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Transformation of Propane into Aromatic Hydrocarbons over ZSM-5 Zeolites

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Transformation of propane into aromatic hydrocarbons over H-ZSM-5 and Ga-exchanged ZSM-5 (Ga-ZSM-5) zeolites were studied. Over H-ZSM-5, the mode of activation of propane changes with the conversion level of propane. Thus, propane undergoes cracking into methane and ethylene by its interaction with acidic hydroxyl groups at low conversion levels, while, at higher conversion levels, it undergoes hydride abstraction by its interaction with carbenium ions. Lower olefins thus formed give oligomerized products, which in turn, undergo dehydrogenation to give aromatic hydrocarbons. The loading of Ga^{3+} of ZSM-5 greatly improves the selectivity to aromatics as well as the total conversion of propane. Thus, a selectivity of 71% was obtained at 500°C. Ga species are quite effective for the transformation of intermediate products (i.e., lower olefins) into aromatic compounds, while they have no direct role in propane activation.

INTRODUCTION

Transformation of lower alkanes into more useful compounds like aromatics is of significant importance since this expands the sources for hydrocarbon products. Csicsery described the dehydrocyclodimerization of lower alkanes over bifunctional catalysts (*1–5*). For example, propane was converted into aromatic hydrocarbons with a 21% selectivity over platinum supported on alumina (*2*). Recently, ZSM-5 zeolites in combination with transition metals have been reported as the catalysts for the aromatization of ethane (*6, 7*) and propane (*8*). Furthermore, ZSM-5 zeolites modified with gallium or zinc species are claimed to give the high selectivity to aromatics (*9–11*). Thus, the yield of aromatics from pentane over H-ZSM-5 and Ga-ZSM-5 were 23 and 52%, respectively, at 550°C (*12*). However, the mechanism of the activation of lower alkanes is not well established. This work deals with the transformation of propane into aromatic hydrocarbons over ZSM-5 zeolites. The mechanistic pathway of propane into aromatics over ZSM-5 was studied, and the effect of Ga ion exchange on the catalytic behavior was examined. The modification of the reaction pathway by gallium loading was discussed.

METHODS

ZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 62 was synthesized by the method described by a patent (*13*). The structures of the synthesized materials were confirmed by X-ray diffractions to be that of ZSM-5 zeolite. The synthesized materials were converted into the ammonium form (NH_4-ZSM-5) by using the procedures described by Jacobs (*14*). A part of NH_4-ZSM-5 was exchanged with Ga^{3+} cation. Thus, NH_4-ZSM-5 was stirred in an aqueous solution of $Ga(NO_3)_3 \cdot 9H_2O$ under refluxing conditions for 24 h, filtered, washed with water, and dried. NH_4-ZSM-5 and Ga^{3+}-exchanged ZSM-5 (Ga-ZSM-5) were pressed, crushed, and sorted into grains of 16–32 mesh.

The reactions were carried out with a continuous flow reactor operating at atmospheric pressure. The catalyst was packed in a reactor of silica-tubing (10 mm i.d.)

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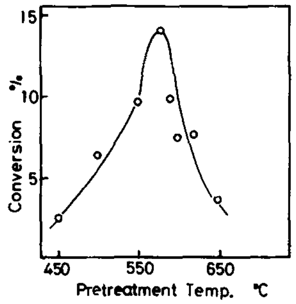


FIG. 1. Effect of pretreatment temperature on the conversion of propane over NH_4-ZSM-5. Reaction temperature, 450°C, $W/F = 7.0$ g h mol^{-1}, pretreatment, 1.5 h in a dry-air stream.

placed in a vertical furnace, and then heated under an air stream at 580°C for 90 min. Under this treatment, NH_4-ZSM-5 was expected to be converted into the proton form of the zeolite (H-ZSM-5). Propane was obtained from Takachiho Ind. and introduced into a preheating zone of the reactor through a flowmeter. The products were withdrawn periodically from the outlet of the reactor and analyzed by gas chromatography. Aliphatic and aromatic hydrocarbons were determined on a 2-m-long Porapack Q column and a 30-m-long OV-101 column, respectively, with gas chromatographs equipped with a flame ionization detector. The conversion, the yield, the selectivity, and the product distribution were calculated on the carbon number basis, if not described otherwise, as follows.

Conversion

$$= \frac{\text{Number of moles of propane consumed}}{\text{Number of moles of propane fed}}$$

Yield of a given hydrocarbon
= (Number of moles of the hydrocarbon produced) × (Number of C atoms in the molecular formula)/(Number of moles of propane fed) × 3

Selectivity to a given hydrocarbon
= (Number of moles of the hydrocarbon produced) × (Number of C atoms in the molecular formula)/(Number of moles of propane consumed) × 3.

RESULTS AND DISCUSSION

1. CONVERSION OF PROPANE OVER H-ZSM-5

Effect of Pretreatment of NH_4-ZSM-5

The conversion of propane was carried out at 450°C with NH_4-ZSM-5 zeolites, which were pretreated at various temperatures in a dry air stream for 1.5 h. The percentage conversion of propane is plotted as a function of the pretreatment temperature in Fig. 1. The propane conversion had its maximum at 580°C. It is worthy of note that the desorption of ammonia from NH_4-ZSM-5 occurs at much lower temperatures than at 580°C. Thus, the temperature-programmed desorption spectrum of ammonia into flowing nitrogen has a peak around 400°C. This suggests that all of acidic hydroxyl groups are not active centers for propane activation. Two possibilities are plausible. (1) The heterogeneity of hydroxyl groups; NH_4^+ groups are intrinsically heterogeneous, and very strong acid sites are formed only from NH_4^+ groups which release ammonia at higher temperatures. (2) Superacid sites, which arise from the synergism between the dislodged aluminohydroxyl groups and framework hydroxyls, as proposed by Midrodatos and Barthomeuf (*15*). It is not possible to distinguish these two possibilities at the moment. The decline of the catalytic activity at higher temperatures is undoubtedly attributed to the decrease in acidic hydroxyl groups in the zeolites by dehydroxylation.

Effect of Reaction Temperature

Temperature dependence of the total conversion of propane and the selectivity to aromatics in the transformation of propane over H-ZSM-5 is shown in Fig. 2. The total conversion as well as the yield of aromatics increased with reaction temperature. The selectivity to aromatic hydrocarbons increased with the reaction temperature.

The product distribution strongly depended on the reaction temperature (Fig.

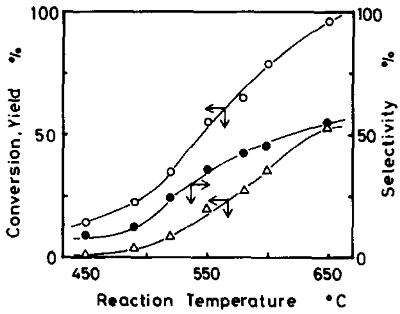


FIG. 2. Change in the total conversion (○), the yield of aromatics (△), and the selectivity to aromatics (●) with reaction temperature in the propane conversion over H-ZSM-5. W/F = 7.0 g h mol^{-1}.

3). At 450°C, the half of carbon atoms of the converted propane were found in the product hydrocarbons with four or five carbon atoms. The selectivity to these hydrocarbon decreased with the reaction temperature. As the reaction temperature increased, the fractions of methane, ethane, and aromatics in the products increased. The distribution among aromatic hydrocarbons at 500°C was: benzene 30%, toluene 50%, xylenes, 18%, others 2% (in molar basis). In the temperature range studied, aliphatic hydrocarbons with six or more carbon atoms were found only sluggishly in the products. This indicates that these hydrocarbons, if formed in the zeolite cavities, are converted immediately either into smaller molecules by cracking, or into aromatic hydrocarbons by dehydrogenation. The selectivity data show that the probability for the latter is favored at higher temperatures.

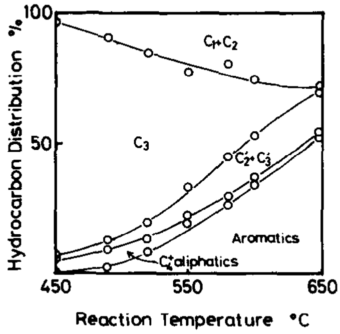


FIG. 3. Distribution of hydrocarbons produced in the propane conversion over H-ZSM-5 with the reaction temperature. W/F = 7.0 g h mol^{-1}.

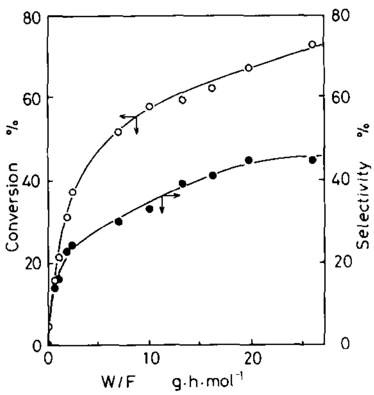


FIG. 4. Change in the total conversion (○), and the selectivity to aromatics (●) with contact time in propane conversion over H-ZSM-5 at 550°C.

Reaction Pathway over H-ZSM-5

The changes of the total conversion, and the selectivity to aromatics with contact time (W/F, W, weight of catalyst and F, flow rate of propane) were examined at 550°C. The total conversion increased with the contact time as shown in Fig. 4. The selectivity to aromatics increased very sharply with increasing contact time, being 45% at W/F of 26.1 g h mol^{-1}.

Figure 5 shows the change in the yields of hydrocarbon species as a function of percentage conversion of propane.

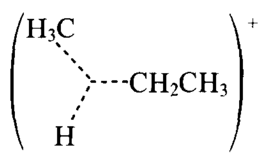
The behavior of each hydrocarbon species gives important information on the reaction pathway.

(1) *Aromatic hydrocarbons.* It is evident that aromatic hydrocarbons are not primary products, since the rate of formation of aromatics increased progressively with increasing conversion level of propane. Plausibly, they are formed by secondary reactions of lower olefins.

(2) *Methane.* At low conversion of propane, the main products are methane and ethylene. Thus, at the conversion of 5%, the products consist of CH_4 (49%), C_2H_4

(36%), C_2H_6 (7%), C_3H_6 (5%), and smaller quantity of hydrocarbons with four or five carbon atoms. Here, the numbers in parentheses are the molar percentages of the corresponding hydrocarbons. This shows that the main reaction at the first stage is the decomposition of propane into methane and $C_2H_5^+$ through the attack of protons on C—C bonds of propane rather than on C—H bonds.

$C_3H_8 + H^+ \rightarrow$



$\rightarrow CH_4 + \overset{+}{C}H_2CH_3$

This tendency agrees with the observation in the reaction of propane in the superacid medium (*16*). However, as seen in Fig. 5, the yields of methane did not increase proportionally with an increase in the propane conversion and apparently their formation came to a halt at a higher conversion range. This strongly suggests that the mode of the propane activation changes as the reaction proceeds. Thus, at the next stage, propane is plausibly activated by the abstraction of hydride ions by carbenium ions (R^+).

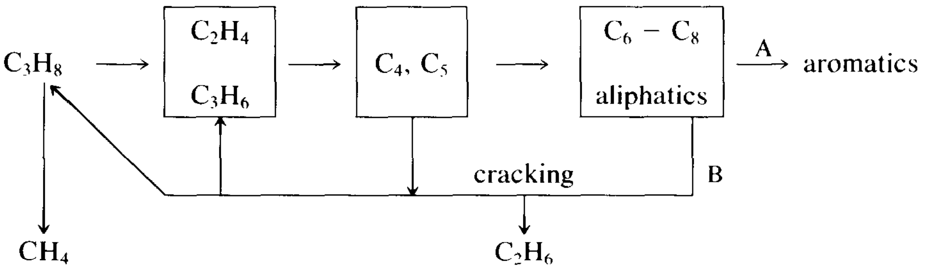
$$C_3H_8 + R^+ \rightarrow RH + CH_3\overset{+}{C}HCH_3$$

The dimethyl carbenium ions formed ($C_3H_7^+$) may give C_3H_6 or react with alkenes to form larger carbenium ions. A similar change in the mode of activation was recently reported in the cracking of hexanes by Haag and Dessau (*17*), who pointed out that the first type of the activation occurred preferentially at lower conversion levels, the second type being predominant at the next stage.

(3) *Ethane.* The change in the yield of ethane with propane conversion is very characteristic. Thus, the pattern of its increase with the conversion is very similar to that of aromatic hydrocarbons, indicating that both species are formed from a common intermediate species. Thus, the main source of ethane at the next stage is not the cracking of propane, but that of the larger molecules, part of which are converted also to aromatics.

(4) *Lower olefins.* The lower olefins and the hydrocarbons with four or five carbon atoms are transitional products, since their yields decreased at higher conversion levels. Lower olefins may oligomerize to give heavier hydrocarbons, which may reproduce smaller molecules by cracking or react with carbenium ions to form large species (C_6–C_8 intermediates).

In conclusion, the main reaction pathway of propane to aromatics may be summarized as follows.



Thus, propane gives C_2H_4 and C_3H_6, which oligomerize in the zeolite cavities. The oligomerized products either give smaller molecules by cracking (Path B), or aromatics by dehydrogenation (Path A). The main final products from propane are thus aromatics and alkanes under the reaction conditions studied.

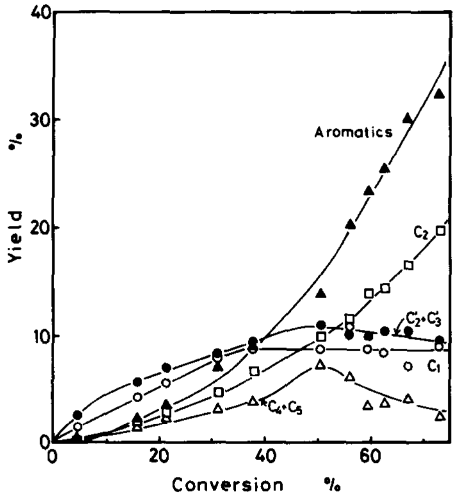


FIG. 5. Variation of yields of hydrocarbons with the total conversion of propane over H-ZSM-5 at 550°C. (○) Methane, (●) ethylene + propylene, (□) ethane, (△) hydrocarbons with four or five carbon atoms, (▲) aromatics.

2. CONVERSION OF PROPANE OVER Ga-ZSM-5

Effect of Reaction Temperature

Temperature dependence of the total conversion of propane, the yield of aromatics and the selectivity in the transformation of propane over Ga-ZSM-5 (SiO_2/Al_2O_3 = 62 and Ga content 1.6 wt%) are shown in Fig. 6. The details of the product composition are given in Fig. 7. From the comparison of Figs. 6 and 7 with Figs. 2 and 3, it is clear that the loading of gallium improves both the total conversion and the selectivity to aromatics, which exceeds 70% over 500°C for Ga-ZSM-5. The distribution of aromatics was not modified greatly by Ga loading. Thus, the distribution of aromatic hydrocarbons at 550°C was as follows: benzene 35%, toluene 52%, and xylenes 13%. Another feature seen in Fig. 7 is smaller accumulation of the intermediates (lower olefins, C_4, C_5), indicating that Ga loading enhances the transformation of these substances into aromatic hydrocarbons.

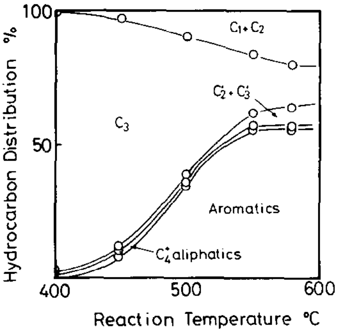


FIG. 7. Change in the distribution of hydrocarbons produced in the propane conversion over Ga-ZSM-5 with the reaction temperature. W/F = 7.0 g h mol^{-1}.

Effect of Ga Content

Figure 8 shows the change in the total conversion and the selectivity to aromatics

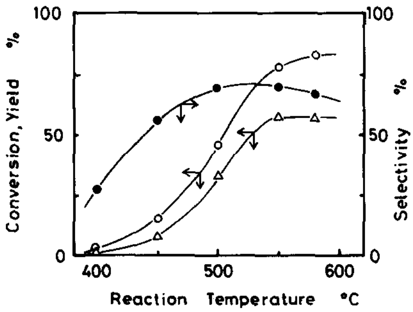


FIG. 6. Change in the total conversion (○), the yield of aromatics (△), and the selectivity to aromatics (●) with reaction temperature in the propane conversion over Ga-ZSM-5. W/F = 7.0 g h mol^{-1}.

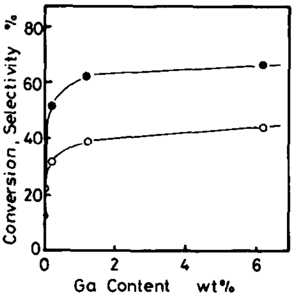


FIG. 8. Change in the total conversion of propane (○) and the selectivity to aromatics (●) with Ga content of ZSM-5 zeolites. Reaction temperature, 500°C. W/F = 7.0 g h mol^{-1}.

with the content of gallium in the zeolites. The total conversion and the selectivity to aromatics increased sharply with increasing Ga content up to 1 wt%, but the further increase in the Ga content caused only slight increase of the conversion and the selectivity. For the ZSM-5 sample studied (SiO_2/Al_2O_3 = 62), the Ga content of 1.2 wt% corresponded to the ion-exchange degree of 100%. Therefore, at least for the samples with higher Ga content, part of the gallium species is not in the form of Ga^{3+} cation. Figure 8 indicates that the Ga species introduced as Ga^{3+} cation is most effective for aromatization.

As discussed earlier, the activation of propane is probably caused by protons or carbenium ions, whose concentration relies on the number of hydroxyl groups. Enhancement of the conversion of propane with Ga-containing zeolites might be ascribed to the modification of the acidic properties with gallium species. However, this idea must be refuted by the following experimental results. To test the acidity of the zeolites, the cracking of hexane was carried out at 240 and 280°C over H-ZSM-5 and Ga-ZSM-5. Over H-ZSM-5, hexane conversions at 240 and 280°C were 16 and 22%, respectively, while the conversion over Ga-ZSM-5 at the two temperatures were 15 and 21%, respectively. Ga loading did not affect the rate of the reaction of pentane at 500°C, though the selectivity to aromatic hydrocarbons was greatly enhanced (*12*). The fact that the acidic property of H-ZSM-5 is not altered by Ga loading is also confirmed by a close similarity of the temperature-programmed desorption spectra of ammonia of the two zeolites. Therefore, the activity increase by Ga ion exchange is not caused by the change in the acid properties of the zeolites, but is related to the higher aromatization activity of Ga cations. As discussed earlier, the intermediate products undergo either aromatization or cracking as shown in Scheme 1. Ga species plausibly promotes the rate of the aromatization of the intermediates (Path A in Scheme 1), and as a result, their cracking to smaller molecules (Path B) is relatively repressed. Since propane is one of the most predominant products in the hydrocarbon cracking, the modification by Ga ion exchange leads to the decrease in the rate of propane conversion, which could be expressed as the difference between the real rate of propane conversion and that of propane regeneration by cracking reactions.

The conclusion that the role of Ga ion exchange is not in the activation step of the reactant propane but in the aromatization of the intermediates, is also supported by the fact that the yield of aromatics from lower olefins increases appreciably by Ga loading. For example, the yields of aromatic compounds from propylene over H-ZSM-5 and Ga-ZSM-5 were 40 and 77%, respectively, when propylene was passed through the zeolites under the conditions of W/F = 40 g h mol^{-1}, propylene pressure of 20 kPa, and 500°C.

Modification of Reaction Path by Ga Loading

The effect of the contact time (W/F) on the total conversion of propane, and the selectivity to aromatics were examined at 500°C. The results are given in Fig. 9. The total conversion of propane and the yield of aromatics increased with contact time and

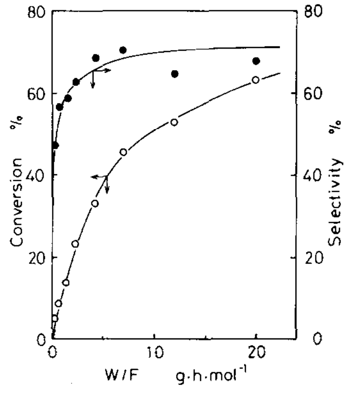


FIG. 9. Change in the total conversion (○), and the selectivity to aromatics (●) with contact time in propane conversion over Ga-ZSM-5 at 500°C.

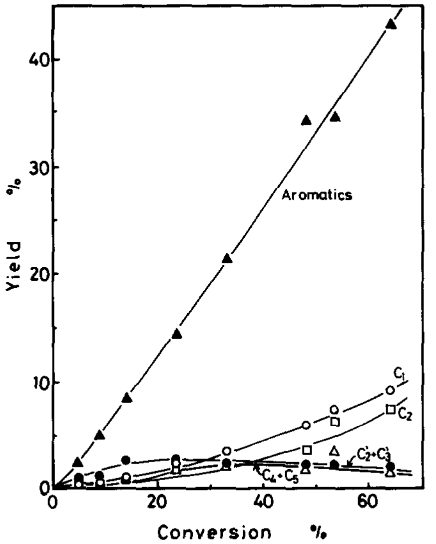


FIG. 10. Variation of yields of hydrocarbons with the total conversion of propane over Ga-ZSM-5 at 500°C. (○) Methane, (●) ethylene + propylene, (□) ethane, (△) hydrocarbons with four or five carbon atoms, (▲) aromatics.

reached 63 and 43%, respectively, at $W/F = 20.2$ g h mol^{-1}. The selectivity to aromatics reached at 65% even at contact times as small as $W/F = 2.5$ g h mol^{-1}. This is in sharp contrast with the conversion over H-ZSM-5, where the selectivity to aromatics was very small at smaller contact times (Fig. 4), indicating that the intermediate species are very efficiently transformed into aromatics over Ga-ZSM-5 before they leave the pores of the zeolites.

Figure 10 shows the yields of hydrocarbon species as a function of the percentage conversion of propane. The yield of aromatics increases almost proportionally with the propane conversion, in agreement with the statement described above. Another important characteristic of the conversion over Ga-ZSM-5 is much smaller production of ethane even at high conversion levels in comparison with the conversion over H-ZSM-5 (Fig. 5). As described earlier, ethane is plausibly produced by cracking of higher aliphatic hydrocarbons formed as intermediates. Smaller yield of ethane thus implies that the intermediate species are effectively converted into aromatics before they are cracked to produce ethane and other smaller molecules.

In conclusion, Ga species does not directly participate in the activation of propane, but serves for the efficient transformation of the intermediate species like olefins into aromatic hydrocarbons. The actual mode of the interaction between olefins and Ga species will be discussed elsewhere (*18*).

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