## NOTES

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# Promoting Action of Inorganic Gases on the Rate of Dehydration of 2-Propanol over Ca-Y Zeolite

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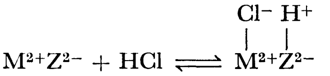
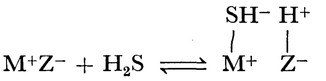
**Synopsis.** The dehydration of 2-propanol over Ca-Y zeolite has been enhanced in the presence of $NO_2$, $SO_2$, and $Cl_2$ at 100 °C. This promoting action has been ascribed to the formation of acidic hydroxyl groups resulting from the reaction of the inorganic gases with zeolitic water or basic hydroxyl groups attached to the metal cations.

The promoting action of inorganic gases on the rate of dehydration of alcohol or hydrocarbon conversion, such as cracking, alkylation or isomerization has been recognized specifically on zeolites.[1–3] The favorable action of gases which contain hydrogen atom or atoms in their structure, such as $H_2O$, HCl, or $H_2S$, has been ascribed to their ability to generate protonic sites by the dissociation of the hydrogen atoms as follows:[4–9]

$$M^{2+} + H_2O \rightleftharpoons M(H_2O)^{2+} \rightleftharpoons M(OH)^{+} + H^{+} \qquad (1)^{4,10,11)}$$



$$M^{2+}Z^{2-} + HCl \rightleftharpoons \overset{\overset{Cl^-}{|}}{M^{2+}}\overset{\overset{H^+}{|}}{Z^{2-}} \qquad (2)^{6,7,12,13)}$$



$$M^{+}Z^{-} + H_2S \rightleftharpoons \overset{\overset{SH^-}{|}}{M^{+}}\ \overset{\overset{H^+}{|}}{Z^{-}} \qquad (3)^{14)}$$

where, $M^{2+}$ or $M^+$ and $Z^{2-}$ or $Z^-$ represent the exchange-able cation and the anionic framework of the zeolite, respectively. The promoting action of compounds possessing no hydrogen atoms, such as $NO_2$, $SO_2$, or $Cl_2$, has however not satisfactorily been interpreted.

In this work, the promoting action of $NO_2$, $SO_2$, $Cl_2$, $CO_2$, HCl, and $H_2S$ on the dehydration of 2-propanol over Ca-Y zeolite has been studied in connection with the formation of acidic hydroxyl groups by the foreign gases. The dehydration of 2-propanol is a typical reaction catalyzed by protonic sites over zeolites[2] and consequently has been used as a test reaction.

## Results and Discussion

The effect of the gases on the rate of propylene and diisopropyl ether formation, denoted by $R_{prp}$ and $R_{ether}$, over Ca-Y zeolite is shown in Fig. 1, where the initial rate has been plotted as a function of the amount of adsorbed gases measured during the course of reaction. The reaction was conducted at 100 °C under 24 Torr of 2-propanol using a conventional gas circulation system. Prior to each run, the Ca-Y zeolite (79% exchanged) was calcined at 500 °C in dried oxygen and degassed for 2 h at the same temperature. After the adsorption of the foreign gas at 100 °C for 20 min, 2-propanol was fed into the system thereby initiating reaction. The amount of gas adsorbed during the course of the reaction was calculated by measuring the amount of foreign gas in the gas-phase by gas-chromatography. The pressure of the foreign gas under the reaction conditions was less than 1.5 Torr. The Ca-Y was prepared from Na-Y (Linde SK-40) by a conventional ion-exchange method using an aqueous solution of $CaCl_2$ at 25 °C. The 2-propanol (spectro grade) and the inorganic gases (purity>99%) were purified by trap to trap distillation *in vacuo*. The results illustrated in Fig. 1 indicate that $NO_2$, $Cl_2$, $SO_2$, and HCl considerably enhance the dehydration of 2-propanol over Ca-Y zeolite. In the case of $CO_2$, the promoting action developed when the gas was pre-adsorbed at temperatures in excess of 300 °C up to 500 °C.

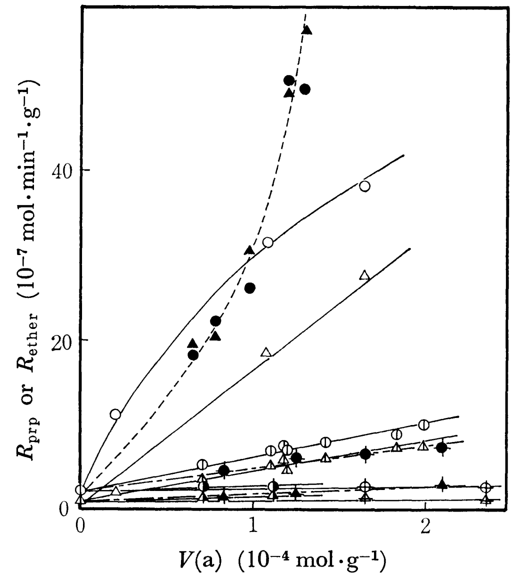


Fig. 1. Effect of inorganic gases on the rate of dehydration of 2-propanol over Ca-Y zeolite : Circle; propylene, triangle; diisopropyl ether, ●, ▲; $NO_2$, ○, △; $Cl_2$, ⦶, △; $SO_2$, ◐, ▲; $CO_2$, ●, ▲; HCl, ⊕, △; $H_2S$.

The formation of acidic hydroxyl groups after adsorption of the six inorganic gases onto the zeolite has been examined as follows. A wafer of the zeolite (3—4 mg/cm²) was calcined in dried oxygen at 450 °C for 1 h, and degassed for 2 h at the same temperature. The wafer was then allowed to come into contact with $D_2O$ vapour 9 Torr for 4 h at 200 °C in order to exchange OH by OD groups since the broad OH stretching band around 3600 cm$^{-1}$, probably due to

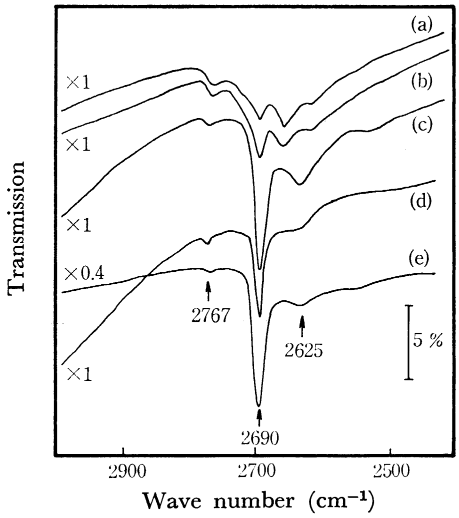


Fig. 2. Spectra of the deuteroxyl stretching vibrations of Ca-Y zeolite : (a) evacuated for 1 h at 450 °C after $D_2O$ treatment, (b) exposed to $SO_2$ after (a), (c) exposed to $NO_2$ after (a), (d) exposed to $Cl_2$ after (a), (e) exposed to DCl after (a). The bands at 2767, 2690, and 2625 cm$^{-1}$ are due to silica-type deuteroxyl groups, acidic deuteroxyl groups in supercages, and those in hexagonal prisms or sodalite cages, respectively.

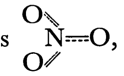
strongly held water molecules on the zeolite, and the absorption of infrared beam by water in the air make it difficult to identify the different kinds of OH group. After the exchange, the wafer was degassed again for 1 h at 450 °C. Figure 2 shows the spectra of the OD stretching vibrations of Ca-Y zeolite after adsorption of $NO_2$, $Cl_2$, $SO_2$, and DCl for 20 min at 100 °C (16 Torr for each compound; 9 Torr for $NO_2$). The spectra have been measured at 100 °C after condensing the adsorbate in the gas phase in a liquid nitrogen trap. For these four compounds, it is clear that the intensity of the 2690 cm$^{-1}$ band due to the acidic deuteroxyl groups[12)] increases greatly after the adsorption of the gas. This band corresponds to the band at 3640 cm$^{-1}$ attributed to the acidic hydroxyl groups in the supercages for the undeuterated Ca-Y zeolite.[11,15)]

The high promoting action of $NO_2$, $Cl_2$, and $SO_2$ indicated in Fig. 1 can be ascribed to the newly formed acidic hydroxyl groups. The lower promoting action of $H_2S$ and $CO_2$ can be accounted for by the low ability to generate acidic hydroxyl groups, substantiated by a very small increase in intensity of the acidic OD band after adsorption of the gas. In the case of $CO_2$, a much higher temperature was needed for the generation of the acidic hydroxyl groups.[2,16)] The promoting action of HCl was not as large as anticipated from the evidence in Fig. 2.

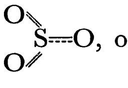
The following schemes are proposed for the generation of protonic sites after the adsorption of $NO_2$, $SO_2$, and $Cl_2$ from an analogy to the mechanisms suggested in the case of $CO_2$:[2,16)]

$$Ca^{2+}(H_2O)_x + A \longrightarrow Ca^{2+}[B]^{2-} + 2H^+ + (H_2O)_{x-1} \tag{4}$$

where, A is $NO_2$, $SO_2$, or $Cl_2$ and B is



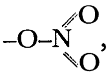
$\mathrm{(O)(O)N{=}O}$,



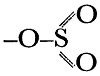
$\mathrm{(O)(O)S{=}O}$, or $\overset{\mathrm{OCl}}{\mathrm{Cl}}$, respectively, or

$$Ca(OH)^+ + A \longrightarrow Ca^+B^- + H^+ \tag{5}$$

where, A is $NO_2$, $SO_2$, or 1/2$Cl_2$ and B is



$\mathrm{{-}O{-}N(=O)_2}$,



$\mathrm{{-}O{-}S(=O)_2}$, or OCl, respectively. $Ca^{2+}(H_2O)_x$ is the divalent cation coordinated by water, and $Ca(OH)^+$ is the basic species formed through the dissociation of hydrating water during the pretreatment of the zeolite. Further infrared spectroscopic studies on this point are in progress.

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