The Role of Zinc Cations in the Conversion of Isobutane into Aromatics over Mechanical Mixtures of ZnO and H-ZSM-5

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(Received November 10, 1992)

Mechanical mixtures of ZnO and H-ZSM-5 show high activities and selectivities for the aromatization of isobutane. The temperature-programmed desorption spectra of ammonia and the infrared spectra of adsorbed pyridene revealed that a solid–solid ion-exchange occurs between ZnO and H-ZSM-5. The presence of Zn cations in the zeolite channels not only enhances the dehydrogenation, but also the C–C bond cleavage of isobutane. A mechanism for the activation of isobutane is proposed.

ZSM-5 zeolites loaded with metal cations, such as gallium and the zinc cations, show high selectivity for aromatic hydrocarbons in transformation of lower alkanes.[1—8] The metal cations can be incorporated by ion exchange or impregnation from aqueous solutions of the corresponding salts.

It is known that mechanical mixtures of metal oxides (Ga_2O_3 and ZnO) and H-ZSM-5 are also highly active and selective for the aromatization of lower alkanes.[9—24] The role and state of metallic species in mechanical mixtures under the reaction conditions have been the subject of much discussion.

Gnep et al.[9,10] and Meriaudeau and Naccache[11] revealed that Ga_2O_3 has a catalytic activity for propane dehydrogenation and proposed a bifunctional mechanism: Ga_2O_3 functions as a dehydrogenation catalyst to form alkenes, while H-ZSM-5 functions as a catalyst for the oligomerization of alkenes. Later, Meriaudeau and Naccache[12,13] proposed a synergetic action of Ga_2O_3 and protons in the zeolite in the step of propane dehydrogenation.

Several authors proposed a back-spillover mechanism.[15—19] In this mechanism, the activation of alkane molecules occurs by the action of Brønsted acid sites, as in the case of the conversion over ordinary H-ZSM-5. The monoatomic hydrogen species formed in the system migrate into the metal oxide, which facilitates the recombination of a monoatomic hydrogen species to produce molecular hydrogen. However, it is not clear what are the migrating species (H^+, H^-, or H), or how they recombine on the oxide surface.

Recently, Kanazirev and Price[20—22] revealed by tempreture-programmed reduction and X-ray diffraction studies that a solid-solid reaction occurs between Ga_2O_3 and H-ZSM-5 to form Ga(I) cations in H-ZSM-5 pore structures:

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O,$$

$$Ga_2O + 2H^+Z^- \rightarrow 2Ga^+Z^- + H_2O.$$

Tan et al.[23] reached a similar conclution that Ga ions in a reduced state migrate into the channels of ZSM-5.

A solid state reaction between ZnO and H-ZSM-5 has also been proposed by Yang et al.[24] They observed a 20% loss of adsorption capacity for ammonia in a temperature-desorption study, and the loss of Brønsted acid sites upon heating H-ZSM-5 with ZnO at 853 K for 1 h.

The present work concerns the interaction between ZnO and H-ZSM-5 in mechanical mixtures, and provides further evidence for the solid-state ion-exchange between ZnO and H-ZSM-5. This work also concerns the mechanism for the activation of isobutane molecules in a catalytic system.

Experimental

The ZSM-5 zeolite with $SiO_2/Al_2O_3=43.5$ was ion-exchanged to NH_4-ZSM-5. ZnO was obtained from Kanto Chemical Co.

The physical mixture of ZnO and NH_4-ZSM-5 was prepared by mixing powders of the two materials in an agate mortar. For catalytic use, the mixture was pressed, crushed and sorted into grains of 16—32 mesh.

The reactions were carried out with a continuous-flow reactor at atmospheric pressure. The catalyst was packed in a reactor of silica tubing (10 mm i.d.) placed in a vertical furnace and heated under an air stream at 773 K for 1.5 h. Isobutane was fed through a flowmeter. The effluent gas was withdrawn periodically and analyzed by gas chromatography. The conversion, the yield, and the product distribution were expressed on a carbon-number basis, if not described otherwise. The selectivity for hydrogen was expressed as the number of moles of hydrogen produced per 100 moles of isobutane reacted.

The temperature-programmed desorption of ammonia was performed as follows. The catalyst was heated under vacuum at 773 K, then exposed to ammonia of 5.3 kPa at 423 K for 30 min, and evacuated at 353 K for 30 min. The temperature of the catalyst was raised at a rate of 5 $K\,min^{-1}$, desorbed ammonia was detected by a quadrupole mass-spectrometer.

The infrared spectra of the adsorbed pyridine were measured with a Shimadzu IR-460 spectrophtometer. A catalyst wafer was placed in a cell, which was connected to a conventional gas-evacuation system.

Results and Discussion

Infrared Spectrum of Adsorbed Pyridine. In order to find the difference in the acidic properties between H-ZSM-5 and a mechanical mixture of ZnO and H-ZSM-5 (ZnO–H-ZSM-5), the infrared spectra of pyridine adsorbed on H-ZSM-5 Na-ZSM-5, Zn-ZSM-5 (ion-exchanged), and two mechanical mixtures, ZnO–H-ZSM-5 and ZnO–Na-ZSM-5 were measured. All of the samples were treated in an air stream at 773 K for 1.5 h and degassed at the same temperature for 1.5 h. The sample wafers were exposed to pyridine vapor at 473 K for 1 h, then evacuated at 473 K for 1 h. The spectra are shown in Fig. 1.

In the case of H-ZSM-5, the band characteristic of pyridinium ions (1548 cm^{-1}) was observed; no bands due to pyridine molecules interacting with Lewis acid sites were observed. In the case of Na-ZSM-5, no bands due to pyridinium ions were observed; a band which appeared at 1444 cm^{-1} was attributable to pyridine molecules interacting with Na^+ ions. In the case of Zn-exchanged H-ZSM-5, in addition to a band due to pyridinium ions (1548 cm^{-1}), a band was observed at 1454 cm^{-1}. This band was assigned to pyridine molecules interacting with Zn cations.

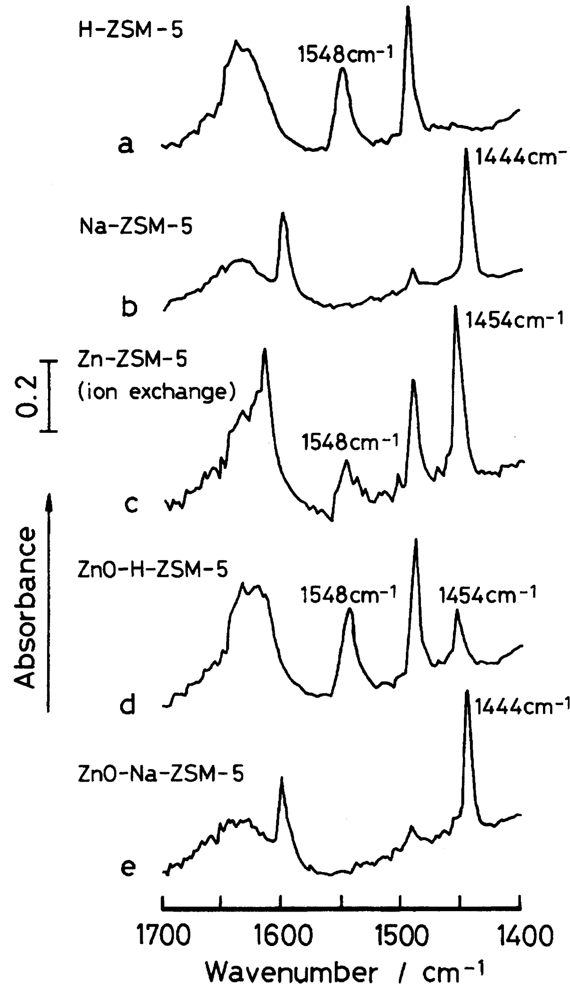


Fig. 1. Infrared spectra of pyridine adsorbed on (a) H-ZSM-5, (b) Na-ZSM-5, (c) Zn ion -exchanged H-ZSM-5, (d) a mechanical mixture of ZnO and H-ZSM-5, and (e) a mechanical mixture of ZnO and Na-ZSM-5.

The spectrum of pyridine adsorbed on ZnO–H-ZSM-5 is similar to that of pyridine adsorbed on Zn-exchanged ZSM-5. Thus, the development of the band at 1454 cm^{-1} clearly shows that Zn cations were present in ZSM-5 channels. This is a strong indication of cation exchange between ZnO and H-ZSM-5:

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O.$$

On the other hand, the spectum of pyridine adsorbed on a mixture of ZnO and Na-ZSM-5 was essentially the same as that of pyridine adsorbed on Na-ZSM-5. Although bands due to pyridene molecules interacting with Na^+ ions were observed, there was no indication of the presence of Zn^{2+} cations or Brønsted acid sites. This indicates that no chemical interaction occurred in Na-ZSM-5 upon heating it with ZnO.

Recently, works have been reported on solid–solid ion-exchange reactions between metal oxides and proton forms of zeolites.[26—30] In no case, however, has a solid–solid ion-exchange between metal oxides and the Na-form of zeolites been successful,[26—29] thus confirming the result from this study.

Temperature Programmed Desorption of Ammonia. Figure 2 shows the temperature-programmed desorption spectra of ammonia (t.p.d.) from H-ZSM-5 and a mechanical mixture of ZnO(15 wt%) and H-ZSM-5.

The t.p.d. spectrum from H-ZSM-5 has two desorption maxima at around 370 and 570 K. The 370 K-peak corresponds to physisorbed ammonia; the other corresponds to ammonia interacting Brønsted acid sites.

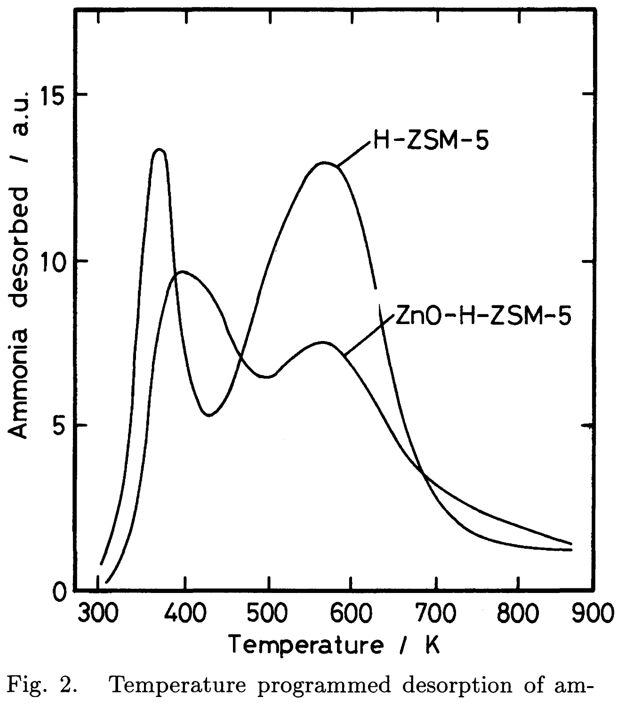


Fig. 2. Temperature programmed desorption of ammonia from H-ZSM-5 and a mechanical mixture of ZnO and H-ZSM-5.

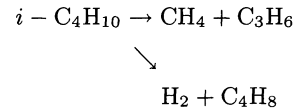
The t.p.d. spectrum from ZnO–H-ZSM-5 differs from that of H-ZSM-5 regarding two important points: (1) The intensity of the peak at 570 K diminished considerably. This indicates the loss of Brønsted acid sites by heating H-ZSM-5 with ZnO. The extent of the loss amounted to ca. 40%, much larger than the value reported by Yang et al.[24] (2) The lower temperature peak was shifted to a higher temperature, indicating the interaction of ammonia molecules with zinc species.

Both facts show that H-ZSM-5 chemically interacts with ZnO to greatly modify the acidic properties. Thus, the t.p.d. results support the conclusion from infrared spectroscopy that protons in H-ZSM-5 undergo a cation-exchange with Zn(II) cations during the heat-treatment.

Conversion of Isobutane over ZnO–H-ZSM-5 Mixtures. The catalytic activities of H-ZSM-5 and mechanical mixtures of ZnO (5, 15, 30 wt%) and H-ZMS-5 for isobutane conversion were compared under the following conditions: reaction temperature of 773 K, an isobutane pressure of 34.2 kPa and a contact time of $W/F=4.2$ g h mol^{-1}, where W and F are the weight of catalyst and flow rate of isobutane plus nitrogen, respectively. The results are summarized in Table 1. Over H-ZSM-5, the conversion of isobutane was 26.4% and the yield of aromatic hydrocarbons was only 1.1%. By adding ZnO of 5% in weight of H-ZSM-5, the conversion increased to 95.9%, and the yield of aromatics also increased to 53.3%. A further increase of ZnO did not appreciably change the conversion of isobutane or the yield of aromatics. The significant increase in the conversion and selectivity for aromatics indicates that zinc species added to H-ZSM-5 play an essential role in aromatization. The large increase in hydrogen formation indicates that zinc species added to H-ZSM-5 bring about dehydrogenation activity.

The conversion of isobutane was also carried out over Na-ZSM-5 and a mechanical mixture of ZnO (15 wt%) and Na-ZSM-5. Na-ZSM-5 has essentially no catalytic activity, the isobutane conversion being 1.6%. In contrast to ZnO–H-ZSM-5, the addition of ZnO to Na-ZSM-5 did not improve the catalytic activity. This indicates that ZnO, itself, has no activity, even for the dehydrogenation of isobutane, and that the coexistence of zinc species and protons are necessary for the catalysis.

In order to further examine the role of zinc species during the initial stage of the conversion, the reaction products of isobutane over H-ZSM-5 and ZnO–H-ZSM-5 were compared at low isobutane pressure and at low contact time. The results are shown in Table 2. In previous studies, we found that the initial reactions in isobutane conversion over H-ZSM-5 and Zn-ZSM-5 (ion-exchanged) can be expressed by following two reactions:[7,25]



$$\begin{array}{l} i-C_4H_{10} \rightarrow CH_4 + C_3H_6 \\ \qquad\qquad\quad \searrow \\ \qquad\qquad\qquad H_2 + C_4H_8 \end{array}$$

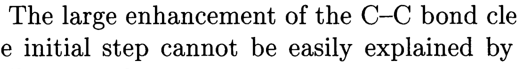
Table 2 shows that this proposition is also operative for ZnO–H-ZSM-5, though secondary reactions (alkene disproportionation, aromatization) seem to be involved.

From the data given in Table 2, the rate of isobutane conversion, and the rates for the formation of methane, propene, and butenes were calculated (listed in Table 3).

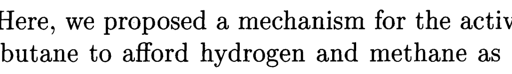
The rates of isobutane conversion over H-ZSM-5 and ZnO–H-ZSM-5 were 7.5×10^{-3} and 0.39 mol g^{-1} h^{-1}, respectively. Thus, about a 50-times increase in isobutane activation was observed by mixing ZnO with H-ZSM-5. The rates of dehydrogenation (formation of butenes) were 2.6×10^{-3} and 0.28 mol g^{-1} h^{-1} over H-ZSM-5 and ZnO–H-ZSM-5, respectively. The dehydrogenation activity was enhanced by about 110 times by adding ZnO to H-ZSM-5, while the rates of methane formation over the two catalysts were 4.6×10^{-3} and 7.0×10^{-2} mol g^{-1} h^{-1}, respectively. The rate of methane formation was enhanced by 15 times by adding ZnO to H-ZSM-5.

The main reaction over H-ZSM-5 was C–C bond cleavage (methane and propene formation), while it was the C–H bond cleavage (dehydrogenation) over ZnO–H-ZSM-5. As expected, the dehydrogenation of isobutane is enormously enhanced by the addition of ZnO to H-ZSM-5. It is worthy of note that the addition of ZnO to H-ZSM-5 not only promotes C–H bond cleavage, but also greatly promotes the C–C bond cleavage in isobutane conversion. These features of a reaction over a mechanical mixture of ZnO and H-ZSM-5 are essentially the same as those over Zn ion-exchanged ZSM-5.[7] This again suggests that zinc cations are ion-exchanged and that the mechanism of isobutane activation over ZnO–H-ZSM-5 is completely different from that over H-ZSM-5. The large enhancement of the C–C bond cleavage in the initial step cannot be easily explained by a back-spillover mechanism.

Here, we proposed a mechanism for the activation of isobutane to afford hydrogen and methane as primary products over Zn-containing ZSM-5.



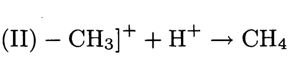
$$C-\overset{C}{\overset{|}{C}}-C + Zn(II) \rightarrow C-\underset{+}{\overset{C}{\overset{|}{C}}}-C + [Zn-H]^{+} \tag{1}$$



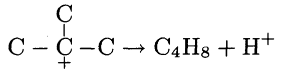
$$C-\overset{C}{\overset{|}{C}}-C + Zn(II) \rightarrow C-\underset{+}{C}-C + [Zn-CH_3]^{+} \tag{2}$$

$$[Zn(II)-H]^{+} + H^{+} \rightarrow H_2 + Zn(II) \tag{3}$$

$$[Zn(II)-CH_3]^{+} + H^{+} \rightarrow CH_4 + Zn(II) \tag{4}$$



$$C-\underset{+}{\overset{C}{\overset{|}{C}}}-C \rightarrow C_4H_8 + H^{+} \tag{5}$$



$$C-\underset{+}{C}-C \rightarrow C_3H_6 + H^{+} \tag{6}$$

Table 1. Transformation of Isobutane over Mechanical Mixtures of ZnO and H-ZSM-5 (or Na-ZSM-5)

Catalyst	H-ZSM-5	H-ZSM-5 +5 wt% ZnO	H-ZSM-5 +15 wt% ZnO	H-ZSM-5 +30 wt% ZnO	Na-ZSM-5	Na-ZSM-5 +15 wt% ZnO
Total conversion/%	26.4	95.9	98.6	98.3	1.6	0.4
Yield of aromatics/%	1.1	53.3	57.3	46.4	0.0	0.0
		Product distribution/%				
CH_4	7.1	9.2	10.0	14.4	6.3	0.0
C_2H_6	2.5	10.2	12.0	14.5	0.0	0.0
C_2H_4	12.8	1.1	1.2	1.7	0.0	0.0
C_3H_8	30.0	13.5	12.1	13.6	6.3	25.0
C_3H_6	22.3	3.1	2.6	3.8	25.0	25.0
n-C_4H_{10}	6.1	4.3	2.6	3.3	62.4	50.0
C_4H_8	10.5	2.5	1.2	1.7	0.0	0.0
C_5+aliphatics	4.7	0.6	0.3	0.1	0.0	0.0
Aromatics	4.0	55.5	58.0	46.9	0.0	0.0
		Hydrogen selectivity/mol per 100 mol isobutane conveted				
H_2	23	143	106	125	0.0	0.0

Reaction conditions: 773 K, 34.2 kPa isobutane pressure, W/F=4.2 g h mol^{-1}.

Table 2. Product Distribution over H-ZSM-5 and a Mechanical mixture of ZnO and H-ZSM-5 at Low Conversion of Isobutane

Catalyst	H-ZSM-5	ZnO-H-ZSM-5
W/F/g h mol^{-1}	0.020	0.014
Conversion/%	0.19	6.8
	Product distribution/%	
CH_4	15.2	4.5
C_2H_6	0.0	0.2
C_2H_4	0.9	2.6
C_3H_8	0.0	0.0
C_3H_6	53.2	17.0
n-C_4H_{10}	0.0	1.8
C_4H_8	30.7	72.1
Aromatics	0.0	1.8
H_2/mol per 100 mol isobutane converted		
	0.0	128

Reaction conditions: 773 K, 8 kPa isobutane pressure.

Table 3. The Rates of Primary Reactions of Isobutane Transformation

Catalyst	H-ZSM-5(A)	H-ZSM-5(B) + ZnO	B/A
Conversion rate/ mmol g^{-1} h^{-1}	7.5	390	52
Formation rate/mmol g^{-1} h^{-1}			
CH_4	4.6	70	15
C_3H_6	5.3	88	17
C_4H_8	2.6	280	108

Zinc cations in the zeolite channels abstract H^- or CH_3^- ions from isobutane to give carbenium ions, Eqs. 1 and 2. Zinc cations are regenerated by the reaction of Zn-H and Zn-CH_3 species with protons of the zeolites, Eqs. 3 and 4. The carbenium ions are decomposed into alkenes and protons Eqs. 5 and 6.

The negligible activity of ZnO–Na-ZSM-5 for alkane activation is explained as follows. Firstly, there is no ion-exchange reactions between ZnO and Na-ZSM-5 to give Zn cations in the zeolite channels. Secondly, the concentration of protons in the channel required for reactions Eqs. 3 and 4 is very low.

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