NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (11), 3443—3444 (1979)

SO_2-Produced Acidic Hydroxyl Groups and the Catalytic Activities of Alkaline Earth X Zeolites

Kiyoshi Otsuka,* Yuji Wada, Kimiaki Tanaka, and Akira Morikawa

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received January 30, 1979)

Synopsis. The generation of Brönsted acid sites by SO_2-adsorption on alkaline earth X zeolites has been examined by infrared spectroscopy. The SO_2-induced catalytic activities of the zeolites in the double-bond isomerization of butenes can be ascribed to both the increase in the number of acidic hydroxyl groups and the enhancement in the catalytic activities of the groups after the SO_2 adsorption.

The kinetic studies of the SO_2-induced isomerization of 2-butene over various cation-exchanged X zeolites have been reported in the previous paper.[1,2] It was inferred that the promoting action of SO_2 on the rate of double-bond isomerization of butenes is caused by the generation of acidic hydroxyl groups. The formation of acidic hydroxyl groups by the adsorption of NO_2, SO_2, or Cl_2 has been confirmed on CaY zeolites, and the induced catalytic acitivity of the zeolite in dehydration of 2-propanol by these inorganic gases has been attributed to the formation of the acidic hydroxyl groups.[3] The object of the present work is to examine these suggestions by studying the generation of the Brönsted acid sites after SO_2-adsorption by infrared spectroscopy.

Experimental

The alkaline earth X zeolites used were prepared by a conventional ion exchange of a NaX zeolite (13X from Linde) with aqueous solution of the appropriate chlorides. The percentages of cation exchange, expressed by 100 ([Al]−[Na])/[Al], were as follows: MgX (78), CaX (78), SrX (94), and BaX (93).

The apparatus and the materials used and the analysis of butene isomers were described elsewhere.[1]

Prior to every run, the catalyst in the reactor was degassed under vacuum for 2 h at the required temperature. After the adsorption of SO_2 at 25 °C for 30 min, the isomerization was started at the same temperature by feeding *cis*-2-butene (1.29×10^{-3} mol) and circulating the gas through the catalyst bed.

Infrared-spectra measurements were made with the zeolite in the form of a self-supporting wafer (3—4 mg/cm^2). The sample wafer was calcined in dried oxygen at 400 °C in the IR-cell and degassed in a vacuum at the same temperature for 1 h. The wafer was then brought into contact with 15 Torr of D_2O vapor for 1 h at 200 °C to exchange OH by OD groups, because the broad OH stretching band around 3600 cm^{-1}, probably due to adsorbed water molecules on the zeolites, makes it difficult to identify the different kinds of OH groups. After this treatment, the wafer was outgassed again in a vacuum for 1 h at 400 °C. The spectra of the wafer were recorded, before and after a required amount of SO_2 was adsorbed at 100 °C, using a Shimadzu IR-430 grating spectrometer. It was confirmed that all the SO_2 introduced was adsorbed on the zeolites under the experimental conditions applied here.

Results and Discussion

Figure 1 shows the infrared spectra of the zeolites at the region of OD-stretching vibration, taken before and after the adsorption of SO_2. For all the zeolites, the intensities of the bands for OD groups around 2695 cm^{-1}, corresponding to the band at ≈3640 cm^{-1} due to acidic OH groups in the super cage for the undeuterated alkaline earth faujasites,[4-6] increased after the adsorption of SO_2. The shift in the frequency of the acidic OD band to a lower frequency of about 4 cm^{-1} has been confirmed by repeated experiments for the infrared spectra of the MgX zeolite. This shift caused by SO_2 was not clear within experimental error (±2 cm^{-1}) for the other three zeolites.

The increase in the absorbance of the acidic OD band at the maximum caused by the SO_2-adsorption and the rate of SO_2-induced double-bond isomerization of *cis*-2-butene have been plotted in Fig. 2 as functions of the amount of SO_2 on the zeolites. The dotted-lines or curve for the rate of the isomerization were from the data for the zeolites pretreated at 500 °C in the previous work.[2] For the CaX zeolite pretreated

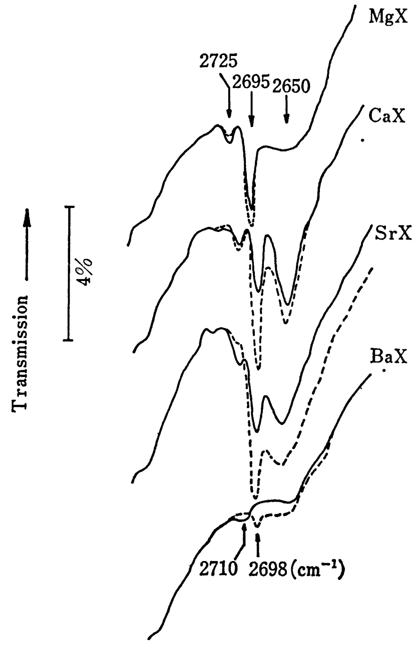


Fig. 1. The effect of SO_2 on the OD stretching bands of the alkaline earth zeolites: ——, without adsorbed SO_2; ----, after the addition of SO_2. The amount of SO_2 adsorbed (10^{-4} mol g^{-1}): MgX, 1.3; CaX, 1.5; SrX, 3.2; BaX, 1.3.

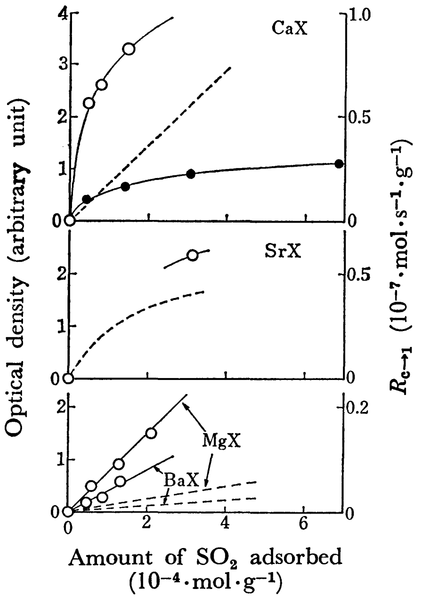


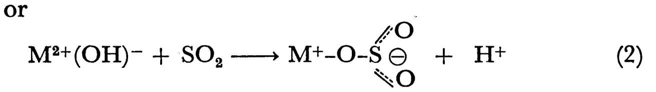
Fig. 2. The optical density of the acidic OD band generated by SO_2 and the rate of the double-bond isomerization as a function of the amount of pre-adsorbed SO_2: ○, optical density of the SO_2-induced acidic OD band; ●, the rate of double-bond conversion, $R_{c\to 1}$, over the CaX pretreated at 400 °C; ----, $R_{c\to 1}$ obtained for the zeolites pretreated at 500 °C.

at 400 °C, the catalytic activity in the isomerization increases with a rise in the concentration of SO_2 adsorbed in the similar way as that of the increase for the absorbance of acidic OD groups. Although the pretreatment temperatures for MgX, SrX, and BaX zeolites are different in the experiments of activity test and infrared spectra measurement, the identical order observed in the SO_2-induced activities among the four zeolites, *i.e.*, CaX$\simeq$SrX>MgX>BaX, has been confirmed in the generation of acidic OD groups.

The schemes proposed for the formation of Brönsted acid sites are as follows:[2,3)]

$$M^{2+}(H_2O)_x + SO_2 \longrightarrow M^{2+}[SO_3]^{2-} + 2H^+ + (H_2O)_{x-1} \qquad (1)$$

or



$$M^{2+}(OH)^- + SO_2 \longrightarrow M^+\text{-}O\text{-}\overset{\nearrow O}{\underset{\searrow O}{S}}\ominus + H^+ \qquad (2)$$

where, $M^{2+}(H_2O)_x$ is the divalent cation coordinated by water, and $M^{2+}(OH)^-$ is the basic hydroxyl groups formed through the following reaction:[5,7)]

$$M^{2+} + H_2O \rightleftharpoons M^{2+}(OH)^- + H^+ \qquad (3)$$

Mirodatos, Pichat, and Barthomeuf have suggested that the OH band at 3685 (MgY) (2710 cm^{-1} in the case of the corresponding OD band) or 3675 cm^{-1} (CaY) should be attributed to the basic OH group of $M^{2+}(OH)^-$ which is responsible for the generation of acidic OH group after CO_2 addition.[8)] The OD bands at 2725—2710 cm^{-1} shown in Fig. 1 correspond to the band due to the basic OD groups. In fact, for MgX, SrX, and BaX, the intensities of these OD bands decreased after the introduction of SO_2, accompanying the increase in intensities of acidic OD groups at ≈2695 cm^{-1} as shown in Fig. 1. However, the relatively greater increase in the intensities of the latter bands compared to the decrease in the former bands suggests that the generation of acidic OH groups cannot be attributed only to the reaction of Scheme 2. We believe that Scheme 1 is also important for the generation of the acid sites.

The spectra in Fig. 1 demonstrate the presence of OD groups at ≈2695 cm^{-1} even in the absence of SO_2 on MgX, CaX, and SrX. These OD groups, however, do not catalyse the isomerization of *cis*-2-butene at 100 °C. The reactivity of the acidic OH group at ≈3640 cm^{-1} with *cis*-2-butene has been examined at 100 °C for MgX before and after the adsorption of SO_2. In the absence of SO_2, the intensity of the OH band did not change by the addition of *cis*-2-butene. On the other hand, the intensity of the band decreased considerably with time in the presence of SO_2. These results suggest that the reactivity of the acidic OH group at ≈3640 cm^{-1} or of the OD group at ≈2695 cm^{-1} increases after the addition of SO_2. Hence, the favorable action of SO_2 on the catalytic activities of the zeolites can be ascribed not only to the increase in the number of acidic hydroxyl groups but also to the enhancement in the catalytic activities of the groups. The little or no change in the frequency of the OD band after the adsorption of SO_2 does not give us any information about the difference in the nature of the OD groups in the presence and absence of SO_2. A possible explanation for the increase in the reactivities of OD groups is that the acidic strength of the OD groups has been totally enhanced through the inductive effect of SO_2 adsorbed on the surface. An alternative explanation is that SO_2 may release the OD or OH groups which had been inhibited in regard to catalysis by the basic $M^{2+}(OD)^-$ or $M^{2+}(OH)^-$ species (Eq. 3).[9)] Further studies are needed to clarify these points.

Addition of SO_2 onto alkaline earth hydroxides, such as $Mg(OH)_2$, $Ca(OH)_2$, and $Sr(OH)_2$, which contain a large number of basic hydroxyl groups and water molecules, causes neither the catalytic activities of these compounds in the double-bond isomerization of butene nor the generation of new hydroxyl groups. These tests have been carried out at 25 °C on the hydroxides pretreated at various temperatures between 100 and 400 °C. These results indicate that the reactions of Schemes 1 and 2 are found specifically on zeolites. A strong electrostatic field in the zeolite cavity must play an important role for the generation of the acidic OH groups.

References

1) K. Otsuka and A. Morikawa, *J. Catal.*, **46**, 71 (1977).
2) K. Otsuka and A. Morikawa, *J. Catal.*, **56**, 88 (1979).
3) Y. Ishinaga, K. Otsuka, and A. Morikawa, *Bull. Chem. Soc. Jpn.*, **52**, 933 (1979).
4) C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, **69**, 3463 (1965).
5) J. W. Ward, *Adv. Chem. Ser.*, **101**, 380 (1971).
6) J. W. Ward, *J. Phys. Chem.*, **72**, 4211 (1968).
7) A. E. Hirschler, *J. Catal.*, **2**, 428 (1963).
8) C. Mirodatos, P. Pichat, and D. Barthomeuf, *J. Phys. Chem.*, **80**, 1335 (1976).
9) C. Mirodatos, A. A. Kais, J. C. Vedrine, P. Pichat, and D. Barthomeuf, *J. Phys. Chem.*, **80**, 2366 (1976).