

Catalytic Transformation of Methane over In-Loaded ZSM-5 Zeolite in the Presence of Ethene

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Methane is shown to react with ethene over In-loaded ZSM-5 to higher hydrocarbons such as propene and toluene at around 673 K. Such methane conversion is not catalyzed by proton-exchanged ZSM-5 (H-ZSM-5) under the same conditions, only C₂H₄ being converted to higher hydrocarbons. By using ¹³C-labeled methane (¹³CH₄) as a reactant, the reaction paths for the formation of propene, benzene and toluene were examined. ¹³C-labeled propene (¹³CC₂H₆) is formed by the reaction of ¹³CH₄ with C₂H₄. The lack of ¹³C-labeled benzene revealed that propene is not transformed to benzene, which instead originates entirely from C₂H₄. The ¹³C atom is inserted both into the methyl group and benzene ring in the toluene formed. This indicates that toluene is formed by two reaction paths; the reaction of ¹³CC₂H₆ with butenes formed by the dimerization of C₂H₄ and the reaction of benzene with ¹³CH₄. The existence of the latter path was proved by the direct reaction of ¹³CH₄ with benzene. The reaction of methane with benzene was also carried out in a continuous flow system over In-loaded ZSM-5. The reaction afforded 7.6% and 0.9% yields of toluene and xylenes, respectively, at 623 K.

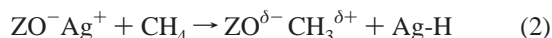
Introduction

The heterolytic dissociation of hydrogen on Ag⁺-exchanged zeolites such as Ag-Y and Ag-A has been shown unequivocally by proton magic angle spinning nuclear magnetic resonance (¹H MAS NMR).^{1,2} Thus, the exposure of Ag⁺-exchanged zeolites to hydrogen leads to the formation of acidic protons and silver hydride species (Ag-H). The amount of acidic protons and silver hydride species are reversibly changed with hydrogen pressure. The process may be expressed as follows

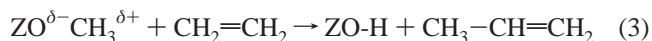


where ZO[−] is the zeolite lattice and ZO-H represents acidic OH groups. The Ag-H may actually exist as cationic silver clusters (Ag_n-H).^{1,2}

We have also reported that CH₄ is activated on Ag⁺-exchanged zeolites such as Ag-Y.² Thus, the formation of Ag-H upon exposure of Ag-Y to CH₄ at 423 K has been confirmed by ¹H MAS NMR. This result suggests that Ag⁺ cations cause the heterolytic dissociation of the C–H bond of CH₄, and that Ag-H and methyl cation-like species (CH₃^{δ+}) are formed over Ag⁺-exchanged zeolites by the following reaction:



Thus, if C₂H₄ coexists with CH₄ in the reaction system, CH₃^{δ+} should react with C₂H₄ to form C₃H₆, as follows:



We have reported that the transformation of CH₄ to C₃H₆ in the initial stage of the transformation of CH₄ in the presence of C₂H₄.^{3,4} This is proven by employing ¹³C-labeled methane (¹³CH₄) as the reactant over Ag⁺-exchanged zeolites. In this reaction, the formation of singly ¹³C-labeled propene (¹³CC₂H₆) and hydrogen progressed selectively, with the latter explainable by the reaction of Ag-H with acidic protons (ZO-H) formed by reaction 3 to regenerate Ag⁺ cations, as follows.



This reaction is the reverse of the heterolytic dissociation of hydrogen molecules expressed by reaction 1. According to reactions 2–4, the transformation of CH₄ to propene and hydrogen proceeds catalytically.

ZSM-5 zeolites loaded with Ga or Zn cations are known to catalyze the conversion of lower alkanes such as propane into aromatic hydrocarbons.^{5,6} However, such zeolites exhibit no practical catalytic activity for CH₄ conversion.⁵ Naccache et al. also reported that H-gallosilicate did not activate CH₄ and that ¹³CH₄ could not be inserted into products such as propene and butene in the conversion of C₂H₄/CH₄ or C₃H₈/CH₄ mixtures.⁷ In contrast, our group recently found that ZSM-5 zeolites loaded with metal cations such as Ga, when prepared by calcining the mixture of NH₄⁺-exchanged ZSM-5 (NH₄-ZSM-5) and the metal salt such as Ga(NO₃)₃, exhibit a catalytic activity for CH₄ conversion in the presence of C₂H₄.⁸ Furthermore, singly ¹³C-labeled propene was formed when ¹³CH₄ was reacted with ethene over metal-loaded zeolites. This suggests that CH₄ is activated on metal cations (Mⁿ⁺) to form metal

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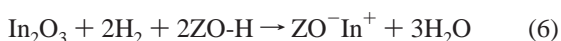
hydride species ($[M - H]^{(n-1)+}$) and methyl cation-like species ($CH_3^{\delta+}$), similar to the case for Ag^+ -exchanged zeolites:



Of the metal cations examined to date, the mixture of NH_4 -ZSM-5 and $In(NO_3)_3$, upon calcination, exhibits a high catalytic activity for the transformation of CH_4 in the presence of C_2H_4 .⁸

An important problem identified in the transformation of CH_4 in the presence of C_2H_4 over Ag^+ -exchanged zeolites is that the catalytic activity decreases with running time.^{3,4} The formation of silver metal was confirmed by X-ray diffraction (XRD) analysis after the reaction over Ag -Y at 673 K, and the transformation of CH_4 did not occur over Ag -Y zeolites when pretreated under hydrogen at 673 K for 1 h. These results suggest that the deactivation of the catalyst occurs by the reduction of silver cations to silver metal. There is a possibility that deactivation will be suppressed by the use of In-loaded ZSM-5, as In cations are more resistant to reduction than Ag^+ cations.

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.⁹ The mixture of In_2O_3 and proton-exchanged zeolites undergoes reductive solid ion-exchange to afford In^+ cationic species in the zeolite cavities under hydrogen atmosphere.^{10,11} Kanazirev et al. reported the incorporation of In^+ cations into ZSM-5 by reductive solid-state ion exchange, which proceeded according to



when the mixture of In_2O_3 and H-ZSM-5 was subjected to heat treatment in hydrogen atmosphere at 670–770 K.¹⁰

However, the exchange of In cationic species seems to be more complicated. It was also reported that for mixtures of NH_4^+ -exchanged zeolites and In_2O_3 , such as NH_4 - β zeolites, In_2O_3 was reduced to a few In cationic species, concomitant with incorporation into the zeolite as a lattice cations by heating the mixtures of NH_4^+ -exchanged zeolites and In_2O_3 .^{12,13} For example, Neinska et al. reported that both In^+ and InO^+ cationic species were detected by IR spectroscopic bands attributed to interaction of these ions with adsorbed pyridine in β -zeolite when the mixture of In_2O_3 and as-synthesized β -zeolite was heated under vacuum at 670 K.¹³ On the other hand, Kikuchi and co-workers examined IR study of OH groups on the mixture of In_2O_3 and H-ZSM-5 calcined at around 900 K, and the decrease of intensity of acidic OH band by the calcination temperature was observed.¹⁴ They proposed that InO^+ species were formed by calcining the mixture of NH_4 -ZSM-5 and In_2O_3 at 823–973 K.



Beyer et al. reported that InO^+ was reduced to In^+ with hydrogen at 600–770 K.¹¹ They also reported that both InO^+ and In^+ cations were observed by IR spectroscopic bands attributed to interaction of these cations with adsorbed pyridine when the mixture of In_2O_3 and H- β zeolite was treated with hydrogen.¹⁵ They concluded that the interconversion between InO^+ and In^+ cationic species was reversible.



The preparation conditions of In-loaded ZSM-5 influence the conversion of CH_4 , and the various chemical states of In cationic species, such as InO^+ and In^+ cationic species, which are formed by calcination and/or hydrogen treatment, exist possibly in ZSM-5. In this work, catalysts were prepared from NH_4 -ZSM-5 and In_2O_3 by calcination or by pretreatment under hydrogen after calcination. The catalytic performance of the In-loaded ZSM-5 catalyst thus prepared, referred to an In/ZSM-5 catalyst, for the transformation of CH_4 in the presence of C_2H_4 is examined with respect to various reaction variables. $^{13}CH_4$ was used for elucidating the reaction path for the formation of propene and the higher hydrocarbons (e.g., benzene and toluene). It is also shown that methane reacts with benzene to form toluene over In/ZSM-5.

Experimental Section

Preparation of NH_4^+ -Exchanged ZSM-5. ZSM-5 ($SiO_2/Al_2O_3 = 23.8$) containing template molecules was obtained from Tosoh Co. Ltd., Japan. The zeolite was converted into the Na form (Na-ZSM-5) by calcination followed by ion exchange. NH_4 -ZSM-5 was obtained by repeating the ion exchange of the Na-ZSM-5 with an NH_4Cl solution. Neither Na^+ cations nor extra framework aluminum were detected by atomic absorption spectrometry or ^{27}Al MAS NMR, respectively.

Preparation of In/ZSM-5. Indium cation-loaded ZSM-5 (In/ZSM-5) was prepared by a solid ion-exchange method. The powder mixture of NH_4 -ZSM-5 and In_2O_3 was packed in a continuous flow reactor (10 mm i.d. silica tubing) in a vertical furnace and heated under an air stream at $0.8\ K\ min^{-1}$ from room temperature to the prescribed temperature. The sample was then calcined at the prescribed temperature for 3 h. Some of the samples were exposed to hydrogen flow ($200\ cm^3\ min^{-1}$) at 101 kPa for 1 h at the prescribed temperature after calcination.

Reaction Procedures for the Transformation of CH_4 in the Presence of C_2H_4 . After calcination or hydrogen pretreatment of a catalyst, the air or hydrogen in the reactor was immediately replaced with helium, and the temperature was reduced to the prescribed reaction temperature. The reaction of CH_4 with C_2H_4 was then carried out under continuous flow at atmospheric pressure. The reactants (CH_4 (33.8 kPa) and C_2H_4 (33.8 kPa)) were fed along with helium (33.8 kPa) into the reactor through mass flow meters. In this work, helium served as both a carrier gas and an internal standard for determination of the amounts of hydrogen, CH_4 , and C_2H_4 by gas chromatography using an activated carbon column and a thermal conductivity detector. Aliphatic hydrocarbons with fewer than four carbon atoms were determined using a Porapak Q column, and hydrocarbons with more than three carbon atoms were determined using an OV-101 column. The conversions of CH_4 and C_2H_4 and the selectivities for hydrocarbon products are expressed in mol %, where the latter is defined as (the amount of a hydrocarbon product (mol))/(total amount of hydrocarbon products (mol)) $\times 100$ (%).

Reaction Procedures for the Reaction of Benzene with CH_4 . The reaction of benzene with CH_4 was carried out in a continuous flow reactor operating at atmospheric pressure. Benzene was delivered into the preheating zone of the reactor by a motor-driven syringe. The reaction products were collected and analyzed by a gas chromatograph equipped with an OV-101 column. The conversion of benzene and the yields of the reaction products (e.g., toluene and xylenes) were determined using propylbenzene as an internal standard, while the conversion of CH_4 was determined using helium as an internal standard.

Transformation of $^{13}\text{CH}_4$ in a Gas Circulation Reaction System. The transformation of $^{13}\text{CH}_4$ in the presence of C_2H_4 was carried out in a gas-circulation system (reactor volume: 308 cm^3). The mixture (0.1 g) of $\text{NH}_4\text{-ZSM-5}$ ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23.8$) and In_2O_3 ($\text{In}/\text{Al} = 0.17$) was heated in a quartz tube reactor at 0.3 K min^{-1} from room temperature to 903 K under a dry air flow of $200\text{ cm}^3\text{ min}^{-1}$, and then calcined at 903 K for 3 h. After calcination, the catalyst was cooled to 723 K and treated under flowing hydrogen ($100\text{ cm}^3\text{ min}^{-1}$) at 723 K for 1 h. The catalyst was then cooled to 673 K , and then connected to the gas circulation glass system for evacuation at 673 K for 1 h.

After preparation of the catalyst, the reaction of $^{13}\text{CH}_4$ with C_2H_4 was initiated at 673 K by introducing the mixture into the reactor containing the catalyst. Side reactions, such as ethylene self-condensation and cracking of hydrocarbon products were minimized by carrying out the reactions at a high molar ratio of $^{13}\text{CH}_4$ to C_2H_4 ($39.4\text{ kPa } ^{13}\text{CH}_4$ to $0.35\text{ kPa } \text{C}_2\text{H}_4$). The reaction products, $^{13}\text{CH}_4$ and C_2H_4 in gas phase, were collected using a gas sampler and analyzed by gas chromatographs equipped with Porapak Q and OV-101 columns with flame ionization detectors. $^{13}\text{CH}_4$ and hydrogen were simultaneously analyzed using an activated carbon column and thermal conductivity detector. The conversion of C_2H_4 and the yields of reaction products were determined using $^{13}\text{CH}_4$ as an internal standard. The amount of converted $^{13}\text{CH}_4$ is negligible because of a large excess of $^{13}\text{CH}_4$ used as a reactant. The conversion of ethylene was ca. 10%.

The reaction products were collected by a gas sampler and identified by gas chromatography mass spectrometry (GC-MS) using a Shimadzu (Japan) QP 5000 spectrometer. The amounts of ^{13}C -labeled hydrocarbons were determined by employing selected-ion monitoring techniques in all analyses. For example, the mole fractions of ^{13}C -labeled propene ($^{13}\text{CC}_2\text{H}_6$) and ^{13}C -labeled toluene were determined in reference to the respective calibration graphs. In the case of propene, the calibration graph was prepared by plotting the ratio of ion abundance at m/z 42 to that at m/z 43 against the ratio of the known concentration of propene-2- ^{13}C ($\text{CH}_3^{13}\text{CH}=\text{CH}_2$, purity 99%) to that of unlabeled propene (C_3H_6). Here, m/z is defined as the ratio between the mass (m) of an ion and the number (z) of electron charges on it. Propene-2- ^{13}C was obtained from Sigma-Aldrich Fine Chemicals, Milwaukee, WI. The ratio of ^{13}C -labeled toluene ($^{13}\text{C}^{12}\text{C}_6\text{H}_8$) to unlabeled toluene (C_7H_8) was determined by plotting the ratio of the ion abundance at m/z 92 to that at m/z 93 against the known ratio of the concentration of toluene-1- ^{13}C (ring ^{13}C , $\text{CH}_3\text{-}^{13}\text{CC}_5\text{H}_5$) to unlabeled toluene. The ratio of the ion abundance at m/e 51 to that at m/e 52 was also plotted. Toluene- α - ^{13}C ($^{13}\text{CH}_3\text{-C}_6\text{H}_5$) was also used to obtain the calibration graph. Toluene-1- ^{13}C (ring ^{13}C , $\text{CH}_3\text{-}^{13}\text{CC}_5\text{H}_5$) and toluene- α - ^{13}C ($^{13}\text{CH}_3\text{-C}_6\text{H}_5$) were obtained from Nippon Sanso, Japan.

Results and Discussion

Catalytic Activity of In/ZSM-5 and H-ZSM-5. Table 1 lists the conversion results for $\text{CH}_4 - \text{C}_2\text{H}_4$ reaction and the selectivity for hydrocarbon product over the In-loaded ZSM-5 catalysts, which were calcined at 903 K or pretreated with hydrogen at 723 K after calcination at 903 K . The ratio of In/Al in the catalyst was 0.17. The reaction was carried out at 623 K , and the pressures of CH_4 and C_2H_4 were set equal at 33.8 kPa . The catalytic activity of H-ZSM-5 prepared by calcining $\text{NH}_4\text{-ZSM-5}$ at 903 K is also shown.

Several distinct features can be seen in Table 1. Most importantly, CH_4 was not converted over H-ZSM-5, as reported

TABLE 1: Conversions of CH_4 and C_2H_4 and Selectivity for Hydrocarbon Products over H-ZSM-5 and In/ZSM-5^a

	H-ZSM-5 ^a	In/ZSM-5 ^b	In/ZSM-5 ^c
conversion/mol %			
CH_4	0.0	3.2	6.8
C_2H_4	85.4	78.5	76.4
selectivity/mol %			
C_3H_6	15.5	23.7	29.6
C_4H_8	25.3	22.5	22.3
C_5H_{10}	7.9	9.2	11.1
lower alkenes	48.7	55.4	63.0
C_2H_6	3.4	3.0	2.5
C_3H_8	17.9	13.5	7.8
C_4H_{10}	14.6	12.5	11.7
C_5H_{12}	4.3	3.7	3.1
lower alkenes	40.2	32.7	3.1
C_6^+	6.3	6.6	6.3
aromatics	4.6	5.2	5.6

^a Reaction Conditions: reaction temperature = 623 K , $\text{CH}_4 = \text{C}_2\text{H}_4 = 33.8\text{ kPa}$, $\text{In}/\text{Al} = 0.17$, $W/F = 3.6\text{ g h mol}^{-1}$. ^b H-ZSM-5 was prepared by calcinations of $\text{NH}_4\text{-ZSM-5}$ at 903 K . ^c $\text{In}_2\text{O}_3/\text{NH}_4\text{-ZSM-5}$ calcined at 903 K . ^d $\text{In}_2\text{O}_3/\text{NH}_4\text{-ZSM-5}$ calcined at 903 K and then treated with hydrogen at 723 K .

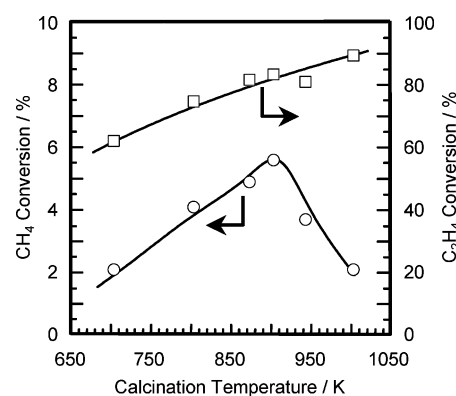


Figure 1. Effect of temperature of catalyst calcination on the conversion of CH_4 (○) and C_2H_4 (□). Results are shown for In/ZSM-5 catalyst prepared by calcination of a mixture of $\text{NH}_4\text{-ZSM-5}$ and In_2O_3 ($\text{In}/\text{Al} = 0.17$) at each temperature for 3 h. Reaction temperature: 623 K . $W/F = 3.6\text{ g h mol}^{-1}$, $\text{CH}_4 = 33.8\text{ kPa}$, $\text{C}_2\text{H}_4 = 33.8\text{ kPa}$.

previously,³ only C_2H_4 being converted to higher hydrocarbons, such as propene and aromatic hydrocarbons, which are benzene, toluene and xylenes. Furthermore, the transformation of CH_4 proceeded over both versions of the In/ZSM-5 catalyst, and the selectivity for lower alkenes (propene (C_3H_6) + butenes (C_4H_8) + pentenes (C_5H_{10})) was increased by introducing the In cationic species into ZSM-5. The hydrogen-pretreated In/ZSM-5 catalyst displayed higher selectivity for lower alkenes than the simply calcined In/ZSM-5 catalyst. As the amount of converted CH_4 was about one tenth of the amount of converted C_2H_4 , the hydrocarbon products originate almost entirely from C_2H_4 .

Effect of Calcination Temperature without Hydrogen Pretreatment. As shown in Table 1, the In/ZSM-5 catalyst calcined at 903 K without hydrogen pretreatment exhibits a catalytic activity for the transformation of CH_4 . The effect of calcination temperature on the catalytic activity of In/ZSM-5 was examined by performing calcination at various temperatures for 3 h.

Figure 1 shows the conversion results for CH_4 and C_2H_4 at 623 K after 1 h, plotted as a function of calcination temperature. The conversion of CH_4 exhibits a clear dependence on calcination temperature, with a maximum conversion achieved at calcination temperature of 903 K .

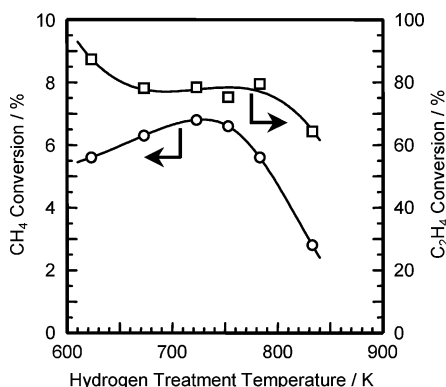


Figure 2. Effect of temperature of catalyst hydrogen pretreatment on the conversion of CH₄ (O) and C₂H₄ (□). Results are shown for In/ZSM-5 catalyst treated with hydrogen at each temperature for 1 h, after calcination of a mixture of NH₄-ZSM-5 and In₂O₃ (In/Al = 0.17) at 903 K for 3 h. Reaction temperature: 623 K. W/F = 3.6 g h mol⁻¹, CH₄ = 33.8 kPa, C₂H₄ = 33.8 kPa.

In contrast to the variation in CH₄ conversion, C₂H₄ conversion increased continuously with calcination temperature, indicating that the activation mechanism for CH₄ differs from that for C₂H₄. There is a possibility that CH₄ is activated on InO⁺ species, which were formed by calcining the mixture of NH₄-ZSM-5 and In₂O₃.¹⁴

Effect of Hydrogen Treatment. As mentioned in the Introduction, InO⁺ species in zeolite lattice was reduced to In⁺ cations under hydrogen.¹¹ In this section, the effect of the temperature of hydrogen pretreatment on the catalytic activity was examined. In/ZSM-5 was prepared by hydrogen pretreatment, after calcining the mixture of NH₄-ZSM-5 and In₂O₃ at 903 K. The conversions of CH₄ and C₂H₄ after 1 h are plotted as a function of the temperature of hydrogen pretreatment in Figure 2. The conversion of C₂H₄ gradually decreased with increasing temperature of hydrogen treatment, decreasing from 83.3% at 623 K to 74.3% at 833 K. This suggests that the amount of acidic protons is decreased by exchanging them with In⁺ cationic species.

In contrast, the conversion of CH₄ gradually increased with hydrogen pretreatment temperature to a maximum of 6.8% at 723 K. The amount of In⁺ cations possibly increased by hydrogen treatment, and In⁺ cationic species as well as Ag⁺ seem to activate CH₄ and the formation of CH₃^{δ+} may progress by the abstraction of H⁻ ions from CH₄. It has been proposed that the abstraction of H⁻ ions from lower alkanes (other than CH₄) occurs with metal cations such as Zn²⁺ to form metal-hydride species ([Zn-H]⁺).^{16,17}

The increase in the catalytic activity after hydrogen treatment as a result of In cationic species formation, does not contradict the fact that InO⁺ species can also activate methane. The reaction expressed by the eq 8 was reversible. Minalyi et al. reported the detection of trivalent In cationic species (InO⁺) and In⁺ cationic species in ZSM-5, after hydrogen treatment.¹⁵ At this stage, the active In species involved in the transformation of CH₄ cannot be determined in this work. The characterization of these In species, such as InO⁺ and In⁺ cations, is currently in progress.

Effect of In Content. The optimum In content in In/ZSM-5 was investigated by examining the effect of the In/Al atomic ratio on the catalytic activity of In/ZSM-5. Figure 3 shows the change in the catalytic activity of In/ZSM-5 with the ratio of In/Al in the catalyst at 623 K. These catalysts were prepared by treatment with hydrogen at 723 K for 1 h, after calcination at 903 K for 3 h.

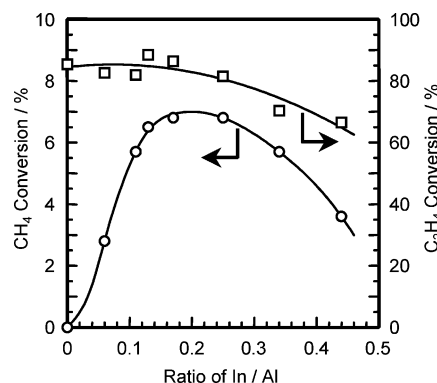


Figure 3. Effect of In content in In/ZSM-5 catalyst on the conversion of CH₄ (O) and C₂H₄ (□). Results are shown for In/ZSM-5 catalyst treated with hydrogen at 723 K for 1 h, after calcination of a mixture of NH₄-ZSM-5 and In₂O₃ (In/Al = 0.17) at 903 K for 3 h. Reaction temperature: 623 K. W/F = 3.6 g h mol⁻¹, CH₄ = 33.8 kPa, C₂H₄ = 33.8 kPa.

TABLE 2: Effect of Reaction Temperature on Conversions of CH₄ and C₂H₄ and Selectivity for Hydrocarbon Products^a

	reaction temperature/K						
	553	598	623	653	673	703	773
conversion/mol %							
CH ₄	0.1	1.4	6.8	10.1	11.8	7.9	3.1
C ₂ H ₄	1.6	15.3	76.4	87.7	90.3	99.0	99.2
selectivity/mol %							
C ₃ H ₆	55.6	33.7	29.6	20.2	20.8	11.4	12.4
C ₄ H ₈	33.2	32.7	22.3	20.4	16.1	3.2	4.6
C ₅ H ₁₀	0	12.7	11.1	6.2	5.9	1.6	0.2
lower alkenes	88.8	79.1	63.0	46.8	42.8	16.2	17.2
C ₂ H ₆	0	2.7	2.5	1.7	1.8	0.9	6.4
C ₃ H ₈	11.2	4.6	7.8	12.2	14.2	30.5	29.6
C ₄ H ₁₀	0	4.2	11.7	15.9	19.5	27.4	7.8
C ₅ H ₁₂	0	1.8	3.1	8.1	7.2	4.3	12.0
lower alkanes	11.2	13.3	25.1	37.9	42.7	63.1	55.8
C ₆ ⁺	0	6.6	6.3	5.9	2.3	1.6	0.5
aromatics	0	1.0	5.6	9.4	12.2	19.1	26.5

^a W/F = 3.6 g h mol⁻¹, CH₄ = C₂H₄ = 33.8 kPa, In/ZSM-5 (In/Al = 0.17) prepared by pretreatment with hydrogen at 723 K, followed by calcining the mixture of NH₄-ZSM-5 with In₂O₃ at 903 K.

The conversion of CH₄ increased with the In/Al ratio to a maximum of 6.8% at In/Al = 0.17, decreasing gradually at higher ratios. At larger amount of In loading, hydrocarbon products may undergo cracking to afford products including CH₄, and the apparent conversion of CH₄ decreases.

Effect of Reaction Temperature. The effect of reaction temperature on the conversions of CH₄ and C₂H₄ and the selectivities for hydrocarbon products was examined. In/ZSM-5 catalysts were pretreated with hydrogen at 723 K, after the calcination at 903 K. The results are shown in Table 2. The conversion of C₂H₄ was as low as that of CH₄ at 553 K but increased with reaction temperature from 15.3% at 598 K to 90.3% at 673 K. The conversion of CH₄ increased more slowly with reaction temperature, reaching 11.8% at 673 K, and decreased with further increases in reaction temperature to 773 K. At higher temperatures, higher hydrocarbons formed from ethene may undergo cracking to afford products including CH₄. This leads to the decrease in the apparent conversion of CH₄ at higher temperatures.

A change in the conversions of CH₄ over running time in the reaction with C₂H₄ at 673 K is shown in Figure 4. The conversion of CH₄ did not change over the running time of 10 h, while that of C₂H₄ gradually decreased with running time.

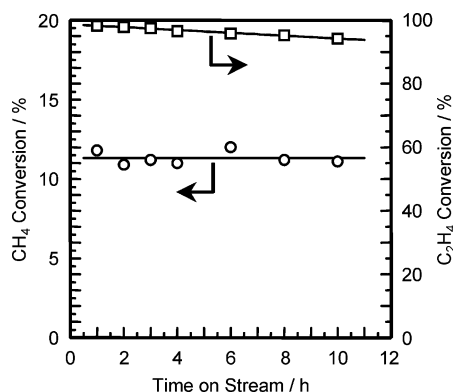


Figure 4. Conversion of CH₄ (O) and C₂H₄ (□) plotted against time on stream at 673 K. Results are shown for In/ZSM-5 catalyst treated with hydrogen at 723 K for 1 h, after calcination of a mixture of NH₄-ZSM-5 and In₂O₃ (In/Al = 0.17) at 903 K for 3 h. Reaction temperature: 673 K. W/F = 3.6 g h mol⁻¹, CH₄ = 33.8 kPa, C₂H₄ = 33.8 kPa.

The catalytic activity of In/ZSM-5 is more stable than that of Ag/ZSM-5, over which the conversion of CH₄ was 13.2% after 1 h, and almost zero after 5 h under the same reaction conditions.³

Effect of contact time. Figure 5 shows the dependence of the conversions of CH₄ and C₂H₄ on the contact time (W/F) at 673 K, where *W* is the weight of the catalyst (g) and *F* is the total flow rate of (CH₄ + C₂H₄ + He) (mol h⁻¹). The conversion of CH₄ reached a maximum of 11.8% at 3.6 g h mol⁻¹, but decreased with further increasing contact time. This indicates that CH₄ is produced by the cracking of products derived from ethane at longer contact times. When the conversion of ethene was carried out in the absence of CH₄ at 3.6 g h mol⁻¹, the conversion of ethene was 94.2% and the selectivity for CH₄ was 0.9%. This may lead to the decrease in the net production of CH₄.

The effect of contact time on the selectivities for hydrocarbon products is also shown in the figure. At W/F of 0.2 g h mol⁻¹, the main products were C₃H₆ and C₄H₈, and no aromatic

hydrocarbons were formed. This selective formation of C₃H₆ suggests that C₃H₆ is almost exclusively by the reaction of CH₄ with C₂H₄ in the initial stage, while the conversion of ethene to propene also proceeds. With increasing W/F, the selectivity for C₃H₆ and C₄H₈ decreased, while the selectivity for C₃H₈ and aromatic hydrocarbons increased. The aromatic hydrocarbons are presumably formed via C₃H₆ and C₄H₈.

Conversion of ¹³CH₄ in the Presence of C₂H₄. To further investigate the reaction pathway of the transformation of CH₄, the reaction of ¹³CH₄ with C₂H₄ was examined over In/ZSM-5 at 673 K using a gas circulation system. To minimize side reactions such as the oligomerization of C₂H₄ and the cracking of the hydrocarbon products, a large excess of ¹³CH₄ (39.4 kPa) to C₂H₄ (0.35 kPa) was used as the reactant, and the reaction was performed in 1 min. Under these conditions, the conversion of C₂H₄ was 13%, and ethane (17%), propene (23%), benzene (41%) and toluene (19%) were observed as gaseous hydrocarbons (values in parentheses denote selectivities in mol %).

Ethane and benzene produced contains only negligible amount of ¹³C-labeled products. The GC-MAS spectrum of benzene produced gave the ratio of the ion abundance at *m/z* 78 to *m/z* 79 was 100/6.6, showing the mole fraction of ¹³C¹²C₅H₆ in benzene was 7%, almost equivalent to the natural abundance. Similarly, the mole fraction of ¹³C¹²CH₆ was 2%. These results indicate that ethane and benzene is entirely derived from ethene.

On the other hand, ¹³C was inserted in propene and toluene. Only one ¹³C from ¹³CH₄ was inserted into propene and toluene, no significant amounts of multi-¹³C-labeled propene or toluene being observed.

The mole fractions of ¹³C¹²C₂H₆ in propene and ¹³C¹²C₆H₈ in toluene were then determined by reference to the calibration graphs. The ion abundance peaks were measured at *m/z* 42 and 43 for propene, and at *m/z* 92 and 93 for toluene. The calculated mole fraction of ¹³C¹²C₂H₆ in propene was 39%, while that for ¹³C¹²C₆H₈ in toluene was 54%. Thus, propene was formed by both the reaction of ¹³CH₄ with C₂H₄ and the transformation (oligomerization-cracking) of C₂H₄. As ¹³C-labeled benzene was

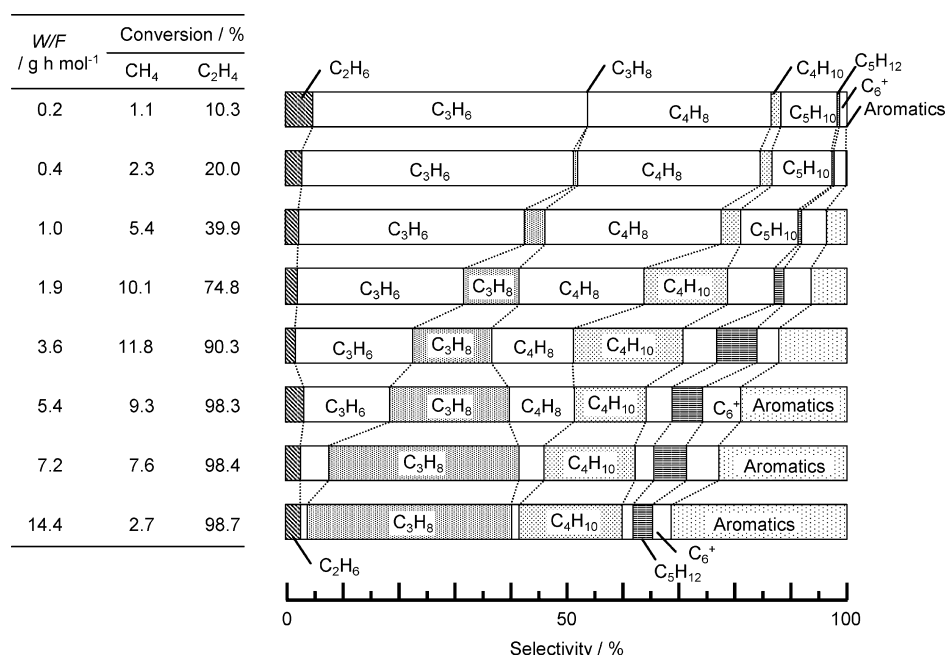


Figure 5. Effect of contact time (W/F) on the catalytic activity of In/ZSM-5 at 673 K. Results are shown for In/ZSM-5 catalyst treated with hydrogen at 723 K for 1 h, after calcination of a mixture of NH₄-ZSM-5 and In₂O₃ (In/Al = 0.17) at 903 K for 3 h. Reaction temperature: 673 K. CH₄ = 33.8 kPa, C₂H₄ = 33.8 kPa.

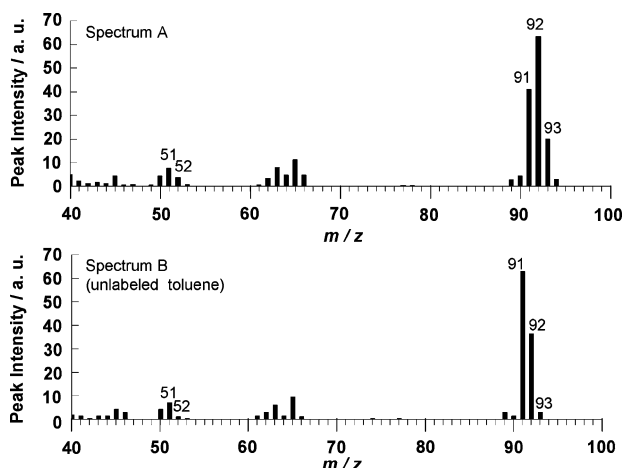


Figure 6. Mass spectrum of toluene after the reaction of $^{13}\text{CH}_4$ with C_2H_4 at 673 K. Spectrum A: toluene formed by the transformation of $^{13}\text{CH}_4$ over In/ZSM-5 in the presence of C_2H_4 at 673 K for 1 min. Spectrum B: unlabeled toluene.

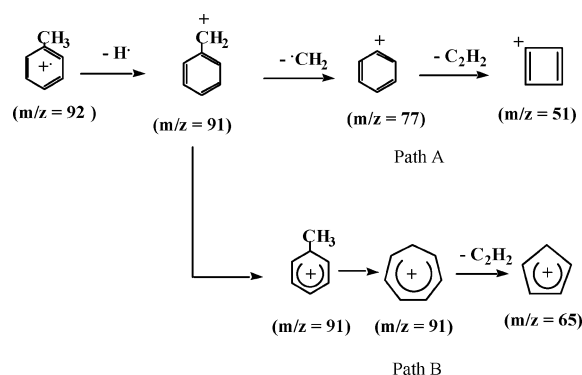


Figure 7. Fragmentation of toluene.

not formed, propene was not transformed to benzene under the reaction conditions.

The reaction path for toluene formation was investigated by recording the fragmentation spectrum of toluene (Figure 6, spectrum A) produced in the transformation of $^{13}\text{CH}_4$ in the presence of C_2H_4 . For comparison, the spectrum of unlabeled toluene ($^{12}\text{CH}_3\text{--}^{12}\text{C}_6\text{H}_5$) is also shown (spectrum B). In spectrum A, the main peak occurs at m/z 92, due to $^{13}\text{C}^{12}\text{C}_6\text{H}_7^+$, while in spectrum B, the main peak is at m/z 91, attributable to $^{12}\text{C}_7\text{H}_7^+$.

Two paths (paths A and B) for toluene fragmentation are well-known (Figure 7).¹⁹ In path A, methyl groups are ejected from toluene to give a molecular ion with m/z of 51. Therefore, the mole fraction of toluene labeled with a single ^{13}C atom in benzene ring ($^{12}\text{CH}_3\text{--}^{13}\text{C}^{12}\text{C}_5\text{H}_5$) can be determined from the calibration graph by measuring the ion abundance peaks at m/z 51 and 52. This determination of the mole fraction of $^{12}\text{CH}_3\text{--}^{13}\text{C}^{12}\text{C}_5\text{H}_5$ in toluene gives a result of 37%, which can be compared with the total mole fraction of ^{13}C -labeled toluene ($^{13}\text{C}^{12}\text{C}_6\text{H}_8$) of 54%. On this basis, the mole fraction of toluene with labeled methyl group ($^{13}\text{CH}_3\text{--}^{12}\text{C}_6\text{H}_5$) is estimated to be 17% ($54 - 37 = 17\%$). Thus, the molar ratio of $^{12}\text{CH}_3\text{--}^{13}\text{C}^{12}\text{C}_5\text{H}_5$ to $^{13}\text{CH}_3\text{--}^{12}\text{C}_6\text{H}_5$ is $37/17 = 2.2$. Singly ^{13}C -labeled toluene is therefore plausibly formed by two reactions; the reaction of $^{13}\text{C}^{12}\text{C}_2\text{H}_6$ with butenes formed by the dimerization of C_2H_4 and the reaction of benzene with $^{13}\text{CH}_4$.

Reaction of Methane with Benzene. To confirm the reaction path for the formation of $^{13}\text{CH}_3\text{--}^{12}\text{C}_6\text{H}_6$ by the reaction of benzene with $^{13}\text{CH}_4$, the reaction of benzene with $^{13}\text{CH}_4$ was carried out over In/ZSM-5 under the conditions of 39.8 kPa of $^{13}\text{CH}_4$, and

1.63 kPa of benzene at 673 K. The In/ZSM-5 was prepared by treatment with hydrogen at 723 K for 1 h, after calcination at 903 K for 3 h.

The reaction products were toluene and hydrogen, and no other hydrocarbon products were observed. The conversion of benzene was 6.4%, which is almost the same as the yield of toluene (6.2%) based on benzene, suggesting that other side reactions such as disproportionation of toluene to benzene and xylenes did not occur. The fraction of $^{13}\text{CH}_3\text{--C}_6\text{H}_5$ in toluene was 96%, showing that $\text{CH}_3^{\delta+}$ species are formed on In/ZSM-5 and react with benzene to form toluene. H-ZSM-5 exhibits no catalytic activity for the reaction of $^{13}\text{CH}_4$ with benzene under the same reaction conditions.

The reaction of benzene with CH_4 was also carried out in a flow reactor by using In/ZSM-5 at 623 K. Partial pressures of both CH_4 and benzene were 33.8 kPa. The conversion of CH_4 and that of benzene were 8.5 and 8.3 mol %, respectively at running time of 1 h. The reaction products were toluene and xylenes, whose selectivities were 89 mol % (yield 7.6%) and 11 mol % (yield 0.9%), respectively. Xylenes are presumably formed by the methylation of toluene with CH_4 and/or by the disproportionation of toluene on acidic sites of In/ZSM-5.

Conclusion

This work demonstrates that CH_4 reacts with C_2H_4 proceeds to afford higher hydrocarbons over In/ZSM-5. In/ZSM-5 pretreated with hydrogen at 723 K after calcining at 903 K, exhibited the highest conversion of CH_4 of 11.8% at a reaction temperature of 673 K. The conversion of CH_4 was about one-eighth of the conversion of C_2H_4 . Use of $^{13}\text{CH}_4$ revealed that propene was found to be formed by two reaction paths; the reaction of CH_4 with C_2H_4 , and the oligomerization-cracking of C_2H_4 . Toluene is also formed plausibly by two reaction paths; the reaction of C_3H_6 with butenes, and the reaction of benzene with CH_4 . The latter path was confirmed by the direct reaction.

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