Conversion of methane over Ag$^+$-exchanged zeolite in the presence of ethene

Toshihide Baba*

Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Midori-ku, 226-8502, Yokohama, Japan

Methane is shown to react with ethene over silver-exchanged zeolites at around 673 K to form higher hydrocarbons. Methane conversion of 13.2% is achieved at 673 K over Ag–ZSM–5 catalyst. Under these conditions, H–ZSM–5 does not catalyze the methane conversion, only ethene being converted into higher hydrocarbons. Zeolites with extra-framework metal cations such as In and Ga also activate methane in the presence of ethene. Using $^{13}$C-labeled methane as a reactant, propane is shown to be a primary product from methane and ethene. $^{13}$C atoms were not found in benzene molecules produced, indicating that benzene is entirely originated from ethene. On the other hand, in toluene, $^{13}$C atoms are found in both the methyl group and the aromatic ring. This implies that toluene is formed by the reaction of propene with butenes formed by the dimerization of ethene, and also by the reaction of benzene with methane. The latter path was confirmed by direct reaction of $^{13}$CH$_4$ with benzene. In this case, $^{13}$C atoms are found only in methyl groups of toluene produced. The heterolytic dissociation of methane over Ag$^+$-exchanged zeolites is proposed as a reaction mechanism for the catalytic conversion of methane, leading to the formation of silver hydride and CH$_4^{+}$ species, which reacts with ethene and benzene to form propene and toluene, respectively. The conversion of methane over zeolites loaded with metal cations other than Ag$^+$ is also described. The reaction of methane with benzene over indium-loaded ZSM–5 afforded toluene and xylenes in yields of up to 7.6% and 0.9% at 623 K when the reaction was carried out in a flow reactor.

KEY WORDS: methane conversion; Alkylation with methane; Ag$^+$-exchanged zeolite; Heterolytic dissociation of methane; Heterolytic dissociation of hydrogen; $^1$H MAS NMR.

1. Introduction

Methane, as a principal component of natural gas, is being considered as a potential resource for energy and chemical production in this century [1]. However, methane is the most inert among hydrocarbons, and it is difficult to directly convert methane into higher hydrocarbons. Nevertheless, some success has been achieved by the oxidative coupling of methane to ethane and/or ethene over a number of basic catalysts, such as MgO [2–5]. In 1993, Xu et al. reported that methane could be transformed into benzene over molybdenum-modified H–ZSM–5 under non-oxidative conditions at atmospheric pressure at 973 K with conversion of approximately 10% [6]. 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 propane into aromatic hydrocarbons, but the same zeolites exhibit negligible catalytic activity for the transformation of methane [7–9]. In 1997, Choudhary et al. reported the conversion of methane into higher hydrocarbons over Ga/ZSM–5 by feeding a lower alkene (C$_3$H$_4$, C$_3$H$_6$, or 1-butene) together with methane under non-oxidative conditions at temperatures, much lower than those required for the oxidative coupling of methane [10,11]. Naccache et al., however, reported that methane was not inserted into the hydrocarbon products in the conversion of the mixtures of $^{13}$CH$_4$ and propene (or ethene) over H-galloaluminosilicate zeolite by the use of [12].

Our group, however, has recently found that Ag$^+$-exchanged zeolites exhibit catalytic activity for methane conversion in the presence of ethene [13–16]. Here, after briefly reviewing the heterolytic adsorption of hydrogen and methane, the conversion of methane into higher hydrocarbons over Ag$^+$-exchanged zeolites are described. Evidence for methane insertion into the products by the use of $^{13}$CH$_4$ is also presented.

2. Hydrogen chemisorption over Ag$^+$-exchanged zeolites

2.1. Reversible interconversion between Ag$^+$ cations and silver metal in Ag$^+$-exchanged zeolites

It is well known that the reduction of zeolites containing silver cations with hydrogen produces both silver metal (Ag$^0$) and acidic protons [17–19], as expressed by

$$\text{ZO}^-\text{Ag}^+ + \frac{1}{2}\text{H}_2 \rightarrow \text{Ag}^0 + \text{ZO–H} \quad (1)$$

where ZO$^-$ and ZO–H stand for zeolite lattice and Bronsted acid sites, respectively. The chemistry of this reduction, however, may be more complex than that expressed by equation (1), and much effort has been devoted to elucidate the state of silver species [20–27]. The formation of silver cationic clusters such as Ag$_2$$^+$ and Ag$_3$$^+$ ions in Ag–Y has been proposed as a potential

---

* To whom correspondence should be addressed.
E-mail: tbaba@chemenv.titech.ac.jp
mechanism for the reduction [20–22], suggesting that silver atoms further react with Ag\(^+\) to form silver cationic clusters Ag\(_n\): \[ \text{ZO}^-\text{Ag}^+ + (n - 1)\text{Ag}^0 \rightarrow \text{ZO}^-\text{Ag}_n^+ \] (2) Ozin et al., based on extensive study of the Ag–Y and Ag–A systems by diffuse reflectance spectroscopy and far-infrared spectroscopy, suggested that several Ag\(_n\) clusters might be present depending on the temperature of hydrogen reduction [25–28]. They also demonstrated a reversible transformation between Ag\(_3^+\) and Ag\(_3\) by treatment with hydrogen and oxygen [25].

Kim and Seff determined the crystal structure of Ag–A (Ag\(_{4.6}\)Na\(_{7.4}\)–A; evacuated at 623 K) by single-crystal X-ray diffraction (XRD) analysis and identified the presence of an Ag\(_6\) \(^3+\) cluster in each large cavity [20]. The cluster is in the form of a nearly linear Ag\(_3\) molecule, in which each constituent atom is coordinated to an Ag\(^+\) ion. The presence of Ag\(_6\)\(^+\) and Ag\(_5\)\(^-\) clusters in Ag–A (Ag\(_{7.6}\)Na\(_{4.4}\)–A) was also identified in a similar manner [21].

The intrazeolitic autoreduction of Ag\(^+\) ions also proceeds upon thermal treatment under vacuum, resulting in the formation of Ag-ion clusters [28] by the following reaction:

\[ 2\text{ZO}^-\text{Ag}^+ \rightarrow 1/2 \text{O}_2 + 2\text{Ag}^0 + \text{ZO}^- + z^+ \] (3)

where Z\(^+\) represents a Lewis acid site.

XRD and CO chemisorption studies have revealed that reversible interconversion occurs between Ag\(^+\) and silver metal in Ag–Y upon low degrees of Ag\(^+\) reduction with hydrogen [29]. Ag\(^+\) ions are reproduced when hydrogen in the system is evacuated. This was confirmed by the disappearance of the XRD lines due to silver metal and the full recovery of the infrared (IR) bands due to CO adsorbed on Ag\(^+\) by evacuation. This reversibility was also confirmed in hydrogen adsorption–desorption experiments at 313 K.

The catalytic activity of Ag–Y for the disproportionation of ethylbenzene to benzene and diethylbenzene has been found by our group to be dependent on the partial pressure of hydrogen in the gas phase [30]. The enhancement effect of hydrogen was reversible, suggesting that the amounts of acidic protons on the catalyst changes reversibly with hydrogen partial pressure. The enhancement effect of catalytic activity by hydrogen has also been observed for several other reactions over Ag-exchanged zeolites [31,32].

2.2. Heterolytic dissociation of hydrogen over Ag–A and Ag–Y zeolites

To understand the enhancement effect of hydrogen on the catalytic activity of Ag\(^+\) exchanged zeolites, the surface hydrogen species were investigated by \(^1\)H magic-angle spinning (MAS) nuclear magnetic resonance (NMR). It provided unequivocal evidence for the heterolytic dissociation of hydrogen over Ag\(_n\)\(^+\) in Ag–A and Ag–Y [33–35]. Figure 1 shows the \(^1\)H MAS NMR spectrum for Ag–A under hydrogen (40 kPa) after the reduction with hydrogen at 313 K for 30 min. Two signals can be observed at 4.0 ppm and –1.8 ppm as shown in figure 1(a). As acidic protons have been observed at 3.9–4.4 ppm in various zeolites [36–37], the peak at 4.0 ppm can be confidently attributed to the acidic protons generated by the reduction of Ag\(^+\) with hydrogen. The signal at –1.8 ppm consists of four peaks with the 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 Ag atoms and/or ions. As metallic silver does not adsorb hydrogen [38], the cationic silver is responsible for the chemisorption of hydrogen molecules. Therefore, it is concluded that the heterolytic dissociation of hydrogen molecule proceeds over the cationic silver species, Ag\(_3^+\).

The reversible change of acidic protons and Ag\(_3\)H with adsorption–desorption cycles was confirmed by \(^1\)H MAS NMR measurements of Ag–A. Upon evacuation of the hydrogen-reduced Ag–A at 313 K for 2 h, the \(^1\)H MAS NMR peaks due to acidic protons and Ag\(_3\)H (figure 1(b)) weakened by about 87% compared with that before evacuation (figure 1(a)). This result indicates that both acidic protons and Ag\(_3\)H are transformed back into \(\text{H}_2\) and Ag\(^+\) when \(\text{H}_2\) is eliminated from the system. Re-exposure of the evacuated Ag–A to hydrogen (40 kPa) at 313 K for 30 min caused the peaks at 4.0 ppm and –1.8 ppm to reappear (figure 1(c)) with the original intensities. These results represent clear evidence of the reversible dissociation of hydrogen molecules on Ag–A, as expressed by

\[ \text{ZO}^-\text{Ag}_3^+ + \text{H}_2 \rightarrow \text{Ag}_3^- + \text{H} + \text{ZO}-\text{H} \] (4)

However, the extent of reversibility was found to be decreased as the degree of Ag\(^+\) reduction increased, which is consistent with the expectation that the number of Ag\(_3^+\) will decrease with increasing degree of reduction due to the increasing population of larger silver clusters such as Ag\(_n\)\(^+\) \((n > 3)\). It has been shown previously that larger metallic silver crystals are formed at the external surface of zeolites under highly reductive conditions [22, 23].

The dissociative adsorption of hydrogen has also been observed on Ag–Y. The \(^1\)H MAS NMR spectrum of Ag–Y under hydrogen (40 kPa) at room temperature after its exposure to hydrogen (40 kPa) at 373 K for 15 min is shown in figure 2. Three peaks are present, the chemical shifts of which were determined after deconvolution to be (4.7 ± 0.1), (3.9 ± 0.1) and (–0.1 ± 0.1) ppm. The peaks at 4.7 and 3.9 ppm are attributed to acidic protons in the sodalite cages and in the supercages,