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HEATS OF IMMERSION IN RELATION TO WATER LOSSES OF SYNTHETIC SODIUM MORDENITE

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ABSTRACT

Synthetic sodium mordenite was thermally dehydrated in vacuo at different temperatures. Effects of thermal treatment upon water losses and the heats of immersion using different immersion liquids are reported. The results clearly indicate the existence of more than one mordenite structure based on the physical characteristics, which are controlled according to the pre-treatment conditions.

INTRODUCTION

The particular physico-chemical properties of mordenite-type zeolite have been the subject of numerous investigations in the field of adsorption and catalysis. Nevertheless, very little is known regarding their surface characteristics.

Mordenite is one of the zeolitic family in which the fundamental building units (AlO_4 and SiO_4 tetrahedra) are linked together by sharing the oxygen ions at the corners in such a regular way as to produce large elliptical channels having a free diameter of ~7 Å, the main channels being interconnected by smaller channels of ~3 Å free diameter. The exchangeable cations are believed to be located in these channels[1] and are not localized[2]. Moreover, the existence of more than one mordenite framework structure based on the particular physical properties is possible[3]. Recent scanning electron microscopic examination[4] revealed that the synthetic sodium mordenite has a composite structure. The SEM micrographs indicate that the trapezohedral crystals are the dominant form; orthorhombic prisms with basal pinacoids together with stacked orthorhombic bipyramid crystals and micro-crystallites with semi-amorphous characters also appeared.

In the present investigation, we study the energetic aspects of adsorption by measuring the heats of immersion using different adsorbates of different physical properties, namely, water, methanol and cyclohexane. In addition, heats of immersion supply further evidence concerning the surface characteristics of mordenite.

TABLE 1

SURFACE CHARACTERISTICS FROM NITROGEN ADSORPTION AND HEATS OF IMMERSION H_i (cal g^{-1}) OF Na MORDENITE USING WATER, METHANOL AND CYCLOHEXANE AS WETTING LIQUIDS

Sample	*Temp. (°C)*	W_0 *water loss* ($g\,H_2O\,g^{-1}$) ($\times 10^2$)	V_0^{DR} *(molecules* g^{-1}) ($\times 10^{20}$)	V_m^{DR} (*ml* g^{-1})	H_i^{w} (*cal* g^{-1})	H_i^{me} (*cal* g^{-1})	H_i^{cyc} (*cal* g^{-1})
NaM (100)	100	6.51	10.22	0.051	2.28	1.88	1.51
NaM (200)	200	9.90	12.28	0.071	5.16	3.68	
NaM (300)	300	11.90	25.08	0.146	6.21	4.12	1.18
NaM (400)	400	13.09	26.26	0.152	8.23	6.78	0.26
NaM (480	480	13.84	26.26	0.152	7.55	4.41	0.26
NaM (550)	550	14.86	26.26	0.152	7.15		

EXPERIMENTAL

Synthetic sodium mordenite of chemical formula $Na_2(AlO_2)_2(SiO_2)_{10} \cdot 7H_2O$ was thermally dehydrated in vacuo over the temperature range 100–550 °C. The temperatures of the pre-treatment selected are 100, 200, 300, 400, 480, and 550 °C, and the corresponding samples are designated as NaM(100), NaM (200), NaM (300), NaM (400), NaM (480) and NaM (550), respectively. Heating was carried out using an electrical tubular furnace programmed at a heating rate of 2.5–3 °C min^{-1}.

Using a calorimetric method[5], the heats of immersion, H_i (cal g^{-1}), were determined at 35 ± 0.05 °C whereby the temperature of the immersion liquid could be kept constant to within ±0.002 °C during the experimental run.

Sample ampoules, each containing a certain weight of the sample (~0.2 g) were evacuated for 3 h at the required temperature, then sealed under vacuum and transferred to the calorimeter. All the heat values reported in this investigation represent the average of at least two independent determinations. Necessary radiation corrections have also been computed[5]. Water losses were accurately estimated and are listed in Table 1.

RESULTS AND DISCUSSION

Synthetic sodium mordenite dehydrates upon heating at different temperatures in the range 100–550 °C. At any temperature, the loss of water starts rapidly from the lowest temperature studied until 300 °C, beyond which the increase in the pre-treatment temperature results in a relatively decreased rate of water loss. The last traces of water were lost on heating about 300 °C.

The variation of the heats of immersion, H_i (cal g^{-1}), with the pre-treatment temperatures, for the various immersion liquids together with water losses are listed in Table 1 and are graphically represented in Fig. 1.

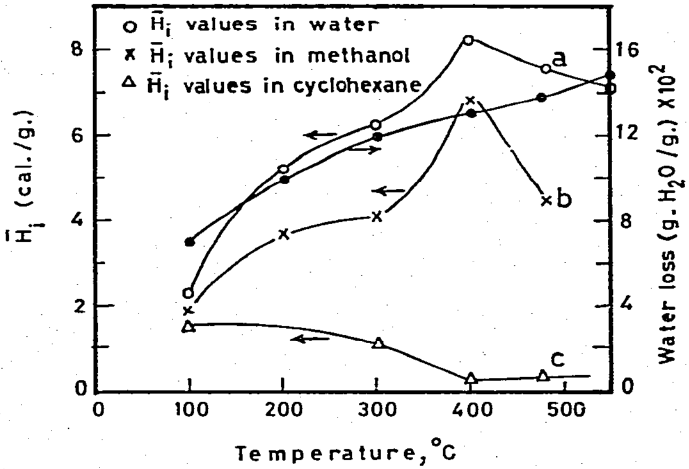

Fig. 1. Variation of the heat of immersion, H_i(cal g^{-1}), and the water loss, (g H_2O g^{-1}), as a function of the pre-treatment temperature.

From these results, there appeared some characteristic features which may be summarized as follows.

(1) It was observed that as the temperature rises the water loss increases. The rate of dehydration seems to be accelerated in the low temperature range and then proceeds with a slower rate in the high temperature range.

(2) The heats of immersion, H_i (cal g^{-1}), in water and in methanol were found to increase with increase of the pre-treatment temperature in a manner parallel with the water loss until 300 °C, followed by a sharper increase in the heat values with further loss up to 400 °C. At temperatures above 400 °C, the heat of immersion decreases until the temperature reaches 550 °C.

The early increase in the heats of immersion may be attributed to the removal of the physically bound water, then at higher temperatures, of the chemically bound water from the mordenite structure leaving a system of continuous channels. Hence, the mordenite channels thus vacated by the water are available for the molecules of the immersion liquid to diffuse through. This diffusion is an activated process[6], which increases with rise in pre-treatment temperature (increased dehydration).

The decrease in the heat values observed when the pre-treatment temperature exceeds 400 °C resulted from the partial collapse of the mordenite structure caused by heating under high vacuum. This phenomenon was previously reported in two earlier publications[4, 7]. Evidently more than one mordenite structure may exist, based on the physical characteristics and controlled according to the pre-treatment conditions.

(3) As a general trend, the heats of immersion in methanol are smaller than in water, which may be attributed to the enhanced accessibility of the small water molecules in the mordenite channels rather than the bulkier methanol molecules. The steeper drop in H_i values at pre-treatment temperatures above 400 °C for methanol, compared with water, may be related to the partial collapse of the mordenite structure according to an inaccessibility factor involved for bulkier methanol molecules.

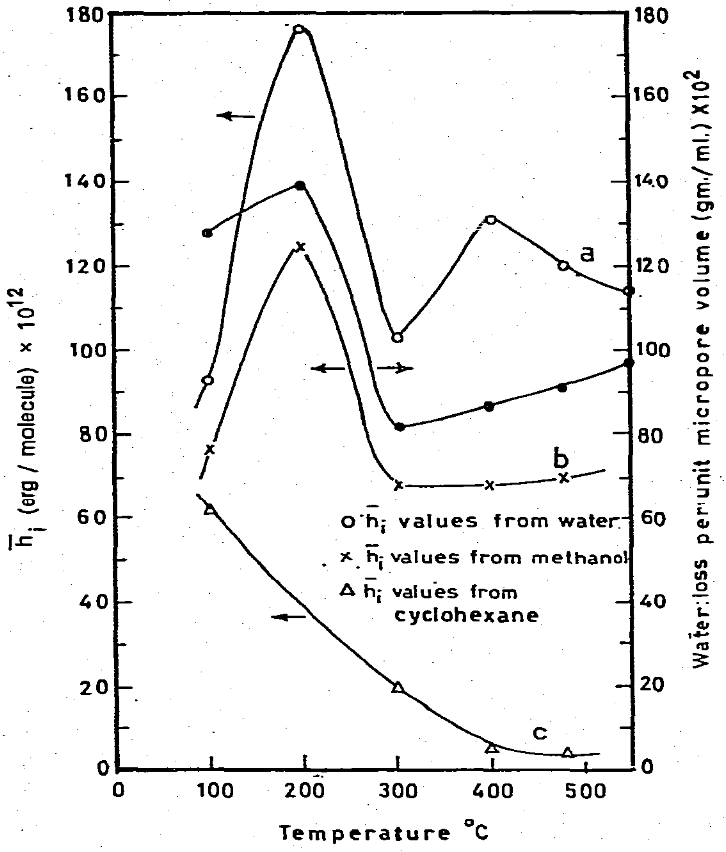

Fig. 2. Variation of the heat of immersion, $\bar{h}_i$(erg molecule^{-1}), and the water loss (g H_2O/V_0^{DR}) as a function of the pre-treatment temperature.

TABLE 2

AVERAGE HEATS OF IMMERSION PER SINGLE MOLECULE OF THE WETTING LIQUID MOLECULES LOCATED IN MICROPORES OF Na MORDENITE SAMPLES

Sample	*Water loss (× 10²) / micro pore volume*	$\bar{h}_i^w$ *(erg molecule⁻¹) (× 10⁻¹³)*	$\bar{h}_i^{me}$ *(erg molecule⁻¹)*	$\bar{h}_i^{cyc}$ *(erg molecule⁻¹)*
NaM (100)	127.65	932.5	768.9×10^{-13}	617.6×10^{-13}
NaM (200)	139.44	1756.4	1252.6×10^{-13}	—
NaM (300)	81.51	1035.0	686.6×10^{-13}	196.6×10^{-13}
NaM (400)	86.12	1310.0	685.5×10^{-13}	41.4×10^{-3}
NaM (480)	91.05	1201.8	702.0×10^{-3}	41.4×10^{-13}
NaM (550)	97.76	1138.1	—	—

(4) The heats of immersion obtained using cyclohexane as immersion liquid, represent the lowest limited values. However, relatively higher heat values were obtained on heating below 300 °C. Due to the size effect, most of the mordenite channels behave as narrower pores towards cyclohexane molecules. Cyclohexane molecules are mostly accessible to the inter-crystalline pore system. Nevertheless,

the inaccessibility towards inter-crystalline pores increases notably upon heating above 300 °C and this again confirms the existence of more than one mordenite structure, previously reported in other investigations[4, 7].

The variations of the average heats of immersion per molecule $\bar{h}_i$ (erg molecule^{-1}), for water (curve a), methanol (curve b) and cyclohexane (curve c) together with water losses per unit micropore volume, each as a function of the pre-treatment temperature are graphically represented in Fig. 2 and are listed in Table 2. As shown in Fig. 2, water heats show a pronounced maximum located at 200 °C, and another less intense peak at 400 °C. The presence of these two peaks is attributed to widely different reasons; the intense peak located at 200 °C represents the hydration of the out-gassed mordenite sample involving the rehydration of metal cations[8], which is accompanied by the evolution of the heat of ion hydration, and as a consequence, the average heat contribution increases until 200 °C is reached. The decrease of the average heat of immersion of different immersion liquids in the order water > methanol > cyclohexane, provides strong support for the above interpretation.

As evident from Table 2, heating at temperatures above 300 °C results in a variable loss of water molecules despite the constancy of monolayer equivalents (26.26×10^{20} molecules g^{-1}), this indicates the development of some pores which are sufficiently inaccessible in nitrogen adsorption[6], but may be involved in heats of immersion. Therefore, over a range of 300–400 °C, the removal of the last trace amounts of water enhances the increase in water heats at 400 °C; such behaviour is absent in methanol heats, as shown in Fig. 2. The immersion process after heating at 400 °C represents the immersion on a surface which is mostly depleted of zeolitic water and the onset of structural collapse in the mordenite channels is not yet observed. These two factors lead to the second peak in water heats at 400 °C and the constancy of the methanol heats upon heating above 300 °C.

The continuous decrease in the heat of immersion values for cyclohexane, $\bar{h}_i$

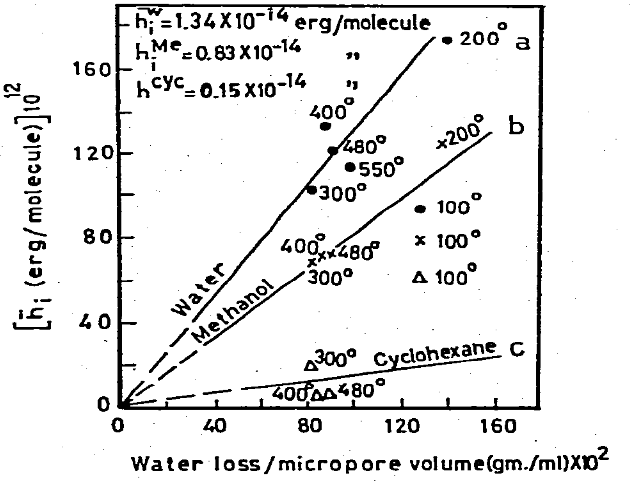

Fig. 3. Variation of heat of immersion, h_i(erg molecule^{-1}) as a function of water loss per unit micropore volume (g H_2O/V_0^{DR}).

(erg molecule^{-1}), is attributed to the decrease in the dispersion interactions involved.

The variation of the average heat contribution per molecule, $\bar{h}_i$ (erg molecule^{-1}), as a function of the water loss per unit micropore volume is illustrated in Fig. 3. The origin of such a plot represents the immersion of a sample without any water loss. In this case, the mordenite pore system is densely populated by water molecules and a minimum values of heats of immersion may be observed (zero heat). Figure 3 shows also a noticeable linear increase in the average heat contribution, $\bar{h}_i$ (erg molecule^{-1}) with the increase in water loss per unit micropore volume, for all immersion liquids used in this investigation; the slopes of these linear relations were found to decrease in the order water > methanol > cyclohexane.

For all immersion liquids, a small heat value was recorded at 100°C, which indicates that the immersion occurred in pore volumes which were still populated with zeolitic water. Definite deviations from the linear plots were observed in some of the higher temperature samples (300, 400 and 480°C). The heat values at 400°C are larger than those assumed basically on the linear plot as shown in Fig. 3, which may be attributed to the increased water loss at 400°C and the structural collapse is not yet observed.

The average contribution of single molecules of different immersion liquids was calculated from the slopes of the linear plots and is shown in Fig. 3. The results are

$$h_i^{w} = 1.93 \times 10^{-1} \text{ kcal mole}^{-1}$$
$$h_i^{Me} = 1.20 \times 10^{-1} \text{ kcal mole}^{-1}$$
$$h_i^{cyc} = 0.22 \times 10^{-1} \text{ kcal mole}^{-1}$$

The lowest heats of immersion were obtained with cyclohexane, which may be attributed to the limited interaction between the bulky cyclohexane molecules and the mordenite surface, whereas in the other immersion liquids (water and methanol), other contributions of ion hydration and polar interactions are involved. These contributions are greater for the smaller water molecules.

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