

High Selective Skeletal Isomerization of 1-Butene over Phosphorus-Modified Silica-Alumina

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Abstract—Silica-alumina catalysts modified with different loadings of phosphorus have been used for the skeletal isomerization of 1-butene to investigate the effects of the phosphorus modification on the conversion of 1-butene and the selectivity for *iso*-butene. Increasing the phosphorus loading led to a decrease in conversion of 1-butene over phosphorus-modified silica-alumina catalysts, while the selectivity for *iso*-butene increased. Silica-alumina catalyst with phosphorus of 9.8 wt% showed an extremely high selectivity for *iso*-butene. The results of NH_3 -TPD, adsorption-desorption behavior of 1-butene and TG analysis of used catalysts indicate that the considerable decrease of strong acid sites by phosphorus modification causes the high selectivity for skeletal isomerization of 1-butene.

Key words : 1-Butene, Skeletal Isomerization, Silica-Alumina, Phosphorus Modification, Monomolecular Reaction

INTRODUCTION

Skeletal isomerization of 1-butene to *iso*-butene over acid catalysts is an interesting research topic because of the distinct difference in selectivity according to the kind of catalyst. Ferrierite [Mooiweer et al., 1994], clinoptilolite [Seo et al., 1998c], MCM-22 [Asensi et al., 1996], aluminophosphate [Gielgens et al., 1995a], $\text{F}/\text{Al}_2\text{O}_3$ [Lee et al., 1997; Seo et al., 1998a], $\text{WO}_3/\text{Al}_2\text{O}_3$ [Gielgens et al., 1995b] and mesoporous material [Seo et al., 1999] catalysts are reported to exhibit a high selectivity for skeletal isomerization producing *iso*-butene. On the other hand, the selectivity for *iso*-butene is very low over catalysts such as ZSM-5 [Seo et al., 1997], mordenite, beta [Seo et al., 1998b] zeolites and silica-alumina [Butler and Nicolaides, 1993; Kim et al., 1998] catalyst.

It is generally acceptable to explain the difference in the selectivity for *iso*-butene by pore structures of ferrierite, clinoptilolite and ZSM-5 zeolites [Seo et al., 1997, 1998c], but it is not proper for amorphous catalysts such as silica-alumina, alumina and mesoporous material. Based on the results of molecular simulations of 1-butene adsorption in ferrierite, we suggested that the high selectivity for *iso*-butene on ferrierite was due to the suppression of dimerization of activated 1-butene molecules in the specifics of its pore structure [Seo et al., 1996]. If the distribution of activated 1-butene molecules on the catalyst surface were a primary factor determining the selectivity for *iso*-butene, the high selectivities of zeolite, amorphous and mesoporous material catalysts could be explained by the same reason.

It is widely known that zeolite modified with phosphorous exhibits the reduction of strong acid sites [Kaeding et al., 1981;

Seo et al., 1990]. If silica-alumina shows a poor selectivity for *iso*-butene due to its high concentration of acid sites, the phosphorous modification gives rise to the enhancement of selectivity by reducing its strong acid sites. In this paper, we report variations in the selectivity for the skeletal isomerization of 1-butene with the loading of phosphorus over silica-alumina catalyst. The differences in the coke deposition and the adsorption-desorption behavior of 1-butene along the loading of phosphorus of silica-alumina catalysts are also discussed relating to the selectivity for *iso*-butene.

EXPERIMENTAL

Silica-alumina (Al content ; 13 wt%, designated as SA) was obtained from Davidson Co. of USA. The surface area and the average pore diameter of SA were measured from the adsorption of nitrogen at -196°C (Micromeritics, ASAP-2400), and were $340\text{ m}^2\cdot\text{g}^{-1}$ and 98 \AA , respectively. The SA modified with phosphorus oxide, designated as SA-P, was prepared by impregnation of SA with aqueous ammonium dihydrogen phosphate (Wako, 98 %) solution followed by drying at 110°C for 2 h and calcined at 550°C for 5 h in an air stream. The loading amounts of phosphorus of the SA-P catalysts were determined by ICP (Jobin Yvon Co., JY. 38 plus, Korea Basic Science Institute) after digestion of the samples using aqueous hydrofluoric acid, and were denoted as SA-P(x); x in the parentheses indicates the amount of phosphorus loaded in wt%.

The apparatus and procedure for the measurement of the temperature-programmed desorption of ammonia (NH_3 -TPD) are described in the literature [Seo et al., 1996].

The adsorption-desorption behaviors of 1-butene on SA and SA-P (9.8) catalysts were measured by a gravimetric apparatus equipped with a quartz spring [Seo et al., 1998a]. The catalyst of 0.2 g was evacuated at 400°C for 1 h, and then

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exposed to 30.4 kPa of 1-butene at 30 °C. The weight change of the catalyst was recorded during the adsorption-desorption process of 1-butene.

The weight loss of the used catalyst was recorded under an oxygen flow with a thermogravimetric analyzer (TA Instruments, TGA 2050) to compare the amount of carbon deposit.

The apparatus and procedure for the skeletal isomerization of 1-butene are described in the literature [Seo et al., 1996]. The conversion was calculated in terms of mole percent of 1-butene consumed and selectivity for *iso*-butene in terms of the yield of *iso*-butene divided by the conversion of 1-butene. 2-Butenes were not considered as products, since the isomerization between 1-butene and 2-butene is much faster than the skeletal isomerization and 2-butenes can also be converted into *iso*-butene.

RESULTS AND DISCUSSION

Fig. 1 shows the conversions of 1-butene and selectivities for *iso*-butene at 450 °C on SA catalysts with different loading amounts of phosphorus. The conversion decreases with an increase in the loading level of phosphorus. SA-P (9.8) catalyst with a high level of phosphorus loading shows the lowest conversion, while the conversion of unmodified SA catalyst has the highest conversion. On the other hand, the selectivity for *iso*-butene of SA-P (9.8) catalyst is very high, as much as 98 %. The decrease of the conversion and the increase of the selectivity according to the time on stream were observed on SA and SA-P (2.6) catalysts. However, there is no remarkable change in the conversion or selectivity over the SA-P (9.8) catalyst.

The profiles of NH₃-TPD are distinct from the loading amount of phosphorus on SA. Fig. 2 shows that the amount of ammonia desorbed above 250 °C in the profiles of NH₃-TPD decreases with an increase in the loading level of phospho-

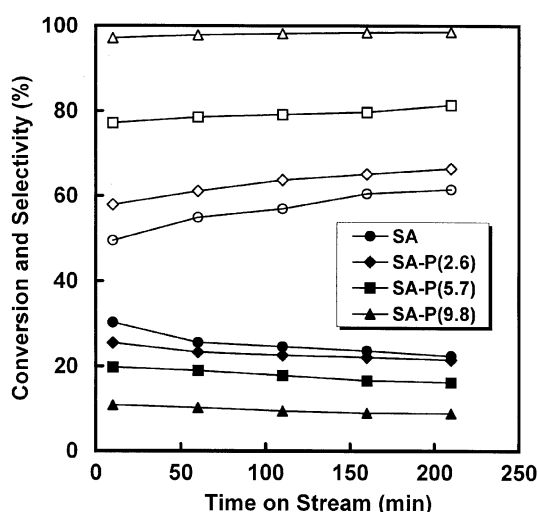


Fig. 1. The time dependences in the conversions (closed) and the selectivities (open) for *iso*-butene in the skeletal isomerization over SA and SA-P(x) catalysts. Reaction temperature=450 °C, $P_{1\text{-butene}}$ =31.5 kPa, WHSV=3.1 h⁻¹.

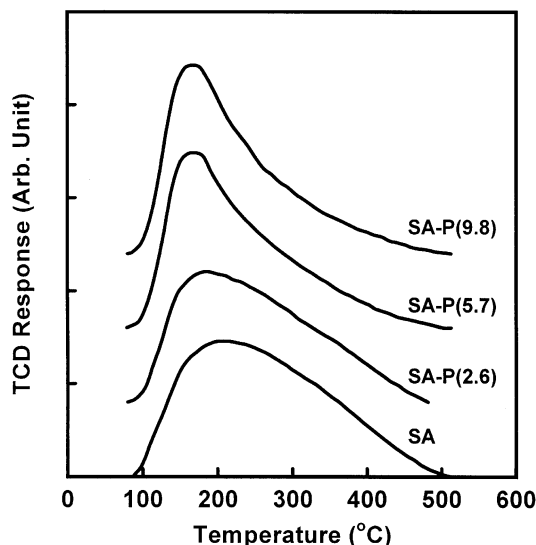


Fig. 2. NH₃-TPD profiles from SA and SA-P(x) catalysts.

rus. On the other hand, the amount of ammonia desorbed at about 150 °C corresponding to the physisorbed ammonia, increases with increasing the loading level of phosphorus. The number of strong acid sites was decreased by phosphorus modification, while that of weak acid sites was increased. This is a well-known phenomenon observed in phosphorus-modified HZSM-5 zeolite, due to the formation of weak acid sites by phosphorus oxide [Kaeding et al., 1981]. Since SA catalyst is amorphous and heterogeneous compared with crystalline zeolite, it is not completely correct to discuss the acidities of SA-P(x) catalysts from NH₃-TPD results only. However, the decrease in the amount of strong acid sites with increasing the loading amount of phosphorus is clear.

The conversion of 1-butene and the selectivity for *iso*-butene on the SA catalyst vary with the charging amount of catalyst as shown in Fig. 3. The conversion increases with increasing the charging amount of SA catalyst, while the change in the conversion on SA-P (9.8) catalyst is negligible. The selectivity on SA catalyst decreases significantly with increasing the charging amount, while that of SA-P (9.8) catalyst shows a very high value of 95 % or above, irrespective of the charging amount of catalyst. This finding indicates that the preferable reactions of SA-P (9.8) catalyst are different from those of SA catalyst.

Fig. 4 shows the adsorption-desorption behavior of 1-butene on SA and SA-P (9.8) catalysts at 30 °C. 1-Butene is adsorbed only slightly over SA-P (9.8) catalyst, and is also desorbed quickly, even by evacuation at the same temperature. On the other hand, a large amount of 1-butene is adsorbed on SA catalyst, and about 50 % of the adsorbed 1-butene is retained after evacuation. The differences in the adsorbed amount of 1-butene and the reversibility of the adsorption-desorption process reveal that the adsorbed states of 1-butene are not the same on SA and SA-P (9.8) catalysts.

Fig. 5 shows the results of the TG analysis at a range of 200-650 °C under an oxygen atmosphere for catalysts used in the 1-butene reaction at 450 °C for 210 min. The weight loss is different for the loading level of phosphorus. The weight

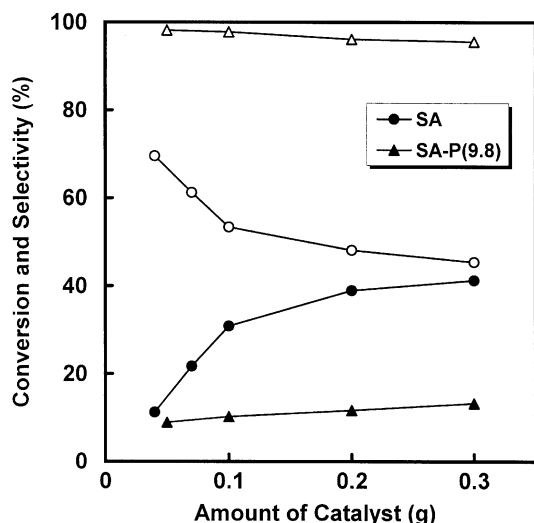


Fig. 3. Variations of the conversion (closed) and the selectivity (open) for *iso*-butene with the charging amount of SA and SA-P (9.8) catalysts in the skeletal isomerization of 1-butene.

Reaction temperature=450 °C, $P_{1\text{-butene}}$ =31.5 kPa, WHSV=3.1 h⁻¹.

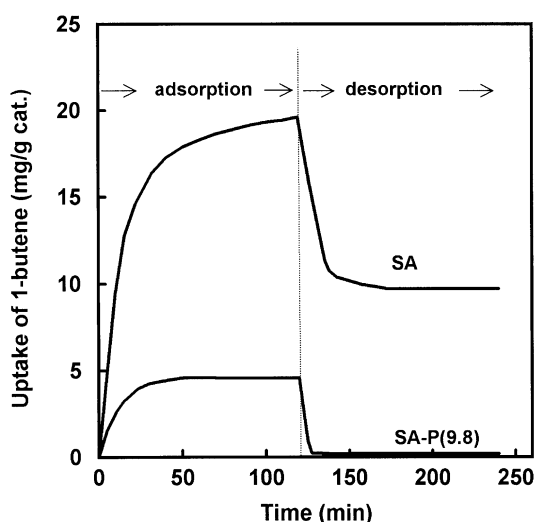


Fig. 4. Adsorption-desorption behaviors of 1-butene over SA and SA-P (9.8) catalysts at 30 °C. Catalysts are exposed to 30.4 kPa of 1-butene during the adsorption process.

loss relating the amount of carbon deposit is large for the used SA catalyst, while it is negligible for used SA-P (9.8) catalyst. A large amount of carbon is deposited on the SA catalyst, illustrating the low selectivity. On the contrary, the carbon deposition is extremely small on the high selective SA-P (9.8) catalyst. These findings suggest that the formation of a high-boiling intermediate in the skeletal isomerization is suppressed by phosphorus modification.

We have suggested already that the high selectivity for skeletal isomerization is due to the distant location of adsorbed 1-butene molecules through restriction of the pore structure of ferrierite [Seo et al., 1996], or because of the low concentration of strong acid sites on alumina catalyst with low levels of fluorine loading [Seo et al., 1998a]. The sparse distribution

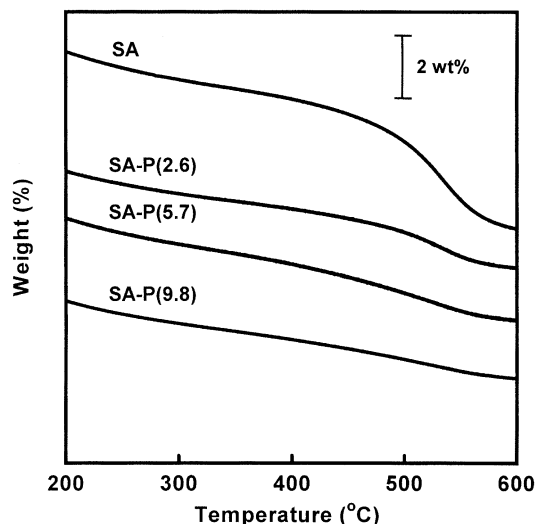


Fig. 5. TG curves of used SA and SA-P (x) catalysts for 210 min and 450 °C.

of activated 1-butene molecules refers to the monomolecular skeletal isomerization, thus, the oligomerization lowering the selectivity for *iso*-butene is suppressed. Easy formation of dimer or the strong interaction of activated 1-butene molecules causes the retention of adsorbed 1-butene and severe coke formation. Accordingly, the solely adsorbed 1-butene due to the low concentration of strong acid sites is a plausible reason for the high selectivity of SA-P (9.8) catalyst with a high level of phosphorus loading.

We conclude as follows: The selectivity for skeletal isomerization of 1-butene on the SA-P(x) catalysts depends on the loading level of phosphorus. On the catalyst with a high level of phosphorus loading of 9.8 wt%, the extremely high selectivity for *iso*-butene is observed because the dimerization is suppressed by the distant location of activated 1-butene molecules due to the low concentration of strong acid site.

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