Highlight Review

Heterolytic Dissociation of C–H Bond of Methane over Ag^+-exchanged Zeolites and Conversion of Methane into Higher Hydrocarbons in the Presence of Ethene or Benzene

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Abstract

The heterolytic dissociation of CH_4 over silver cationic clusters (Ag_n^+) in Ag^+-exchanged zeolites leads to the formation of silver hydride (Ag_n–H) and methyl cations, which then reacts with C_2H_4 to form C_3H_6. This process provides methane conversion of 13.2% at 673 K to afford higher hydrocarbons, such as toluene. Under these reaction conditions, H–ZSM-5 only catalyzes ethene conversion to higher hydrocarbons, such as butenes, and no methane conversion occurs. The reaction of CH_4 with benzene also proceeds to form toluene and xylenes over Ag–ZSM-5 at 673 K. Zeolites prepared by exchange with other metal cations, including In and Ga, also activate CH_4 in the presence of C_2H_4. Using ^{13}C-labeled methane ($^{13}CH_4$) as a tracer, propene is shown to be a primary product for the ethene reaction based on the observation of a significant proportion of singly ^{13}C-labeled propene ($^{13}CC_2H_6$). In–ZSM-5 catalyzes the formation of not only propene, but also benzene and toluene. ^{13}C label atoms are not found in the benzene thus produced, indicating that benzene originates entirely from C_2H_4. However, the occurrence of singly ^{13}C-labeled toluene ($^{13}CC_6H_8$) implies that toluene is formed by the reaction of benzene with $^{13}CH_4$. The alternative reaction path, involving $^{13}CC_6H_8$ formation by reaction of propene with *n*-butenes generated by ethene dimerization, can be refuted by confirmation of the toluene origin through direct reaction of $^{13}CH_4$ with benzene.

♦ 1. Introduction

Methane, 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 material. However, as a principal component of natural gas, CH_4 is now under consideration as a potential resource for energy and chemical production.[1] In the past few decades, there has been significant basic and applied research on methane-related topics, ranging from synthesis gas production to direct oxidation of CH_4 to CH_3OH or formaldehyde[2,3] and oxidative coupling to C_2H_4 or C_2H_6.[4–6] However, in the direct oxidation and oxidative coupling of CH_4, the selectivity for the desired products is high only at low conversion rates, and the process produces relatively large volumes of undesirable products such as CO_2 and CO. Although CH_4 conversion under non-oxidative conditions is thermodynamically unfavorable, CH_4 is converted in such process to higher hydrocarbons without the formation of CO_2 and CO. For example, the non-oxidative homologation of CH_4 proceeds over metal catalysts, such as Pt and Ru.[6]

In 1993, Wang et al. reported that CH_4 could be transformed to benzene over molybdenum-modified H–ZSM-5 zeolite under non-oxidative conditions at atmospheric pressure and 973 K, and achieved conversion of approximately 10%.[7] Naphthalene, toluene, C_2H_4, and C_2H_6 were also formed associated with the parallel deposition of coke on the surface of the catalyst.[8] ZSM-5 zeolites loaded with Ga or Zn (Ga/ZSM-5 or Zn/ZSM-5) are also known to catalyze the transformation of lower alkanes, such as propene, to aromatic hydrocarbons, but the same zeolites exhibit negligible catalytic activity for the transformation of CH_4.[9,10] In 1997, Choudhary et al. reported the conversion of CH_4 to higher hydrocarbons over Ga/ZSM-5 by feeding a lower alkene (ethene, propene, or 1-butene) together with CH_4 under non-oxidative conditions at temperatures much lower than those required for oxidative coupling.[11] Naccache et al., however, reported that CH_4 was not inserted into the hydrocarbon products in the conversion of the mixtures of $^{13}CH_4$ and propene (or ethene) over H-galloaluminosilicate zeolites.[12]

Our group has found that Ag^+-exchanged zeolites are catalytically active for CH_4 conversion in the presence of alkenes (C_2H_4 or propene), and the reaction of CH_4 with benzene to form toluene has been shown to proceed at around 650 K.[13,14] Furthermore, exchange with other metal cations, such as In and Ga, has also been found to activate CH_4, driving conversion to higher hydrocarbons in the presence of C_2H_4.[15,16]

Recently, Pierella et al. reported that CH_4 is converted to higher hydrocarbons in the presence of C_2H_6 over Zn–ZSM-11,[17] and Choudhary et al. demonstrated simultaneous conversion of CH_4 and CH_3OH to gasoline over ZSM-5 modified with metal cations, such as Ga, In, and Zn.[18]

Our work focuses on the development of a new activation method for CH_4 conversion over metal cation-exchanged zeolites, such as Ag–Y. This review examines the catalysis of Ag^+-exchanged zeolites for heterolytic dissociation of the C–H bond of CH_4, the conversion of CH_4 in the presence of ethene, and the reaction of CH_4 with benzene. Reaction mechanisms for CH_4 activation and the formation of various hydrocarbons, such as propene, benzene, and toluene, are also proposed.

♦ 2. Activation of CH_4 over Ag^+-exchanged Zeolites

2.1 Reversible Heterolytic Dissociation of H_2 Molecules

Much attention has been drawn to the reduction behavior of

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silver cations and the chemistry of silver species in zeolites, such as Ag–A.[19–23] Uytterhoeven et al. found that vacuum thermal treatment of Ag–A and Ag–Y promotes the intrazeolitic autoreduction of Ag^+ ions and the formation of a color center,[19] as described by

$$2(ZO^-Ag^+) \rightarrow 1/2O_2 + 2Ag^0 + ZO^- + Z^+, \quad (1)$$

where ZO^- represents the zeolite lattice and Z^+ is a Lewis acid site. At 600 K, the degree of reduction amounts to almost 8% in fully exchanged Ag–A. Gellens et al. determined through X-ray powder diffraction (XRD) studies that Ag–A contains linear Ag_3^{2+} clusters.[20] The formation of Ag_2^+ and Ag_3^+ clusters in Ag–Y zeolite was similarly identified.[21]

Silver cations in zeolites are also reduced by H_2 to generate protons (Brønsted acid sites, ZO–H) and silver metal:[22]

$$ZO^-Ag^+ + 1/2H_2 \rightarrow Ag^0 + ZO\text{–}H. \quad (2)$$

The chemistry of this reduction, however, may be more complex than that expressed by Eq 2, and much effort has been devoted to elucidate the state of the silver species.[23–25] The formation of silver cationic clusters, such as Ag_2^+ and Ag_3^+ ions, in Ag–Y has been proposed as a potential mechanism for the reduction, suggesting that silver atoms further react with Ag^+ to form silver cationic clusters Ag_n^+:

$$ZO^-Ag^+ + (n-1)Ag^0 \rightarrow ZO\text{–}Ag_n^+. \quad (3)$$

Our group's ^1H magic-angle spinning (MAS) nuclear magnetic resonance (NMR) studies of surface hydrogen species have provided unequivocal evidence for the heterolytic dissociation of H_2 over silver cationic clusters (Ag_n^+) in Ag–Y and Ag–A.[26,27] The ^1H MAS NMR spectrum for Ag–Y under H_2 at room temperature after exposure to H_2 at 373 K is shown in Figure 1.

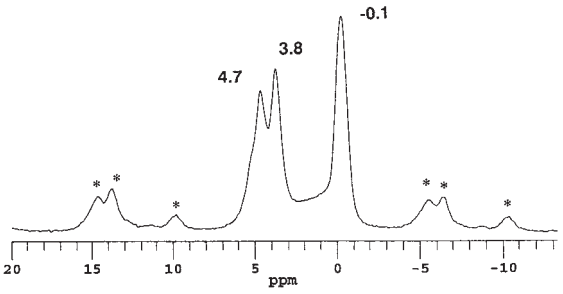

Figure 1. ^1H MAS NMR spectrum for Ag–Y at 298 K in the presence of H_2 (40 kPa) after reduction by exposure to H_2 (40 kPa) at 373 K for 15 min.[15]

Three peaks are present, the chemical shifts of which were determined after deconvolution to be (4.7 ± 0.1), (3.8 ± 0.1), and (-0.1 ± 0.1) ppm. The peaks at 4.7 and 3.8 ppm are attributable to acidic protons in the 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), as expressed by Eq 2. The peak at -0.1 ppm, which was not observed in H–Y, is ascribed to silver hydride species (Ag_n–H) adsorbed on cationic silver clusters (Ag_n^+):

$$ZO^-Ag_n^+ + H_2 \rightarrow Ag_n\text{–}H + ZO\text{–}H. \quad (4)$$

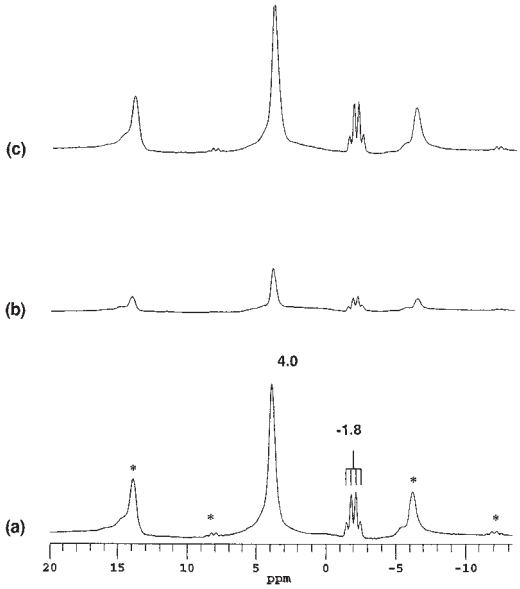

Figure 2. ^1H MAS NMR spectra for Ag-A at 298 K in the presence and absence of hydrogen.[15] (a) After reduction under H_2 (40 kPa) at 313 K for 30 min (R–Ag–A), (b) after evacuation of R–Ag–A at 313 K for 2 h (O–Ag–A), and (c) after re-exposure of O–Ag–A to H_2 (40 kPa) at 313 K for 30 min.

The existence of the silver hydride species is more clearly exhibited by exposure of Ag–A to H_2 than Ag–Y. Figure 2 shows the ^1H MAS NMR spectrum for Ag–A under H_2 after reduction with H_2 at 313 K.[26] Two signals can be observed, at 4.0 and -1.8 ppm (Figure 2a). As acidic protons have been observed at 3.9–4.4 ppm in various zeolites,[28] the peak at 4.0 ppm can be confidently attributed to the acidic protons generated by the reduction of Ag^+ cations under H_2. The signal at -1.8 ppm consists of four peaks with a peak intensity ratio of 1:3:3:1 and a coupling constant of (131 ± 1) Hz. It is thus considered to represent protons interacting with three equivalent Ag atoms and/or ions. As metallic silver does not adsorb H_2,[29] cationic silver must be the chemisorption center for H_2. Therefore, the heterolytic dissociation of H_2 is concluded to proceed over the cationic silver species, Ag_3^+ and to form Ag_3–H and acidic protons.

As mentioned above, the peak at -0.1 ppm, observed on Ag–Y upon exposure to H_2, did not split as seen for Ag–A. These differences suggest that Ag_3^+ in Ag–A is smaller than Ag_n^+ in Ag–Y.

The reversible change of acidic protons and Ag_3–H was confirmed by ^1H MAS NMR measurements of Ag–A in the presence and absence of H_2.[26] Evacuation of the hydrogen-reduced Ag–A at 313 K resulted in an 87% weakening of the ^1H MAS NMR peaks due to acidic protons and Ag_3–H (Figure 2b). This result indicates that both acidic protons and Ag_3–H are transformed back into H_2 and Ag^+ when H_2 is eliminated from the system. Re-exposure of the evacuated Ag–A to H_2 at 313 K caused the peaks at 4.0 and -1.8 ppm to reappear (Figure 2c) with the original intensities. These results represent clear evidence of the reversible dissociation of H_2 molecules on Ag-A, as described by

$$ZO\text{–}Ag_3^+ + H_2 \leftrightarrows Ag_3\text{–}H + ZO\text{–}H. \quad (5)$$

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However, the extent of reversibility was found to decrease as the degree of Ag^+ reduction increased, which is consistent with the expectation that the number density of Ag_3^+ will decrease with increasing degree of reduction as a result of the increasing population of larger silver clusters such as Ag_n^+ ($n > 3$). Previous studies have shown that the larger metallic silver crystals are formed on the external surface of zeolites under highly reductive conditions.[24]

The reversibility of the transformations among Ag_n^+, hydrogen molecules, Ag_n–H and acidic protons over Ag-Y zeolites has also been confirmed:[26,27]

$$ZO\text{–}Ag_n^+ + H_2 \leftrightarrows Ag_n\text{–}H + ZO\text{–}H. \quad (6)$$

2.2 Heterolytic Dissociation of C–H Bond of CH_4

Heterolytic dissociation of the C–H bond of CH_4 has been confirmed to proceed over Ag–Y zeolite.[35] The ^1H MAS NMR spectrum of Ag–Y under CH_4 at room temperature after exposure to CH_4 at 393 K is shown in Figure 3.

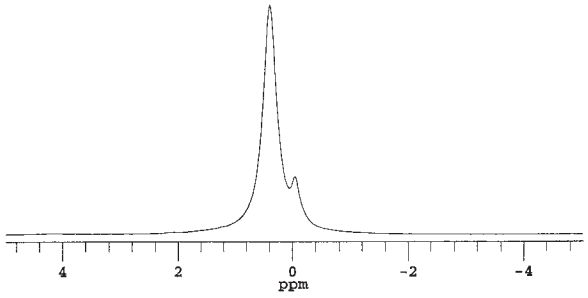


Figure 3. ^1H MAS NMR spectrum for Ag–Y in the presence of CH_4 (14 kPa) after exposure to CH_4 (14 kPa) at 393 K for 15 h.[26]

Two peaks can be observed, with chemical shifts of 0.4 and −0.1 ppm. The peak at 0.4 ppm was also observed for both Na–Y and H–Y, while the peak at −0.1 ppm was not observed in either of these catalysts upon exposure to CH_4. The peak at 0.4 ppm can therefore be assigned to the protons of CH_4 physisorbed on these zeolites. The peak at −0.1 ppm is in good agreement with that for silver hydride species formed by exposure of Ag–Y zeolite to H_2 and thus can be attributed to silver hydride species adsorbed on cationic silver clusters (Ag_n^+), which was formed by intrazeolitic autoreduction of Ag^+ to Ag^0 (Eq 1) and reaction of Ag^0 with Ag^+ (Eq 3). The following scheme for heterolytic cleavage of the C–H bond of CH_4 is proposed as a plausible mechanism for this reaction:[26]

$$ZO\text{–}Ag_n^+ + CH_4 \rightarrow Ag_n\text{–}H + ZO^{\delta-}CH_3^{\delta+}. \quad (7)$$

2.3 Reaction of $^{13}CH_4$ with Benzene

The highly polarized methoxy groups ($ZO^{\delta-}CH_3^{\delta+}$) formed by adsorption of CH_4, as expressed by Eq 7, should be very reactive. It is thus expected that $CH_3^{\delta+}$ reacts with benzene to form toluene. Using $^{13}CH_4$ as a tracer, the reaction of $^{13}CH_4$ with benzene was carried out over Ag–ZSM-5 at 673 K in a gas-circulation system.[13,14] The pressures of $^{13}CH_4$ and benzene in this reaction were 39.8 and 1.6 kPa, respectively. The reaction over Ag–ZSM-5 yielded 5.8% toluene in 2 min with 6.1% benzene conversion. No other hydrocarbons (e.g., xylenes) were observed. The proportion of singly ^{13}C-labeled toluene was 96%, indicating that the majority of the toluene was produced by methane–benzene reaction. This is strongly suggestive of electrophilic attack of the CH_3^+ moiety ($CH_3^{\delta+}$) toward the aromatic ring, indicating that heterolytic dissociation of the C–H bond of CH_4 proceeds over Ag^+-exchanged zeolites to form $CH_3^{\delta+}$. This is the first report of such a methane activation mechanism. H–ZSM-5 did not exhibit catalytic activity for the reaction of $^{13}CH_4$ with benzene under the same reaction conditions, as expected.

$ZO^-Ag_n^+$ may be regenerated by the reaction of Ag_n–H with an acidic proton on the Brønsted acid site accompanied by the formation of H_2, as expressed by

$$Ag_n\text{–}H + ZO\text{–}H \rightarrow ZO^-Ag_n^+ + H_2. \quad (8)$$

As mentioned above, this reaction is the reverse reaction of Eq 4. The conversion of CH_4 thus proceeds catalytically over Ag^+-exchanged zeolites.

2.4 Reaction of Benzene with CH_4 in a Flow Reactor

The reaction of benzene with CH_4 in a flow reactor over Ag–ZSM-5 at 673 K at partial pressures of 33.8 kPa for both CH_4 and benzene resulted in CH_4 and benzene conversions of 2.2 and 1.6%.[21] The reaction products were toluene and xylenes, with yields of 0.02 and 1.1%, respectively, after a running time of 1 h. Xylenes are presumably formed by the disproportionation of toluene at acidic sites of Ag–ZSM-5 and/or by the methylation of toluene with CH_4.

♦ 3. Conversion of CH_4 in the Presence of Ethene over Ag^+-exchanged Zeolites

3.1 Reaction of $^{13}CH_4$ with Ethene

The formation of toluene by the reaction of CH_4 with benzene suggests the formation of highly polarized methoxy groups ($ZO^{\delta-}CH_3^{\delta+}$) over Ag–ZSM-5. The highly polarized methoxy groups formed by the adsorption of CH_4, as expressed by Eq 7, should be very reactive. It is thus expected that the $CH_3^{\delta+}$ react with ethene (C_2H_4) to form C_3H_6 as follows.

$$ZO^{\delta-}CH_3^{\delta+} + CH_2{=}CH_2 \rightarrow ZO^{\delta-}(CH_3CHCH_3)^{\delta+}$$
$$\rightarrow CH_3CH{=}CH_2 + ZO\text{–}H. \quad (9)$$

$ZO^-Ag_n^+$ may be regenerated by the reaction of Ag_n–H with an acidic proton on the Brønsted acid site accompanied by the formation of H_2, as expressed by Eq 8.

To examine whether propene is formed from CH_4 and ethene, the reaction of ^{13}C-labeled methane ($^{13}CH_4$) with ethene was performed in a gas-circulation system over Ag^+-exchanged zeolites at 673 K.[13] To minimize side reactions, such as the dimerization/oligomerization of ethene, a large excess of $^{13}CH_4$ to ethene was used. The reaction was performed for 1 min. Under these reaction conditions, propene was produced over Ag–A, Ag–Y, and Ag–ZSM-5 (Table 1). Over Ag–A and Ag–Y, ethane was formed in addition to propene as a gaseous product.

In all cases, a significant proportion of propene was singly ^{13}C-labeled ($^{13}CC_2H_6$), indicating that $^{13}CC_2H_6$ is formed by the reaction of $^{13}CH_4$ with ethene. Undoubtedly, ^{13}C-labeled propene was formed. Although not quantified, the formation of H_2 in the reaction was confirmed. Unlabeled propene (C_3H_6)

was also obtained and must have been formed by oligomerization/cracking of ethene. Ethane was formed, but was not labeled with ^{13}C.

In the case of the H–ZSM-5 catalyst, ethane, propene, and butenes were observed as gaseous hydrocarbon products. However, the mole fraction of $^{13}CC_2H_6$ in propene was only 6%, similar to the natural abundance of $^{13}CC_2H_6$. This shows that H–ZSM-5 is unable to activate CH_4, and that acidic protons catalyze only the transformation of ethene to higher hydrocarbons, such as propene and butenes.[13] H–Y was also found to be unable to activate CH_4 (not shown). These results clearly demonstrate that CH_4 reacts with ethene and that the inclusion of silver species is indispensable for activating CH_4.

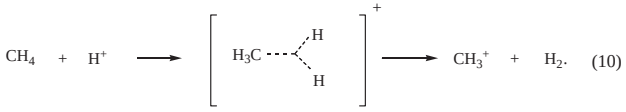
Proton-exchanged zeolites (H–ZSM-5 and H–Y) only catalyzed ethene to propene, as well as ethane and butanes, showing that propene is formed solely by the conversion of ethene over Brønsted acid sites. This indicates that the ethenium ion ($C_2H_5^+$) is formed over Brønsted acid sites, although $C_2H_5^+$ cannot attack and insert itself into the C–H bond of CH_4.

Olah et al. reported the polycondensation of CH_4 in FSO_3H–SbF_5[30] and suggested that methane is protonated in the solution to CH_5^+, which then loses H_2 to form CH_3^+, as expressed by

Table 1. Reaction of $^{13}CH_4$ with C_2H_4 over Ag^+-exchanged zeolites[a]

Catalyst	Ag(51%)–Y	Ag(60%)–A	Ag–ZSM-5[b]	H–ZSM-5[c]
Pressure/kPa				
$^{13}CH_4$	39.4	38.8	39.5	39.5
C_2H_4	1.21	1.12	0.412	0.399
Conversion/mol %				
C_2H_4	10	37	10	0.8
Selectivity/mol %				
C_2H_6	35	72	0	10
C_3H_6	65	28	100	71
C_4H_8	0	0	0	19
(Singly ^{13}C labeled hydrocarbon/hydrocarbon) × 100				
$^{13}CCH_6$ in C_3H_6	86	80	87	6

[a]Catalyst, 0.1 g; temperature, 673 K; reaction time, 1 min; reactor volume, 408 cm^3. Values in parentheses denote the degree of Ag^+ exchange. [b]$Ag^+/Al^{3+} = 0.17$ by mole. [c]H(100%)–ZSM-5.



The reaction of this intermediate with excess CH_4 initiates a growth or polycondensation reaction to form higher hydrocarbons such as ethane and ethene. Since CH_4 does not react over proton-exchanged zeolites such as H–ZSM-5, the mechanism of the activation of CH_4 for the formation of $CH_3^{\delta+}$ over silver-exchanged zeolites appears to differ from that for super acid catalysts.

3.2 *Catalytic Activity of Ag^+-exchanged Zeolites*

The reaction of CH_4 with C_2H_4 over Ag^+-exchanged at 673 K in a flow reactor proceeded as expected (Table 2).[13] In this experiment, an equimolar mixture of CH_4 and C_2H_4 (partial pressure of 33.8 kPa each) was reacted with a contact time of $W/F = 3.6\,g\,h\,mol^{-1}$, where W and F are the weight of the catalyst (g) and the total feed rate (mol h^{-1}), respectively. CH_4 was successfully converted over Ag^+-exchanged zeolites. It is possible that silver cationic clusters, over which CH_4 is activated, form in the presence of CH_4 and C_2H_4 by the reduction of Ag^+ cations with these hydrocarbons and/or by the intrazeolitic autoreduction of Ag^+ cations. For the Ag–Y catalyst, the conversions of CH_4 and C_2H_4 were 6.5 and 15.9%, respectively, where C_2H_6 was the main product, accompanied by C_3H_6, butenes and butanes.

The results of the ($CH_4 + C_2H_4$) reaction over H–Y after 1 h are also listed in Table 2. In contrast with the reaction over Ag–Y, H–Y did not catalyze the conversion of CH_4 as expected, although C_2H_4 conversion did proceed. Saturated hydrocarbons, such as C_2H_6, were the main products, indicating that extensive hydride-transfer reactions occurred according to the higher acidity of H–Y.

In the absence of CH_4, appreciable amounts of saturated hydrocarbons were also produced over Ag–Y. For example, the selectivity for C_3H_6 was approximately half than that achieved in the presence of CH_4. These results suggest that C_3H_6 is produced by the reaction of C_2H_4 with CH_4 over Ag–Y, although C_3H_6 is also produced by the reaction of C_2H_4 over

Table 2. Conversion of CH_4 over silver-exchanged zeolites in the presence of C_2H_4[a]

Catalyst	Ag(46%)–Y	Ag(46%)–Y	H(68%)–Y	Ag(60%)–A	Ag–ZSM-5[b]	H(100%)–ZSM-5
Reaction temperature/K	673	673	673	623	673	673
CH_4/kPa	33.8	0	33.8	33.8	33.8	33.8
C_2H_4/kPa	33.8	33.8	33.8	33.8	33.8	33.8
Conversion/mol %						
CH_4	6.5	—	0	2.1	13.2	0
C_2H_4	15.9	13.2	11.8	3.2	86.3	93.9
Selectivity/mol %						
CH_4	—	5.3	—	—	—	—
C_2H_6	41.0	42.9	62.6	33.6	1.8	2.0
C_3H_6	29.7	13.6	10.3	38.9	20.6	10.3
C_3H_8	4.2	5.0	4.5	0	11.7	26.5
C_4H_8	7.5	6.9	4.2	27.5	9.9	9.0
C_4H_{10}	11.7	16.7	13.5	0	13.7	18.2
C_{5+} Aliphatics	5.9	9.6	4.9	0	30.3	22.1
Aromatics	0	0	0	0	30.3	22.1

[a]Running time, 1 h; $W/F = 3.6\,g\,h/mol$; He carrier gas and internal standard for hydrocarbon determination. Values in parentheses denote the degree of Ag^+ exchange. [b]$Ag^+/Al^{3+} = 0.17$ by mole.

Brønsted acid sites, which are generated by the reaction of H_2 with cationic silver species.

The transformation of CH_4 did not occur over Ag–Y pretreated with H_2 at 673 K for 1 h. Under this condition, silver metal particles developed, which are likely to be inactive for CH_4 activation.

Ag–A and Ag–ZSM-5 also catalyzed the transformation of CH_4 in the presence of C_2H_4. The conversions of CH_4 and C_2H_4 over Ag–A were 2.1 and 3.2%, respectively, where ethane, propene, and butenes were formed. The selectivity for lower alkenes (propene and butenes) was 66.4%. The small pore size of A-type zeolite promotes the selective formation of lower alkenes, and the acidity of acidic protons generated on Ag–A is not sufficient to convert lower alkenes into aromatic hydrocarbons. Furthermore, highly acidic protons are not required in the generation of Ag_n^+ by the reaction of Ag_n–H with acidic protons.

Over Ag–ZSM-5, the conversions of CH_4 and C_2H_4 at 673 K were 13.2 and 86.3%, respectively. Benzene, toluene, and xylenes were formed under these reaction conditions. The selectivity for benzene was very low, while that for C_3H_6 was relatively high (20.6%). The conversion of CH_4 did not proceed over H–ZSM-5 or H–Y.

♦ 4. Activation of CH_4 over Metal Cation-exchanged ZSM-5

4.1 Conversion of $^{13}CH_4$ in the Presence of Ethene

It is well known that many metal salts and metal oxides undergo solid ion exchange on proton-exchanged zeolites such as H–ZSM-5 to form metal cations in zeolite cavities.[31] The catalytic synergy of metal cations and protons in ZSM-5 loaded with metal cations (Ag, Ga, and Zn) has been proposed for the aromatization of lower alkanes[9] and selective removal of NO using oxygen and CH_4 (Ga).[32] In the case of In cation exchange, the mixture of In_2O_3 and proton-exchanged zeolites undergoes reductive solid ion exchange to afford In^+ in the zeolite cavities under H_2.[33] Kanazirev et al. reported the incorporation of In^+ cations into ZSM-5 by reductive solid-state ion exchange, which proceeded according to

$$In_2O_3 + 2H_2 + 2ZO\text{–}H \rightarrow 2ZO^-In^+ + 3H_2O, \quad (11)$$

when the mixture of In_2O_3 and H–ZSM-5 was subjected to heating at 670–770 K in a hydrogen atmosphere.[33]

There is a possibility that the heterolytic dissociation of the C–H bond of CH_4 occurs on zeolites exchanged with metal cations (M^{n+}) other than Ag^+. This reaction is described by

$$ZO^-M^{n+} + CH_4 \rightarrow [M - H]^{(n-1)+} + ZO^{\delta-}CH_3{}^{\delta+}. \quad (12)$$

If highly polarized methoxy groups ($ZO^{\delta-}CH_3{}^{\delta+}$) form in addition to the metal-hydride species $[M - H]^{(n-1)+}$, as in the case of Ag^+-exchanged zeolites, the conversion of CH_4 may proceed in the presence of C_2H_4.[15,16]

The conversion of $^{13}CH_4$ in the presence of C_2H_4 was carried out at 673 K over ZSM-5 zeolite exchanged with various metal cations (In, Fe, Mo, and Ag).[15,16] The main product in these cases was propene (Table 3), and ^{13}C from $^{13}CH_4$ was found in propene to varying extents. This indicates that CH_4 is activated over metal cationic species and that $^{13}CC_2H_6$ is produced by the CH_4–C_2H_4 reaction, demonstrating that CH_4 is also activated over other metal cationic species. In the case of In–ZSM-5 (In/Al = 0.17), the conversion of C_2H_4 was 13%, and ethane (17%), propene (23%), benzene (41%), and toluene (19%) were observed as gaseous hydrocarbon products (values in parenthesis denote selectivities in mol %).[16] Among these hydrocarbons, ^{13}C-labeled ethane ($^{13}CCH_6$) and benzene ($^{13}CC_5H_6$) were negligible, with mole fractions of only 2 and 9%, respectively (close to natural abundances). This result indicates that ethane and benzene originate solely from C_2H_4. On the other hand, ^{13}C atoms from $^{13}CH_4$ were found in propene and toluene, the fractions of ^{13}C-labeled propene ($^{13}CC_2H_6$) in propene and singly ^{13}C-labeled toluene ($^{13}CC_6H_8$) in toluene being 33 and 54%, respectively. No significant amounts of multi-^{13}C-labeled propene ($^{13}C_2CH_6$) or toluene ($^{13}C_2C_5H_8$) were observed. Propene was formed by the reactions of $^{13}CH_4$ with C_2H_4 and the oligomerization/cracking of C_2H_4. As ^{13}C-labeled benzene was not formed, propene was not converted to benzene in these reactions.

Table 3. Reaction of $^{13}CH_4$ with C_2H_4 over metal cation-exchanged zeolites[16]

Catalyst[a]	In–ZSM-5	Fe–ZSM-5	Mo–ZSM-5
Pressure/kPa			
$^{13}CH_4$	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	65	28	100
Benzene (C_6H_6)	41	0	0
Toluene (C_7H_8)	19	0	0
(Singly ^{13}C labeled hydrocarbon/hydrocarbon) × 100			
$^{13}CCH_6$ in C_3H_6	33	62	24
$^{13}CC_5H_6$ in C_6H_6	9	—	—
$^{13}CC_6H_8$ in C_7H_8	54	—	—

[a]Catalyst, 0.1 g; temperature, 673 K; reaction time, 1 min; reactor volume, 408 cm^3. Metal cation/Al^{3+} = 0.17 by mole.

To further investigate the reaction path of toluene formation, the fragmentation of the mass spectroscopy (MS) spectrum of toluene was also examined.[16] The mole fraction of toluene singly labeled with ^{13}C in the benzene ring (CH_3–$^{13}CC_5H_5$) was 37%, and the mole fraction of toluene with labeled methyl group ($^{13}CH_3$–C_6H_5) was 17% (54% − 37% = 17%). Thus, the molar ratio of CH_3–$^{13}CC_5H_5$ to $^{13}CH_3$–C_6H_5 was 37/17 = 2.2, which is lower than that expected (6/1) from the statistical distribution. Singly ^{13}C-labeled toluene is therefore plausibly formed by two reactions; (i) the reaction of benzene with $^{13}CH_4$, and (ii) the reaction of $^{13}CC_2H_6$ with butenes formed by the dimerization of C_2H_4.

4.2 Reaction of $^{13}CH_4$ with Benzene over In–ZSM-5

The formation of ^{13}C-labeld toluene and the absence of ^{13}C-labeled benzene suggest that a fraction of the toluene is formed by reaction between CH_4 and benzene.[16] To further investigate the formation of toluene, the reaction of benzene with $^{13}CH_4$ was carried out over In–ZSM-5 under $^{13}CH_4$ (39.8 kPa) and benzene (1.63 kPa) at 673 K. The sole reaction products were toluene and H_2. The comparable conversion of benzene (5.6%)

Table 4. Catalytic activities for methane conversion over various metal cation-exchanged ZSM-5 catalysts in the presence of C_2H_4[a,15]

Metal cation[b]	Ag	Mo	In	Fe	V	Ga	Pd	Pb	La	Zn	Cu	H[c]
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_2H_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
Selectivity for hydrocarbons/%[d]	68.9	94.6	98.6	76.3	75.7	92.1	82.5	80.5	96.7	99.8	99.2	91.3
Distribution/mol %												
C_2H_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_3H_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_3H_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_4H_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_4H_{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	15.8	15.8	20.1	26.9	31.2	19.4	25.8	39.1	18.8	22.1

[a]$CH_4 = C_2H_4 = 33.8$ kPa; running time, 1 h; $W/F = 3.6$ g h mol^{-1}; reaction temperature, 673 K. [b]Metal cation/$Al^{3+} = 0.17$ by mole. [c]H–ZSM-5. [d]Moles of carbon in hydrocarbon products per 100 mole of carbon ($CH_4 + C_2H_4$) converted.

and yield of toluene (4.9%) suggest that other side reactions such as the disproportionation of toluene to benzene and xylenes did not occur. The high ^{13}C-labeled toluene fraction (97%) indicates that the $CH_3^{\delta+}$ species formed on In–ZSM-5 subsequently reacts with benzene to form toluene. Thus, CH_4 can be activated not only over cationic Ag^+ clusters but also over other metal cations and/or cationic species, such as In cations. H–ZSM-5 did not exhibit catalytic activity for the reaction between $^{13}CH_4$ and benzene under the same reaction conditions.

4.3 Catalytic Activity of Metal Cation-exchanged ZSM-5

As mentioned above, $^{13}CH_4$ is activated in the presence of ethene over metal cation-exchanged ZSM-5 to form propene and toluene. This result motivated the investigation of the conversion of CH_4 over ZSM-5 exchanged with various metal cations. The reaction of CH_4 in the presence of C_2H_4 was carried out at 673 K in a flow reactor.[15] All of the metal cation-exchanged ZSM-5 zeolites were active for CH_4 conversion to higher hydrocarbons, as expected (Table 4). CH_4 conversion over Ag–ZSM-5 was 13.2%. These results show that In, Mo, Fe, V, Ga, Pd, and Pb are particularly suitable for CH_4 conversion, and that the catalytic activity is related to the metal cation used. H–ZSM-5 is not active in CH_4 conversion, and only C_2H_4 was converted to hydrocarbons (e.g., aromatics) in this case.

The activities of almost all of the investigated catalysts decreased with time on stream. The decay in activity was most rapid for Ag–ZSM-5, reaching zero after 5 h time on stream. In contrast, In–ZSM-5 exhibited much more stable activity for CH_4 conversion, actually increasing from 8.1% conversion after 1 h to 8.6% after 5 h time on stream. Indium cations are more resistant to reduction compared to Ag^+. The catalytic activity of In–ZSM-5 was also found to vary with the temperature of catalyst calcination and hydrogen pretreatment. The conversion of CH_4 over this catalyst was 11.8% at 673 K and remained relatively constant with time on stream when the catalyst was pretreated with hydrogen at 723 K after calcination at 903 K.[16]

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