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Selective Conversion of Methanol into Aromatic Hydrocarbons over Zinc-exchanged ZSM-5 Zeolites

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The conversion of methanol into hydrocarbons over ZSM-5 zeolites has been studied with a special emphasis on improving the selectivity to aromatic hydrocarbons. The introduction of zinc or gallium cations to ZSM-5 appreciably increased the yield of or selectivity for aromatic hydrocarbons. Thus, under the reaction conditions of 700 K, methanol pressure of 40 kPa and $W/F = 9.0$ g h mol^{-1}, the yields of aromatic hydrocarbons over H-ZSM-5, Ga-ZSM-5, and Zn-ZSM-5 were 40.3, 48.2 and 67.4%, respectively. Over Zn-ZSM-5 the distribution of aromatic products on a molar basis was as follows; benzene (5.8%), toluene (28.0%), xylenes + ethylbenzene (45.6%) and C_{9^+}(20.6%). The reaction conditions were optimized to obtain the highest yield of aromatic hydrocarbons over Zn-ZSM-5. The yield of aromatics increased with temperature up to 700 K, but a further temperature increase led to the decomposition of methanol to carbon oxides. The selectivity for aromatics gave a maximum of 70% at a methanol partial pressure of 22 kPa. The yield of aromatic hydrocarbons increased with the degree of cation-exchange of H-ZSM-5 with Zn-cations, indicating the essential role of zinc species in the enhancement of the selectivity to aromatics. It is concluded that the zinc species has a capability of efficiently converting alkene intermediates to aromatic hydrocarbons.

ZSM-5 zeolites are known to convert methanol into hydrocarbons of petroleum-range boiling products.[1–5] The petroleum produced by the methanol-to-petroleum process includes *ca.* 60 wt% aromatic hydrocarbons.[1] However, the one-pass yield of aromatic hydrocarbons is not necessarily high. Thus, Chang and Silvestri[2] reported that under the conditions of 644 K and atmospheric pressure, the fraction of aromatics in the hydrocarbon products was 41.1 wt%. The yield of aromatics was pressure-dependent, a high pressure favouring the formation of aromatics and a low pressure favouring the formation of lower alkenes.[3]

According to the accepted mechanism, aromatic hydrocarbons are formed *via* hydrogen transfer between the precursors such as alkenes and carbenium ions, the formation of aromatics inevitably accompanying the formation of alkanes.[6] This sets a limit to the yield of aromatic hydrocarbons. Therefore, if aromatics were produced through a direct dehydrogenation of alkene intermediates, the formation of alkanes could be suppressed and the yield of aromatics, which are considered to be more valuable chemicals, could be enhanced. It has been shown that gallium or zinc cations incorporated into ZSM-5 are effective in the aromatization of alkenes.[7–11] Here, we describe the selective conversion of methanol into aromatic hydrocarbons over Zn-ZSM-5.

Experimental

ZSM-5 zeolite was synthesized by a patented method.[12] The structure of the synthesized material was confirmed to be that of ZSM-5 by X-ray diffraction. The synthesized material was converted into the ammonium form (NH_4-ZSM-5) by using the procedure described by Jacobs.[13] Zn-ZSM-5 was made by exchanging the ammonium form twice with a zinc nitrate solution at 353 K for 24 h. The gallium-exchanged form of ZSM-5 (Ga-ZSM-5) was made by refluxing an aqueous solution of $Ga(NO_3)_3 \cdot 9H_2O$ containing NH_4-ZSM-5 for 24 h. The catalysts were pressed, crushed and sorted into grains of 16–32 mesh. The reactions were carried out in 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 then heated under an air stream at 853 K for 90 min. By this treatment NH_4-ZSM-5 was expected to be converted into the proton form of the zeolite (H-ZSM-5). Methanol was fed by a motor-driven syringe into the preheating zone of the reactor. Helium was fed through a flow-meter. The effluent gas was withdrawn periodically and analysed by a gas chromatograph equipped with a flame ionization detector. Aliphatic hydrocarbons, aromatics and carbon oxides were determined in a 2 m long Porapak Q column, a 50 m long OV-101 capillary column and a 2 m long active carbon column, respectively. The conversion, yield, selectivity and product distributions are expressed on a carbon-number basis, if not otherwise indicated.

Results and Discussion

Conversion over H-ZSM-5, Ga-ZSM-5 and Zn-ZSM-5.

The reaction of methanol over H-ZSM-5 ($SiO_2/Al_2O_3 = 42$) was carried out at a methanol partial pressure of 40 kPa in the temperature range 600–800 K. Under these conditions the conversion was complete; neither methanol nor dimethyl ether were detected in the reactor effluent. The change in the product distribution with reaction temperature is shown in fig. 1. The yield of aromatic hydrocarbons was 30% at 600 K, gradually increasing with reaction temperature and reaching 44% at 800 K. Another main product was propane. Above 700 K, the yields of methane, ethane and lower alkenes increased. The decomposition to carbon oxides was small in the temperature range studied.

The effect of the reaction temperature on the product distribution in the conversion of methanol over Ga-ZSM-5 ($SiO_2/Al_2O_3 = 47$; Ga, 1.9 wt%) was examined and is shown in fig. 2. As expected, the yield of aromatic hydrocarbons over Ga-ZSM-5 was higher than that over H-ZSM-5. Thus the yield of aromatics was 36% at 600 K, increased with increasing temperature and reached 64% at 800 K. In spite of the increasing yield of aromatics, the yield of propane was appreciably lower over Ga-ZSM-5 than over H-ZSM-5. This indicates that hydrogen transfer between carbenium ions and alkene intermediates was suppressed as a result of the faster conversion of the latter into aromatics by direct dehydrogenation.

The conversion of methanol was also greatly affected by the introduction of zinc cations into ZSM-5. Fig. 3 shows the change in the product distribution with reaction temperature in the conversion of methanol over Zn-ZSM-5 ($SiO_2/Al_2O_3 = 47$; Zn, 2.0 wt%). Below 700 K the yield of aromatic hydrocarbons was higher than that over H-ZSM-5 or Ga-ZSM-5. At 700 K the yield reached 67% over Zn-ZSM-5, with the yield of propane being much smaller than that over H-ZSM-5 or Ga-ZSM-5. Over 750 K, however, the decomposition of methanol to carbon oxides became appreciable and the yield of aromatics was greatly depressed.

The product distributions at 700 K over the three catalysts are given in table 1, together with that over Ga-ZSM-5 at 800 K. At 700 K the yield of aromatics was the highest over Zn-ZSM-5, followed by Ga-ZSM-5 and then by H-ZSM-5. The great difference between Zn-ZSM-5 and the other two zeolites is also seen in the rest of the products. The main products other than aromatics were lower alkanes over H-ZSM-5 and Ga-ZSM-5. On the other hand, appreciable amounts of lower alkenes were found

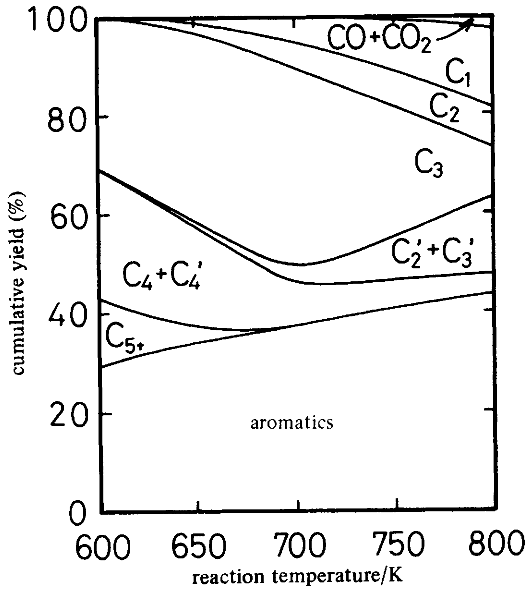

Fig. 1. Change in the product distribution with reaction temperature in methanol conversion over H-ZSM-5. P(MeOH) = 40 kPa, $W/F = 9.0$ g h mol^{-1}.

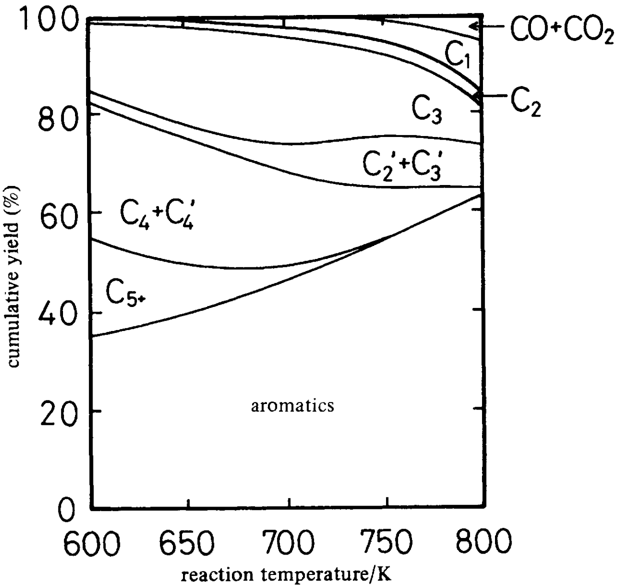

Fig. 2. Change in the product distribution with reaction temperature in methanol conversion over Ga-ZSM-5. P(MeOH) = 40 kPa, $W/F = 9.0$ g h mol^{-1}.

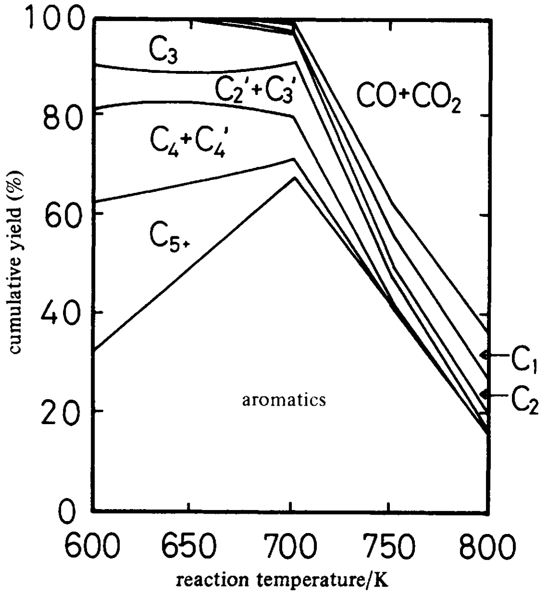

Fig. 3. Change in the product distribution with reaction temperature in methanol conversion over Zn-ZSM-5. *P*(MeOH) = 40 kPa, *W*/*F* = 9.0 g h mol^{-1}.

in the products over Zn-ZSM-5. Since alkenes can be converted into aromatics much more easily than alkanes, the ultimate yield of aromatics could be further increased. Although the yield of aromatics can be increased by raising the reaction temperature over Ga-ZSM-5, the yield of methane increased greatly at 800 K. Methane may be produced by the cracking of propane and the dealkylation of alkylbenzenes. This has been confirmed by the reactions of propane[10] and xylene[9] over Ga-ZSM-5.

Table 1 also gives the distribution of aromatic hydrocarbons. At 700 K over Zn-ZSM-5, the main aromatic products were xylenes. Trimethylbenzenes and toluene were also formed in large quantities. Similar distributions for aromatics were also found for H-ZSM-5 and Ga-ZSM-5. By raising the reaction temperature to 800 K over Ga-ZSM-5, the benzene fraction was doubled, again indicating the dealkylation of alkylbenzenes.

Effect of Reaction Conditions

The effect of the partial pressure on the product distribution was studied at a constant contact time, with the results being shown in fig. 4. When the methanol partial pressure was low, the formation of carbon oxides was observed. As the methanol pressure increased, the formation of carbon oxides diminished, becoming negligible above 22 kPa. The selectivity for aromatic hydrocarbons went through a maximum at 16 kPa and decreased at higher pressures. This trend is the opposite of that found in the conversion of methanol over H-ZSM-5, where the yield of aromatics increases with increasing methanol pressure.[3] The lowering of the aromatic yield at higher partial pressure of methanol may be caused by a thermodynamic limitation of the dehydrogenation reactions.

Fig. 5 shows the variation in the selectivity among aromatic products with the partial pressure of methanol. At low pressures the main aromatic products (expressed on a molar basis) were trimethylbenzenes. As the partial pressure increased, toluene and

Table 1. Methanol conversion over ZSM-5

catalyst T/K	H-ZSM-5 700	Ga-ZSM-5 700	 800	Zn-ZSM-5 700
products		C(%)		
$CO+CO_2$	0.4	0.6	3.6	0.7
C_1	2.2	2.2	12.8	1.5
C_2–C_4	46.7	42.2	10.8	13.0
C_2'–C_4'	6.7	4.2	8.8	13.1
C_{5^+}	3.7	2.6	0.0	4.3
aromatics	40.3	48.2	64.0	67.4
aromatics		C(%)		
benzene	9.3	8.5	17.2	4.5
toluene	31.5	33.8	34.3	25.1
C_8	35.0	39.4	23.0	46.7
C_{9^+}	24.2	18.3	25.5	23.7

$CH_3OH = 40$ kPa, $W/F = 9.0$ g h mol^{-1}.

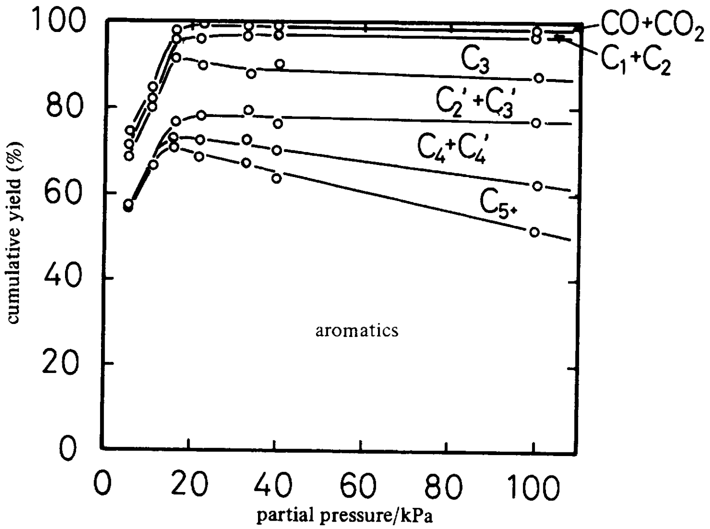

Fig. 4. Change in the product distribution with the methanol partial pressure for the methanol conversion over Zn-ZSM-5. $T = 700$ K, $W/F = 9.0$ g h mol^{-1}.

xylenes increased at the expense of trimethylbenzenes. Above 20 kPa, xylenes were the main products and accounted for *ca.* 50% of all aromatic products.

Fig. 6 shows the variation in the product distribution with the contact time at 700 K and at a methanol partial pressure of 22 kPa. Here, the contact time is expressed by W/F(g h mol^{-1}), where W and F stand for the weight of the catalyst used and the flow rate (mol h^{-1}) of the feed (methanol + helium), respectively. Except for the case of a very short contact time, the conversion of methanol was complete. The yield of aromatics increased with contact time and reached 70% at $W/F = 9.0$ g h mol^{-1}. A further increase

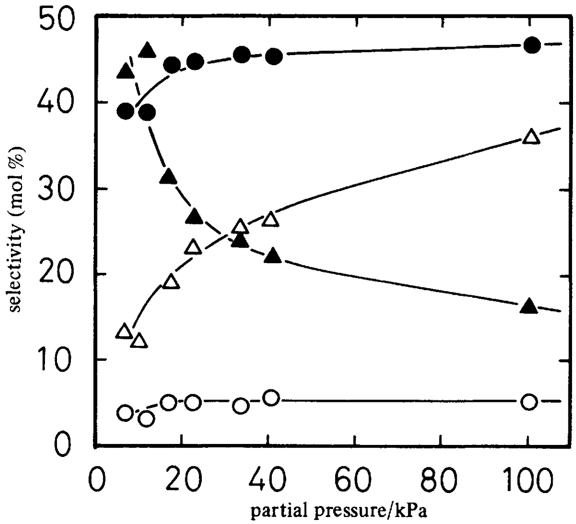

Fig. 5. Effect of the methanol partial pressure on the selectivity among aromatic hydrocarbons produced in the methanol conversion over Zn-ZSM-5. $T = 700$ K, $W/F = 9.0$ g h mol^{-1}. ○, Benzene; △, toluene; ●, C_8; ▲, C_{9+}.

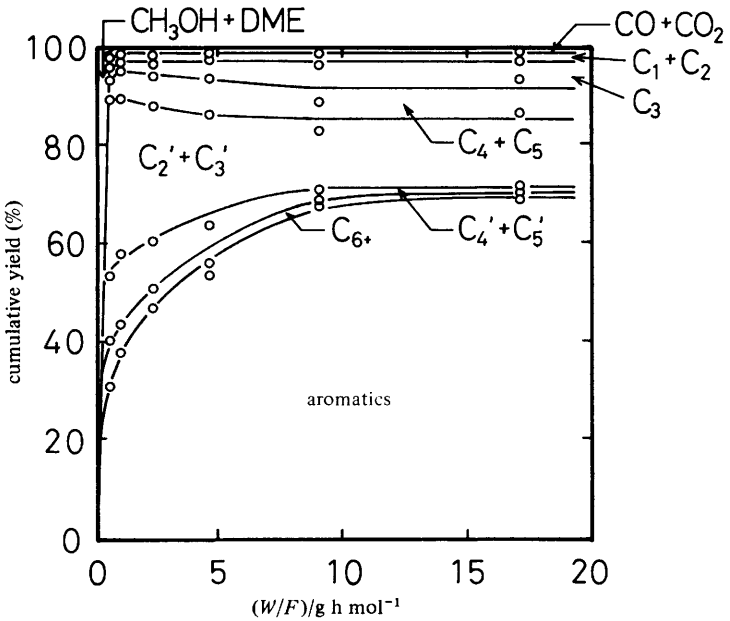

Fig. 6. Change in the product distribution with contact time for the methanol conversion over Zn-ZSM-5. $T = 700$ K, $P(\text{MeOH}) = 22$ kPa.

in the contact time did not alter the product distribution. Large amounts of alkenes were also found with the aromatic hydrocarbons. This indicates that the system was probably in a dehydrogenation–hydrogenation equilibrium. Since alkenes may be easily transformed into aromatics if the equilibrium is favourable, the selectivity to aromatics could have been further improved by the elimination of hydrogen from the system, *e.g.* through the use of a separation membrane.

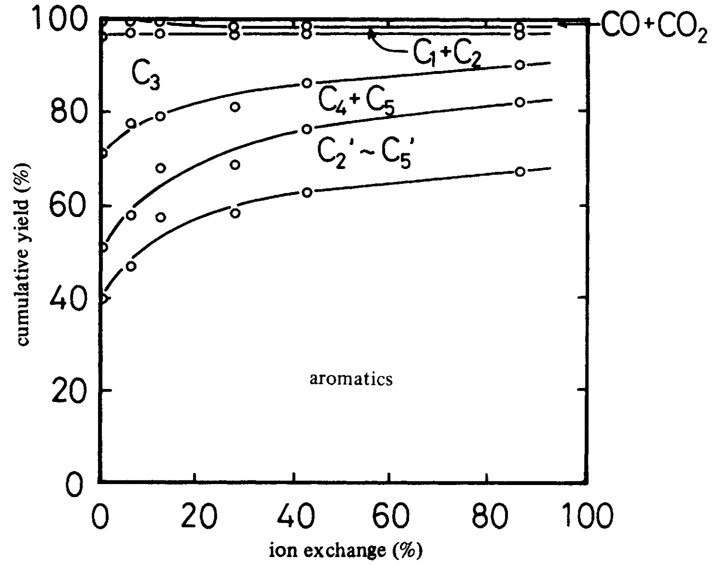

Fig. 7. Change in the product distribution with the degree of cation exchange of H-ZSM-5 with zinc cations for the methanol conversion. $T = 700$ K, P(MeOH) = 22 kPa, $W/F = 9.0$ g h mol^{-1}.

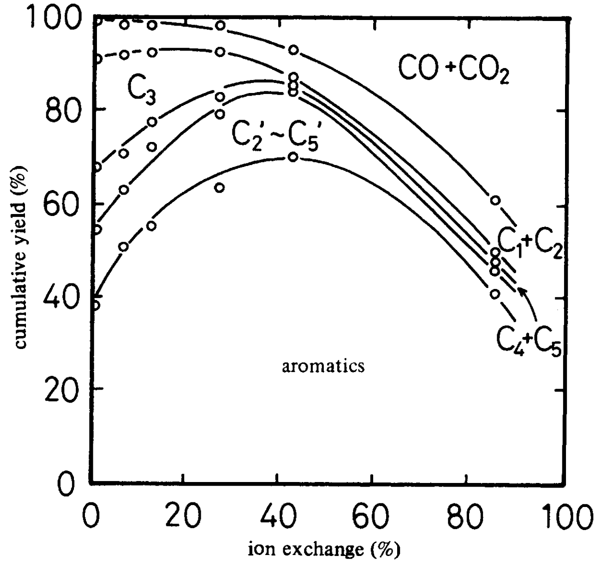

Fig. 8. Change in the product distribution with the degree of cation exchange of H-ZSM-5 with zinc cations for the methanol conversion. 750 K, P(MeOH) = 22 kPa, $W/F = 9.0$ g h mol^{-1}.

Role of the Zinc Cations

In order to gain information on the role of the zinc cations, the effect of the degree of cation-exchange with zinc cations on the product distribution was examined at 700 and 750 K, and the results are shown in fig. 7 and 8, respectively. At 700 K the yield of aromatic hydrocarbons increased with the zinc content. The formation of carbon oxides was low at all degrees of cation exchange. At 750 K the formation of carbon oxides

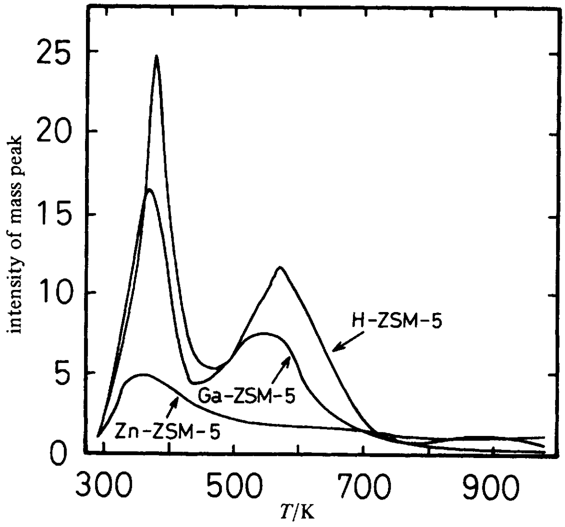

Fig. 9. Temperature-programmed desorption of ammonia from H-ZSM-5, Ga-ZSM-5 and Zn-ZSM-5.

increased with an increase in the degree of cation exchange, and, as a result, the yield of aromatics exhibited a maximum *versus* the degree of cation exchange.

Zinc cations bring about two adverse effects on methanol conversion: they act as a catalyst for alkene dehydrogenation but also as a catalyst for the decomposition of methanol to carbon oxides. The first effect is favourable to the enhancement of the selectivity to aromatics, while the second depresses the selectivity. It is therefore important to maintain a correct balance between the two effects, which depends on the reaction temperature, methanol pressure and the degree of cation exchange.

Acidic Properties of Zn-ZSM-5

To examine the acidic properties of Zn-ZSM-5, temperature-programmed desorption (t.p.d.) of ammonia was carried out on H-ZSM-5, Ga-ZSM-5 and Zn-ZSM-5. Each catalyst was exposed to 5.3 kPa of ammonia at 423 K for 30 min. The temperature was raised at a rate of 5 K min^{-1}. The spectra thus obtained are shown in fig. 9. The t.p.d. spectrum of H-ZSM-5 has two maxima. The low-temperature peak at 380 K is caused by physisorbed ammonia, while the high-temperature peak at 570 K is caused by strong Brønsted-acid sites. The t.p.d spectrum of ammonia from Ga-ZSM-5 was essentially the same as that from H-ZSM-5, although the high-temperature peak was shifted to a lower temperature. The t.p.d. spectrum of Zn-ZSM-5, however, was quite different, as there was no discrete peak caused by the Brønsted-acid sites. It is thus clear that the acidity of Zn-ZSM-5 is much less than that of H-ZSM-5 or Ga-ZSM-5. This may be related to a reduction in the formation of alkanes, since hydrogen transfer between carbenium ions and alkenes (or alkanes) is an acid-catalysed reaction. Thus the introduction of zinc cations acts in two different ways in the selective production of aromatic hydrocarbons. First, zinc species act as a catalyst for the dehydrogenation of alkenes. Secondly, exchange with zinc cations greatly depresses the acidity of the zeolite, and this in turn reduces the rate of the hydrogen-transfer reaction which suppresses the formation of alkanes.

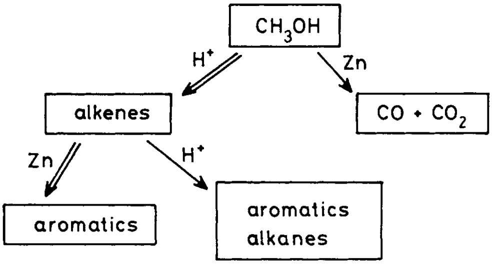

Fig. 10. Reaction scheme of methanol conversion over Zn-ZSM-5.

Reaction Scheme

The reaction scheme for methanol conversion over Zn-ZSM-5 can be summarized as is shown in fig. 10, where the role of protons and zinc ions is emphasized. Lower alkenes are formed from methanol by the catalytic action of protons. Methanol may decompose to give carbon oxides by the action of zinc ions.

The lower alkenes are dehydrogenated to give aromatic hydrocarbons by the action of zinc ions. They can be transformed into alkanes and aromatics through hydride-transfer reactions by the action of protons.

It is thus clear that both protons and zinc cations have two adverse effects on the aromatization of methanol. Protons are essential to form alkenes from methanol. At the same time, they catalyse hydride transfer to promote the formation of alkanes, and this leads to a reduction in the yield of aromatics. Zinc ions are important as a catalyst for the dehydrogenation of alkenes to give aromatics, but their presence in excess promotes the decomposition of methanol. It therefore seems essential to achieve an appropriate balance between the two catalytic species, zinc cations and protons, in the zeolite structure in order to obtain the highest yield of aromatic hydrocarbons from methanol.

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