An Infrared Study of the CaA Zeolite Reacted with CO_2

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An infrared study was made on the CaA zeolite reacted with CO_2 gas. It was found that a carbonate ion (CO_3^{2-}) is formed by binding of CO_2 to an oxygen, and this carbonate ion coordinates to a Ca^{2+} cation in the zeolite in the unidentate way.

Key words: IR; CO_2; CaA Zeolite.

The use of zeolites for the adsorption of harmful gases has widened [1, 2]. In [2] we have studied the ionic states, motional behavior and binding degrees of SO_2 and CO_2 reacted with type 5A (CaA) zeolite, and we have concluded that SO_2 is adsorbed on the surfaces while CO_2 is absorbed in the deep pores of this zeolite.

In the present work the binding states of CO_2 on the same zeolite was investigated by IR spectroscopy.

Experimental Details

Synthetic CaA was purchased from the British Drug House (BDH). The content of its unit cell is given in [3]. Firstly, the zeolite was kept for 5 h at 350 °C to remove the water from the pores. 5 g of $CaCO_3$ were placed in a glass container, and HCl was dropped on it while it was heated. Then CO_2 gas was passed through the mixture, resulting in the reaction

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O\,.$$

The IR spectra were taken from disks of powdered material with a Perkin Elmer Model 1430 Infrared Spectrophotometer.

Results and Discussion

Figure 1 shows the IR spectra of pure and CO_2 reacted CaA zeolite. The IR active modes of free CO_2, which are bonding and antisymmetrical stretching modes, are at 667 and 2350 cm^{-1}, respectively [4]. As seen in the figure, the vibration modes of CO_2 reacted on the zeolite CaA appear at quite different energies from those of

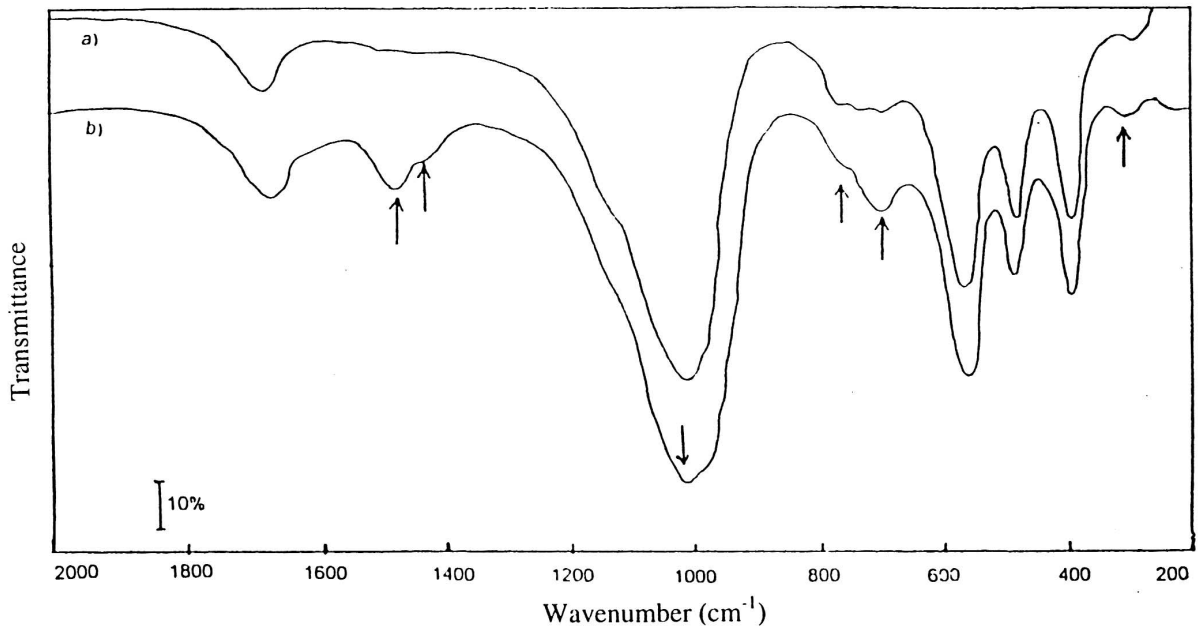


Fig. 1. IR spectra of the zeolite CaA. a) pure b) CO_2 reacted. The arrows indicate the frequencies given in Table 1.

Assignment	$\nu(C{-}O_{II})$ $+\nu(C{-}O_I)$	$\nu(C{-}O_I)$ $+\nu(C{-}O_{II})$	$\delta(O_{II}CO_{II})$	$\nu(Co{-}O_I)$ $\nu(Ca{-}O_I)$	$\nu(C{-}O_{II})$	$\varrho_r(O_{II}CO_{II})$
$[Co(NH_3)_5CO_3]Br$*	1373	1070	756	362	1453	678
$[Co(NH_3)_5CO_3]I$*	1366	1065	776	360	1449	679
CaA + Co_3	1420	1010	750	340	1470	680

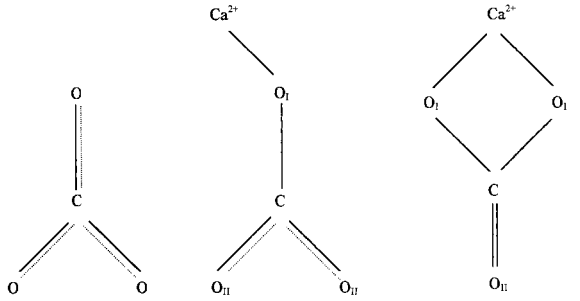
* [5]

Table 1. Vibration modes and frequencies of CO_3 in $[Co(NH_3)_5CO_3]Br$, $[Co(NH_3)_5CO_3]I$ and the CaA zeolite. Results are in cm^{-1}. ν shows stretching, the δ bending and ϱ_r the rocking modes.

free CO_2. The reason for this is the formation of a carbonat ion (CO_3^{2-}) by the binding of CO_2 to an oxygen. The reactions must be

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+,$$
$$HCO_3^- \rightarrow CO_3^{2-} + H^+.$$

This carbonat ion can be bound to a Ca^{2+} cation in the zeolite in two ways. This is like the binding of carbonat ions with metals [5]. The two ways are shown in Scheme 1 on the right.



Free ion (D_{3h}) Unidentate (C_s) Bidentate (C_{2v})

Scheme 1

The free carbonat ion has 4 vibration modes. Two of them are degenerate. The binding of CO_3 to a Ca^{2+} cation lowers the symmetry. In this situation, the vibration of ν_1, which is forbidden in the free form, becomes infrared active, and each of the doubly degenerate vibrations, ν_3 and ν_4, splits into two bands. The splitting of the degenerate vibrations is larger in the bidentate way than in the unidentate way. Since the two CO splitting is small (1420–1470 cm^{-1}) as seen in Fig. 1, the binding of the CO_3^{2-} ion to the Ca^{2+} cation is in the unidentate way in the zeolite CaA. Thus, the combination bands $\nu(C{-}O_{II})$ and $\nu(C{-}O_I)$ are at 1470 and 1420 cm^{-1}, respectively. These values are close to the values, for the same bands, in $[Co(NH_3)_5CO_3]Br$ and $[Co(NH_3)_5CO_3]I$ [5]. The measurements in the present study and those in [5] are given in Table 1. Their spectra have also a band π around at 850 cm^{-1}. But it has not been observed in our spectrum.

As a result, a carbonat ion is formed on the zeolite CaA reacted with CO_2, and this carbonat ion is bound to a Ca^{2+} cation in the unidentate way.

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