

The Determination of Mobility and Immobility of Water Adsorbed in Type 5A and 13X Zeolites by IR and DTA

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In this study, infrared (IR) and differential thermal analysis (DTA) data were used to investigate the mobility of water adsorbed in synthetic zeolites of type 5A and 13X with pore diameters of 5 and 10 Å, respectively. The results indicate that there are at least two types of water, mobile and immobile ones, in the narrow pore zeolite, while there is only mobile water in the wide pore zeolite.

Key words: IR; DTA; Mobility of Water; Type 5A Zeolite; 13X Zeolite.

The dynamics of water molecules adsorbed in porous systems can be studied by using metal ion complexes as paramagnetic probes [1–3]. Such studies give information about the localization and structure of adsorbed complexes and about the behavior of the adsorbed water.

In our previous study, by electron spin resonance (ESR) the mobility and freezing properties of water adsorbed in synthetic zeolites of type 3A, 4A, 5A, and 13X with pore diameters of 3, 4, 5, and 10 Å, respectively, and the natural zeolites heulandite and clinoptilolite were studied using the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex as paramagnetic probe [4]. It was found that in the narrow-pore zeolites type 3A, 4A, and 5A the first layers of water molecules on the surfaces are restricted in motion even at room temperature, whereas beyond these the water molecules are mobile, the water molecules in wide pore and natural zeolites behaving like liquid water. These results are good agreement with our other study, where $\text{VO}(\text{H}_2\text{O})_5^{2+}$ and $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ complexes were adsorbed on the same zeolites [5].

In the present study these results were confirmed by analysis of IR and DTA spectra of water adsorbed in type 5A and 13X zeolites.

Experimental Details

The synthetic zeolites of the type 5A and 13X were purchased from the British Drug House (BDH). The

unit cells of these zeolites were given in [1]. Firstly the zeolites were activated at 473 K for 4 h. Then, aqueous solutions of CuCl_2 of $5 \cdot 10^{-3}$ M were prepared in distilled water. 1 g of the zeolites was put into 20 cm³ of this solution, stirred and stored at room temperature for 24 h. Then, the solutions were filtered and the zeolites were dried at room temperature.

The IR spectra were recorded on disks of powdered material with a Perkin Elmer Model 1430 Infrared Spectrophotometer. The DTA and thermogravimetry (TG) curves were obtained from the Thermal Analysis Station Rigaku TAS 100.

Results and Discussion

The IR spectra of the zeolites of type 5A and 13X adsorbed CuCl_2 + water with taken at room temperature, are shown in Fig. 1 with the spectra of their pure states. The IR spectrum of the type 5A zeolite has two peaks, showing that there are two kinds of water. These are mobile and immobile water, which can be seen in Fig. 1a) ①. The peak at 3420 cm⁻¹ belongs to the mobile water and that at 3590 cm⁻¹ belongs to the zeolitic water. The peak at 3520 cm⁻¹ (Fig. 1a) ②) in the IR spectrum of the type 5A zeolite adsorbed CuCl_2 + water that appears at higher energy with then the others is attributed to the vibration of zeolitic water. The peaks at 3350 and 3445 cm⁻¹ in Fig. 1a) ② are attributed to mobile and immobile water in zeolitic pores, respectively. Since the environment of the zeolitic water changes with the inclusion of water adsorbed on the type 5A zeolite, the IR peak seen at 3590 cm⁻¹ in Fig. 1a) ① shifts towards 3520 cm⁻¹ in Fig. 1a) ②. It is impossible to state these for the 13X zeolite because there it gives only a peak in the water region of the IR spectrum was shown in Fig. 1b). This peak contains zeolitic and mobile water.

The DTA plays an important role in the detection of mobile and immobile water. DTA and TG curves of water adsorbed in type 5A zeolite have three dehydration steps at 318, 401, and 460 K (Fig. 2a). Dehydration in three steps is attributed to the difference in bonding strength of the water molecules in the type 5A zeolite. These dehydration steps exist also in the DTA curve of pure type 5A zeolite but appear at higher temperatures and lower intensities. Mobile water on surfaces and in pores are removed at 318 and 401 K, respectively. Immobile water in pores is removed at 460 K.

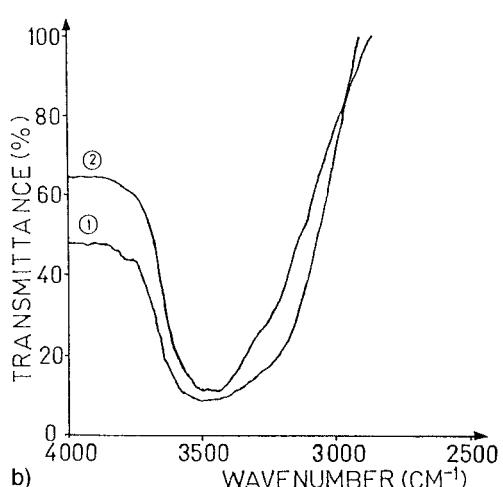
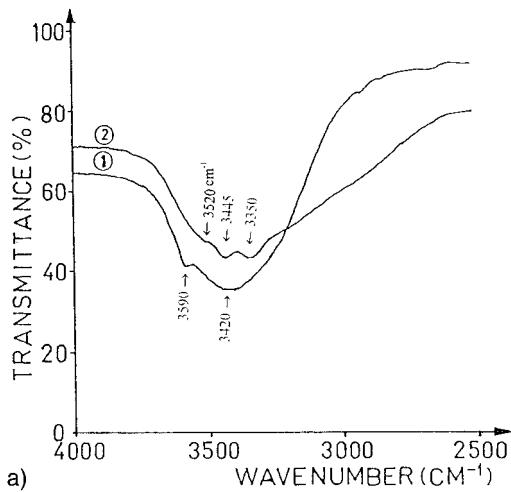


Fig. 1. IR spectra of a) ① zeolite of type 5A pure, ② zeolite of type 5A with adsorbed CuCl₂ + water. b) ① zeolite of type 13X pure, ② zeolite of type 13X with adsorbed CuCl₂ + water.

The DTA curve of the 13X zeolite shows almost only one step of dehydration at 369 K (Fig. 2b). We attribute this dehydration step to mobile water. Essentially, the very low endothermic peak at 319 K does not appear in the DTA trace of pure 13X zeolite. It gives only a wide peak at 420 K which belongs to mobile water.

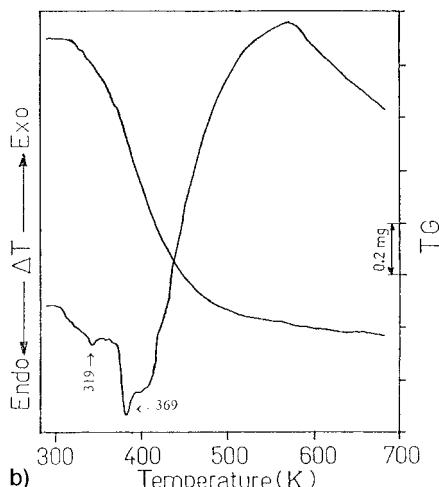
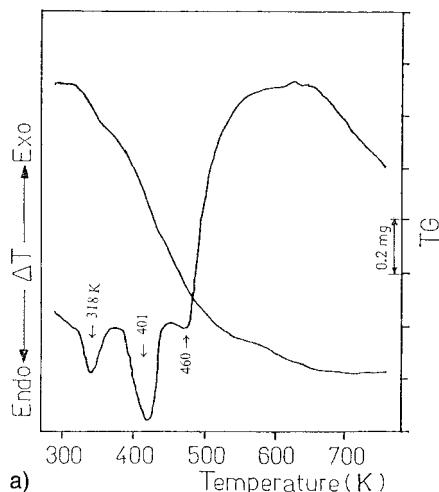


Fig. 2. DTA and TG results for a) zeolite of type 5A with adsorbed CuCl₂ + water, 5.72 mg, and b) zeolite of type 13X with adsorbed CuCl₂ + water, 5.42 mg.

Conclusion

From these results it is concluded that at least two types of water are adsorbed in the narrow pore type 5A zeolite. These are mobile and immobile water. Only mobile water is adsorbed in the wide pore zeolite 13X.

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