Olefin Hydrogenation over ZSM-5 Type Zeolite Catalysts Modified with Alkaline Earth Metals

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Synopsis. Olefin hydrogenation was carried out over ZSM-5 type zeolite catalysts modified with various alkaline earth metals. It was found that the catalytic activity of H-ZSM-5 for the olefin hydrogenation decreases upon such a modification.

Several papers have claimed that alumina, silica-alumina gels, and crystalline aluminosilicates (mordenite) are effective for the hydrogenation of ethylenic double bonds.[1-5)] Recently, our previous communications have dealt with the conversion of the synthesis gas to hydrocarbons in a two-stage system consisting of a methanol synthesis reactor, followed by a hydrocarbon-forming reactor containing H-ZSM-5 zeolite. It has also been shown that the H-ZSM-5 zeolite catalyst is active for olefin hydrogenation.[6,7)]

In this paper, it will be shown that the activity of the H- ZSM-5 zeolite catalyst in the olefin hydrogenation decreases when it is modified with alkaline earth metals.

Experimental

The H-ZSM-5 catalysts modified with alkaline earth metals were synthesized hydrothermally from ZSM-5 zeolite in the presence of alkaline earth metal acetates. Crystallization was carried out in a 300 ml stainless steel autoclave at 150—160 °C for 15—24 h. The precipitate was filtered off, washed thoroughly with distilled water, and calcined at 500 °C for 15 h in order to remove an organic base. It was then protonated in a hydrochloric acid solution of 1 M (1 M=1 mol dm^{-3}) and calcined in air at 500 °C for 6 h. Some analytical data are given in Table 1. The synthetic alkaline earth metal-modified ZSM-5 catalyst had a well defined ZSM-5 type structure, as demonstrated by the X-ray powder diffraction pattern.

Table 1. Preparation of various alkaline earth metal-modified H-ZSM-5 type zeolite catalysts

Catalyst	Atomic ratios[a)] Si/Al	Alkaline earth metal/Al	BET surface area (m^2 g^{-1})
1. H-ZSM-5	120		342
2. Mg-H-ZSM-5	94	1.30	336
3. Ca-H-ZSM-5	117	1.63	341
4. Sr-H-ZSM-5	93	1.29	301
5. Ba-H-ZSM-5	90	1.35	301
6. Silicalite[b)]	—		345

a) Determined by X-ray fluoresence spectrometry.
b) Prepared from tetraethoxysilane.

The silicalite and silica gel used were prepared as follows. The silicalite was synthesized from tetraethoxysilane in the method described above. The silica gel was obtained by the hydrolysis of tetraethoxysilane. The precipitate was filtered off, dried at 100 °C, and then calcined at 500 °C for 10 h.

Hydrogenation was carried out at 400 °C and at a space velocity (SV) of 5000 h^{-1} under 40 kg cm^{-2}, using a high-pressure fixed-bed system. The reaction gas was composed of 2.5 mol% C_2H_4 (or C_3H_6), 50 mol% H_2, and 47.5 mol% Ar. The catalyst was packed into a quartz tube reactor, which was set in the pressure vessel. The effluent gas was led directly to sampling valves of a Yanaco AG-1000TFH auto gas chromatograph for analysis. The ethylene (or propylene)-based yields of the products were calculated by using argon as the internal standard.

The temperature programmed desorption (TPD) spectra of NH_3 over various catalysts were measured using a conventional TPD apparatus. The measurement was done from 100 °C to 600 °C with a heating rate of 5 °C min^{-1} and with nitrogen as the carrier gas (flow rate, 100 ml min^{-1}). The catalyst charged was 0.30 g.

Results and Discussion

Figure 1 shows some typical results for the hydrogenation of ethylene or propylene over various alkaline earth metal-modified ZSM-5 catalysts. The shaded parts in Fig. 1 indicate C_2 to C_5 olefins. Products both lower and higher in molecular weight were formed through a variety of reactions, such as polymerization, isomerization, cracking, and hydrogenation. The yields of light olefins and higher-carbon-number hydrocarbons (C_6^+) increased in the following order: H-ZSM-5≈Mg-H-ZSM-5<Ca-H-ZSM-5<Sr-H-ZSM-5<Ba-H-ZSM-5. In the case of the C_2H_4 (or C_3H_6)-H_2 system over these catalysts, hardly no aromatic hydrocarbons(BTX) were obtained as compared with those obtained in the C_2H_4 (or C_3H_6)-He system over the H-ZSM-5 catalyst (self-hydrogenation). In addition, the hydrogenation of these olefins was carried out over silicalite and silica gel of a very high purity. However, these olefins were hardly hydrogenated at all over these catalysts.

The TPD spectra of H-ZSM-5 zeolite exhibited two peaks, whose temperatures at the peak maximum were about 170 and 450 °C. By the addition of alkaline earth metals, the amount of desorbed NH_3 above 350 °C, which corresponded to that of the second peak, of various catalysts decreased in the following order: H-ZSM-5>Ca-H-ZSM-5>Mg-H-ZSM-5>Sr-H-ZSM-5>Ba-H-ZSM-5. In Fig. 2 are plotted the molar ratios of the C_2 to C_5 paraffins (C_2^-—C_5^-) to the C_2 to C_5 olefins ($C_2^=$—$C_5^=$) over these catalysts (given in Fig. 1) against the normalized amount of desorbed NH_3 [based on that of H-ZSM-5]. Except for Mg-H-ZSM-5, the (C_2^-—C_5^-)/($C_2^=$—$C_5^=$) molar ratio decreased as the amount of

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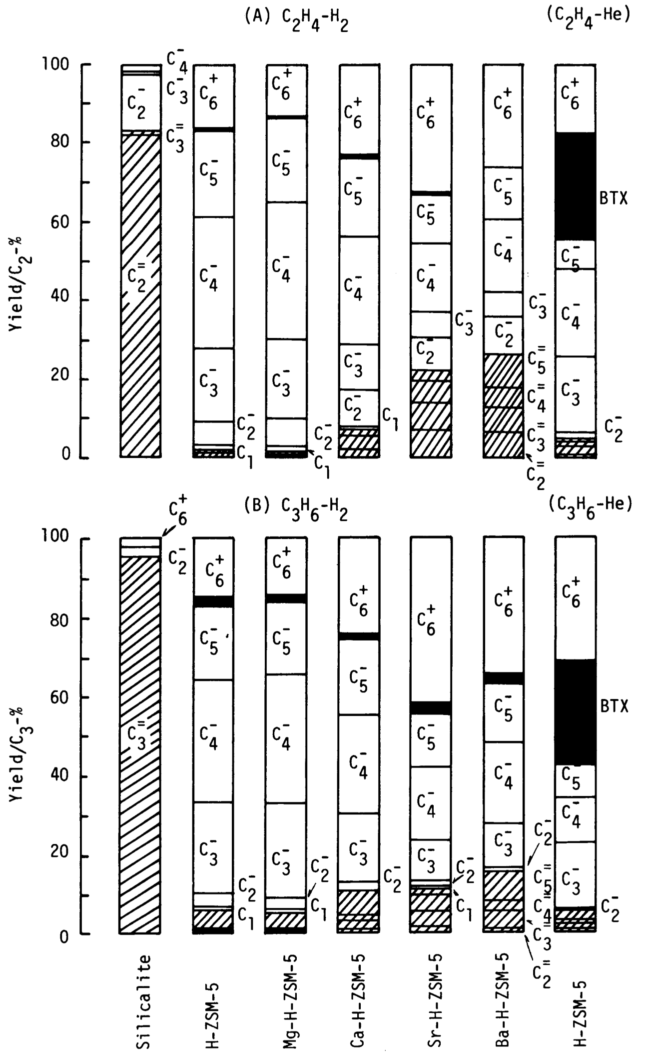

Fig. 1. Olefin hydrogenation over ZSM-5 type zeolite catalysts modified with various alkaline earth metals. Reaction conditions: $P=40$ kg cm^{-2}, $T=400$ °C, SV $=5000$ h^{-1}
Shaded parts indicate C_2 to C_5 olefins.

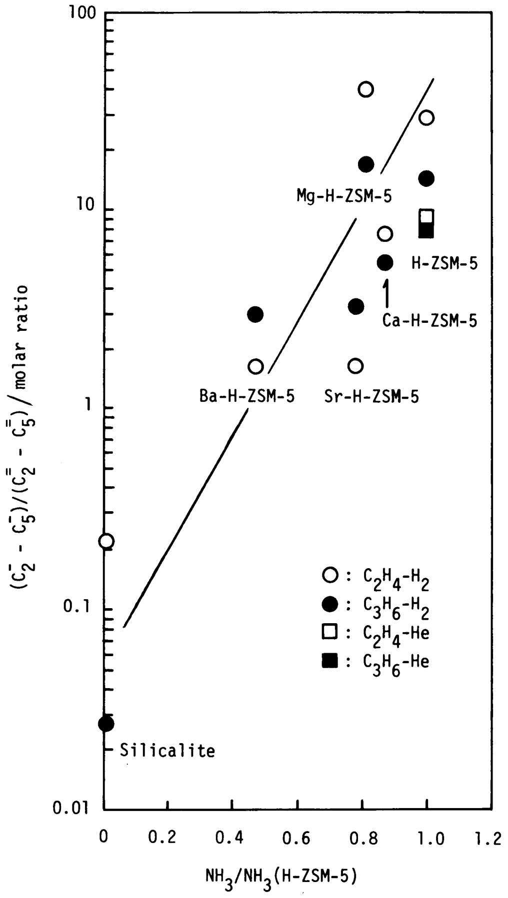

Fig. 2. Relation between the (C_2^-—C_5^-)/($C_2^=$—$C_5^=$) molar ratio and the amount of desorbed NH_3 of various catalysts. (C_2^-—C_5^-):C_2 to C_5 paraffins, ($C_2^=$—$C_5^=$): C_2 to C_5 olefins.

desorbed NH_3 decreased, namely, the basicity of alkaline earth metal increased. The temperature at the peak maximum of the second peak of the Mg-H-ZSM-5 catalyst hardly differed from that of H-ZSM-5.

Moreover, the impurities presented in the H-ZSM-5 zeolite were carefully analyzed by means of X-ray fluoresence spectrometry and inductively coupled argon plasma emission spectrometry. Only a trace amount of Fe (0.0065 wt%) was detected. The other metals were far below the detection limit of the inductively coupled argon plasma emission spectroscope (Shimadzu ICPS-50).

From these results, it can be concluded that the olefins are hydrogenated on the acidic sites of the H-ZSM-5 zeolite catalyst and that this hydrogenation activity decreases upon modification with alkaline earth metals.

The increase in the C_6^+ yield over the catalyst modified with alkaline earth metals may be attributed to the occurrence of the other reactions, such as polymerization, isomerization, and cracking, which take place in preference to the hydrogenation.

The limited data of the present work can not serve to clarify the detailed mechanism of this alternation of the acid property in zeolites.

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