JOURNAL OF CATALYSIS 50, 379–381 (1977)

NOTE

Isomerizations of Butenes Caused by Adsorbed Sulfur Dioxide via Different Mechanisms over ZnX Zeolite

Sulfur dioxide adsorbed on various alkali or alkaline earth cation-exchanged-X zeolites or on metal oxides such as Al_2O_3, NiO, or MnO_2 causes the *cis–trans* geometrical isomerization of 2-butenes without enhancing the rate of double-bond migration (*1, 2*). This selective geometrical isomerization occurs through the addition and elimination of butene molecules at the terminal of the polysulfone during the progress of the copolymerization of SO_2 and 2-butenes (*2, 3*). However, SO_2 adsorbed on various transition metal cation- or rare-earth metal cation-exchanged-X zeolites causes not only the *cis–trans* isomerization but also the double-bond migration of 2-butenes at room temperature (*4*). It is not clear whether the two isomerizations caused by SO_2 over these zeolites occur via the same reaction intermediate or via different ones. In this brief note, we intend to clarify this point using ZnX zeolite (79% exchanged, surface area = 579 m²/g) as an example of the transition metal cation-exchanged-X zeolites.

ZnX zeolite degassed in a vacuum at a high temperature (>500°C), does not show any catalytic activity for the isomerizations of butenes at 25°C. Addition of a small amount of SO_2 on it causes the geometrical isomerization and the double-bond migration of butenes at considerable rates. The effects of the reaction temperature upon the rates of these two isomerizations are very different as shown in Fig. 1. The rate of geometrical isomerization, $R°_{c\to t}$ (closed circles), shows its maximum at around 25°C; on the other hand, the rate of double-bond migration, $R°_{1\to c,t}$ (triangles) or $R°_{c\to 1}$ (squares), increases steadily with a rise in temperature from −15 to 90°C. The effects of the degassing temperature for the zeolite on the catalytic activities for the SO_2-induced isomerizations are also very different for the two reactions as shown in Fig. 2; i.e., the rate of double-bond migration decreases with a rise in the degassing temperature from 300 to 700°C, in contrast with the sharp increase in the rate of geometrical isomerization. Nitric oxide in an amount of 1% of the preadsorbed SO_2 poisons the geometrical isomerization, but it does not exert any effect on the rate of double-bond migration.

In the case of catalytic isomerization of butenes over oxides or zeolites, it is the usual case that the two isomerizations proceed via a common reaction intermediate on a common active site. However, the kinetic results described above show that the two reactions do take place by means of different mechanisms over different active sites. As suggested previously, the selective *cis–trans* isomerization must occur by means of the polysulfone-accompanying isomerization mechanism (*1–3*). The selective poisoning of this reaction by nitric oxide must be due to its effective quenching of the terminal radicals of the polysulfone formed from butene and SO_2. The decrease in the rate of *cis–trans* isomerization at temperatures greater than 25°C can

ISSN 0021-9517

be ascribed to the decrease in the number of polysulfone sites necessary for the isomerization (*3*); the ceiling temperature for the polysulfone formation must lie at about 25°C (*3*). The active site for the *cis–trans* reaction may be an exposed zinc cation of the zeolite expected from the desorption of the water molecules coordinated on it by degassing in a vacuum at high temperatures (Fig. 2). Using 1-butene as the starting olefin, it has been shown that the product ratio of *cis-* to *trans*-2-butene is always about unity, suggesting that the reaction intermediate of the double-bond migration is a secondary butyl carbonium ion (*5*, *6*). It is probable that the active site for the double-bond migration is a strong Brönsted acid site produced from the reaction between SO_2 and surface hydroxyl groups.

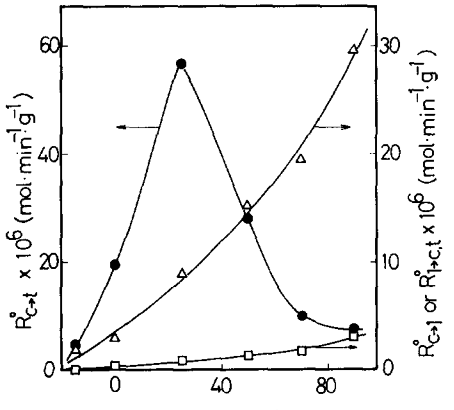

FIG. 1. Temperature effect on the initial rates of the two isomerizations: (△) $R^{\circ}_{1\to c,t}$, the rate of double-bond migration of 1-butene; (□) $R^{\circ}_{c\to 1}$ and (●) $R^{\circ}_{c\to t}$, the rates of double-bond migration and of geometrical isomerization, respectively, using *cis*-2-butene as the starting olefin. Before the run, ZnX zeolite had been calcined at 500°C in oxygen flow, then degassed in a vacuum at the same temperature. The temperature of SO_2 preadsorption was same as the reaction temperature. The pressure of butenes was 120 Torr and the amount of SO_2 adsorbed was 4.1×10^{-5} mol/g. After the addition of butene, all of the SO_2 preadsorbed was still adsorbed even at the highest temperature of 90°C, which was checked by the analysis of SO_2 in gas phase during the progress of the reactions.

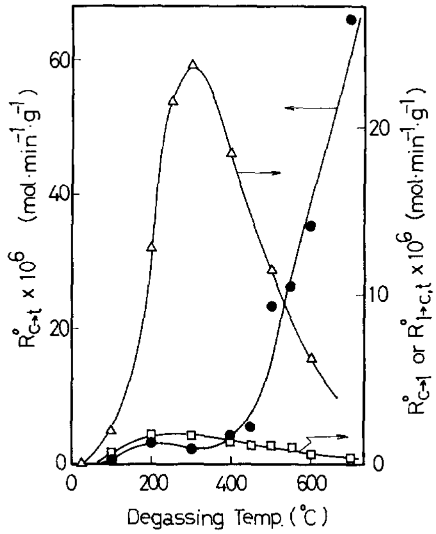

FIG. 2. The initial rates of the two isomerizations as a function of the degassing temperature: (△) $R^{\circ}_{1\to c,t}$, (□) $R^{\circ}_{c\to 1}$, and (●) $R^{\circ}_{c\to t}$. Before the run, ZnX zeolite, without treatment in oxygen flow, was degassed in a vacuum at the desired temperature. The isomerizations were carried out at 25°C. The pressure of butenes was 120 Torr and the amount of SO_2 adsorbed was 4.1×10^{-5} mol/g. The zeolite degassed at temperatures lower than 400°C showed considerable catalytic activities for the two isomerizations even in the absence of SO_2. The rates plotted are the values induced by SO_2, i.e., the differences in rates between those measured in the presence and in the absence of SO_2.

The contribution of the isomerization via the carbonium-ion mechanism to the net rate of *cis* to *trans* isomerization of *cis*-2-butene can be estimated on the bases of the rates measured before and after the addition of nitric oxide which was used as a selective poison for the polysulfone-accompanying geometrical isomerization. The results obtained at 25°C have shown that the rate of *cis–trans* isomerization via the carbonium-ion intermediate is less than 4% of that due to the polysulfone-accompanying isomerization.

REFERENCES

1. Otsuka, K., and Morikawa, A., *J. Chem. Soc. Chem. Commun.*, 218 (1975).

2. Otsuka, K., and Morikawa, A., *J. Catal.* **46**, 71 (1977).

3. Otsuka, K., Tanabe, T., and Morikawa, A., *J. Catal.* **48**, 333 (1977).
4. Otsuka, K., Eshima, K., and Morikawa, A., unpublished data.
5. Foster, N. F., and Cvetanovic, R. J., *J. Amer. Chem. Soc.* **82**, 4274 (1960).
6. Hightower, J. W., and Hall, W. K., *J. Catal.* **5**, 99 (1966).

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Received April 26, 1977