Unusually Active Sodium Ions in NaY Zeolite for the SO₂-induced *cis-trans* Isomerization of *cis*-But-2-ene

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Received 31st March, 1980

The presence of very active sodium ions in NaY zeolite for the SO_2 -induced *cis-trans* isomerization of *cis*-but-2-ene has been suggested. The sodium ions were removed by exchange with multivalent cations at a low level of exchange. It was inferred that a sodium ion in the six-membered rings (site II or II*) containing one (or zero) aluminium ion or a delocalized sodium ion somewhere in the supercages is responsible for the active site. The presence of active univalent cations has been also confirmed in K-L and Na-mordenite.

The specific *cis-trans* isomerization of but-2-enes caused by adsorbed SO₂ over NaX and NaY zeolites has been explained by a mechanism assuming the formation of a sulphone complex as a reaction intermediate.^{1,2} The reaction is very sensitive to exchangeable cations in the supercages of the zeolites.^{1,3} In the case of NaX, the exchange of sodium ions by Zn²⁺ increased the catalytic activity of the zeolite in the SO₂-induced *cis-trans* conversion.³ On the other hand, for NaY, preliminary experiments showed that exchange by multivalent cations decreased the activity of the zeolite. Hence, in this report we intend to elucidate the negative effect of the exchange of sodium ions by multivalent cations on the *cis-trans* isomerization of *cis*-but-2-ene over NaY

EXPERIMENTAL

MATERIALS

The samples of parent NaY (Linde SK-40), NaX (Linde 13X), Na-mordenite (Zeolon 100Na) and K-L (Linde SK-45) were twice exchanged with 1.0 mol dm⁻³ solutions of NaCl and KCl at 343 K to reduce the impurity cation content. The NaY and NaX samples thus prepared indicated, during the washing procedure with distilled water, Na⁺ decationization to the extents of 4 and 8%, respectively. The unit-cell compositions of the four univalent cation zeolites are as follows:

where it was assumed that the decationated sites of the NaY and NaX zeolites were filled by protons. The degrees of exchange of the zeolites were determined by flame-photometric analysis of the residual sodium or potassium in the zeolites. The error in the degree of exchange was within $\pm 3\%$.

PROCEDURE

The apparatus employed was a conventional static gas-circulation system with 235 cm^3 dead volume. Before each run the zeolite sample was degassed in a vacuum with the temperature increasing to 773 K (10 K min⁻¹). The catalyst was then calcined in dried oxygen at 773 K for

1 h and further degassed for 2 h at the same temperature. After the adsorption of SO₂ at 298 ± 0.1 K for 30 min, the isomerization of *cis*-but-2-ene was started by feeding the gas at a pressure of 13.7×10^3 Pa. The reproducibility of the kinetic data was $\pm 3\%$. No desorption of the preadsorbed SO₂ was confirmed during the isomerization under the experimental conditions applied in this work.

RESULTS AND DISCUSSION

The univalent cation-exchanged zeolites tested here did not show any catalytic activity for the isomerization of *cis*-but-2-ene at 298 K. However, preadsorption of SO₂ on the zeolites caused selective *cis*-*trans* isomerization. The kinetic curves of the reaction for the Na-mordenite and K-L showed a rapid initial formation of *trans*-but-2-ene during the first few minutes followed by a steady formation of the product for *ca*. 60 min. In the cases of NaY and NaX, *trans*-but-2-ene was formed linearly with time from the beginning of the reaction for *ca*. 30 min. In the presence of SO₂, the kinetic curves showed rapid initial isomerization followed by a steady decrease in the rate of the reaction with time irrespective of the type of zeolite. The average quantities of the butene isomers formed per second, which had been calculated from the quantities of the products within the initial 150 s, were tentatively chosen as a measure of the initial rates of the reactions. R_{c-t}^{0} and R_{c-1}^{0} represent the initial rates thus calculated for the formations of *trans*-but-2-ene and but-1-ene, respectively.

Fig. 1 shows the effect of SO₂ concentration on the rates of the SO₂-induced isomerizations over the various X zeolites. The cation-exchange of NaX always increased the catalytic activity of the zeolite for the *cis-trans* conversion irrespective of the degree of exchange. The SO₂ adsorbed on NaX zinc-exchanged to 76%, Zn(76)X, also induced double-bond migration of *cis*-but-2-ene. Fig. 2 shows the rates



FIG. 1.—Rate of SO₂-induced isomerization of *cis*-but-2-ene over X zeolites as functions of SO₂ concentration: R_{c-t}^0 : \bigcirc , NaX; \bigcirc , Zn(22)X; \bigcirc , Zn(38)X; \square , Zn(76)X; \triangle , La(29)X. R_{c-1}^0 : \blacksquare , Zn(76)X. The reactions were carried out at 298 K.

of the SO_2 -induced or -enhanced isomerizations for the various Y zeolites. In contrast to the results observed for the X zeolites, a slight exchange of sodium ions by multivalent cations [Zn(12)Y, Ca(24)Y or La(28)Y] caused a sharp decrease in the catalytic activity for the SO_2 -induced *cis-trans* isomerization. When the degree of exchange is high enough [Zn(78)Y and Ca(79)Y], the activities of the exchanged zeolites exceeded the activity of NaY zeolite. The enhancing action of SO_2 on the rate of the double-bond shift is also indicated for the highly exchanged Y zeolites in fig. 2. The promoting effect of SO_2 on the *cis-trans* isomerization, however, is very much greater than that on the double-bond shift.



FIG. 2.—Rate of SO₂-induced or -enhanced isomerization over Y zeolites at 298 K as functions of SO₂ concentration: R_{c-t}^0 : \bigcirc , NaY; \triangle , Zn(12)Y; \triangle , Zn(83)Y; \square , Ca(24)Y; \square , Ca(79)Y; \bigcirc , La(28)Y. R_{c-1}^0 : \triangle , Zn(83)Y; \blacksquare , Ca(79)Y.

It has been suggested that the sodium ions in NaY are the active sites for the SO_2 -induced *cis-trans* isomerization of but-2-enes.² The reaction is initiated by means of a polarization of the charge-transfer complex, formed from SO_2 and but-2-ene, under the influence of the exchangeable metal cations in zeolites.¹ When the exchange levels were high enough (*ca.* > 60%), the multivalent-cation-exchanged zeolites showed greater catalytic activities than the univalent-cation-exchanged zeolites.¹ This is true for both the X- and Y-type zeolites in fig. 1 and 2. However, when the level of exchange is low, we must take into account the number and the location of the exchangeable cations in the zeolite structure. The exchange of sodium ions by multivalent cations would decrease the number of metal cations in the supercages. Moreover, when the multivalent cations locate preferentially in the small cavities (hexagonal prisms and sodalite units), as has been pointed out by many workers,³⁻⁶ the catalysis effect of the internal cations on the SO₂-induced *cis-trans*

conversion must be weak compared with the multivalent cations in the supercages. In the case of zinc-exchanged X zeolites, the activity of the zeolite for the *cis-trans* isomerization increased sharply at levels of exchange greater than *ca.* 40%.³ The results have been explained by the appearance of the Zn^{2+} in the supercages above a degree of exchange of *ca.* 40%.³ The high catalytic activities of Zn(76)X in fig. 1 and of Zn(83)Y and Ca(79)Y in fig. 2 for the *cis-trans* isomerization can be attributed to the divalent ions in the supercages.

The results for Zn(22)X, Zn(38)X and La(29)X in fig. 1 suggest that the internal multivalent cations have a catalytic activity higher than that of the sodium ions in the supercages. The charge-transfer complexes of SO_2 and butenes in the supercages may be activated by the electrostatic field of the multivalent cations in the sodalite cages (probably at site I' or II') leaking through the tetrahedral SiO_4^{4-} and AlO_4^{5-} framework of the cages. In the case of Y zeolite, we expect a less effective shielding of the electric field of the cations in the sodalite cages by the framework oxygens compared with the shield which occurs in X zeolites because of the higher Si/Al ratios for Y zeolites. Therefore, the introduction of multivalent cations in Y zeolite must enhance the activity of the zeolite more effectively than the enhancement by the multivalent cations in X zeolite at any level of exchange. However, the results in fig. 2 show considerable decreases in the catalytic activities of NaY at low levels of exchange with multivalent cations [Zn(12)Y, Ca(24)Y] and La(28)Y]. The activity of Zn(12)Y, for example, decreased to one fourth of the activity of NaY at an SO₂ concentration of 2×10^{-4} mol g⁻¹. For a Y zeolite containing 58 monovalent cations per unit cell the optimum distribution allows 32 in site II, 6 in I and 20 in I'.⁷ X-ray diffraction studies have indicated the location of 31 univalent cations at site II.⁸ The large decrease in the activity of NaY zeolite after zinc-exchange (6 Na⁺ exchanged) cannot be explained by the decrease in the number of sodium ions even when the Na⁺ in the supercages had selectively been exchanged by Zn²⁺, because such a selective exchange of Na⁺ could only decrease the number of Na⁺ in the supercages to ca. 80%. Hence, we hypothesize here that the NaY zeolite contains an especially active sodium ion in the supercages. The ions must be removed first by exchange with multivalent cations, causing the sharp drop in the activity of the NaY due to the introduction of small quantities of Zn²⁺, Ca²⁺ or La³⁺. In the case of X zeolites which have a Si/Al ratio close to unity, it is probable that there is only one kind of six-membered ring, composed of tetrahedral SiO₄⁴⁻ and AlO₅⁴⁻ arranged alternately. On the other hand, for Y zeolite having Si/Al ratios greater than unity (2.56 for the NaY used here), various kinds of arrangement of the tetrahedra in the rings may occur, *i.e.* rings containing three, two, one or zero aluminium ions. This is true no matter whether the distribution of aluminium ions in the structure is random or ordered.^{9,10} The sodium ions in the supercages of NaY would first occupy site II of the rings containing three aluminium ions, then the site surrounded by two aluminium ions. The rest of the sodium ions may sit on the rings containing one (or zero) aluminium ion. We speculate that the highly active sites in NaY may be attributed to the sodium ions whose charges are not fully compensated by negative charges on the six-membered rings containing one (or zero) AlO_4^{5-} . Alternative species responsible for the active sites might be a delocalized sodium ion somewhere in the supercages. Such an unstable sodium ion on the site could be easily removed by exchange with multivalent cations. If the above consideration is true, we can expect the presence of a highly active univalent cation in any zeolite having a high Si/Al ratio. In order to examine this prediction the SO₂-induced isomerization was carried out over L zeolites (Si/Al = 3.0) and mordenites (Si/Al = 7.0).



FIG. 3.—Rate of SO₂-induced isomerization at 298 K over L zeolites: R_{c-t}^0 : \bigcirc , K-L; \bigcirc , Zn(8)-L. R_{c-1}^0 : \triangle , Zn(8)-L.



FIG. 4.—Rate of SO₂-induced or -enhanced isomerization over mordenites at 298 K. R_{r-t}^0 : \bigcirc , Na-mordenite: \bigcirc , Zn(9)-mordenite; \frown , Zn(52)-mordenite. R_{r-1}^0 : \bigcirc , Na-mordenite; \frown , Zn(9)-mordenite; \frown , Zn(52)-mordenite.

The effects of SO₂ concentration on the rates of the isomerizations for L zeolites are shown in fig. 3. The slight exchange of potassium of the K-L zeolite by zinc [Zn(8)-L] decreased the catalytic activity of the K-L in the SO₂-induced *cis-trans* isomerization. The results for mordenites are indicated in fig. 4. The exchange of Na-mordenite by zinc cations increased the activities of the mordenite in the absence of SO₂ for both the isomerizations, *cis-trans* and double-bond conversions. For the zinc-exchanged mordenites, there is not much difference in the ratios of R_{c-t}^0/R_{c-1}^0 in the presence and in the absence of SO₂. Note that the ratios R_{c-t}^0/R_{c-1}^0 are small, less than 4, even in the presence of SO₂. These facts show the absence of the selective *cis-trans* isomerization which was observed for Na-mordenite. The SO₂-enhanced *cis-trans* isomerization over the zinc-exchanged mordenites may be interpreted using the same mechanism as that of the double-bond shift invoking a sec-butyl carbenium ion as a reaction intermediate.^{1, 2} In any case, it is clear that an active sodium ion essential for the selective *cis-trans* conversion has disappeared from the zinc-exchanged mordenites.

Since zeolite L and mordenite have totally different structures to those of X and Y zeolites, with quite different channel sizes and ion sites, the sites for the specially active univalent cations in L and mordenite structures are, of course, quite different to those of X and Y zeolites. It is difficult to speculate the exact position of the active cations. However, it is not unreasonable to postulate the presence of unusually active univalent cations whose charges are not fully compensated by negative charges of oxygen ions in the channels of K-L and Na-mordenite on the similar basis as described in the case of Y zeolite. In conclusion, the results of K-L and Na-mordenite support the prediction that the zeolite having a high Si/Al ratio contains very active univalent cations for the *cis-trans* specific isomerization of but-2-enes.

The enhancing action of SO_2 on the carbenium-ion-type reactions, such as dehydration of propan-2-ol¹¹ and double-bond shift of but-2-enes,^{2, 12} has been ascribed to the increase in the number of acidic hydroxyl groups formed through the reaction of SO_2 with the basic hydroxyl groups or with the water coordinated to the metal cations.^{11, 12} The enhancement in the acidity of the groups due to the electron-withdrawing character of the adsorbed SO_2 is also important for the favourable effect of SO_2 .^{2, 12} The double-bond isomerization enhanced by SO_2 over the highly zinc- or calcium-exchanged X and Y zeolites and over the Zn(8)-L and the mordenites may be interpreted on a similar basis.

The NaY zeolites used in this work contained *ca.* 4% Na⁺-decationated sites which had been formed during the washing treatment by distilled water after the exchange in NaCl solution. Hence, in order to decrease the decationation of sodium ions, the NaY was again exchanged in 1.0 mol dm⁻³ NaCl solution at 353 K and then washed by NaOH solution of pH 10 until no chloride ion was detected. Another method applied to decrease the decationation was the exchange of NaY (4 g) using 100 cm³ of 0.01 mol dm⁻³ NaOH solution at 298 K for 3 h. The zeolite was then filtered and washed with 100 cm³ distilled water. The NaY prepared by the former and by the latter methods showed 2.1 and 2.4 times increases in the activities for the *cis-trans* conversion, respectively, at an SO₂ concentration of 1.2×10^{-4} mol g⁻¹. The results can be explained on the basis of the recovery of the active sodium ions which had been washed out during the washing treatment of the zeolite by distilled water. Thus the results for the SO₂-induced *cis-trans* isomerization over the mordenites, L and Y zeolites strongly suggest the presence of very active sodium ions, although the concentration of the sodium ions is very low.

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