

## Aromatization of *n*-Hexane over ZnO/H-ZSM-5 Catalysts

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The mechanism of transformation of *n*-hexane into aromatics over ZnO/H-ZSM-5 catalyst has been investigated. The yields of aromatics in the transformation of *n*-hexane over H-ZSM-5 are enhanced by mechanical mixing of ZnO as well as by ion exchange or impregnation of zinc cation. It is concluded that aromatization of *n*-hexane over ZnO/H-ZSM-5 is a bifunctional reaction, and that ZnO as well as H-ZSM-5 takes part both in the activation of *n*-hexane and in the aromatization of lower olefins. By contrasting the conversion of *n*-hexane with that of 1-hexene, it is found that aromatization of *n*-hexane over ZnO/H-ZSM-5 involves both the dehydrogenation of *n*-hexane into hexene and that of the oligomerized products into aromatics. It is proposed that ZnO catalyzes the dehydrogenation of *n*-hexane into hexene and of the oligomerized products into aromatics. © 1988

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### INTRODUCTION

Naphtha reforming catalysts, Pt/Al<sub>2</sub>O<sub>3</sub>, have been used industrially to transform heavy naphtha (C<sub>7</sub>–C<sub>10</sub>) into aromatics, but lower paraffins (C<sub>2</sub>–C<sub>6</sub>) are hardly converted into aromatics over these catalysts. It has recently been reported that H-ZSM-5 combined with zinc or gallium cations can convert lower paraffins into aromatics (1–7). However, few results have been reported with respect to the reaction mechanism and the role of metal cations. Mole *et al.* (4) suggested that in the conversion of propane over Zn-ZSM-5 the zinc cation acts as a hydride acceptor to give a transient species such as [Zn–H]<sup>+</sup> in the dehydrogenation step between C<sub>3</sub>H<sub>7</sub><sup>+</sup> and C<sub>3</sub>H<sub>8</sub>. Ono *et al.* (5–7) suggested that zinc or gallium cations are quite effective for the transformation of lower olefins into aromatics, although these cations have no direct role in paraffin activation. Industrial interest and the mechanistic aspects prompted us to do the present investigation on the reaction mechanism of *n*-hexane over ZnO/H-ZSM-5 catalyst.

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### EXPERIMENTAL

ZSM-5 zeolite with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 100 was synthesized by the method described in a patent (8). The structure of the synthesized material was confirmed by X-ray diffraction to be that of ZSM-5. SEM analysis of the catalyst revealed aggregates of around 1 μm consisting of small crystallites of around 0.1 μm. After calcination at 823 K for 8 h, the ammonium form of the catalyst (NH<sub>4</sub>-ZSM-5) was obtained by exchanging twice with 1 M NH<sub>4</sub>NO<sub>3</sub> solution at 353 K for 3 h.

H-ZSM-5 catalyst was prepared by calcining NH<sub>4</sub>-ZSM-5 at 823 K for 4 h. ZnO/H-ZSM-5 catalysts (ZnO content, 0.2–10.0 wt%) were prepared by mechanically mixing ZnO and NH<sub>4</sub>-ZSM-5, then calcining at 823 K for 4 h. They were pressed, crushed, and sorted into sizes of 16–32 mesh. SEM measurements showed ZnO particles to be uniformly fixed on the external surface of H-ZSM-5.

Reactions were carried out in a quartz tubular microflow reactor containing 0.5 g of catalyst. After the catalyst zone was heated to 773 K under nitrogen, *n*-hexane or 1-hexene diluted with nitrogen (molar ratio of N<sub>2</sub>/feed = 5) was fed to the preheat-

ing zone of the reactor. Experiments were conducted at 773 K and 1 atm. Analysis of the reaction products (hydrocarbons) was carried out by on-line gas chromatography 1–4 h from the start of reaction; conversion and selectivity remained constant for the period. Aliphatic and aromatic hydrocarbons were determined in a 3-m-long VZ-10 column and a 50-m-long OV-101 capillary column, respectively. The amount of hydrogen produced was calculated by carbon balance and hydrogen balance between the feed and the reaction products (hydrocarbons).

Conversion, selectivity, and product distribution were calculated on the carbon basis, and H<sub>2</sub> production ratio was defined as moles of H<sub>2</sub> produced divided by feed moles converted.

## RESULTS AND DISCUSSION

### 1. Conversion of *n*-Hexane

The conversion of *n*-hexane was carried out over H-ZSM-5 and ZnO/H-ZSM-5, with WHSV ranging from 2 to 32 h<sup>-1</sup>.

The changes in *n*-hexane conversion and product selectivity with contact time over ZnO/H-ZSM-5 (ZnO 2.0 wt%) are shown in Fig. 1. At short contact time, it is remarkable that the selectivities for lower olefins are higher than those for lower paraffins.

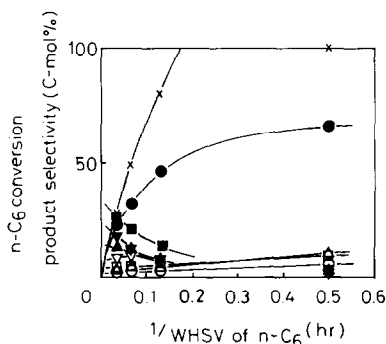


FIG. 1. Variation of product selectivity with contact time in the conversion of *n*-hexane over ZnO(2 wt%)/H-ZSM-5. ×, *n*-hexane conversion; ●, aromatics; ○, methane; △, ethane; □, propane; ▽, butane; ▲, ethylene; ■, propylene; ▼, butene.

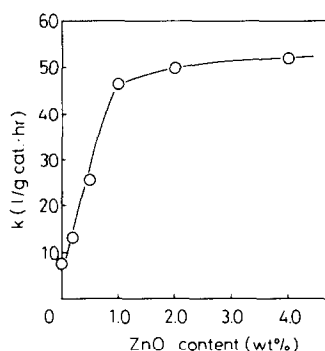


FIG. 2. Change in the apparent reaction rate constant of *n*-hexane with ZnO content. WHSV of *n*-hexane = 8–32 h<sup>-1</sup>.

This agrees with the results reported by Simmons *et al.* (9) that olefins were produced predominantly in the cracking reaction of butane over steamed gallosilicate. *n*-Hexane conversion and the selectivities for aromatics, methane, ethane, and propane increased with contact time, whereas the selectivity for olefins decreased. This indicates that *n*-hexane is converted into aromatics via olefins over ZnO/H-ZSM-5. Aromatics were mainly benzene, toluene, and xylene.

The apparent rate constants for reaction of *n*-hexane over H-ZSM-5 and ZnO/H-ZSM-5 were obtained from the slopes of first-order plots of *n*-hexane conversion against contact time. These were found to be first order with respect to the concentration of *n*-hexane, since *n*-hexane conversions obey first-order kinetics fairly well. As shown in Fig. 2, the apparent reaction rate constant of *n*-C<sub>6</sub> increased with ZnO content, indicating that ZnO as well as H-ZSM-5 takes part in the activation of *n*-hexane. These results differ from those of Ono *et al.* (7), who reported that zinc cations have no direct role in paraffin activation. Ono *et al.* (5–7) have studied the conversion of propane, pentane, and hexane over Ga-ZSM-5, but only the conversion of propylene over Zn-ZSM-5. The differences between the results reported here and those reported by Ono *et al.* may be attributed to

the differences in dehydrogenation activity between zinc and gallium cations and the changes in acidity of zeolite combined with metal cations. Studies on the conversion of *n*-hexane over Ga-H-ZSM-5 have been described in detail elsewhere (10).

In Fig. 3, H<sub>2</sub> production ratio is shown as a function of the selectivity for aromatics over H-ZSM-5 and ZnO/H-ZSM-5. H<sub>2</sub> production ratio extrapolated to zero selectivity for aromatics tends to 1.0 as ZnO content increases. This indicates that one mole hydrogen is produced from one mole of *n*-hexane in the initial stage of formation of aromatics when the ZnO content is high enough. In Fig. 3, over H-ZSM-5, H<sub>2</sub> production ratio extrapolated to zero selectivity for aromatics is no more than 0.2, indicating that *n*-hexane is directly converted by the penta-coordinated carbenium ion mechanism (11, 12). On the other hand, over ZnO/H-ZSM-5, if *n*-hexane were converted only by cracking via hexene, H<sub>2</sub> production ratio extrapolated to zero selectivity for aromatics might be expected to become 1.0, whereas it increases only 0.5–0.8 in the presence of ZnO. We suggest that since ZnO/H-ZSM-5 has acidic sites, the direct cracking of *n*-hexane is always operative together with the cracking of *n*-hexane via hexene, and that the latter reaction increases with ZnO content.

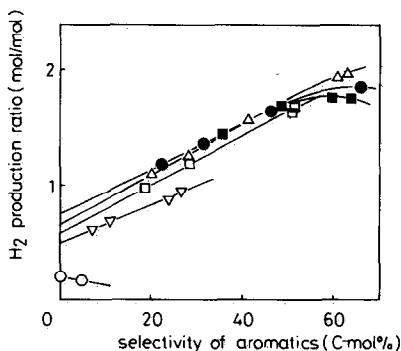


FIG. 3. Relation between H<sub>2</sub> production ratio and the selectivity of aromatics in the conversion of *n*-hexane. ZnO content (wt%): ○, 0; ▽, 0.2; □, 0.5; △, 1.0; ●, 2.0; ■, 4.0.

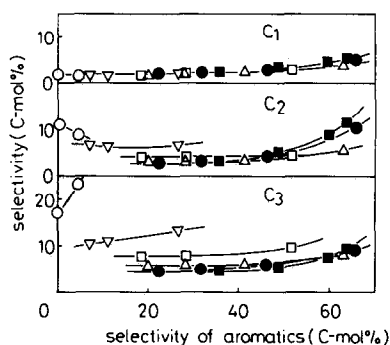


FIG. 4. Relation between the selectivities of methane, ethane, and propane and the selectivity of aromatics in the conversion of *n*-hexane. ZnO content (wt%): ○, 0; ▽, 0.2; □, 0.5; △, 1.0; ●, 2.0; ■, 4.0.

Repetition of oligomerization of lower olefins and cracking of the oligomerized products leads to the formation of a variety of olefins, which yield a variety of oligomerized products with longer carbon chains, which are the intermediates for aromatics. In Fig. 3, H<sub>2</sub> production ratio increased with selectivity for aromatics over ZnO/H-ZSM-5, but was almost constant over H-ZSM-5. As proposed by Mole *et al.* (4), this indicates that over H-ZSM-5, aromatics are formed by the hydrogen transfer between lower olefins (or carbenium ions) and the oligomerized products. On the other hand, it seems that over ZnO/H-ZSM-5, aromatics are formed by dehydrogenation of the oligomerized products over ZnO. If the dehydrogenation of the oligomerized products were operative, the slopes of H<sub>2</sub> production ratio might be expected to be 3. Practically, however, since ZnO/H-ZSM-5 has acidic sites, and the hydrogen transfer is always operative together with the dehydrogenation of the oligomerized products, the actual slopes must be no more than 2.

In Fig. 4, the selectivities for methane, ethane, and propane are plotted respectively against the selectivity for aromatics over H-ZSM-5 and ZnO/H-ZSM-5. The following features can be seen.

1. The selectivities for ethane and propane extrapolated to zero selectivity for

aromatics decrease with increasing ZnO content.

2. Below 40% of selectivity for aromatics, the selectivity for propane sharply increases with the selectivity for aromatics over H-ZSM-5, but is almost constant over ZnO/H-ZSM-5.

3. Over 40% of the selectivity for aromatics over ZnO/H-ZSM-5, the selectivities for methane, ethane, and propane increase with ZnO content as well as with the selectivity for aromatics.

Similar to the results shown in Fig. 3, feature 1 shows that the conversion of *n*-hexane via hexene into lower olefins without the formation of lower paraffins increases with ZnO content. And feature 2 shows that aromatics are formed by the hydrogen transfer between propylene (or  $C_3H_7^+$ ) and the oligomerized products over H-ZSM-5, but mainly by the dehydrogenation of the oligomerized products over ZnO/H-ZSM-5.

As shown in Fig. 3, over ZnO/H-ZSM-5 the higher the selectivity for aromatics, the higher is the hydrogen pressure in reaction atmosphere. Therefore, feature 3 implies that over ZnO, ethane and propane are formed by hydrogenation of ethylene and propylene or by hydrogenolysis of the oligomerized products. The influence of ZnO content on *n*-hexane conversion and product selectivity is shown in Fig. 5 at a WHSV of  $2\text{ h}^{-1}$  over ZnO/H-ZSM-5. The selectivities for aromatics and methane increased with ZnO content up to 2.0 wt% and then gradually decreased. On the other hand, the selectivities for ethane and propane decreased with increasing ZnO content up to 2.0 wt% and then gradually increased. Since methane is formed only by hydrogenolysis, the differences among the trends of the selectivities for methane, ethane, and propane lead us to the conclusion that ethane and propane are formed over ZnO by hydrogenation of ethylene and propylene. It has been reported (13) that over Ga-H-ZSM-5, the formation of aromatics is enhanced by the introduction of ethane

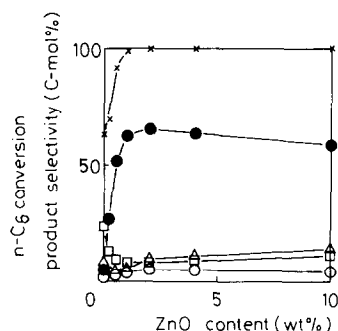


FIG. 5. Influence of ZnO content on product selectivity in the conversion of *n*-hexane. ×, *n*-hexane conversion; ●, aromatics; ○, methane; △, ethane; □, propane.

(10–50 vol%) to the feed gas ( $C_3$ – $C_4$ ). We suggest that the hydrogenation of ethylene to ethane is prevented due to the equilibrium between ethane and ethylene. This effect leads to an increase in the formation of aromatics. Since the trend of the selectivity for methane is similar to that of the selectivity for aromatics, we suggest that methane is formed by demethylation of aromatics over ZnO as proposed by Ono *et al.* (7).

## 2. Conversion of 1-Hexene

Since it has been suggested that *n*-hexane is converted into lower olefins by cracking via hexene in the activation of *n*-hexane, the conversion of 1-hexene was also carried out over H-ZSM-5 and ZnO/H-ZSM-5, with WHSV ranging from 2 to  $32\text{ h}^{-1}$ .

1-Hexene conversions were 100% in all experiments, because over H-ZSM-5 cracking of 1-hexene is faster than that of *n*-hexane by two orders of magnitude (14). At short contact time, only the cracking of 1-hexene into lower olefins prevails in the absence of added hydrogen.

Over H-ZSM-5 and ZnO/H-ZSM-5, the cracking of 1-hexene into lower olefins is much faster than the aromatization of lower olefins; therefore, the apparent rate constants for formation of aromatics from lower olefins over H-ZSM-5 and ZnO/H-ZSM-5 were obtained from the slopes of first-order plots of lower olefins conversion

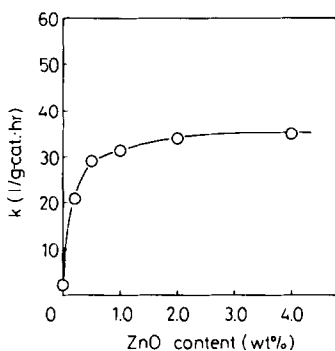


FIG. 6. Change in the apparent formation rate constant of aromatics from lower olefins with ZnO content. WHSV of 1-hexene = 8–32 h<sup>-1</sup>.

against contact time. These were found to be first order with respect to the concentration of lower olefins since lower olefin conversion obeys first-order kinetics fairly well. As shown in Fig. 6, the apparent formation rate constant increased with ZnO content. This indicates that the formation of aromatics from lower olefins is catalyzed over ZnO as well as over H-ZSM-5.

In Fig. 7, H<sub>2</sub> production ratio is plotted against the selectivity for aromatics over H-ZSM-5 and ZnO/H-ZSM-5. In contrast to the case of *n*-hexane, H<sub>2</sub> production ratio extrapolated to zero selectivity for aromatics becomes zero. Compared with the results of Fig. 3, it is found that the dehydrogenation of *n*-hexane into hexene over ZnO/H-ZSM-5 takes place in the conversion reaction of *n*-hexane. On the other hand, in Fig. 7, the slope of H<sub>2</sub> production ratio is also about 2, indicating that the hydrogen transfer between lower olefins and the oligomerized products is always operative together with the dehydrogenation of the oligomerized products in the aromatization of lower olefins.

In Fig. 8, the selectivities for methane, ethane, and propane are plotted against the selectivity for aromatics over H-ZSM-5 and ZnO/H-ZSM-5. Contrary to the case of *n*-hexane, the selectivities for methane, ethane, and propane extrapolated to zero selectivity for aromatics become zero,

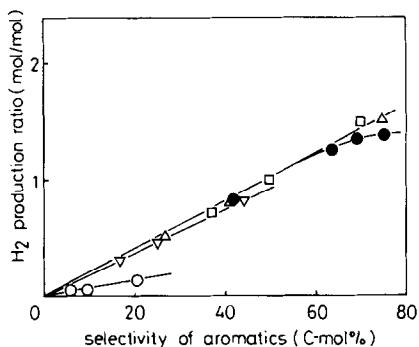


FIG. 7. Relation between H<sub>2</sub> production ratio and the selectivity of aromatics in the conversion of 1-hexene. ZnO content (wt%): ○, 0; ▽, 0.2; □, 0.5; △, 1.0; ●, 2.0.

because only olefins are formed in the cracking reaction of 1-hexene.

### 3. Mechanism of Aromatization of *n*-Hexane over ZnO/H-ZSM-5

Based on their study of the conversion of propane over H-ZSM-5, zinc-exchanged H-ZSM-5, and nonacidic silicalite, Mole *et al.* (4) suggest that both zinc cations and hydrogen forms of ZSM-5 contain catalytic functions. Moreover, we have shown that the yields of aromatics from *n*-hexane over H-ZSM-5 are enhanced by mechanical mixing of ZnO as well as by ion exchange or impregnation of zinc cation. Under reducing atmosphere, ZnO may be reduced to Zn

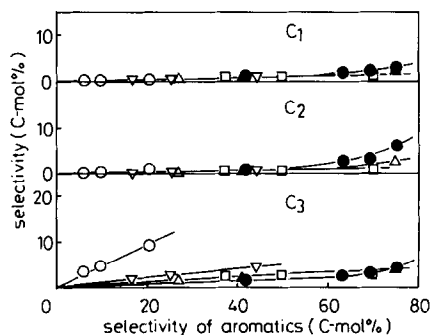
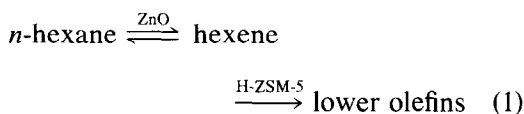


FIG. 8. Relation between the selectivities of methane, ethane, and propane and the selectivity of aromatics in the conversion of 1-hexene. ZnO content (wt%): ○, 0; ▽, 0.2; □, 0.5; △, 1.0; ●, 2.0.

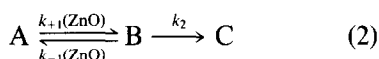
metal and then Zn metal may be vaporized and dispersed on H-ZSM-5. However, ZnO/H-ZSM-5 catalysts prepared by mechanical mixing were not exposed to reducing atmosphere before reaction, and no change was observed in conversion or selectivity up to at least 4 h from the start of reaction. Furthermore, if aromatization of *n*-hexane over ZnO/H-ZSM-5 were a monofunctional reaction and the interface between ZnO and H-ZSM-5 were the active site, the number of active sites over ZnO/H-ZSM-5 prepared by mechanical mixing would be much smaller than that over ZnO/H-ZSM-5 prepared by ion exchange or impregnation. Therefore, we conclude that aromatization of *n*-hexane over ZnO/H-ZSM-5 is a bifunctional reaction.

Since it has been found that over ZnO/H-ZSM-5, *n*-hexane is converted only into lower olefins via hexene, we hypothesize scheme (1) for the activation of *n*-hexane over ZnO/H-ZSM-5: dehydrogenation into hexene (either hexene itself or an adsorbed hexene) over ZnO, followed by cracking of hexene into lower olefins over H-ZSM-5.



Temperature-programmed desorption (TPD) measurements with ammonia were carried out to study the effect of acidity at various ZnO contents. No change was observed in TPD spectra of H-ZSM-5 and ZnO/H-ZSM-5, suggesting that mechanical mixing of ZnO does not affect the acidity of zeolite, and the reaction rate constant of the reaction over acidic site does not change with the ZnO content.

By assuming all steps to be first order, the kinetic scheme



where A = *n*-hexane, B = hexene, C = lower olefins, and (ZnO) = ZnO content, can be solved as follows.

$$\begin{aligned} -dC_A/dt &= k_{+1}(\text{ZnO})C_A - k_{-1}(\text{ZnO})C_B \\ dC_B/dt &= k_{+1}(\text{ZnO})C_A \\ &\quad - [k_{-1}(\text{ZnO}) + k_2]C_B \\ &= 0 \quad (\text{with a steady-state approximation}) \end{aligned}$$

$C_A$  = *n*-hexane concentration, and  $C_B$  = hexene concentration. Thus,

$$-dC_A/dt = \frac{k_{+1}k_2(\text{ZnO})}{k_{-1}(\text{ZnO}) + k_2} C_A \quad (3)$$

If  $(\text{ZnO}) \ll k_2/k_{-1}$ , Eq. (3) reduces to

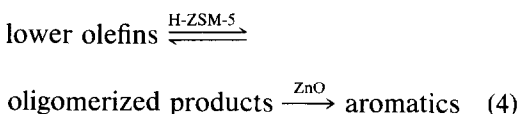
$$-dC_A/dt = k_{+1}(\text{ZnO})C_A.$$

If  $(\text{ZnO}) \gg k_2/k_{-1}$ , Eq. (3) reduces to

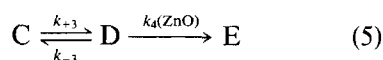
$$-dC_A/dt = \frac{k_{+1}k_2}{k_{-1}} C_A.$$

When the ZnO content is low, dehydrogenation of *n*-hexane over ZnO is the rate-determining step and the reaction rate of *n*-hexane depends on the ZnO content. On the other hand, when the ZnO content is high enough, cracking of hexene over H-ZSM-5 is the rate-determining step and the reaction rate of *n*-hexane does not depend on the ZnO content. The reaction rate equation (3) is found to correlate the results of Fig. 2, which show that the apparent reaction rate constant of *n*-hexane increased with ZnO content, but leveled off at about 1.0 wt%.

We hypothesize scheme (4) for the formation of aromatics from lower olefins over ZnO/H-ZSM-5: oligomerization of lower olefins over H-ZSM-5, followed by dehydrogenation of the oligomerized products into aromatics over ZnO.



By assuming all steps to be first order, the kinetic scheme



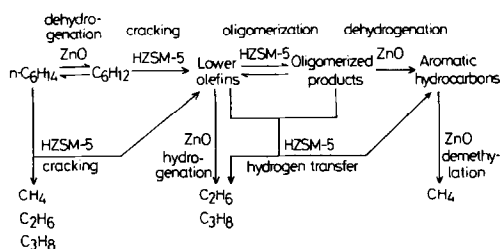


FIG. 9. Reaction mechanism of *n*-hexane over ZnO/H-ZSM-5.

where C = lower olefins, D = oligomerized products, E = aromatics, and (ZnO) = ZnO content, can be solved as follows.

$$\begin{aligned} dC_E/dt &= -dC_C/2dt \\ &= \frac{k_{+3}k_4(\text{ZnO})}{2[k_{-3} + k_4(\text{ZnO})]} C_C. \quad (6) \end{aligned}$$

If  $(\text{ZnO}) \gg k_{-3}/k_4$ , Eq. (6) reduces to

$$dC_E/dt = \frac{k_{+3}k_4(\text{ZnO})}{2k_{-3}} C_C.$$

If  $(\text{ZnO}) \gg k_{-3}/k_4$ , Eq. (6) reduces to

$$dC_E/dt = \frac{k_{+3}}{2} C_C.$$

As well as the conversion of *n*-hexane, scheme (4) correlates the results of Fig. 6, which show that the apparent rate constant for formation of aromatics from lower olefins increased with ZnO content, but leveled off at about 0.5 wt%. Figure 6 leveled off at a smaller amount of ZnO than Fig. 2;  $k_{-3}/k_4 < k_2/k_{-1}$ . Since  $k_{-3}$  seems to be almost equal to  $k_2$ ,  $k_4$  (dehydrogenation) should be faster than  $k_{-1}$  (hydrogenation of hexene). Therefore, we suggest that the oligomerized products in scheme (4) must be naphthenes, as proposed by Csicsery (15). Finally, Fig. 9 shows the reaction mechanism as described above, for the reaction of *n*-hexane over ZnO/H-ZSM-5 catalyst.

#### CONCLUSION

We have shown here that aromatization of *n*-hexane over ZnO/H-ZSM-5 involves

dehydrogenation of *n*-hexane into hexene and that of oligomerized products into aromatic hydrocarbons. Moreover, contrary to Ono *et al.* (7), it was found that ZnO as well as H-ZSM-5 takes part in the activation of *n*-hexane.

We conclude that aromatization of *n*-hexane over ZnO/H-ZSM-5 is a bifunctional (ZnO and H-ZSM-5) reaction and that ZnO catalyzes the dehydrogenation of *n*-hexane into hexene and of the oligomerized products into aromatics.

*n*-Hexane is converted into only lower olefins by cracking via hexene, but into both lower olefins and lower paraffins by direct cracking of *n*-hexane. It is necessary to make the former reaction faster than the latter to obtain aromatic hydrocarbons from *n*-hexane in higher yield, because aromatization of lower paraffins is limited to low yield due to the equilibrium between lower paraffins and aromatics.

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