

# SO<sub>2</sub>-INDUCED ISOMERIZATION OF *n*-BUTENES OVER X- AND Y-TYPE ZEOLITES

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(Received 30<sup>th</sup> January, 1978)

The promoting action of SO<sub>2</sub> for the isomerization of *cis*-2-butene over X- and Y- type zeolites has been characterized. Different kinetic behaviour observed for the SO<sub>2</sub>-induced *cis*-*trans* isomerization and double-bond migration of 2-butenes on cation-exchanged zeolites shows that the two reactions take place with different mechanisms over different active sites. The *cis*-*trans* isomerization is accompanied by the copolymerization of SO<sub>2</sub> and 2-butenes. The double-bond migration is caused by acidic OH groups newly generated through the reaction of SO<sub>2</sub> with basic OH groups. On HY zeolite, the creation of basic sites by dehydroxylation is essential for the promoting action of SO<sub>2</sub>. SO<sub>2</sub> adsorbed on the basic sites may enhance the acid strength of BRONSTED sites by its attracting negative charge from the catalyst.

## Introduction

The favourable action of guest molecules to reactant transformation has been recognized, specifically on zeolites [1, 2] with a few exceptions [3]. The promoting action of SO<sub>2</sub> for hydrocarbon conversion such as cracking, alkylation or isomerization over X- and Y-type zeolites has been reported in patents over ten years ago [4, 5]. However, not detailed study on this subject has since been reported. Hence, in order to elucidate the promoting action of SO<sub>2</sub> in zeolite catalysis, we have investigated kinetics of the SO<sub>2</sub>-induced isomerization of olefins over cation-exchanged-X, NaX and HY zeolites. The reaction mechanism and the nature of the active sites are discussed.

## Experimental

All the zeolites used were prepared by an usual ion exchange method of NaX and NaY zeolites with aqueous solution of the appropriate chlorides. The percentages of exchange were as follows: LiX (60), KX (79), RbX (61), CsX (64), MgX (76), CaX (83), SrX (94), BaX (81), LaX (83), CeX (84), NdX (87), NH<sub>4</sub>Y (100).

The apparatus employed was a conventional gas circulating system with 225 ml dead volume. Prior to every run, the catalyst was calcinated in dried oxygen and degassed *in vacuo* for 2 hr at 500 °C. HY zeolite prepared by decomposition of NH<sub>4</sub>Y zeolite under vacuum at various temperatures was subjected to the run without calcination in oxygen. At 25 °C, SO<sub>2</sub> was adsorbed on the catalyst and the reaction was started by feeding *cis*-2-butene ( $1.3 \times 10^{-3}$  mol). The initial rates of the two types of isomerizations,  $R_{c \rightarrow t}^0$  and  $R_{c \rightarrow 1}^0$ , were calculated from the amount of *trans*-2- and 1-butene produced within 7 min, respectively.

### Results and discussions

#### Cation-exchanged zeolites

Addition of  $\text{SO}_2$  onto LiX, NaX and KX zeolites induces geometrical isomerization of *cis*-2-butene but no double-bond migration. No isomerization of 1-butene has been further confirmed. The reactions did not occur on RbX and CsX zeolites.  $\text{SO}_2$  on alkaline earth- and rare earth-X zeolites induces the two isomerizations of *cis*-2-

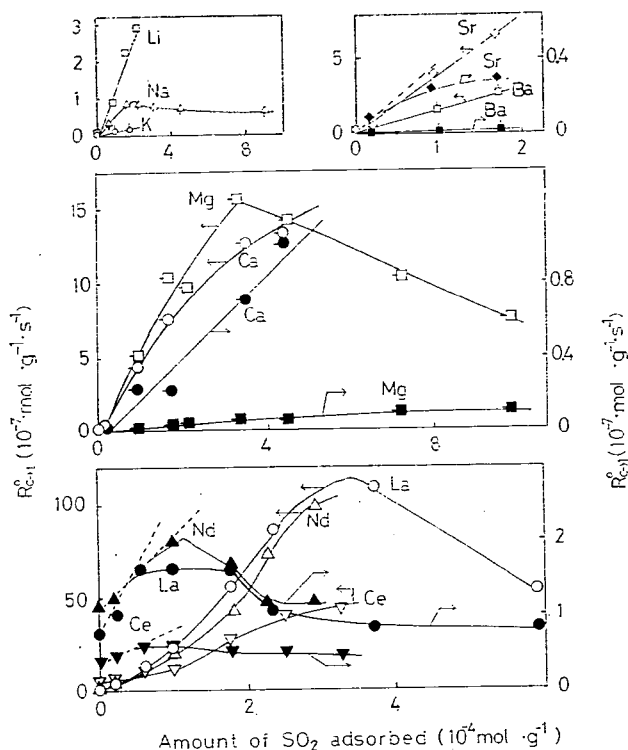
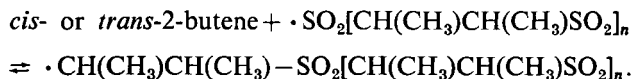


Fig. 1. Rate of  $\text{SO}_2$ -induced isomerizations of *cis*-2-butene as a function of the amount of  $\text{SO}_2$  adsorbed on cation-exchanged-X zeolites. Open signs  $R_{c \rightarrow t}^0$ ; filled signs  $R_{c \rightarrow 1}^0$ .

-butene. The effect of  $\text{SO}_2$  concentrations on the initial rates,  $R_{c \rightarrow t}^0$  and  $R_{c \rightarrow 1}^0$ , is shown in Fig. 1. The promoting action of  $\text{SO}_2$  is unusually greater on geometrical isomerization than on double-bond migration. Nitric oxide in an amount of 1% of preadsorbed  $\text{SO}_2$  poisons geometrical isomerization strongly, but does not affect the rate of double-bond migration.

### Reaction mechanism for *cis-trans* isomerization

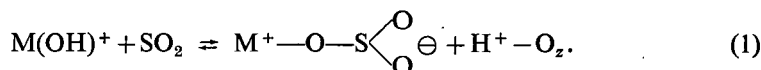
The selective *cis-trans* isomerization can be explained by the addition and elimination of 2-butene molecules at the terminal of the polysulfone formed in the adsorption layer [6—8]:



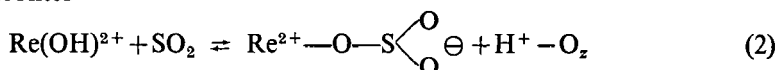
The *cis-trans* isomerization on alkali and alkaline earth zeolites shows an acceleration of its rate with reaction time, being attributed to the accumulation of a radical intermediate. The selective poisoning of nitric oxide to the reaction must be due to its effective quenching of the terminal radical of the polysulfone. The decrease in the rate of *cis-trans* isomerization with increase in the amount of SO<sub>2</sub> under high SO<sub>2</sub> concentrations can be ascribed to an interference of the diffusion of butene molecules by the formed polysulfone in the narrow pores of zeolites. The activities for the zeolites in Fig. 1 for the *cis-trans* isomerization increase with a rise in the electrostatic potential of the exchangeable cations of the zeolites, suggesting the initiation of the reaction under the influence of metal cations.

### Active site for double-bond migration

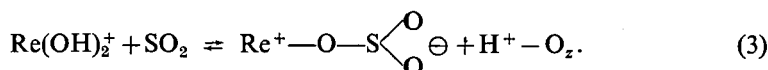
The SO<sub>2</sub>-induced double-bond migration over alkaline earth- and rare earth-X zeolites can be interpreted by assuming generation of acidic hydroxyl groups on SO<sub>2</sub> adsorption at the expense of basic hydroxyl groups [2, 9, 10]. In the case of alkaline earth zeolites, new acidic OH groups may be generated as follows:



For rare earth zeolites



or



The rate of SO<sub>2</sub>-induced double-bond migration is expressed as follows:

$$R_{c \rightarrow 1}^0 \propto [\text{H}_{\text{new}}^+] \quad (4)$$

$$[\text{H}_{\text{new}}^+] = K[\text{M}(\text{OH})^+][\text{SO}_2] \quad (5)$$

where *K* is the equilibrium constant of equation (1). Table I shows the slopes of the linear portion of the curves for the double-bond migration in Fig. 1 at the low concentration of SO<sub>2</sub>. The concentration of M(OH)<sup>+</sup>, produced by the dissociation of water molecules in the electrostatic field around the divalent cations in zeolite, must increase in the order of Ba < Sr < Ca < Mg as the electrostatic potential of the cations increases [11—14], while *K* must decrease in the same order because of an expected decrease in basicity of M(OH)<sup>+</sup>. Thus, it is reasonable that the number of

Table I

Activities of the zeolites for SO<sub>2</sub>-induced double-bond migration of *cis*-2-butene

Zeolites	BaX	SrX	CaX	MgX	NdX	CeX	LaX
Activities (10 <sup>-4</sup> ·s <sup>-1</sup> )	0.075	3.70 <sup>a</sup>	2.18	0.133	15.3 <sup>a</sup>	17.5 <sup>a</sup>	15.1 <sup>a</sup>

a: obtained from the dotted lines in Fig. 1.

new acidic OH groups, or the promoting action of SO<sub>2</sub>, over alkaline earth zeolites is highest in SrX (Table I). The high promoting action of SO<sub>2</sub> for rare earth zeolites might be attributed to the presence of Re(OH)<sub>2</sub><sup>+</sup> which has greater basicity than M(OH)<sup>+</sup>.

### HY and NaY zeolites

For HY zeolites prepared by the decomposition of NH<sub>4</sub>Y zeolite at 200–350 °C, SO<sub>2</sub> acts as a weak poison for the two isomerizations. Its promoting action appears on HY zeolites degassed in a vacuum at temperatures higher than 400 °C. SO<sub>2</sub>-enhanced rates on HY and NaY, R(SO<sub>2</sub>), or the differences between rates measured in the presence and absence of SO<sub>2</sub>, are plotted against the degassing temperatures and the reaction temperatures (zeolites degassed at 600 °C) in Fig. 2 (a) and 2 (b),

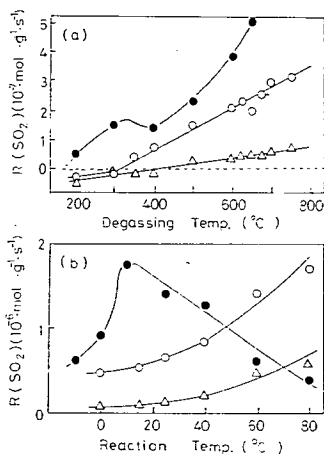


Fig. 2. Effect of (a) degassing temperatures of zeolites ([SO<sub>2</sub>] 2.2 × 10<sup>-5</sup> mol/g) and (b) reaction temperatures ([SO<sub>2</sub>] 9.4 × 10<sup>-5</sup> mol/g for HY, 3.8 × 10<sup>-5</sup> mol/g for NaY; the degassing temperature 600 °C) on the rate of SO<sub>2</sub>-induced isomerizations of *cis*-2-butene. ○ HY(*c*→*t*); △ HY(*c*→*l*); ● NaY(*c*→*t*)

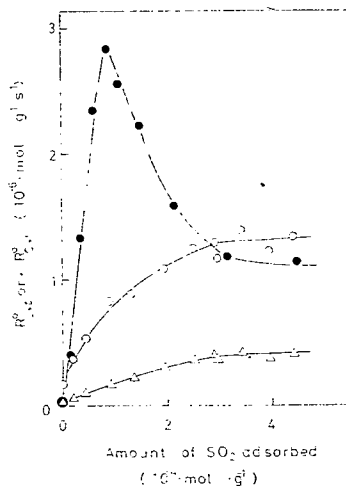
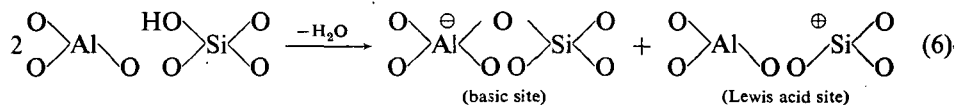


Fig. 3. The plots of net rates of isomerizations against the amount of SO<sub>2</sub> adsorbed. The catalysts were degassed at 600 °C. ○ HY(*c*→*t*); △ HY(*c*→*l*); ● NaY(*c*→*t*).

respectively. SO<sub>2</sub> causes only *cis-trans* isomerization on NaY as well as on alkali-X zeolites. The effect of the adsorbed amounts of SO<sub>2</sub> on the net rates of two isomerizations for NaY and HY zeolites (degassed at 600 °C) is shown in Fig. 3.

In the case of HY zeolite, the similar kinetic behaviour for the two isomerizations (Figs. 2, 3) suggests that they proceed *via* a common reaction intermediate on a common active site. The fact that the promoting action of SO<sub>2</sub> emerges on the catalysts treated at temperatures higher than 400 °C implies that the dehydroxylation of the catalyst, shown below [15], is necessary.



The promotion in catalytic activity might be caused by the adsorption of electrophilic SO<sub>2</sub> on the basic site, *i.e.*, the consequent attraction of negative charge from the catalyst results in an increase in acid strength of OH groups remained on the surface.

The *cis-trans* isomerization for NaY zeolite must occur by means of the polysulfone-accompanying isomerization mechanism described above. The decrease in the rate of *cis-trans* isomerization at temperatures higher than 10 °C (Fig. 2 (b)) can be ascribed to the decrease in the number of effective polysulfone [7]. The active site for the selective *cis-trans* isomerization may be an exposed exchangeable metal cation formed by degassing *in vacuo* at high temperatures (Fig. 2 (a)).

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