

## Transformation of Butanes and 1-Butene into Aromatic Hydrocarbons over Ag ion-exchanged ZSM-5 Catalyst

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은 이온교환된 ZSM-5 상에서 부탄 및 1-부텐의 방향족화 반응

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**Abstract :** The transformation of butanes and 1-butene into aromatic compounds was performed over HZSM-5 catalyst and its Ag ion-exchanged form. The yield of aromatic hydrocarbons appreciably increased by incorporating silver cations into HZSM-5. The silver cations serve as catalysts for dehydrogenation of the starting hydrocarbons.  $Ag^+$  ions could be reduced to  $Ag^0$  metals with resulting in the formation of acidic OH groups by hydrogen produced during the dehydrogenation of butanes and 1-butene. The reaction of 1-butene over ZSM-5 with different loading of Ag was carried out to investigate the effect of acidic properties of these catalysts.

**요 약 :** HZSM-5와 Ag 이온으로 교환된 ZSM-5를 촉매로 사용하여 부탄과 1-부텐으로부터 방향족 화합물로의 전환반응을 수행하였다. 방향족 탄화수소의 수율은 HZSM-5 내에 Ag 이온을 도입함으로써 현저하게 증가하였다. Ag 이온들은 출발원료인 탄화수소의 탈수소 촉매로서 작용하였다. 부탄과 1-부텐의 탈수소 과정에서 생성된 수소는  $Ag^+$  이온을 Ag 금속으로 환원시킴과 동시에 산점의 형성을 유발하였다. Ag의 담지량이 다른 ZSM-5를 촉매로 사용하여 1-부텐의 전환반응을 수행하고, 이들 촉매의 산점특성 변화에 따른 효과를 검토하였다.

### 1. Introduction

Much attention has been drawn to the transformation of lower alkanes into aromatic hydrocarbons from both industrial and academic points of view. The aromatic hydrocarbons can be utilized as a booster for high octane number gasoline and are fundamental raw chemicals in the petroleum chemistry. Csicsery[1-4] has described the dehydrocy-

clodimerization of lower alkanes over bifunctional catalysts such as platinum on alumina and  $Cr_2O_3$  on alumina. Recently, ZSM-5 zeolite in combination with transition metal have been reported as the catalysts for aromatization of ethane[5] and propane [6]. It has been well established that the loading of zinc or gallium cations onto ZSM-5 greatly enhances the selectivity for aromatic hydrocarbons in the transformation of lower alkanes and alkenes. Mole

et al.[7] have studied the conversion of propane over ZSM-5 exchanged with zinc cations(Zn-ZSM-5) and concluded that zinc cations abstract hydride ions from propane molecules. Ono and co-workers [8-10] have shown that, in the conversion of propane, butane and pentane over ZSM-5 zeolite, the metal species in gallium exchanged ZSM-5 act as a catalyst for dehydrogenation of intermediate alkenes. They showed that the alkane molecules such as propane and butane are activated initially by the acidic sites of the zeolite. Ono et al.[11-13] have also shown that Zn-ZSM-5 gives high selectivity for aromatic hydrocarbons in the transformation of propene, 1-butene or methanol.

In this work, we demonstrate that silver ion-exchanged ZSM-5(Ag-ZSM-5) has very high catalytic activities in the transformation of butanes and 1-butene into aromatic hydrocarbons. However Ag-ZSM-5 has never explored as an aromatization catalyst. The reaction of 1-butene over HZSM-5 and Ag-ZSM-5 with different ion exchange level was performed to acquire the knowledge of interaction between olefin molecules and metal cations(or acidic sites).

## 2. Experimental

ZSM-5 zeolites( $\text{SiO}_2/\text{Al}_2\text{O}_3=43.5$  and  $72.1$ ) were obtained from TOSOH and were converted into the ammonium form( $\text{NH}_4\text{-ZSM-5}$ ) using the procedure described by Jacobs[14]. Ag-ZSM-5 was made by exchanging with a silver nitrate solution at room temperature for 48 h. The content of exchanged Ag cations in ZSM-5 was controlled by changing the initial concentration of silver nitrate solution. The catalysts were pressed, crushed and sorted into grains of 16~32mesh. The reaction was carried out with a continuous flow reactor operating at atmospheric pressure. The catalyst was packed in the reactor (10mm I. D. silica tubing) placed in a vertical furnace, and was then heated in a stream of air at 773K for 90min. By this treatment, it was assumed that  $\text{NH}_4\text{-ZSM-5}$  form would be converted into the

proton form(HZSM-5). Gaseous reactants such as n-butane and 1-butene were fed into the reactor through a flowmeter. The effluent gas was withdrawn periodically and analyzed with gas chromatography equipped with a flame ionization detector. Aliphatic and aromatic hydrocarbons were determined in a 2 m-long Porapak Q column and a 30 m-long OV-101 capillary column. Conversion, yield selectivity and product distribution were expressed on a carbon number basis, unless expressed otherwise.

## 3. Results and Discussion

The reaction of 1-butene over HZSM-5, Zn-ZSM-5 and Ag-ZSM-5 was carried out, and their total conversions and product distribution are summarized in Table 1. The yield of aromatic hydrocarbons appreciably increased by introducing silver or zinc cations into ZSM-5. The selectivity to aromatics also increased; 53.6%, 84.5% and 83.6% over HZSM-5, Ag-ZSM-5 and Zn-ZSM-5, respectively. Instead, the selectivity to undesirable products(ethane and propane) decreased by introducing these Zn and Ag cations. The produced aromatic hydrocarbons were mainly toluene and xylenes. The benzene fraction in the aromatics was greater over Zn-ZSM-5 than HZSM-5 and Ag-ZSM-5.

The results obtained in the transformation of isobutane over HZSM-5, Zn-ZSM-5, Ga-ZSM-5 and Ag-ZSM-5 are given in Table 2. The total conversions were slightly higher over Zn-, Ga-, and Ag-ZSM-5 than over HZSM-5. The selectivities to aromatic hydrocarbons were 4.0%, 52.8%, 31.6% and 66.5% over H-, Zn-, Ga- and Ag-ZSM-5 respectively. The small production of lower alkanes like propane was observed over Zn- and Ag-ZSM-5 in comparison with HZSM-5. The great enhancement of the yield of aromatic hydrocarbons supports the idea that metal cations enhance the rate of the aromatization of alkanes and alkenes.

In Table 3, the total conversion and product distribution in the transformation of n-butane over H-

**Table 1.** Transformation of 1-Butene over HZSM-5, Zn-ZSM-5 and Ag-ZSM-5 Catalyst

Catalyst ;	HZSM-5	Ag-ZSM-5 <sup>(a)</sup>	Zn-HZSM-5 <sup>(b)</sup>
Temperature (K)	773	773	773
Conversion (%)	96.7	99.1	99.4
Yield of aromatics (%)	51.8	83.7	83.1
Product distribution (%)			
CH <sub>4</sub>	0.4	0.1	2.3
C <sub>2</sub> H <sub>6</sub>	1.2	0.3	1.9
C <sub>2</sub> H <sub>4</sub>	6.1	2.9	2.0
C <sub>3</sub> H <sub>8</sub>	12.2	3.9	3.4
C <sub>3</sub> H <sub>6</sub>	9.8	3.2	2.4
C <sub>4</sub> H <sub>8</sub>	2.5	0.7	0.4
n-C <sub>4</sub> H <sub>10</sub> +iso-C <sub>4</sub> H <sub>10</sub>	9.6	3.4	3.3
C5+aliphatics	4.6	1.0	0.5
aromatics	53.6	84.5	83.6
Aromatic distribution (%)			
benzene	5.2	3.8	11.5
toluene	25.0	23.6	45.7
xylene+ethylbenzene	51.0	50.1	35.8
C9+aromatics	18.8	22.5	7.0

Reaction conditions ; 1-butene=34.2kPa, W/F=4.2g h mol<sup>-1</sup> (a) 80% Ag ion-exchanged (b) 3wt% Zn loading

**Table 2.** Transformation of Iso-Butane over HZSM-5, Zn-ZSM-5, Ga-ZSM-5 and Ag-ZSM-5 Catalyst

Catalyst ;	HZSM-5	Zn-ZSM-5	Ga-ZSM-5	Ag-ZSM-5
Conversion (%)	26.4	89.2	66.5	71.2
Yield of aromatics (%)	1.1	47.7	21.0	47.3
Product distribution (%)				
CH <sub>4</sub>	7.1	8.6	8.3	1.0
C <sub>2</sub> H <sub>6</sub>	2.5	6.6	2.7	0.8
C <sub>2</sub> H <sub>4</sub>	12.8	2.9	6.9	5.9
C <sub>3</sub> H <sub>8</sub>	30.0	11.0	23.0	8.8
C <sub>3</sub> H <sub>6</sub>	22.3	5.5	10.6	8.1
C <sub>4</sub> H <sub>8</sub>	6.1	5.8	8.0	2.5
n-C <sub>4</sub> H <sub>10</sub> +iso-C <sub>4</sub> H <sub>10</sub>	10.5	5.9	5.8	4.3
C5+aliphatics	4.7	0.9	3.1	2.4
aromatics	4.0	52.8	31.6	66.5
Aromatic distribution (%)				
benzene	20.5	19.9	23.9	8.9
toluene	49.6	37.4	52.0	31.1
xylene+ethylbenzene	29.9	36.3	24.1	41.0
C9+aromatics	0	6.4	0	19.0

Reaction conditions ; 773K, iso-butane=34.2kPa, W/F=4.2g h mol<sup>-1</sup>, 80% Ag ion-exchanged and 3wt% Zn, Ga loading.

ZSM-5, Zn-ZSM-5 and Ga-ZSM-5 at 773 K are listed. The main products over H-ZSM-5 were lower alkanes such as propane. Over Zn-ZSM-5

and Ga-ZSM-5, aromatic hydrocarbons were the main products. The selectivity to propane decreased considerably when Zn cations were introduced into

**Table 3.** Transformation of n-Butane over HZSM-5, Zn-ZSM-5 and Ga-ZSM-5 Catalyst

Catalyst ;	HZSM-5	Zn-ZSM-5	Ga-ZSM-5
Conversion( % )	44.7	38.3	58.0
Yield of aromatics( % )	3.2	17.6	16.4
Product distribution( % )			
CH <sub>4</sub>	4.3	5.8	5.0
C <sub>2</sub> H <sub>6</sub>	9.9	7.2	7.1
C <sub>2</sub> H <sub>4</sub>	9.3	4.7	6.2
C <sub>3</sub> H <sub>8</sub>	44.5	8.0	32.6
C <sub>3</sub> H <sub>6</sub>	9.5	9.5	7.9
iso-C <sub>4</sub> H <sub>10</sub>	4.9	7.5	6.2
C <sub>4</sub> H <sub>8</sub>	7.4	10.2	4.6
C <sub>5</sub> +liphatics	3.0	1.2	2.1
aromatics	7.2	45.9	28.3
Aromatic distribution( % )			
benzene	14.9	28.1	19.2
toluene	41.2	41.4	47.7
xylene+ethylbenzene	39.4	27.8	28.6
C <sub>9</sub> +aromatics <sup>§</sup>	4.5	2.7	4.5

Reaction conditions ; 773K, n-butane=34.2kPa, W/F=4.2g h mol<sup>-1</sup>, 1.2wt% Zn and 1.9wt% Ga loading.

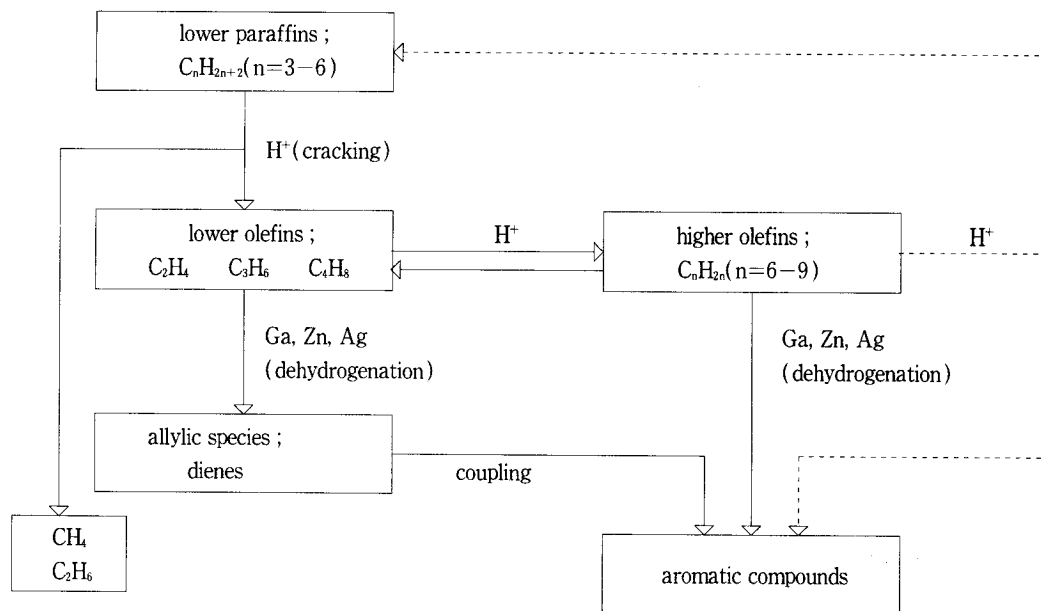
HZSM-5. The production of hydrogen increased sharply after introduction of zinc or gallium cations to H-ZSM-5, indicating that these cations serve as dehydrogenation catalysts. In Table 1~3, the important differences in the transformation of n-butane, iso-butane and 1-butene over HZSM-5 and Zn-, Ga-, Ag-ZSM-5 are the selectivities for propane and aromatics.

As for the mechanism of the formation of aromatic hydrocarbons, Poustma[15] has proposed a mechanism involving Brönsted-acid centres as active sites. Here, he proposed that aromatic molecules were formed from alkene oligomers by successive deprotonation and hydride transfer to carbenium ions. With this mechanism, the formation of one molecule of aromatic hydrocarbons inevitably accompanies the formation of three molecules of alkane. In the results of Table 1~3, the molar ratio of alkanes to aromatics in the products over acidic HZSM-5 was high, indicating that the scheme proposed by Poustma is operative. On the other hand, the lower alkane/aromatics ratio of the products and the enhancement of the aromatic yield over Zn-, Ga- and Ag-ZSM-5 are clear evidence that a

mechanism other than the one described above is operative. One possibility is that zinc and silver species work as a dehydrogenation centre. In the presence of Zn, Ga or Ag cations, alkenes may undergo direct abstraction of a hydrogen atom(or ion) to form allylic species. Aromatic hydrocarbons may be formed by the successive abstraction of hydrogen atoms from higher alkenes or direct coupling of two allylic species with simultaneous production of hydrogen molecules. However, the mechanism of the activation of lower alkanes and the role of metal cations in the aromatization have been well established by Ono et al.[8-10, 11, 12]. In the transformation of butanes and butenes, the general pathway of the conversion over ZSM-5 zeolites can be summarized as follows.

Firstly, if there exist no metal cations such as zinc and silver, lower paraffins undergo cracking over Brönsted sites of the zeolites to give lower olefins and smaller paraffins. Among smaller paraffins, methane and ethane are the end products, since they are not reactive under the reaction conditions.

Lower olefins formed by cracking of alkanes dimerize to yield higher olefins which undergo



cracking to regenerate lower olefins. Isomerization of olefins proceeds simultaneously with dimerization and cracking over acid sites. The combination of these reactions leads to the formation of a variety of olefins. Then, repeated hydride abstraction and deprotonation of higher olefins yield aromatics. Since the formation of one molecule of aromatic hydrocarbons accompanies the formation of three molecules of alkane, the yield of aromatics is limited. Secondary, in the presence of zinc, gallium or silver cations, alkenes may undergo direct abstraction of a hydrogen atom (or ions) to form allylic species. Aromatic hydrocarbons may be formed by the successive abstraction of hydrogen atoms (or ions) from higher alkenes or by direct coupling of two allylic species with simultaneous production of hydrogen. All elementary reactions found over HZSM-5 also proceed over Zn-, Ga- or Ag-ZSM-5 by action of Brønsted-acid sites. But, in contrast to the conversion over HZSM-5, the yields of lower alkanes were very small over metal-ion containing ZSM-5, indicating that the incorporation of zinc and silver species does not generate acidic centres capable of catalysing hydride-transfer reactions. Since the dehydrogenation path with metal cations does not

result in the simultaneous formation of alkanes, there is essentially no limit to higher yield of aromatics. This explains the higher yield of aromatic hydrocarbons over Zn-, Ga- or Ag-containing zeolites. In the transformation of lower alkanes like butane, metal cations should play the same role. Alkenes formed by cracking of alkanes can be effectively transformed to aromatic hydrocarbons by the dehydrogenation activity of these cations. Consequently, it is clear that there exist two types of activation of the reactant alkane molecules over Ga- and Zn-ZSM-5, dehydrogenation by the action of Ga, Zn or Ag cations and cracking on Brønsted acid sites. Thus, relative contribution of the two types of activation seems to depend on both the nature of a reacting alkane and the primary reactions over acid sites.

The changes in the product distribution over Ag-ZSM-5 with on-stream time in the transformation of 1-butene and iso-butane are summarized in Table 4 and Table 5 respectively. The important feature of 1-butene and iso-butane reactions observed over Ag-ZSM-5 was the small yield of methane and propane at 1 h. The yield of aromatics decreased but that of methane, ethane and propane increased

Table 4. Conversion of 1-Butene over Ag-ZSM-5 with Reaction Time

Catalyst ;	100% ion-exchanged Ag-ZSM-5(SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =72.1)	
Temperature(K)	773	773
Reaction time(h)	1	3
Conversion(%)	97.8	97.2
Yield of aromatics(%)	72.9	55.8
Product distribution(%)		
CH <sub>4</sub>	0.1	0.4
C <sub>2</sub> H <sub>6</sub>	0.2	1.1
C <sub>2</sub> H <sub>4</sub>	2.3	5.3
C <sub>3</sub> H <sub>8</sub>	5.7	11.7
C <sub>3</sub> H <sub>6</sub>	6.9	8.4
C <sub>4</sub> H <sub>8</sub>	1.6	2.2
n-C <sub>4</sub> H <sub>10</sub> +iso-C <sub>4</sub> H <sub>10</sub>	6.0	9.4
C <sub>5</sub> +aliphatics	2.6	4.1
aromatics	74.5	57.5
Aromatic distribution(%)		
benzene	5.6	5.5
toluene	26.5	32.8
xylene+ethylbenzene	37.5	46.9
C <sub>9</sub> +aromatics	30.4	14.7

Reaction conditions ; 1-butene=34.2kPa, W/F=4.2g h mol<sup>-1</sup>

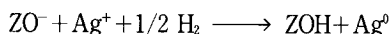
Table 5. Conversion of Iso-Butane over Ag-ZSM-5 with Reaction Time

Catalyst ;	55.4% ion-exchanged Ag-ZSM-5(SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =43.5)			
Temperature(K)	773			
Reaction time(h)	1	2	4	6
Conversion(%)	71.7	68.5	54.1	43.8
Yield of aromatics(%)	47.3	44.9	22.5	16.9
Product distribution(%)				
CH <sub>4</sub>	1.0	1.3	2.7	3.6
C <sub>2</sub> H <sub>6</sub>	0.8	0.9	1.6	1.8
C <sub>2</sub> H <sub>4</sub>	5.9	5.7	9.0	9.6
C <sub>3</sub> H <sub>8</sub>	8.8	10.1	18.2	21.1
C <sub>3</sub> H <sub>6</sub>	8.1	8.0	12.7	13.8
C <sub>4</sub> H <sub>8</sub>	4.3	4.3	6.7	7.3
n-C <sub>4</sub> H <sub>10</sub>	2.5	2.6	4.3	4.6
C <sub>5</sub> +aliphatics	2.3	1.6	3.3	3.3
aromatics	66.5	65.5	41.5	34.9
Aromatic distribution(%)				
benzene	8.9	7.9	14.0	13.3
toluene	31.1	26.9	38.3	36.3
xylene+ethylbenzene	41.0	41.3	34.5	33.3
C <sub>9</sub> +aromatics	19.0	23.9	13.2	17.1

Reaction conditions ; iso-butane=34.2kPa, W/F=4.2g h mol<sup>-1</sup>

with increasing on-stream time. Ag-ZSM-5 was much more effective than HZSM-5 in the aromatization of butanes and 1-butene. The difference in the product distribution between HZSM-5 and Ag-ZSM-5 is brought about by the differences in the acid strength of two catalysts. The silver cations were reduced by hydrogen which was produced during the dehydrogenation of hydrocarbons. Therefore, Ag-ZSM-5 becomes more acidic with prolonged reaction time and the increase in the yield of the lower alkanes can be assigned to the increase in the acid strength of the catalyst. Over acidic zeolites, oligomerization and cracking become more prevailing, so that various type of olefins are formed in the zeolite pores, and various types of hydrocarbons can be formed from a variety of allylic species.

In order to obtain the information on the change in the acidic properties of Ag-ZSM-5, X-ray diffractograms of the fresh and the used catalyst were taken and are shown in Fig. 1. As shown in this figure, the formation of Ag metal was found after using Ag-ZSM-5 as a catalyst for 6 h in the transformation of iso-butane. These result indicate that silver cations were reduced to Ag metal with resulting in the formation of acidic OH groups by hydrogen which was produced during the dehydrogenation of iso-butane.



where  $\text{ZO}^-$  denotes the oxygen anion of the zeolite framework.

As described above, the bifunctional nature of the catalyst is important for aromatization of olefins. The acidic sites are responsible for oligomerization of olefins and the metal cations are responsible for dehydrogenation of olefins or oligomerized products. Acidic sites are also responsible for cracking of oligomers and for hydrogen transfer reactions. Therefore, when the acidic nature of the catalyst is modified, the overall catalytic processes in the zeolite cavities would be greatly changed and the selectivities to the products would be altered. To observe

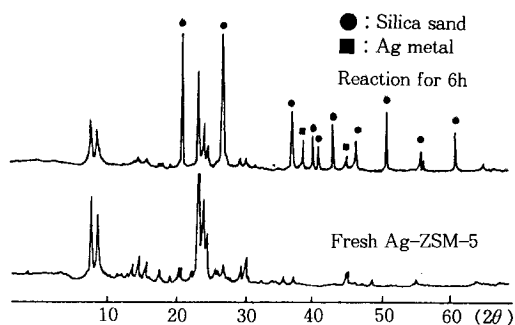


Fig. 1. X-ray diffractograms of Ag-ZSM-5 catalysts before and after use in the transformation of iso-butane to aromatic compounds.

the effect of acidic properties of HZSM-5 by introducing Ag cations, the reaction of 1-butene over ZSM-5 catalyst with different amount of Ag was carried out and their total conversion and product distribution are shown in Fig. 2. The selectivity to aromatic hydrocarbon was 84.5%, when the proton in HZSM-5 were exchanged by Ag cations at 80% level. The higher selectivity to aromatics was obtained with 80% ion-exchange of Ag cations as compared to 100% Ag-ion exchange. This result indicates that the difference in the acidic properties should have a great influence on the reaction pathway of the aromatization. In addition, the transformation of 1-butene was carried out over Ag-ZSM-5 catalyst which was pretreated in a stream of hydrogen at 773 K for 2.5 h. The product distribution and the yields of benzene, toluene and xylenes were very similar to those obtained over HZSM-5, and the results are shown in Fig. 3. This result also suggests the formation of acidic sites with silver metals by the reduction of  $\text{Ag}^+$  ions.

Temperature programmed desorption spectra of ammonia revealed that the acid strength of HZSM-5 was considerably reduced by introducing Zn and Ag cations. Ga-ZSM-5 is more acidic than Zn-ZSM-5 and Ag-ZSM-5. This is reflected in the product distribution. The yields of lower alkenes are very high over Ga-ZSM-5 as compared to Zn-ZSM-5 and Ag-ZSM-5. These alkenes are the primary

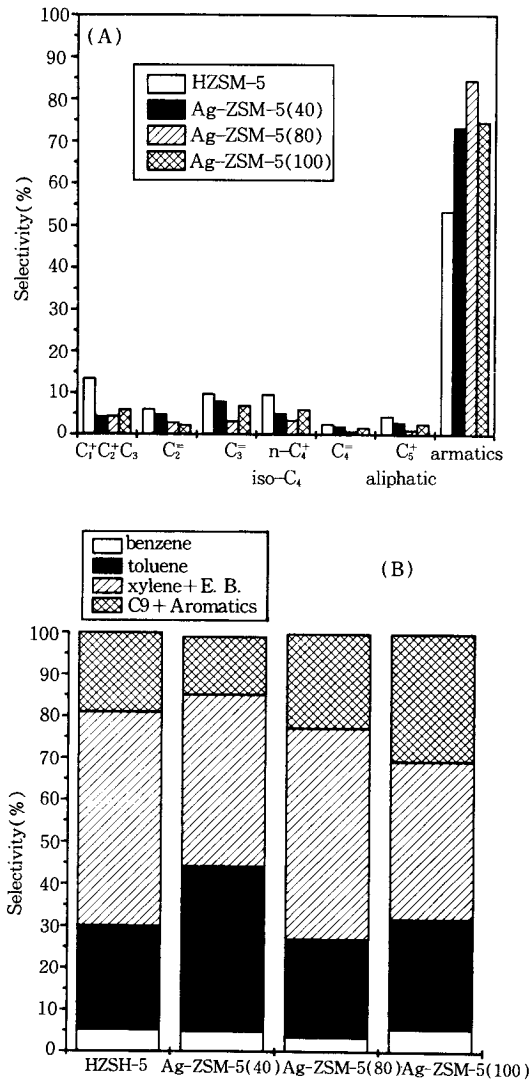


Fig. 2. Product selectivity(A) and the distribution of aromatic hydrocarbons (B) in 1-butene transformation over HZSM-5 and Ag-ZSM-5 with different degree of Ag cation-exchange. Reaction conditions ; 773k, pressure of 1-butene=34.2kPa, W/F=4.2g h mol<sup>-1</sup>.

products, and they are formed by a rapid conversion of butenes. The contribution of acid sites may be reduced in the case of less acidic Zn-ZSM-5. Since propane is formed via hydride transfer reactions, the higher acidity of HZSM-5 and Ga-ZSM-5

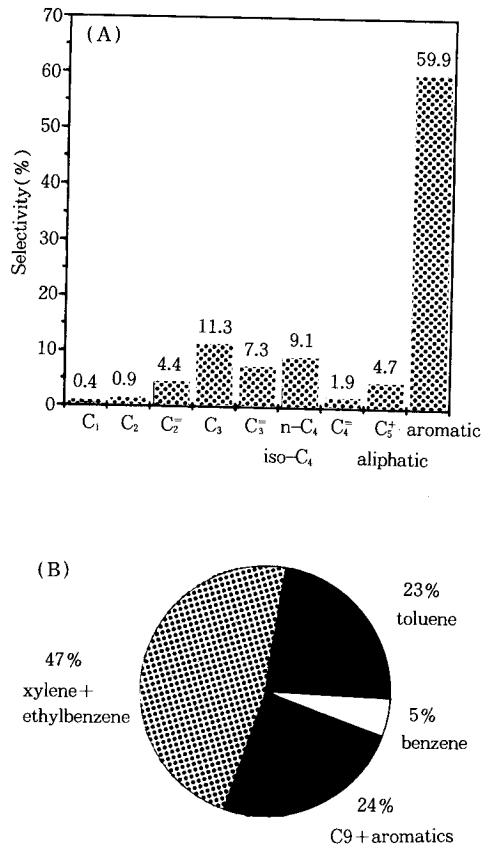


Fig. 3. Product selectivity (A) and the distribution of aromatic hydrocarbons (B) in 1-butene transformation over Ag-ZSM-5 which was pretreated in the stream of hydrogen at 773K for 2.5h.

leads to the higher production of propane as shown in Table 1~3.

The infrared spectra of pyridine adsorbed on HZSM-5, Zn-ZSM-5 and Ag-ZSM-5 were measured. All the samples were treated at 773 K for 1.5 h in an air stream and degassed at the same temperature for 1.5 h. Pyridine vapor was exposed to the samples at 473 K for 1 h and then evacuated at 473 K for 1 h. The results are shown in Fig. 4. In the case of HZSM-5, only the bands due to pyridinium ions were observed but no bands due to pyridine molecules interacting with Lewis acid sites



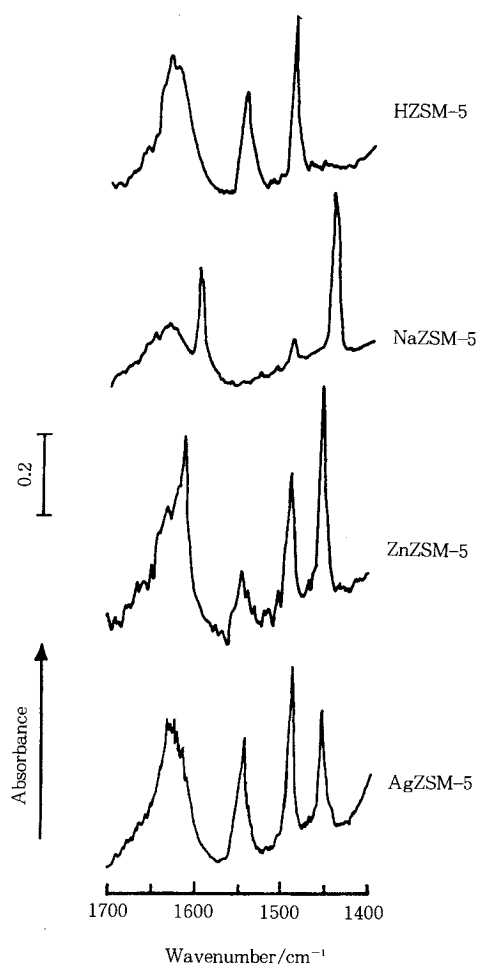


Fig. 4. FT-IR spectra of pyridine adsorbed on HZSM-5, Na-ZSM-5, Zn-ZSM-5 and Ag-ZSM-5 zeolite.

were observed. Over Na-ZSM-5, the bands due to pyridinium ions were not observed, and a band appeared at  $1494\text{cm}^{-1}$ , which was attributed to pyridine molecules interacting with  $\text{Na}^+$  cations. For Zn-ZSM-5 and Ag-ZSM-5, the formation of Brønsted acid sites was confirmed by the presence of a band at  $1548\text{cm}^{-1}$  (pyridinium ion) and a band at  $1454\text{cm}^{-1}$  was observed, which was plausibly due to pyridine molecules interacting with Zn or Ag cations.

Temperature dependence of product distribution in 1-butene conversion over Ag-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3$

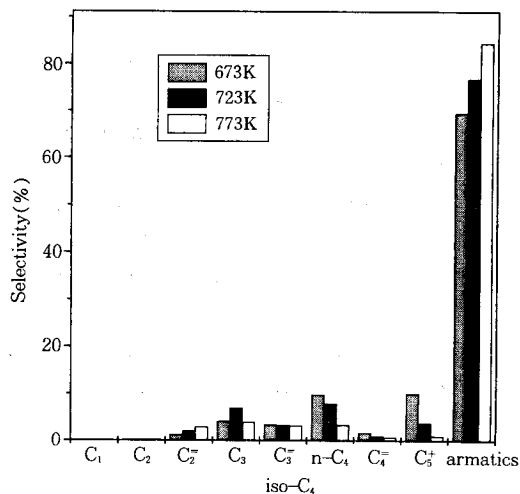


Fig. 5. The change in selectivities to hydrocarbons with increasing reaction temperature in the transformation of 1-butene over Ag-ZSM-5. Reaction conditions; pressure of 1-butene =  $34.2\text{kPa}$ ,  $W/F=4.2\text{g h mol}^{-1}$ .

=  $72.1$ ) is shown in Fig. 5. The general features in the product distribution over Ag-ZSM-5 were similar to those obtained over Zn-ZSM-5 by Ono et al. [12]. The yield of aromatics increased with increasing reaction temperature up to 773 K and it reached to 84.5% at 773 K. The distributions of aromatic hydrocarbons were as follows on the basis of carbon number; benzene 3.8%, toluene 23.6%, xylene + ethylbenzene 50.1% and C<sub>9</sub>+ aromatics 22.5%. In this case, xylenes were the main products. This indicates that the aromatics may be formed by the direct coupling of two butene molecules. The variety of the aromatic hydrocarbons in the products must be a reflection of the distribution of alkenes in the system. This in turn implies that the oligomerization of 1-butene and the aromatization are much faster than the interconversion among alkenes.

### 3. Conclusions

The results described above may be summarized

as follows.

1. The yield of aromatics appreciably increased by introducing  $\text{Ag}^+$  cations into ZSM-5 catalyst in the aromatization of butanes and 1-butene.

2. The selectivity for propane decreased considerably when  $\text{Ag}^+$  cations were introduced into ZSM-5.

3.  $\text{Ag}^+$  ions in ZSM-5 were reduced to  $\text{Ag}^0$  with resulting in the formation of acidic OH groups, and the higher yield of propane was obtained over hydrogen-reduced Ag-ZSM-5.

4. The yield of aromatics increased with increasing reaction temperature up to 773 K.

### References

1. S. M. Csicsery, *J. of Catal.*, **17**, 205(1970).
2. S. M. Csicsery, *J. of Catal.*, **17**, 217(1970).
3. S. M. Csicsery, *J. of Catal.*, **17**, 315(1970).
4. S. M. Csicsery, *J. of Catal.*, **18**, 30(1970).
5. O. V. Bragin, T. V. Vasina, and A. V. Preobrazhenskii, *Izv. Akad. Ser. Khim.*, **56**(1984).
6. T. Inui and F. Okazumi, *J. of Catal.*, **90**, 366 (1984).
7. T. Mole, J. R. Anderson, and G. Crerr, *Applied Catal.*, **17**, 141(1985).
8. H. Kitagawa, Y. Sendoda, and Y. Ono, *J. of Catal.*, **101**, 12(1986).
9. Y. Ono and K. Kanae, *J. Chem Soc. Faraday Trans.*, **87**, 69(1991).
10. G. Sirokman, Y. Sendoda, and Y. Ono, *ZEO-LITES*, **6**, 299(1986).
11. M. Shibata, H. Kitagawa, Y. Sendoda, and Y. Ono, Proc. 7th Int. Zeolite Conf., 717, Kodansha-Elsevier, Tokyo-Amsterdam(1986).
12. Y. Ono, H. Kitagawa, and Y. Sendoda, *J. Chem Soc. Faraday Trans. 1*, **83**, 2913(1987).
13. Y. Ono, H. Adachi, and Y. Sendoda, *J. Chem Soc. Faraday Trans. 1*, **84**, 109(1988).
14. P. A. Jacobs, *J. Phys. Chem.*, **86**, 300(1982).
15. M. I. Poustma, "In Zeolite Chemistry and Catalysis", ed. J. A. Rabo, ACS Monograph, *Amer. Chem. Soc.*, **171**, 437, Washington D. C.(1976).