to direct oxidation of methane to methanol and/or formaldehyde^{2),3)}, and oxidative coupling of methane to ethane and/or ethene^{4)~11)} have been conducted extensively over the past hundred years. The process alternatives now available for C1 chemistry are summarized in **Fig. 1**. As an alternative to the conventional oil route, it may be possible to produce light olefins from natural gas^{12)~14)}. Investigations on alternative routes for light olefin synthesis were conducted following the 1973 oil crisis, leading to four broad categories (**Category 1–Category 4**) of production routes (see **Fig. 1**), as detailed below.

Category 1: Conversion of syngas using Fischer-Tropsch (FT) Fe-, Co-, Ru-, or Rh-based catalysts. Although a large number of studies have been conducted in attempts to improve the FT-type catalyst for the purpose of olefin synthesis, this synthetic route is essentially restricted by the Schulz-Flory law with regard to the carbon number distribution of the products¹⁵⁾. The products are usually aliphatic saturated hydrocarbons.

Category 2: Oxidative coupling of methane to produce ethane and propane^{4)~11)}. This process requires the use of oxygen. The formation of oxygen-containing products, such as CH_3OH and H_2O , provides a thermo-

* To whom correspondence should be addressed.

* E-mail: tbaba@chemenv.titech.ac.jp

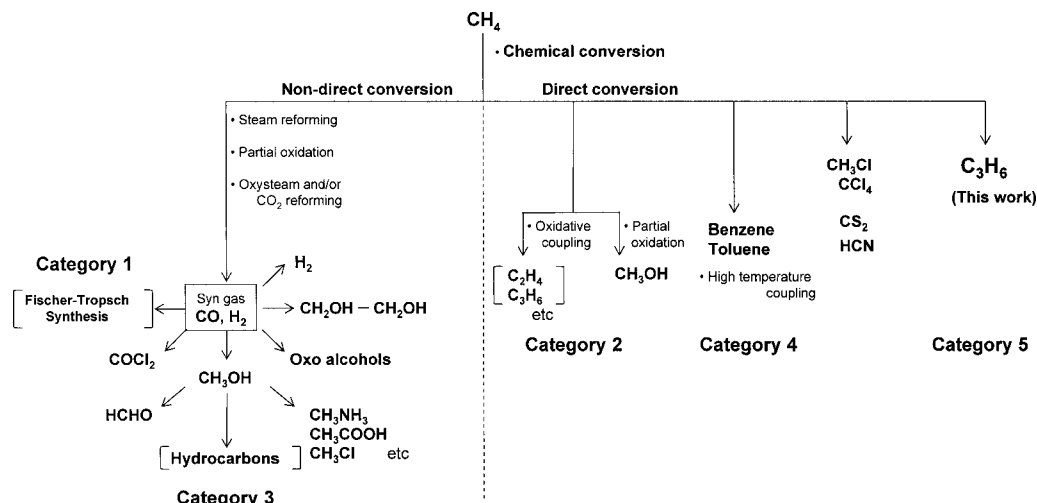


Fig. 1 Methane Utilization by Chemical Conversion

dynamic driving force such that the reaction has negative free energy. However, with the kinetically controlled direct oxidation reaction, the formation of CO_2 , an undesired product, severely limits the yields of light olefins.

Category 3: Conversion of methanol to olefins (MTO) using shape-selective zeolitic catalysts such as H-ZSM-5 and SAPO-34^{16,17}. This route is regarded as an indirect olefin synthesis from natural gas. The potential to realize practical applications for olefin synthesis appears to be higher than for other direct syntheses.

Category 4: Non-oxidative coupling of methane to aromatic hydrocarbons such as benzene (C_6H_6) at high reaction temperatures. Methane conversion under non-oxidative conditions is thermodynamically unfavorable, while methane is converted to higher hydrocarbons without the formation of CO_2 or CO .

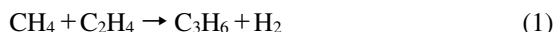
In 1993, Wang *et al.* reported that methane could be transformed into benzene over molybdenum-modified H-ZSM-5 zeolite under non-oxidative conditions at 973 K and at atmospheric pressure with conversion of approximately 10%¹⁸. Naphthalene, toluene ($\text{C}_6\text{H}_5\text{CH}_3$), ethene, and ethane were also formed with the parallel deposition of coke on the surface of the catalyst^{19,20}. ZSM-5 zeolites loaded with gallium or zinc (Ga/ZSM-5 or Zn/ZSM-5) are also known to catalyze the transformation of lower alkanes such as propane into aromatic hydrocarbons, yet the same zeolites exhibit negligible catalytic activity for the transformation of methane^{21–23}.

In this paper, we propose a new category, “**Category 5**” for the production of propene, as shown in Fig. 1.

Category 5 (this work): Two new routes for propene production: methane conversion using silver-exchanged zeolite in the presence of ethene, and direct ethene conversion over proton-exchanged zeolite by a size-

selective process.

The present paper consolidates extensive experimental research by the author’s group on these two methods for the catalytic synthesis of propene. In the conversion of methane and ethene, propene is produced by the reaction



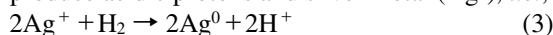
The effectiveness of silver-exchanged zeolite for the activation of methane is investigated in detail through ^1H magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, and the methane activation mechanism is determined through the use of ^{13}C -labeled methane as a reactant. The second synthetic route is suitable for ethene conversion under size-selective control by the reaction

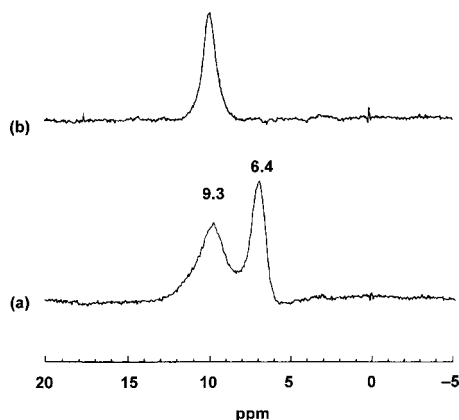


2. Reason Why Silver-exchanged Zeolites Are Used as Catalysts for Methane Activation

2.1. Catalytic Properties of Silver Salts of Heteropoly Acids and Silver-exchanged Zeolites as Solid Acid Catalysts

Silver-exchanged zeolites (*e.g.*, Ag-Y, Ag-A) and silver salts of heteropoly acids (*e.g.*, $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$) do not possess acidic protons (Brønsted acid sites). However, such materials exhibit catalytic activity for acid-catalyzed reactions in the presence of hydrogen^{24,25}. For example, the disproportionation of ethylbenzene to diethylbenzene and benzene, which is a typical acid-catalyzed reaction, is catalyzed by Ag-Y only under reductive conditions in the presence of hydrogen²⁴. It is thus clear that hydrogen plays an essential role in the formation of Brønsted acid sites (acidic protons). It is considered that Ag^+ cations are reduced by hydrogen to produce acidic protons and silver metal (Ag^0), *i.e.*,





(a) $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ heated at 393 K for 1 h and then at 523 K for 1 h under vacuum, followed by reduction under 40 kPa H_2 at 488 K for 25 min. Spectrum was recorded at 298 K under 40 kPa H_2 . Hydrogen consumption: 0.42 mol per equivalent of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$. Consumption corresponds to reduction of one of three Ag^+ cations in $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$. (b) Same sample after evacuation at 298 K for 2 h. Spectrum was recorded at 298 K.

Fig. 2 ^1H MAS NMR Spectra for $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ ⁽²⁵⁾

The characteristics of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ ⁽²⁵⁾, $\text{Ag}-\text{Y}$ ^{(24),(26)}, and $\text{Ag}-\text{A}$ ⁽²⁶⁾ as solid acid catalysts can be summarized as follows.

(1) The catalytic activity of silver-bearing compounds for various acid-catalyzed reaction is enhanced in the presence of hydrogen, while the activity of the parent acids, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and H^+ -exchanged Y zeolite ($\text{H}-\text{Y}$), is independent of hydrogen pressure.

(2) The hydrogen enhancement effect is reversible. For example, after starting the isomerization of *n*-hexane using $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ in the presence of hydrogen, the catalytic activity decreases upon removal of hydrogen from the reaction system, and recovers to the initial level upon the re-introduction of hydrogen⁽²⁷⁾.

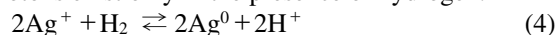
(3) The catalytic activities of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Ag}-\text{Y}$ in the presence of hydrogen are higher than those of the parent acids, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}-\text{Y}$.

2. 2. Effect of Partial Reduction of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$

After evacuation at 523 K for 1 h, $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ exhibits no ^1H MAS NMR response. However, after reduction under hydrogen, $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ produces two distinct peaks (9.3 ± 0.1 ppm and 6.4 ± 0.1 ppm) in the spectrum recorded under hydrogen at 298 K (Fig. 2(a))⁽²⁸⁾. Under these conditions, 33% of Ag^+ in $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ is reduced if all of the consumed hydrogen is consumed by the reduction of Ag^+ to Ag^0 metal, as expressed by Eq. (3).

Evacuation of gas-phase hydrogen at room temperature for 2 h causes the peak at 6.4 ppm to disappear (Fig. 2(b)). The density of protons detected at 6.4 ppm in the ^1H MAS NMR spectra thus changes reversibly with hydrogen pressure, while the density of protons detected at 9.3 ppm appears to be independent

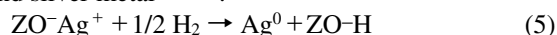
of hydrogen pressure, indicating that the 6.4 ppm protons exist only in the presence of hydrogen.



Partially reduced $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ exhibits catalytic activity for the isomerization of hexane only in the presence of hydrogen, with protons at both 9.3 ppm and 6.4 ppm catalyzing the isomerization of but-1-ene to but-2-ene. The partial reduction $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ thus has a particular effect on catalytic activity in the presence of hydrogen due to the behavior of acidic protons.

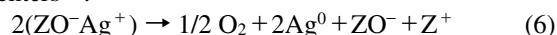
2. 3. Reversible Heterolytic Dissociation on Silver-exchanged Zeolites

Silver cations in zeolites are also reduced by hydrogen to generate protons (Brønsted acid sites, $\text{ZO}-\text{H}$) and silver metal^{(29)~(31)}:



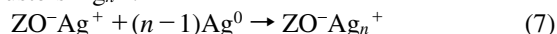
where ZO^- represents the zeolite lattice.

The chemistry of this reduction, however, may be more complex than suggested by Eq. (5), and much effort has been devoted to elucidating the state of silver species^{(32)~(36)}. Jacobs *et al.* found that vacuum thermal treatment of $\text{Ag}-\text{A}$ and $\text{Ag}-\text{Y}$ promotes intra-zeolitic auto-reduction of Ag^+ ion and the formation of color centers⁽³²⁾:



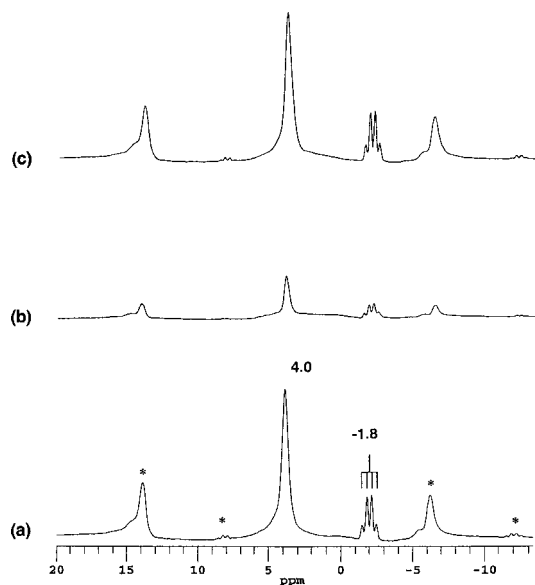
where Z^+ represents Lewis acid sites. At 600 K, up to 8% of Ag^+ in fully exchanged $\text{Ag}-\text{A}$ is reduced.

The formation of silver cationic clusters such as Ag_2^+ and Ag_3^+ ions in $\text{Ag}-\text{Y}$ has been proposed as a potential mechanism for reduction, suggesting that silver atoms further react with Ag^+ to form silver cationic clusters Ag_n^+ :



Ozin *et al.*, based on extensive study of the $\text{Ag}-\text{Y}$ and $\text{Ag}-\text{A}$ systems by diffuse reflectance spectroscopy and far-infrared spectroscopy, suggested that several silver cationic clusters (Ag_n^+) might be present depending on the temperature of hydrogen reduction^{(33)~(36)}.

Investigation of surface hydrogen species by ^1H MAS NMR has provided unequivocal evidence for the heterolytic dissociation of hydrogen over silver cationic clusters in $\text{Ag}-\text{A}$ and $\text{Ag}-\text{Y}$ ^{(37)~(39)}. Figure 3 shows the ^1H MAS NMR spectrum for $\text{Ag}-\text{A}$ under hydrogen after hydrogen reduction at 313 K⁽³⁸⁾. Two signals are apparent, at 4.0 ppm and -1.8 ppm. As acidic protons have been observed at 3.9–4.4 ppm in various zeolites⁽⁴⁰⁾, the peak at 4.0 ppm can be confidently attributed to the acidic protons generated by the reduction of Ag^+ under hydrogen. The signal at -1.8 ppm, consisting of four peaks with peak intensity ratios of 1 : 3 : 3 : 1 and a coupling constant of (131 ± 1) Hz, is considered to represent protons interacting with three equivalent silver atoms and/or ions⁽³⁸⁾. As metallic silver does not adsorb hydrogen, the cationic silver must be the chemisorption center for the hydrogen molecules. It is therefore concluded that the heterolytic dissociation of

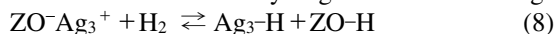


(a) Ag-A reduced under 40 kPa H₂ at 313 K for 30 min, spectrum recorded under 40 kPa H₂. (b) Same sample after evacuation at 313 K for 2 h. (c) Same sample after re-exposed to 40 kPa H₂ at 313 K for 30 min.

Fig. 3 ¹H MAS NMR Spectra of Ag-A Recorded at 298 K in the (a), (c) Presence and (b) Absence of Hydrogen³⁸⁾

hydrogen molecule proceeds over the cationic silver species, Ag₃⁺.

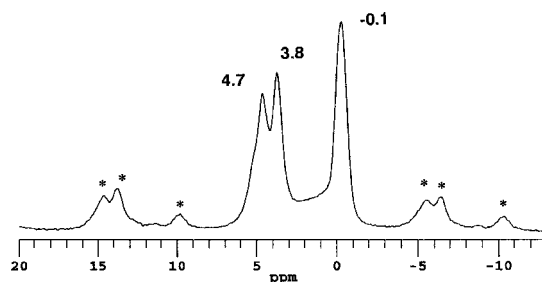
The reversible change of acidic protons and Ag₃-H was confirmed by ¹H MAS NMR measurements of Ag-A in the presence and absence of H₂³⁸⁾. After evacuation of the hydrogen-reduced Ag-A at 313 K, the ¹H MAS NMR peaks due to acidic protons and Ag₃-H (Fig. 3(b)) weakened by approximately 90% compared with that before evacuation (Fig. 3(a)). This result indicates that both acidic protons and Ag₃-H are transformed back into H₂ and Ag⁺ when H₂ is eliminated from the system. Re-exposure of the evacuated Ag-A to hydrogen at 313 K caused the peaks at 4.0 ppm and -1.8 ppm to reappear (Fig. 3(c)) with the original intensities. These results represent clear evidence of the reversible dissociation of hydrogen molecules on Ag-A:



The reversible dissociation of hydrogen molecules satisfactorily explains the reversible enhancement of the catalytic activity of Ag-A for the isomerization of but-1-ene²⁷⁾.

Increasing the temperature of hydrogen exposure from 313 K to 353 K resulted in the emergence of a peak due to silver hydride species (Ag_{*n*}-H) with an indeterminate value of *n* at -0.5 ppm, accompanied by a weakening of the Ag₃-H response. This result suggests that Ag_{*n*}-H species may have formed by further reaction of Ag₃⁺ with silver metal.

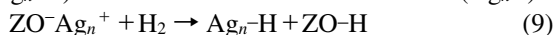
The heterolytic dissociation of hydrogen also occurred in the case of Ag-Y. The ¹H MAS NMR spectrum of



Sample was exposed to 40 kPa H₂ at 373 K for 15 min prior to measurement.

Fig. 4 ¹H MAS NMR Spectrum for Ag-Y Recorded at 298 K under 40 kPa H₂³⁸⁾

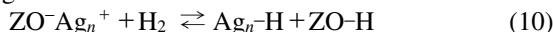
Ag-Y under hydrogen (40 kPa) at room temperature after hydrogen reduction at 423 K is shown in Fig. 4³⁸⁾. Three peaks are present, with chemical shifts of (-0.1 ± 0.1), (3.8 ± 0.1), and (4.7 ± 0.1) ppm. The peak at -0.1 ppm, which was not observed in proton-exchanged Y zeolite (H-Y), is ascribed to silver hydride species (Ag_{*n*}-H) adsorbed on cationic silver clusters (Ag_{*n*}⁺):



The peak at -0.1 ppm did not split as in the case of Ag-A, suggesting that Ag_{*n*}⁺ in Ag-Y is larger than Ag₃⁺ in Ag-A.

The peaks at 4.7 and 3.8 ppm are attributable to acidic protons in sodalite cages and supercages, respectively. This assignment is consistent with that for acidic protons in H(87%)-Y, implying that protons formed upon reduction of Ag⁺ ions are stabilized as bridging hydroxyl groups (ZO-H).

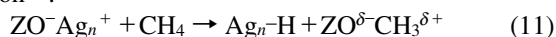
The reversibility of the transformations among Ag_{*n*}⁺, hydrogen molecules, Ag_{*n*}-H and acidic protons over Ag-Y zeolites has also been confirmed³⁸⁾.



2.4. Heterolytic Dissociation of C-H Bond of Methane

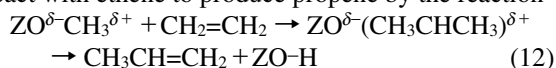
Silver-exchanged Y zeolite (Ag-Y) activates methane by heterolytic dissociation of the C-H bond³⁸⁾. The ¹H MAS NMR spectrum of Ag-Y under methane at room temperature after exposure to methane at 393 K is shown in Fig. 5. Two peaks are observed, with chemical shifts of 0.4 ppm and -0.1 ppm. The former is also observed for both Na-Y and H-Y, whereas the latter is not observed for either Na-Y nor H-Y upon exposure to methane. The peak at 0.4 ppm can therefore be assigned to the protons of methane physisorbed on these zeolites. As the peak at -0.1 ppm is in good agreement with that for silver hydride species formed by exposure of Ag-Y zeolite to H₂, it can be attributed to silver hydride species absorbed on cationic silver clusters (Ag_{*n*}⁺), which are presumably formed by the intra-zeolitic auto reduction of Ag⁺ to Ag⁰ (Eq. (6)) and reaction of Ag⁰ with Ag⁺ (Eq. (7)). The following scheme for heterolytic cleavage of the C-H bond of

CH₄ is proposed as a plausible mechanism for this reaction³⁸:



3. Reaction of ¹³C-labeled Methane with Ethene

The highly polarized methoxy groups (ZO^{δ-}CH₃^{δ+}) formed by the adsorption of methane (Eq. (11)) should be very reactive. It is thus expected that CH₃^{δ+} will react with ethene to produce propene by the reaction



The formation of propene from methane and ethene by this process has been examined by performing conversion reactions using ethene and ¹³C-labeled methane (¹³CH₄) in a closed gas circulation system at 673 K^{42,43}. The results after 1 min of reaction for a number of catalysts, including silver-exchanged zeolite, are listed in **Table 1**⁴⁴. To minimize side reactions, such as the dimerization/oligomerization of ethene, a large excess of ¹³CH₄ to ethene was used. Under these reaction conditions, propene is produced over Ag-A, Ag-Y, and Ag-ZSM-5, and ethane (C₂H₆) is produced as an addi-

tional gaseous product over Ag-A and Ag-Y.

In all cases, a significant proportion of propene is singly ¹³C-labeled (¹³CC₂H₆), indicating that ¹³CC₂H₆ is formed by the reaction of ¹³CH₄ with ethene. No doubly ¹³C-labeled propene (¹³C₂CH₆) is formed in this reaction. Although not quantified, the formation of hydrogen in the reaction can also be confirmed from these experiments. These results are strongly suggestive of electrophilic attack on the double bond of CH₂=CH₂ by the CH₃^{δ+} moiety in silver-exchanged zeolites. This is the first such methane activation mechanism to be reported. ZO-Ag_n⁺ may be regenerated by the reaction of Ag_n-H with an acidic proton on the Brønsted acid site accompanied by the formation of hydrogen, as expressed by

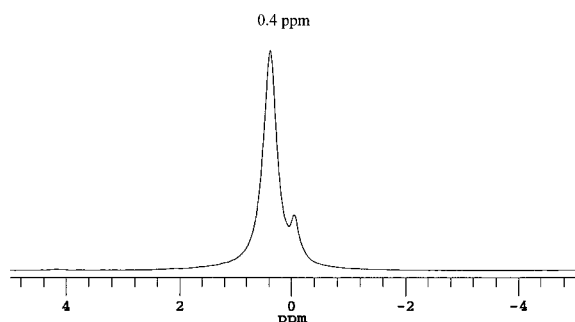


This reaction is the reverse of Eq. (10). The conversion of methane therefore proceeds catalytically over silver-exchanged zeolites.

Unlabeled propene (C₃H₆) is also obtained in these reactions, and is considered to have formed by the oligomerization-cracking of ethene. The ethane formed in this reaction was not labeled with ¹³C.

In the case of Ag₃PW₁₂O₄₀, ethane and propene were obtained as the main products, and selectivity for butenes was low (**Table 1**). The mole fraction of ¹³CC₂H₆ in total propene was 7%, similar to the natural abundance. This result demonstrates that the reaction of methane with ethene does not proceed over Ag₃PW₁₂O₄₀, which is unable to activate methane. The catalytic properties of silver cations in silver-exchanged zeolites thus differ from those for Ag₃PW₁₂O₄₀.

Reaction over H-ZSM-5 resulted in the formation of ethane, propene, and butenes as gaseous hydrocarbon products (**Table 1**). The mole fraction of ¹³CC₂H₆ in propene was 6%, similar to the natural abundance. Methane is thus not activated over H-ASM-5, which catalyzes only the transformation of ethene to higher hydrocarbons such as propene and butenes. H-Y is



Sample was exposed to 14 kPa CH₄ at 393 K for 1 h prior to measurement.

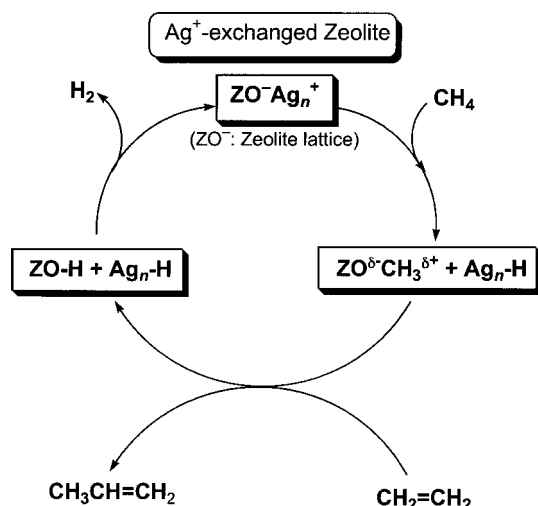
Fig. 5 ¹H MAS NMR Spectrum for Ag-Y Recorded at 298 K under 14 kPa CH₄³⁸

Table 1 Reaction of ¹³CH₄ with C₂H₄ over Ag⁺-exchanged Zeolites and Ag₃PW₁₂O₄₀

Catalyst	Ag(51%)-Y ^{a)}	Ag(60%)-A ^{a)}	Ag(17%)-ZSM-5 ^{a)}	H(100%)-ZSM-5	Ag ₃ PW ₁₂ O ₄₀ ^{b)}
Pressure [kPa]					
¹³ CH ₄	39.4	38.8	39.5	39.50	40.3
C ₂ H ₄	1.21	1.12	0.412	0.399	1.3
Conversion [mol%]					
C ₂ H ₄	10	37	10	0.8	4
Selectivity [mol%]					
C ₂ H ₆	35	72	0	10	68
C ₃ H ₆	65	28	100	71	25
C ₄ H ₈	0	0	0	19	7
(Singly ¹³ C-labeled hydrocarbon/hydrocarbon) × 100					
¹³ C ¹² C ₂ H ₆ in C ₃ H ₆	86	80	87	6	7

a) Catalyst, 0.1 g; reaction temperature, 673 K; reaction time, 1 min. Values in parentheses denote degree of Ag⁺ exchange.

b) Ag₃PW₁₂O₄₀, 0.6 g; reaction temperature, 623 K; reaction time, 3 min.



also unable to activate methane (not shown). These results clearly demonstrate that methane does not react with ethene at Brønsted acid sites, and that the presence of silver species in zeolite pores is indispensable for activating methane for reaction with ethene to produce propene.

4. Production of Propene by Reaction of Methane with Ethene

On the basis of ^1H MAS NMR measurements and the results of conversion of $^{13}\text{CH}_4$ in the presence of ethene, the proposed mechanism for the production of propene is as shown in **Scheme 1**⁴³⁾. Heterolytic dissociation of the C-H bond of methane produces highly polarized methoxy groups ($\text{ZO}^{\delta-}\text{CH}_3^{\delta+}$) and $\text{Ag}_n\text{-H}$, and the $\text{CH}_3^{\delta+}$ moiety thus formed reacts with ethene to produce propene and acidic protons (ZO-H).

According to **Scheme 1**, Ag_n^+ is regenerated by the reaction of $\text{Ag}_n\text{-H}$ with acidic protons at Brønsted acid sites (ZO-H), accompanied by the formation of H_2 . This reaction is the reverse of reaction (10), by which $\text{Ag}_n\text{-H}$ and ZO-H are formed simultaneously by the heterolytic dissociation of H_2 accompanying the formation of propene.

The acidic protons are essential for maintaining the catalytic reaction of methane with ethene. As the acid strength of protons generated in Ag-A is known to be very low compared to that in Ag-Y or Ag-ZSM-5, the role of proton acidity in promoting this catalytic reaction can be understood by comparing the catalytic performance of these three materials in the same reactor system (**Table 2**). The conversion of methane over Ag-A reaches 2.1% after 1 h time on stream, with a corresponding ethene conversion of 3.2%. The reaction over Ag-A thus proceeds effectively, suggesting that silver cationic species are successfully regenerated

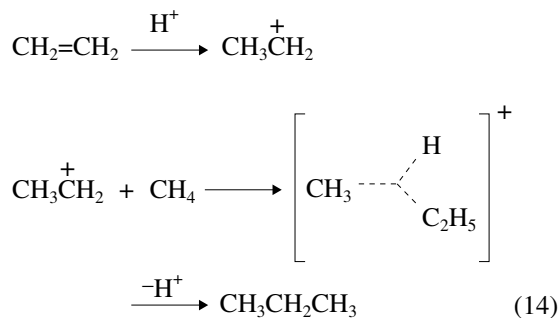
despite the low acid strength of protons. Therefore, highly acidic protons do not appear to be required to regenerate Ag_n^+ by reaction of $\text{Ag}_n\text{-H}$ with acidic protons.

However, the catalytic activities of Ag-ZSM-5 and Ag-Y for the conversion of methane are higher than that achieved over Ag-A. The acid strength of the acidic protons generated on Ag-ZSM-5 and Ag-Y is stronger than that on A-type zeolite. It is plausible that the regeneration of Ag_n^+ expressed by Eq. (13) occurs more readily as the acid strength of protons increases (e.g., ZO-H).

$\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ does not activate methane or promote the heterolytic dissociation of H_2 . These results are consistent with the finding that conversion of $^{13}\text{CH}_4$ in the presence of ethene does not produce $^{13}\text{CC}_2\text{H}_6$ over $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$.

Proton-exchanged zeolites (H-ZSM-5 and H-Y) catalyze only the conversion of ethene to propene, ethane, and butanes. Thus, propene is produced only by the conversion of ethene at Brønsted acid sites. Although C_2H_5^+ will be formed at Brønsted acid sites, the C_2H_5^+ ion does attack and insert into the methane C-H bond.

Olah *et al.* reported that the reaction of $^{13}\text{CH}_4$ and ethene over solid superacid catalysts (38% SbH_5 intercalated into graphite, TaF_5 , and $\text{TaF}_5\text{-AlF}_3$ at 1 : 1 weight ratio) at ambient temperature produces ^{13}C -labeled propane ($^{13}\text{CC}_2\text{H}_8$)^{45),46)}. Singly ^{13}C -labeled propane ($^{13}\text{CC}_2\text{H}_8$) could arise only from a $^{13}\text{CH}_4\text{-C}_2\text{H}_4$ condensation reaction. On the basis of these results, the following reaction mechanism was proposed.



Thus, mechanistically, the ethylation of methane is considered to be initiated by the protonation of ethene to produce the C_2H_5^+ , which then inserts into methane *via* pentacoordinate carbonation, yielding singly ^{13}C -labeled propane ($^{13}\text{CC}_2\text{H}_8$).

The activation of methane, however, does not occur over proton-exchanged zeolites such as H-ZSM-5. Instead, propene is produced. These results indicate that the production of C_2H_5^+ over proton-exchanged zeolites produces propene by the conversion of ethene itself. Therefore, the mechanism of the activation of methane for production of the CH_3^+ moiety in silver-exchanged zeolites appears to differ from that for superacid catalysts. It therefore appears essential to

Table 3 Reaction of $^{13}\text{CH}_4$ with C_2H_4 over Metal-exchanged Zeolites

Catalyst	In-ZSM-5 ^{a)}	Fe-ZSM-5 ^{a)}	Mo-ZSM-5 ^{a)}
Pressure [kPa]			
$^{13}\text{CH}_4$	39.4	39.5	39.6
C_2H_4	0.346	0.359	0.346
Conversion [mol%]			
C_2H_4	13	9.2	4.0
Selectivity [mol%]			
C_2H_6	17	33	37
C_3H_6	23	67	63
Benzene (C_6H_6)	41	0	0
Toluene (C_7H_8)	19	0	0
(Singly ^{13}C labeled hydrocarbon/hydrocarbon) $\times 100$			
$^{13}\text{C}^{12}\text{C}_2\text{H}_6$ in C_3H_6	33	62	24
$^{13}\text{C}^{12}\text{C}_5\text{H}_6$ in C_6H_6	9	—	—
$^{13}\text{C}^{12}\text{C}_6\text{H}_8$ in C_7H_8	54	—	—

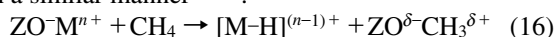
Catalyst, 0.1 g; reaction temperature, 673 K; reaction time, 1 min; reactor volume, 408 cm^3 .a) The molar ratio of metal cation to Al^{3+} was 0.17.

benzene production over Ag-ZSM-5 is very low.

In contrast with the reaction over Ag-Y, H-Y does not catalyze the conversion of methane in the presence of ethene, although ethene is converted. Saturated hydrocarbons such as ethane are the main products, indicating that extensive hydride-transfer reactions proceed due to the higher acidity of H-Y.

6. Activation of Methane over Metal Cation-exchanged ZSM-5 in the Presence of Ethene

There is a possibility that heterolytic dissociation of the C-H bond of methane may occur at metal cation (M^{n+}) sites other than Ag^+ on exchanged zeolites. If the highly polarized methoxy groups ($\text{ZO}^\delta\text{-CH}_3^{\delta+}$) are formed together with metal-hydride species $[\text{M-H}]^{(n-1)+}$ as in the case of silver-exchanged zeolites, the conversion of methane may proceed in the presence of ethene in a similar manner^{47),48)}:



The results of $^{13}\text{CH}_4$ conversion in the presence of ethene at 673 K using various metal cation-exchanged ZSM-5 zeolites are shown in **Table 3**^{47),48)}. The main product in all cases is propene, and ^{13}C was found in propene to varying extents. These results indicate that methane is activated on metal cationic species and that $^{13}\text{CC}_2\text{H}_6$ is produced by the methane-ethene reaction, demonstrating that methane is also activated on metal cationic species other than silver.

In the case of In-ZSM-5 (In/Al = 0.7), ethene conversion reached 13%, and ethane (17%), propene (23%), benzene (41%), and toluene (19%) were observed as gaseous hydrocarbon products (values in parenthesis denote selectivities in mol%)⁴⁸⁾. Among these hydrocarbons, ^{13}C -labeled ethane ($^{13}\text{CCH}_6$ and $^{13}\text{C}_2\text{H}_6$) and ^{13}C -labeled benzene ($^{13}\text{CC}_5\text{H}_6$) are negligible, with

mole fractions of only 2% and 7%, respectively (close to natural abundances). This result indicates that ethane (C_2H_6) and benzene (C_6H_6) originate solely from ethene. Propene and toluene, on the other hand, exhibit singly ^{13}C -labeled fractions of 33% and 54%, respectively. No significant amounts of multi- ^{13}C -labeled propene ($^{13}\text{CC}_2\text{H}_6$) or toluene ($^{13}\text{C}_2\text{C}_5\text{H}_8$) are produced by these reactions. Propene is thus formed by the reactions of $^{13}\text{CH}_4$ with ethene and the oligomerization/cracking of ethene. As ^{13}C -labeled benzene is not formed, propene is not converted to benzene in these reactions.

The formation of ^{13}C -labeled toluene ($^{13}\text{CC}_6\text{H}_8$) and the absence of ^{13}C -labeled benzene suggest that a fraction of the toluene is formed by reaction between methane and benzene⁴⁸⁾. Reaction of benzene over In-ZSM-5 under 39.8 kPa of $^{13}\text{CH}_4$ and 1.63 kPa of benzene at 673 K produced only toluene and hydrogen as reaction products. The similarity in the rates of benzene conversion (5.6%) and toluene yield (4.9%) suggests that side reactions such as the disproportionation of toluene to benzene and xylenes does not occur. The fraction of ^{13}C -labeled toluene is 97%, indicating that $\text{CH}_3^{\delta+}$ species formed on In-ZSM-5 are subsequently reacting with benzene to form toluene. Thus, methane can be activated not only on cationic Ag_n^+ clusters but also on other metal cations and/or cationic species. H-ZSM-5, on the other hand, does not show any catalytic activity for the reaction between methane and benzene under the same reaction conditions, as expected.

7. Catalytic Activity of Metal Cation-exchanged ZSM-5 for Methane Conversion

Motivated by the discovery that methane is activated over metal cation-exchanged ZSM-5 in the presence of

Table 4 Catalytic Activities for Methane Conversion in the Presence of Ethylene over ZSM-5 Exchanged with Various Metal Cations

Metal cation ^{a)}	Ag	Mo	In	Fe	V	Ga	Pd	Pb	La	Zn	Cu	H ^{b)}
Conversion [%]												
CH ₄	13.2	9.5	8.1	7.9	7.6	7.0	5.5	5.4	2.5	1.8	1.7	0
C ₂ H ₄	86.3	80.2	97.6	88.8	94.0	97.2	95.5	78.1	93.2	88.8	97.0	93.9
Composition [mol%]												
C ₂ H ₆	1.8	0.0	1.7	1.0	2.3	3.7	3.7	0.0	1.7	1.2	1.7	2.0
C ₃ H ₆	20.6	20.3	5.5	20.6	11.2	5.9	9.2	24.3	11.5	16.7	6.0	10.3
C ₃ H ₈	11.7	13.7	25.0	18.2	24.8	28.6	22.4	13.0	23.0	7.9	24.6	26.5
C ₄ H ₈	9.9	14.7	3.6	15.7	8.0	4.0	6.3	17.8	8.5	10.8	4.3	9.0
C ₄ H ₁₀	13.7	16.0	24.9	14.8	22.1	23.5	18.5	11.3	18.9	11.9	36.5	18.2
C ₅ -C ₇	12.7	14.2	13.4	13.9	11.5	7.4	8.7	14.2	10.6	12.4	8.1	11.9
Aromatics	30.3	21.1	25.9	15.8	20.1	26.9	31.2	19.4	25.8	39.1	18.8	22.1

CH₄=C₂H₄ = 33.8 kPa; running time, 1 h; W/F, 3.6 g·h·mol⁻¹; reaction temperature, 673 K.

a) Metal cation/Al³⁺ = 0.17.

b) H-ZSM-5.

ethene to produce propene and toluene, the conversion of methane was investigated over a range of metal cation-exchanged ZSM-5 zeolites. The results for the reaction of methane in the presence of ethene at an equimolar ratio are listed in **Table 4**⁴⁷⁾. These experiments were conducted for 1 h time on stream at 673 K in a flow reactor using catalysts with a molar ratio of metal cation to Al³⁺ of 0.17 regardless of the valence of the metal.

All of the metal cation-exchanged ZSM-5 zeolites (M-ZSM-5) tested (M = In, Mo, Fe, V, Ga, Pd, and Pb) are active for the conversion of methane to higher hydrocarbons, as expected. Methane conversion over Ag-ZSM-5 is the highest (13.2%), decreasing to 1.7% over Cu-ZSM-5. Again, H-ZSM-5 is shown to be inactive for methane conversion, converting only ethene to various hydrocarbons such as aromatics.

The activities of almost all of the investigated catalysts decrease with time on stream. The activity decay of Ag-ZSM-5 is the most rapid, with methane conversion decreasing from 13.2% after 1 h to zero after 5 h time on stream. On the other hand, the In-ZSM-5 catalyst is relatively stable with respect to methane conversion, decreasing by just 0.5% over 4 h time on stream. This result is reasonable, since indium cations are more resistant to reduction than silver cations. The catalytic activity of In-ZSM-5 is also dependent on the temperature of catalyst calcination and hydrogen pretreatment: continuous methane conversion of 11.8% is achieved over In-ZSM-5 at 673 K when the catalyst is pretreated with hydrogen at 723 K after calcination at 903 K⁴⁸⁾.

8. Selective Production of Propene by Conversion of Ethene over Proton-exchanged Zeolites

Proton-exchanged zeolites (*e.g.*, H-ZSM-5) have been shown to catalyze the conversion of ethene to pro-

duce propene, yet are unable to activate methane for conversion. In the conversion of methane over silver-exchanged zeolites in the presence of ethene, Ag-A exhibits higher selectivity for the production of propene than Ag-Y due to the smaller pores of the A-type zeolite. It is therefore expected that both the acid strength of Brønsted acid sites and the pore size of the catalyst material influence the rate and selectivity of propene formation in the conversion of ethene.

8. 1. Effect of Pore Size on Selectivity for Propene Formation

To examine the effect of pore size on the selectivity for propene, the conversion of ethene at 723 K was conducted under 33.3 kPa of ethene using the silicoaluminophosphate molecular sieve SAPO-34, the aluminosilicate molecular sieves H-[Al]-ZSM-5 and Ca-A, and the borosilicate molecular sieve H-[B]-ZSM-5 as solid acid catalysts⁴⁹⁾. The catalytic performance of these materials after 1 h time on stream is summarized in **Table 5**⁴⁹⁾. These results indicate that the selectivity for propene formation is strongly dependent on pore size. SAPO-34 exhibits the highest selectivity for propene (*ca.* 80%), while the selectivity for 2-methyl propene (*i*-butene) is very low. The accompanying alkenes are 1- and 2-butenes, produced with selectivities of 3.1% and 8.9%, respectively. The pore size of these catalysts decreases in the order H-[Al]-ZSM-5 = H-[B]-ZSM-5 > Ca-A > SAPO-34. The SAPO-34 structure includes a CHA cage (0.75 nm diameter × 0.82 nm), which is accessible via six eight-member rings (0.45 nm × 0.41 nm)⁴⁹⁾. The pore size of SAPO-34 (0.45 nm × 0.41 nm) is thus approximately equal to the kinetic diameter of propene (0.45 nm) and smaller than the kinetic diameter of 2-methyl propene (0.50 nm). Ethene has a kinetic diameter of 0.39 nm, while that for 1-butene is 0.45 nm).

Table 5 Catalytic Performance of Silicoaluminophosphate and Aluminosilicate Catalysts for the Conversion of Ethene at 723 K

Catalyst	Pore size ^{a)} [nm]	W/F [g·h·mol ⁻¹]	C ₂ ⁼ conv. [%]	Product selectivity [C-atom %]							Rate of C ₃ ⁼ formation [mmol·g ⁻¹ ·h ⁻¹]	Rate of butane conversion ^{c)} [mmol·g ⁻¹ ·h ⁻¹]
				C ₃ ⁼	1-C ₄ ⁼	2-C ₄ ⁼ (C/T ^{b)})	<i>i</i> -C ₄ ⁼	C ₁ -C ₄ alkane	C ₅	C ₆		
SAPO-34												
Si/(P + Al + Si) = 0.1	0.38 × 0.38	2.0	7.9	79.5	3.1	8.9 (0.64)	0.1	6.6	1.8	0.0	7.0	0.29
H-[Al]-ZSM-5 Si/Al = 11.9	0.56 × 0.53 0.55 × 0.51	0.050	6.3	48.4	4.0	11.2 (0.72)	14.3	5.0	16.3	0.8	130	6.3
H-[B]-ZSM-5 Si/B = 64.2	0.56 × 0.53 0.55 × 0.51	47	7.5	37.9	6.0	16.6 (0.72)	16.1	1.4	12.2	9.8	0.13	0.080
Ca-A Si/Al = 1.0	0.50	240	2.0	51.5	5.0	12.7 (0.73)	1.1	24.6	5.1	0.0	0.0095	0.043

C₂⁼: ethene, C₃⁼: propene, 1-C₄⁼: 1-butene, 2-C₄⁼: 2-butene, *i*-C₄⁼: *i*-butene, C₁-C₄ alkane: (CH₄ + C₂H₆ + C₃H₈ + C₄H₁₀), C₅: (pentenes + pentanes), C₆: aliphatic hydrocarbons with 6 carbon atoms.

Ethene pressure = 33.8 kPa, 1 h of time on stream.

a) Crystallographic free diameter (nm).

b) Molar ratio of *cis*-2-butene to *trans*-2-butene.

c) Cracking of *n*-butane: reaction temperature, 773 K; partial pressure of *n*-butane, 4.05 kPa.

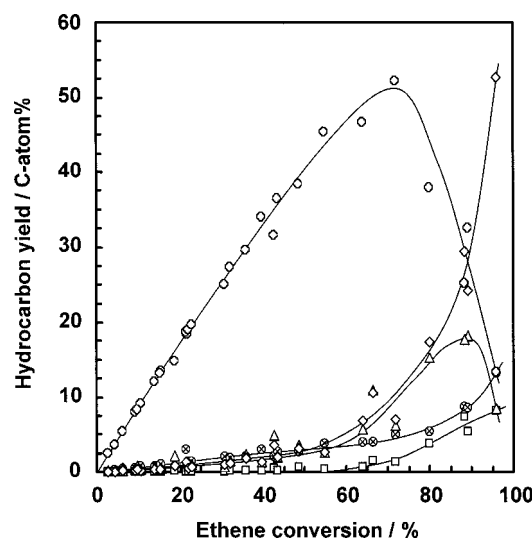
8.2. Effect of Acid Strength on Selectivity for Propene Formation

Although the pore size of A-type zeolite (Ca-A) is similar to that of SAPO-34, SAPO-34 exhibits higher selectivity for propene. The rate of propene formation over SAPO-34 is also much greater than that over Ca-A (Table 5). These results intimate that acid strength is also an important factor determining the activity for propene formation.

The acid strength of the catalysts was thus estimated based on the rate of *n*-butane cracking at 773 K at an *n*-butane pressure of 4.0 kPa⁵⁰). The cracking of *n*-butane is a typical reaction that proceeds on Brønsted acid sites, and it is natural that the reaction rate would increase with acid strength. The rate of *n*-butane cracking over SAPO-34 is 6.7 times greater than that over Ca-A, demonstrating the higher acid strength of SAPO-34.

To examine the effect of acid strength on propene formation, it is reasonable to compare the catalytic performance of H-[Al]-ZSM-5 and H-[B]-ZSM-5, which have the same structure and pore size yet dissimilar acidities. As shown in Table 5, the two catalysts exhibit different activities for *n*-butane cracking. The acid strength of H-[Al]-ZSM-5 is much higher than that of H-[B]-ZSM-5, and the former displays a much faster rate of propene formation than the latter. These results indicate that the rate of propene formation is higher over acid sites with greater acid strength. Ca-A, which has the lowest acid strength of the materials tested, also exhibits the lowest rate of propene formation.

The acid strength, on the basis of the rate of *n*-butane cracking, decreases in the order H-[Al]-ZSM-5 ≫ SAPO-34 ≫ H-[B]-ZSM-5 > Ca-A, whereas the selectivity for propene decreases in the order SAPO-34 > Ca-A > H-[Al]-ZSM-5 > H-[B]-ZSM-5. H-[Al]-ZSM-5,



⊗: CH₄ + C₂H₆ + butanes, ○: propene, ◇: propane, △: butenes, □: C₅+ hydrocarbons.

Fig. 6 Hydrocarbon Yield as a Function of Ethene Conversion over Proton-activated SAPO-34 at 673 K under Ethene Partial Pressure of 33.8 kPa⁴⁹)

which has higher acid strength than SAPO-34, converts propene to other hydrocarbons, such as C₅ hydrocarbons, whereas H-[B]-ZSM-5 and Ca-A, with lower acid strength than SAPO-34, exhibit a lower rate of propene formation than SAPO-34. These results show that SAPO-34, with modest acid strength, achieves the highest selectivity for propene among the catalysts examined.

8.3. Propene Yield and Selectivity over SAPO-34

The reaction of ethene over SAPO-34 at 673 K was further examined as a function of contact time (*W/F*) as a means of controlling the conversion level of ethene.

The yield of propene in the reaction at 33.3 kPa ethene partial pressure is plotted as a function of ethene conversion in **Fig. 6**⁴⁹⁾. The yield of propene increases with ethene conversion to a maximum yield of 52.2% propene at 71.2% ethene conversion. At ethene conversion greater than *ca.* 70%, the yield of propene decreases accompanied by an increase in the yield of propane. These results show that propene formed by catalysis is further converted to propane and higher hydrocarbons, such as hexenes.

9. Conversion of Ethanol to Propene over SAPO-34

It is well known that ethanol readily dehydrates to ethene over solid acid catalysts such as H-[Al]-ZSM-5, and that the conversion of ethanol affords lower alkenes, such as ethene and propene^{51)~53)}. Ethanol is usually produced by the hydration of ethene, yet can also be synthesized by the alcohol fermentation of biomass. It is therefore possible that propene, and hence polypropylene, could be produced without the consumption of petroleum resources.

The reaction pathways for the formation of hydrocarbons have been assumed to be similar to those of the analogous methanol-to-gasoline (MTG) process. In the case of ethanol, it is considered to be first converted to diethyl ether and then subsequently to ethene. The conversion of ethanol to propene was thus attempted using the SAPO-34 catalyst. The reaction was carried out as a function of contact time under 33.8 kPa ethanol at 673 K. Under these reaction conditions, ethanol is completely converted to hydrocarbons such as ethene and propene. The highest yield of propene is 51.0% at 50 g·h·mol⁻¹ (W/F), at which the yield of ethene is 38.1%. SAPO-34 thus afforded propene with high yield by the conversion of ethanol as well as ethene as a reactant. H₂O formed by the dehydration of ethanol to ethene has no influence on the yield of propene. Ethanol and ethene are thus converted to propene in similar yields over SAPO-34 at 673 K for a given contact time.

10. Conclusion

A new approach for the activation of methane over silver-exchanged zeolites was presented based on a consolidation of work by the author's group. Through ¹H MAS NMR measurements and the conversion of ¹³C-labeled methane in the presence of ethene revealed that the formation of silver cation clusters, which promote the reversible heterolytic dissociation of H₂, is essential for the activation of methane to afford highly polarized CH₃^{δ+} and form a Ag_n-H. The CH₃^{δ+} moiety then reacts with ethene to produce propene and acidic protons (ZO-H), as shown in **Scheme 1**, and the silver cation clusters are regenerated by the reaction of

Ag_n-H with ZO-H. Thus, propene is produced by the reaction of methane with ethene over silver-exchanged zeolites. This reaction also proceeds over other metal cation-exchanged zeolites. Catalysis involving metal cations such as Ag_n⁺ in zeolites is a new concept for the activation of methane, and may be expandable to alkane activation for the generation of alkyl carbenium ions by abstraction of hydride propene.

Propene is also produced over proton-exchanged zeolite materials such as SAPO-34 by the conversion of ethene. SAPO-34, which has intermediate acid strength and pore size comparable to the kinetic diameter of propene, selectively affords propene with high yield in the conversion of ethene. SAPO-34 is also an effective catalyst for the selective production of propene by the conversion of ethanol instead of ethene.

References

- 1) Crabtree, R. H., *Chem. Rev.*, **95**, 987 (1995).
- 2) Otsuka, K., Hatano, M., *J. Catal.*, **108**, 252 (1987).
- 3) Pyantnitskii, Y. I., *Theoretical and Experimental Chem.*, **39**, 201 (2003).
- 4) Lee, J. S., Oyama, S. T., *Catal. Rev. Sci. Eng.*, **30**, 294 (1988).
- 5) Hutchings, G. J., Woodhouse, J. R., Scurrel, M. S., *Chem. Soc. Rev.*, **18**, 251 (1989).
- 6) Amenomiya, Y., Birss, V. I., Golezdzinowski, M., Galuszka, J., Sanger, A. R., *Catal. Rev. Sci. Eng.*, **32**, 168 (1990).
- 7) Ashcroft, A. T., Cheethan, A. K., Foord, J. S., Gree, M. L. H., Grey, C. P., Murrell, A. J., Vernon, P. D. F., *Nature*, **344**, 319 (1990).
- 8) Lunsford, J. H., *Angew. Chem. Int. Ed. Engl.*, **34**, 970 (1995).
- 9) Ito, T., Lunsford, J. H., *Nature*, **314**, 9 (1982).
- 10) Shepelev, S. S., Lone, K. G., *J. Catal.*, **117**, 362 (1989).
- 11) Amariglico, M., Just, J. S., Amariglico, A., *Fuel Processing Technol.*, **42**, 291 (1995).
- 12) Anderson, J. R., *Appl. Catal.*, **47**, 177 (1989).
- 13) Lunsford, J. H., *Catal. Today*, **63**, 165 (2000).
- 14) Choudhary, T. V., Aksoylu, E., Goodman, D. W., *Catal. Rev. Sci. Eng.*, **45**, 151 (2003).
- 15) Inui, T., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **35**, (1), 33 (1992).
- 16) For example, Stocker, M., *Microporous Mesoporous Mater.*, **29**, 3 (1999).
- 17) Inui, T., *ACS Symposium Ser.*, **738**, 115 (2000).
- 18) Wang, L., Tao, L., Mie, M., Xu, G., Hunrg, J., Xu, Y., *Catal. Lett.*, **21**, 35 (1993).
- 19) Xu, Y., Liu, S., Wang, L., Xie, M., Guo, X., *Catal. Lett.*, **30**, 135 (1993).
- 20) Onishi, R., Liu, S., Dong, Q., Wang, L., Ichikawa, M., *J. Catal.*, **182**, 92 (1999).
- 21) Ono, Y., *Catal. Rev. Sci. Technol.*, **34**, 179 (1992).
- 22) Inui, T., Ishihara, Y., Kamachi, K., Matsuda, H., *Stud. Surf. Sci. Catal.*, **49**, 1183 (1989).
- 23) Hagen, A., Roessner, F., *Catal. Rev. Eng.*, **42**, 403 (2000).
- 24) Baba, T., Ono, Y., *Zeolites*, **7**, 292 (1987).
- 25) Baba, T., Watanabe, H., Ono, Y., *J. Phys. Chem.*, **87**, 2406 (1983).
- 26) Baba, T., Seo, S. G., Ono, Y., *Stud. Surf. Sci. Catal.*, **37**, 443 (1987).
- 27) Baba, T., Ono, Y., *Appl. Catal.*, **53**, 301 (1989).
- 28) Baba, T., Ono, Y., *J. Phys. Chem.*, **100**, 9064 (1996).
- 29) Beyer, H., Jacobs, P. A., Uytterhoeven, J. B., *J. Chem. Soc.*,

- Faraday Trans. 1*, **72**, 674 (1976).
- 30) Tsutsumi, K., Takahashi, H., *Bull. Chem. Soc. Jpn.*, **45**, 2332 (1972).
 - 31) Wang, P., Yang, Y., Kondo, J. N., Domen, K., Baba, T., *Bull. Chem. Soc. Jpn.*, **77**, 1627 (2000).
 - 32) Jacobs, P. A., Uytterhoeven, J. B., Beyer, H. K., *J. Chem. Soc., Faraday Trans. 1*, **75**, 56 (1979).
 - 33) Ozin, G. A., Hughes, F., *J. Phys. Chem.*, **87**, 94 (1983).
 - 34) Ozin, G. A., Baker, M. D., Godber, J., *J. Phys. Chem.*, **88**, 4902 (1984).
 - 35) Baker, M. D., Ozin, G. A., Godber, J., *J. Phys. Chem.*, **89**, 305 (1985).
 - 36) Baker, M. D., Godber, J., Ozin, G. A., *J. Phys. Chem.*, **89**, 2299 (1985).
 - 37) Baba, T., Komatsu, N., Takahashi, T., Sugisawa, H., Ono, Y., *Stud. Surf. Sci. Catal.*, **125**, 269 (1999).
 - 38) Baba, T., Komatsu, N., Sawada, H., Yamaguchi, Y., Takahashi, T., Sugisawa, H., Ono, Y., *Langmuir*, **15**, 7894 (1999).
 - 39) Baba, T., Tohjo, Y., Takahashi, H., Sawada, H., Ono, Y., *Catal. Today*, **66**, 81 (2001).
 - 40) Pfeifer, H., Freude, D., Hunger, M., *Zeolites*, **5**, 274 (1985).
 - 41) Knal, Z., "Catalysis," eds. by Anderson, J. R., Boudart, M., Springer-Verlag, Berlin (1982), Vol. III, p. 231.
 - 42) Baba, T., Sawada, H., *Phys. Chem. Chem. Phys.*, **4**, 3919 (2002).
 - 43) Baba, T., Inazu, K., *Chem. Lett.*, **35**, 142 (2006).
 - 44) Baba, T., Iwase, Y., Inazu, K., Matsumoto, A., *Microporous Mesoporous Mater.*, **101**, 142 (2007).
 - 45) Olah, G. A., Felver, J. D., Lalmmertsma, K., *J. Am. Chem. Soc.*, **105**, 6529 (1983).
 - 46) Olah, G. A., *Acc. Chem. Res.*, **20**, 422 (1987).
 - 47) Baba, T., Abe, Y., *Appl. Catal. A: General*, **250**, 265 (2003).
 - 48) Baba, T., Abe, Y., Nomoto, K., Inazu, K., Murai, K., *J. Phys. Chem., B*, **109**, 4263 (2005).
 - 49) Oikawa, H., Shibata, Y., Inazu, K., Iwase, Y., Baba, T., *Appl. Catal. A: General*, **312**, 181 (2006).
 - 50) Ito, M., Shimoyama, Y., Saito, Y., Tsurita, Y., Otake, M., *Acta Crystal.*, **C41**, 1698 (1985).
 - 51) Restalli, H., Jr., Lok, B. M., Duisman, J. A., Earls, D. E., Mullhapt, J. T., *Can. J. Chem. Eng.*, **60**, 44 (1982).
 - 52) Talukdar, A. K., Bhattacharyya, K. G., Sivasanker, S., *Appl. Catal. A: General*, **148**, 357 (1997).
 - 53) Ingram, C. W., Lancashire, R. J., *Catal. Lett.*, **31**, 395 (1995).

.....

要 旨

銀イオン交換およびプロトン交換ゼオライトによるメタンとエチレンからのプロピレン合成

稲津 晃司, 小山 徹, 宮地 輝光, 馬場 俊秀

東京工業大学大学院総合理工学研究科化学環境学専攻, 226-8502 横浜市緑区長津田4259-G1-14

筆者らが行ってきた二つのプロピレン合成法について概説する。その一つは、銀イオン交換を用いたエチレン共存下でのメタン転化反応である。もう一つはプロトン交換ゼオライトによるエチレン転化反応である。この反応では、プロピレンはゼオライトの分子ふるい効果によって選択的に生成する。

銀イオン交換ゼオライトはメタンを活性化できる。このことは銀イオン交換 Y 型ゼオライトにメタンを吸着させると、メタンの C-H 結合が不均等解離することが¹H MAS NMR 測定によって明らかとなった。メタンの不均等解離によって生成した CH₃⁺は、400℃ 付近でエチレンと反応して CH₃CH⁺CH₃を生成する。メタンとエチレンとの反応によってプロピレンが生成す

ることは、¹³CH₄と CH₂=CH₂とを反応させると¹³CC₂H₆が生成することから支持される。

一方、¹³CH₄と CH₂=CH₂との反応を試みたとき、プロトン交換ゼオライトでは C₃H₆が生成し、¹³CC₂H₆が生成しない。この結果は、プロトン交換ゼオライトではエチレンからプロピレンが生成していることを示している。なかでも SAPO-34はエチレンからプロピレンを選択的に生成する。たとえば、400℃ で反応を行うと、エチレン転化率が71.2% のときプロピレンの最高収率は52.2% (選択率は73.3%)であった。プロピレンの高い選択性は、SAPO-34の酸性プロトンの性質と分子ふるい効果によってもたらされると思われる。

.....