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High Activity and Selectivity of Sulfided CoNaA Zeolite for Isomerization of 1-Butene

Masatoshi SUGIOKA,* Shin-ichi NAKAYAMA, Daisuke UCHIDA, and Takaji KANAZUKA
Department of Industrial Chemistry, Muroran Institute of Technology,
Mizumoto 27-1, Muroran 050

The effect of sulfiding with H_2S on the catalytic activity and selectivity of CoNaA zeolite in the isomerization of 1-butene was investigated. High activity and selectivity to trans-2-butene were obtained by sulfiding of CoNaA zeolite with H_2S.

In the previous paper,[1-3] we showed that the catalytic activity of some kind of metal Y zeolites for various acid catalyzed reactions were remarkably enhanced by sulfiding with H_2S. In the present paper, we report the effect of sulfiding with H_2S on the catalytic activity and selectivity of CoNaA zeolite in the isomerization of 1-butene.

The isomerization of 1-butene over CoNaA zeolite was carried out at room temperature with 40 Torr of initial pressure by use of a conventional closed circulation system. A 0.05 g of CoNaA zeolite prepared by ion-exchange (67%) was evacuated at 500 °C for 2 h followed by sulfiding with H_2S(40 Torr) for 1 h at various temperatures. Reaction products were analyzed on a gaschromatogragh with propylene carbonate column(5 m) at 0 °C.

Fig. 1 shows the catalytic isomerization of 1-butene over CoNaA and sulfided CoNaA zeolites at room temperature. CoNaA zeolite without sulfiding showed no catalytic activity for the isomerization of 1-butene. However, the catalytic activity of CoNaA zeolite was remarkably enhanced by sulfiding with H_2S at 300 °C as shown in Fig. 1. Enhanced activity of CoNaA zeolite was found to be higher than that of HNaY zeolite(78% ion-exchange). The isomerization of 1-butene over sulfided CoNaA zeolite was highly selective for the formation of trans-2-butene. A selectivity above 90% was obtained constantly during the reaction. The high activity of CoNaA zeolite enhanced by sulfiding with H_2S might be attributed to the formation of new Brönsted acid sites on CoNaA zeolite surface as well as the case of MeY zeolites described in the previous papers.[1-3] The high selectivity of sulfided CoNaA zeolite for the formation of trans-2-butene would be due to the action of shape selectivity of CoNaA zeolite with small pore diameter. Since it has been reported that the diffusion rate of cis-2-butene is two orders of magnitude lower than that of trans-2-butene in the hydrogenation of these 2-butenes on Pt/CaA zeolite,[4] cis-2-butene cannot diffuse from the super cage to outer surface at room temperature even if cis-2-butene is formed inside the super cage of sulfided CoNaA in the isomerization of 1-butene. Fig. 2 shows the effect of sulfiding temperature on the catalytic activity and selectivity of CoNaA zeolite in the isomerization of 1-butene. It was found that the catalytic activity of CoNaA is strongly depended on the sulfiding temperature and it attained maximum at around 300 °C. This indicates that the amount of newly formed acidic hydroxyl group, i.e. Brönsted acid sites, increases with increasing the sulfiding temperature up to 300 °C, but it decreases above 300 °C by the disappearance of acidic hydroxyl groups formed on sulfided CoNaA zeolite. On the other hand, the selectivity to trans-2-butene was independent of the sulfiding temperature of CoNaA zeolite. This suggests that the pore structure of CoNaA zeolite is hardly affected by the sulfiding temperature and the action of shape selectivity of CoNaA zeolite is kept even after the sulfiding with H_2S at high temperature. Further detailed studies with respect to the structure of sulfided CoNaA zeolite and the isomerization of 1-butene over other sulfided metal ion-exchanged A zeolites are in progress in our laboratory.

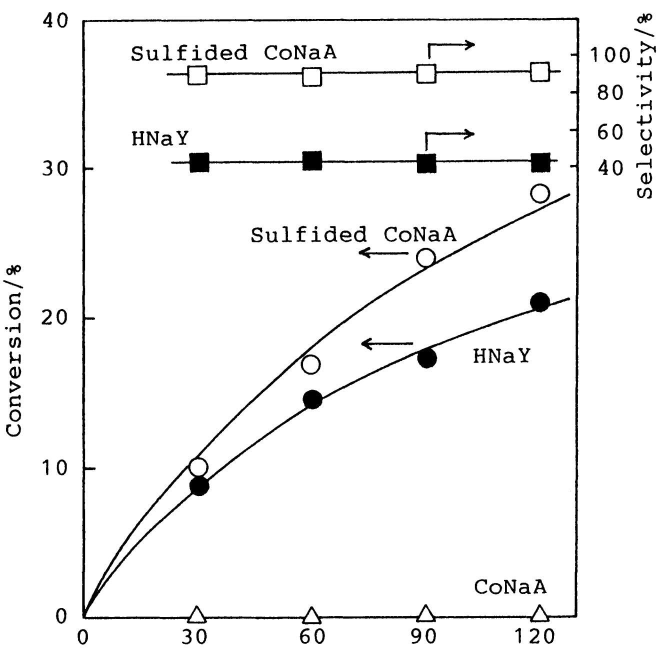

Fig. 1. Catalytic isomerization of 1-butene over CoNaA and sulfided CoNaA zeolites at room temperature.

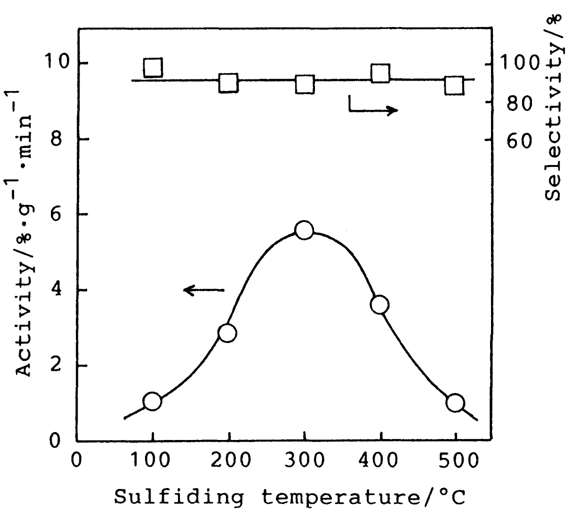

Fig. 2. Effect of sulfiding temperature on the catalytic activity and selectivity to trans-2-butene of CoNaA zeolite in the isomerization of 1-butene. Activity(%·g^{-1}·min^{-1}) was defined as the conversion of 1-butene per unit catalyst weight(g) and unit reaction time(min).

References 1) M. Sugioka, "Hyōmen(Surface)," 25, 525 (1987). 2) M. Sugioka, S. Nakayama, T. Kanazuka, and T. Hosotsubo, Proc. Intern. Symp. Acid-Base Catalysis (Sapporo), p.305 (1988). 3) M. Sugioka, S. Nakayama, T. Nakayama, and T. Kanazuka, Proc. 4th Japan-China-U.S.A. Symp. on Catal. (Sapporo), p.286 (1989). 4) N. Y. Chen and P. B. Weisz, Chem. Eng. Prog. Ser., 63, 86 (1967).

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