Skeletal isomerization of 1-butene into isobutene over Mg-ZSM-22 modified by the deposition of silicon alkoxide

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Received 28 November 1997; accepted 9 April 1998

Mg-ZSM-22, modified by the deposition of silicon ethoxide, was prepared and investigated as a catalyst for the skeletal isomerization of 1-butene to isobutene in a fixed-bed flow reactor. The prepared catalysts were characterized by XRD, TPD, SEM-EDX, ICP and FT-IR. The deposition of silicon alkoxide on Mg-ZSM-22 led to a decrease in the amount of strong acid sites, confirmed by TPD experiments with ammonia and γ-collidine. The treatment also affected the size of pore opening, as evidenced by constraint index measurement and chemisorption experiment using n-hexane. As the deposition time increased, the conversion of 1-butene decreased as the result of reduced acidity, while selectivity to isobutene increased. The deposition of silicon alkoxide resulted in the suppression of side reactions and coke deposition, thus enhancing the skeletal isomerization. The modification of Mg-ZSM-22 by deposition of silicon alkoxide was very effective in terms of catalytic stability and coke removal.

Keywords: skeletal isomerization, isobutene, silicon alkoxide, Mg-ZSM-22

1. Introduction

Isobutene is a valuable raw material for the synthesis of MTBE (methyl *tert*-butyl ether) and TBA (*tert*-butyl alcohol) [1,2]. Since the demand for isobutene has continuously increased, the skeletal isomerization of n-butenes to isobutene has emerged as an attractive route.

A number of reports have appeared recently, dealing with this conversion over γ-alumina [3,4] and various zeolites [5–7]. Acidity, pore size, and pore structure of catalyst are all known to be very important parameters for this reaction [8,9].

The effective selectivity obtained using zeolite as a catalyst can be improved by decreasing the number of unselective active sites. Coke formation on the external surface represents a very serious problem. Therefore, poisoning or blocking the external surface could lead to enhanced selectivity and stability. Many papers [10–12] have reported improvements in selectivity via the poisoning of the external surface of zeolite, which are not responsible for the shape selectivity. In addition, it has been reported that the inactivation of the external surface is essential in order to achieve high selectivity for olefin [13] and acetylene hydrogenation [14].

Based on our previous work [15,16], which reported the skeletal isomerization of 1-butene over Mg-ZSM-22, the strong acid sites of Mg-ZSM-22, on which coke is mainly formed, exist largely on the external surface of the catalyst, and side reactions, such as dimerization and cracking, also take place on those same sites. In this study, Mg-ZSM-22 was modified by deposition of silicon alkoxide in order to inactivate the external surface and the resulting catalysts were evaluated in terms of the skeletal isomerization of 1-butene.

2. Experimental

2.1. Catalysts preparation

K-ZSM-22 was prepared by a hydrothermal method, as previously described in the literature [17]. The synthesized K-ZSM-22 was then ion-exchanged three times with a 0.01 M aqueous $Mg(NO_3)_2$ solution at 80 °C. The resultant Mg-ZSM-22 was filtered, washed, and then calcined at 500 °C for 4 h under a helium flow of 30 ml/min.

In order to modify the external surface, Mg-ZSM-22 was treated by the deposition of silicon ethoxide. The alkoxide was kept in a liquid reservoir at 50 °C, and nitrogen gas was bubbled through the solution. The bubbled nitrogen was then fed to the bed of catalyst. The sample became gray after treatment as the result of carbonaceous deposit. Because of this, the modified catalyst was calcined under a flow of O_2 at 450 °C in order to remove the coke. Sample names for modified Mg-ZSM-22 catalysts are abbreviated according to the treatment time: for example, 2H refers to Mg-ZSM-22 treated with silicon alkoxide for 2 h.

2.2. Characterization

The crystallinity of the prepared catalysts was confirmed by XRD (Rigaku, D/Max 11-A) analysis using Cu Kα as a radiation beam.

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The surface area and pore volume of the catalysts was measured with a BET surface analyzer (Micromeritics ASAP-2000).

The acid amounts and strengths of the catalysts were determined by TPD of ammonia and γ-collidine (trimethyl pyridine), which was carried out using methods described previously [15].

The amount of carbon deposited on the catalysts used was determined by the CHNO analysis method [18].

Elemental analyses were carried out on a Perkin-Elmer P-40 inductively coupled plasma atomic emission spectrophotometer (ICP-AES). The samples were dissolved in hydrofluoric acid, heated by microwave treatment, and then digested in a teflon-lined chamber.

The surface composition of the modified samples was determined by SEM-EDX using Jeol JSM-840A.

Chemisorption experiments were performed in a conventional glass vacuum system using n-hexane as an adsorbate. Catalyst samples of 0.4 g were placed in a quartz adsorption cell and pretreated using nitrogen at a rate of 50 ml/min at 400 °C for 1 h, and then cooled to room temperature. After the samples were evacuated, 0.4 kPa of n-hexane was dosed.

Constraint indices (CI) were measured in a fixed-bed reactor to confirm the contraction of pore opening by the deposition of silicon alkoxide. The catalysts were preheated at 400 °C in a helium flow for 1 h. After adjusting the temperature to 315 °C, the 50 : 50 mixture of n-hexane and 3-methylpentane was injected, and after 10 min reaction the products were analyzed by a gas chromatograph.

2.3. Catalysis

Cracking of 1,3,5-triisopropylbenzene (TIPB) was carried out in a fixed-bed reactor by pulse injection. The catalysts were pretreated by heating at 400 °C in a helium flow for 1 h. After adjusting the temperature to 350 °C, the reactant was injected, and the obtained products were analyzed by a gas chromatograph.

The skeletal isomerization of 1-butene was also carried out in a fixed-bed flow reactor. The catalysts were heated from room temperature to 500 °C at a rate of 10 °C/min under a helium flow of 20 ml/min, and then preheated at 500 °C for 1 h. After adjusting the temperature to 450 °C, 1-butene was fed to the reactor at a rate of 5 ml/min. The products were analyzed by gas chromatography using FID with a HP-PLOT/γ-alumina capillary column.

For purposes of this study, *trans*- and *cis*-2-butene were both regarded as reactants, because an equilibrium between 1-butene and the 2-butenes was established at the reaction temperature range.

3. Results and discussion

3.1. Characterization of modified catalysts

XRD analyses were carried out before and after modification. No significant change was observed. SEM photographs were also taken before and after modification, and no noticeable differences between them were observed. These experiments confirm that the crystallinity and morphology of the catalysts were not changed by the deposition of silicon alkoxide.

Figures 1 and 2 represent the TPD spectra of Mg-ZSM-22 and 2.5H, using ammonia and γ-collidine (trimethyl pyridine) as adsorbates, respectively. Since the molecular size of γ-collidine is much larger than that of ammonia, it is difficult for γ-collidine to diffuse into the pores of Mg-ZSM-22. Therefore, and as expected, the amount of γ-collidine adsorbed was considerably less than that of ammonia. γ-collidine appears to be mainly adsorbed on the external surface of Mg-ZSM-22. In comparing the NH_3

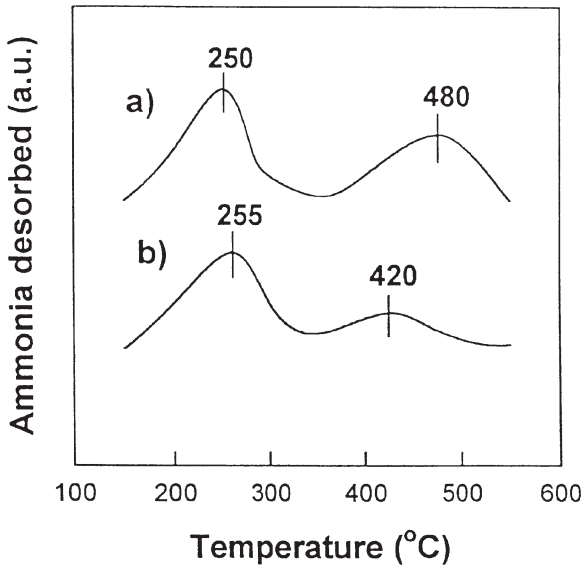

Figure 1. Temperature-programmed desorption of ammonia: (a) Mg-ZSM-22, (b) 2.5H.

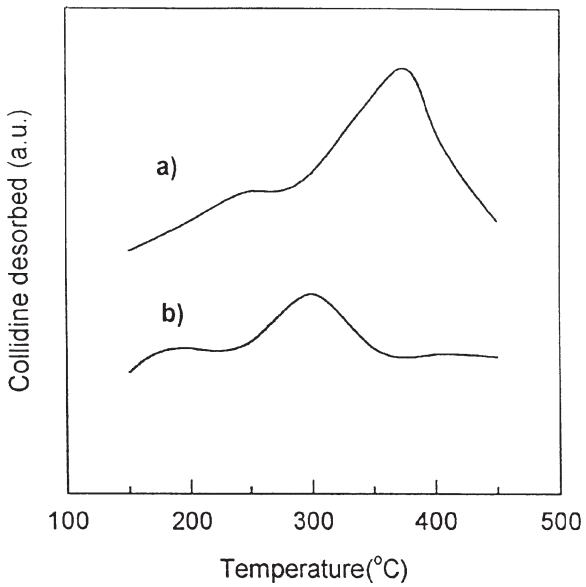

Figure 2. Temperature-programmed desorption of γ-collidine: (a) Mg-ZSM-22, (b) 2.5H.

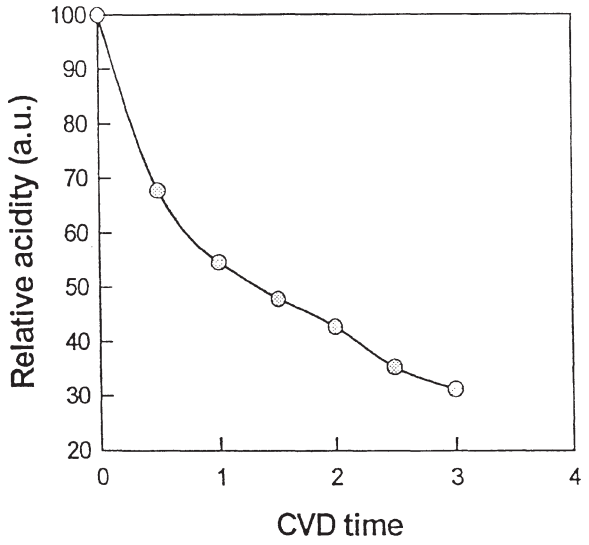

Figure 3. The relative external acidity of modified catalysts as a function of deposition time.

TPD peak of fresh Mg-ZSM-22 with that of 2.5H, it is clear that the large number of strong acid sites in the fresh catalyst are reduced after this modification. The γ-collidine TPD profile also shows that the area around 370 °C decreased significantly and that the peak shifted to a lower temperature of about 300 °C after the deposition of silicon alkoxide. The relative acidity of the external surface of the modified Mg-ZSM-22 calculated based on the results of γ-collidine TPD is shown in figure 3 as a function of treatment time. The relative external acidity rapidly decreased with increasing deposition time. For the case of sample 3H, about 70% of the external acidity was inactivated, as compared to untreated Mg-ZSM-22. Our previous work [15,16] showed that the strong acid sites were located mainly on the surface of Mg-ZSM-22, and that a reduction in the strong acid sites led to a high selectivity to isobutene and an enhanced stability of Mg-ZSM-22. Niwa et al. [19], who reported the modification of H-mordenite by a CVD method, proposed that the deposition of silicon alkoxide resulted in only the contraction of the pore opening, but that there was no reduction in acid sites. In the case of Mg-ZSM-22, however, because the strong acid sites are located mainly on the surface, the external acidity was inactivated by the deposition of silicon alkoxide, as was confirmed by TPD analyses.

The bulk compositions of the Mg-ZSM-22 materials were analyzed by the inductively coupled plasma (ICP) method and the surface compositions by SEM-EDX. Table 1 shows the ratios of silicon to aluminum in bulk and on the surface of modified Mg-ZSM-22. No noticeable difference between the surface and bulk composition of unmodified Mg-ZSM-22 is evident. However, the difference between them rapidly increased with increasing deposition time, and, as a result, the surface acidity was reduced in proportion to the degree of deposition. Aluminum was not detected when the deposition time exceeded 2 h. This suggests that the silica layer gradually covers the surface of the Mg-ZSM-22 catalyst with increasing deposition time and completely covers it for deposition in excess of 2 h.

Table 1
The ratio of silicon to aluminum in the bulk and on the surface of catalysts with respect to treatment time.

CVD time (h)	Bulk Si/Al	Surface Si/Al
0	43.9	39.5
0.5	46.3	57.3
1	48.2	72.4
1.5	45.4	80.7
2	50.1	94.2
2.5	47.3	∞
3	48.8	∞

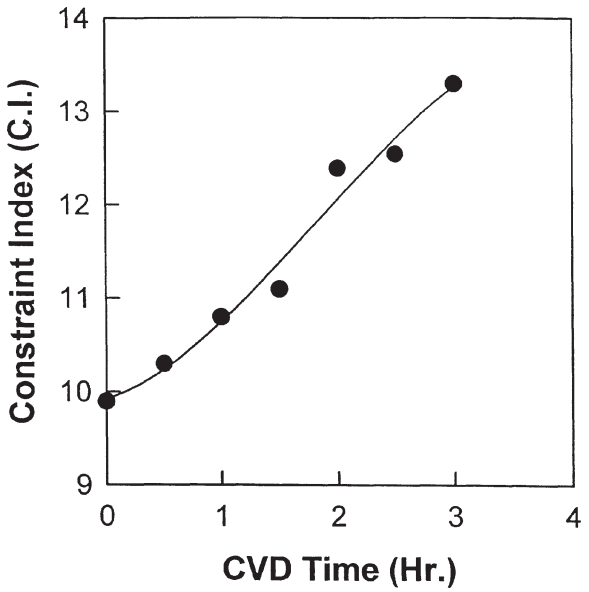

Figure 4. The variation of the constraint indices (CI) of modified catalysts at 315 °C as a function of deposition time.

In order to elucidate the influence of deposition on the size of pore opening, constraint index (CI), defined as the ratio of cracking rate of n-hexane to that of 3-methylpentane, was measured using the mixture of n-hexane and 3-methylpentane as a reactant at 315 °C. Figure 4 shows constraint indices of modified catalysts as a function of deposition time. The measured value of untreated Mg-ZSM-22 was about 9.9 but the CI value increased with the deposition time, as shown in figure 4. These results mean that the size of pore opening of Mg-ZSM-22 was reduced with deposition time.

The contraction of pore opening was also confirmed by a chemisorption experiment using n-hexane as an adsorbate.

The rate of adsorption can be expressed by the following equation [20]:

$$V_{\mathrm{e}} \ln\bigl(V_{\mathrm{e}}/(V_{\mathrm{e}} - V)\bigr) - V = kt,$$

where V and V_{e} represent the amount adsorbed at time t and at equilibrium, respectively, and k is the rate constant for the adsorption. The rate constant for adsorption can be readily obtained from the slope of the linear plot of

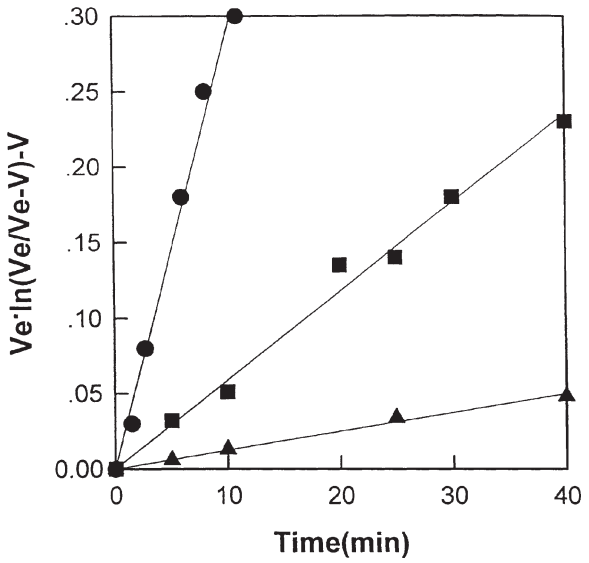

Figure 5. Plots for the rate of n-hexane adsorption over modified catalysts: (●) Mg-ZSM-22, (■) 1.5H, (▲) 3H.

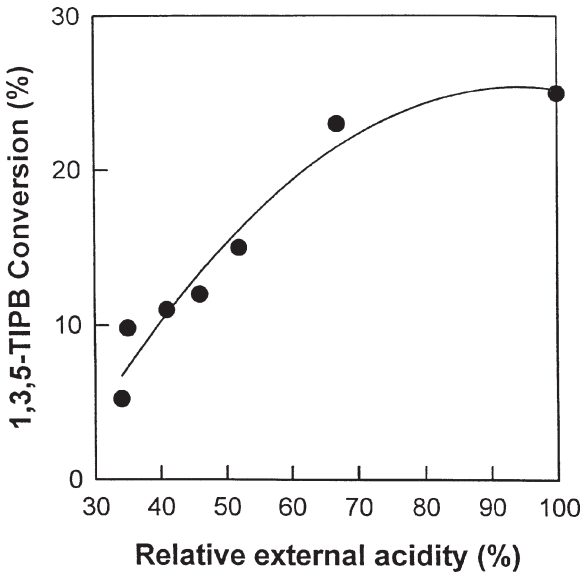

Figure 6. The conversion of 1,3,5-TIPB with respect to the relative external acidity.

the above equation. The linear plots of modified catalysts for n-hexane are shown in figure 5. As the deposition time increases, the rate constant decreases greatly, indicating that the silicon alkoxide is adsorbed on the external acid sites, thus affecting the diffusion of n-hexane. On the other hand, the adsorption amounts of n-hexane at equilibrium were unchanged by the deposition of silicon alkoxide (V_e = 2.46–2.61 mmol/g). From the adsorption results, it can be concluded that the deposition of silicon alkoxide reduces the external acidity and contracts the pore opening.

3.2. 1,3,5-TIPB cracking

1,3,5-TIPB cracking tests were performed in order to measure the strong acid sites on the external surface of modified Mg-ZSM-22. Since its kinetic diameter (approximately 8.5 Å) is larger than the pore size of Mg-ZSM-22, cracking appears to take place only on the external surface of Mg-ZSM-22. Namba et al. [21] also proposed that the cracking of 1,3,5-TIPB takes place in the same manner on the external surface of ZSM-5.

The conversion of 1,3,5-TIPB was plotted with the relative amounts of external acid sites in figure 6. It increased with increasing the relative amounts of external acid sites. The external surface is gradually poisoned with deposition of silicon alkoxide, as confirmed by the results of γ-collidine TPD (figure 3), resulting in the reduction of cracking activity for 1,3,5-TIPB.

3.3. Skeletal isomerization of 1-butene

Figure 7 shows the effect of deposition temperature on 1-butene conversion and isobutene selectivity. The conversion of 1-butene decreased, and isobutene selectivity increased with increasing deposition temperature over the range of 100–400 °C at the early stage of reaction. The

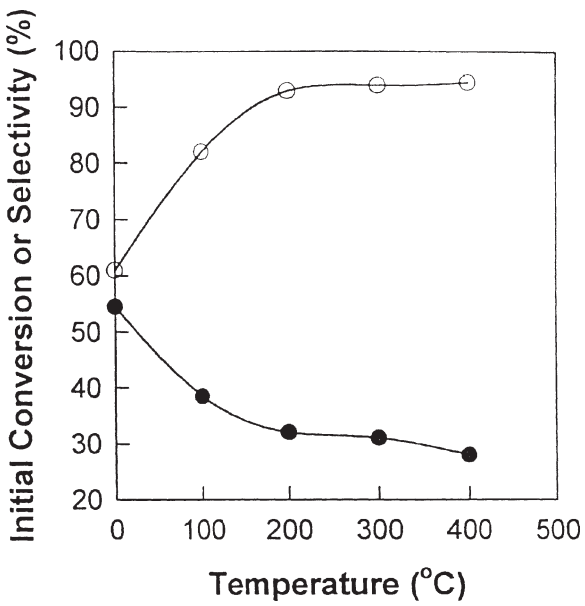

Figure 7. 1-butene conversion and isobutene selectivity as a function of deposition temperature: (●) 1-butene conversion, (○) isobutene selectivity.

highest isobutene yield was realized when the Mg-ZSM-22 was modified with silicon alkoxide at 200 °C. In addition, it exhibited much better catalytic stability than unmodified Mg-ZSM-22.

The conversions and product distribution at the initial stage of reaction over the modified catalysts with respect to deposition time are shown in table 2. The conversion of 1-butene decreased with increasing deposition time, as the result of reduced acidity, while the selectivity to isobutene was enhanced by the modification. The main byproducts over unmodified Mg-ZSM-22 were C_3 and C_5 hydrocarbons, which were probably formed as the result of dimerization and subsequent cracking on the strong acid sites

Table 2
1-butene conversion and product distribution over modified Mg-ZSM-22 with respect to CVD time.

Catalyst	Conversion (%)	Selectivity (mol%)				
		$C^{2=}$	$C^{3=}$	C^4	i-$C^{4=}$	C^{5+}
Mg-ZSM-22	54.7	1.4	17.4	4.6	61.2	12.7
0.5H	47.5	–	10.8	1.0	83.4	4.7
1H	39.7	–	7.4	–	90.3	2.1
2H	32.6	–	5.3	1.0	92.1	1.7
3H	27.4	–	5.5	–	93.4	0.8

Table 3
The amount of coke deposition, percentage deactivation, and recovery factor with respect to deposition time.

Catalyst	Coke amount (wt%)	Percentage deactivation (%)	Recovery factor (%)
Mg-ZSM-22	2.54	37.4	24.5
0.5H	1.32	18.6	63.2
1H	0.89	12.1	67.3
1.5H	0.87	9.4	72.5
2H	0.65	5.7	69.8
2.5H	0.68	5.5	78.7
3H	0.59	4.7	81.5

which contained sufficient space around them to permit this. Xu et al. [22] reported that all side reactions in the skeletal isomerization of n-butene are largely controlled by two factors, i.e., acidity and limitation of pore opening. The data listed in table 2 clearly show that the deposition of silicon alkoxide suppresses side reactions. As described earlier, the deposition of silicon alkoxide affects both the acidity and the pore opening of Mg-ZSM-22. Therefore, both the selective poisoning of strong acid sites and spatial constraints result in reduced side reaction and enhanced isobutene selectivity.

It was also observed that catalytic stability was greatly enhanced by the deposition of silicon alkoxide. Table 3 shows the amount of coke deposition after a 10 h reaction, the percentage deactivation, and the recovery factors of modified catalysts. The percentage deactivation was defined as the ratio of the drop in conversion by deactivation after a 10 h reaction to the initial conversion, and recovery factors were defined in this work by the ratio of the amount of coke removed by calcination under an O_2 flow at 550 °C to the amount of coke deposited after a 10 h reaction. The amount of coke deposition and the percent deactivation decreased rapidly with increasing deposition time, while the recovery factor increased. These results are due mainly to the reduced strong acid sites, as confirmed by the TPD analyses. The strong acid sites of zeolites lead to, not only side reactions, but also rapid coke formation which may be an important factor in the deactivation of zeolites in hydrocarbon related processes.

The deposition of silicon alkoxide resulted in the suppression of side reactions and coke deposition, thus enhancing skeletal isomerization, and was very effective in terms of catalytic stability and coke removal, as is shown in table 3.

4. Conclusions

The modification of Mg-ZSM-22 by the deposition of silicon alkoxide led to the selective removal of strong acid sites and the contraction of pore opening without altering the crystallinity. The cracking activity of 1,3,5-TIPB decreased with increasing deposition time, as a result of reduced acidity of the external surface of Mg-ZSM-22. The enhanced selectivity to isobutene appears to be the result of inactivation of strong acid sites and narrowing of the pore opening. The highest isobutene yield was obtained when Mg-ZSM-22 was modified with silicon alkoxide at 200 °C.

Catalytic stability was also greatly enhanced by the deposition of silicon alkoxide. Carbonaceous deposits on the modified Mg-ZSM-22 were easily removed and did not pose a significant problem.

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