Thermochimica Acta, 31 (1979) 147–151

HEATS OF IMMERSION IN RELATION TO WATER LOSSES OF CHROMIUM EXCHANGED MORDENITE

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(Received 23 May 1978)

ABSTRACT

Chromium-exchanged mordenite samples were thermally dehydrated in vacuo over the temperature range 100–480 °C. The effects of thermal treatment on water losses and heats of immersion in water, methanol, and cyclohexane are discussed.

From the results obtained, it is concluded that the chromium ions reflect smaller heats of ion hydration compared with the sodium ions in sodium mordenite[1]. The displaying parameters are, the hydration of metal cations, filling of the vacated pore structure, and the structural collapse at the high temperature studied. It was found that the heats of immersion decrease with increasing molecular size of the wetting liquid.

INTRODUCTION

Scanning electron microscopic examination[2] showed that the chromium-exchanged form of mordenite-type zeolites has the same composite microstructure as the original synthetic sodium mordenite with one basic difference, namely, the degree of amorphous character which increases with the presence of the transition metal cations in the zeolitic structure. The microstructure of the chromium-exchanged mordenite, obtained from the SEM micrographs, displayed the trapezohedral crystals with orthorhombic bipyramid crystals with an oriented morphology.

Previous investigations on various transition metal cationic forms of mordenite-type zeolites[2, 3] indicate that the high vacuum procedure, when applied at high temperatures, causes a partial collapse in the mordenite structure, and the total pore system, consisting primarily of intracrystalline pores, is inaccessible to the various adsorbates to different extents depending on their molecular sizes.

In this paper, the study of some surface characteristics was followed in an energetic sense. Chromium-exchanged sodium mordenite-type zeolite was chosen as the starting product for this work. The results obtained, using water, methanol and cyclohexane as immersion wetting liquids, were critically compared with each other.

TABLE 1

HEATS OF IMMERSION OF CrNaM USING WATER, METHANOL AND CYCLOHEXANE AS WETTING LIQUIDS

Sample	W_0 *water loss* *(H_2O g^{-1})* *($\times 10^2$)*	V_0^{DR3} *(molecule g^{-1})*	V_m^{DR3} *(ml g^{-1})*	H_i^w *(cal g^{-1})*	H_i^{Me} *(cal g^{-1})*	H_i^{cyc} *(cal g^{-1})*
CrNaM(100)	10.49	0.34×10^{20}	0.002	3.78	2.63	0.435
(200)	14.13	13.47×10^{20}	0.078	6.38	4.49	0.417
(300)	14.49	28.13×10^{20}	0.163	11.39	4.70	0.428
(400)	15.15	30.15×10^{20}	0.175	11.82	3.98	0
(480)	16.58	30.15×10^{20}	0.175	7.22	4.28	0

EXPERIMENTAL

The synthetic sodium mordenite with the chemical formula $Na_2(AlO_2)_2$-$(SiO_2)_{10} \cdot 7H_2O$ was subjected to a certain exchange process during which the chromium cations replace the sodium cations of the original synthetic sodium mordenite sample. Chemical analysis showed that the resulting chromium exchanged mordenite has the chemical formula $Cr_{0.39}Na_{1.23}(AlO_2)_2(SiO_2)_{10} \cdot 7.05\ H_2O$.

The chromium-exchanged mordenite sample, CrNa–M, was thermally dehydrated in vacuo at temperatures of 100, 200, 300, 400, and 480 °C. Heating was carried out using an electrical tubular furnace programmed to increase at a rate of 2.5–3.0 °C min^{-1}.

The integral heats of immersion, H_i (cal g^{-1}), were determined at 35 ± 0.05 °C using a calorimetric method[4], whereby the temperature of the immersion liquid could be kept constant within ±0.002 °C during the experimental run.

An accurately weighed sample (0.2 g) contained in an ampoule was carefully evacuated for 3 h at a pressure of 10^{-5} mm Hg at the required temperature, then sealed under vacuum and transferred to the calorimeter. The measured change in temperature produced on immersion of the samples was corrected for radiation losses[4]. All the heat values reported in columns 5–7 of Table 1 are the averages of at least two independent determinations.

RESULTS AND DISCUSSION

Figure 1 illustrates the variation of the heat of immersion, H_i (cal g^{-1}), and the water loss, g/g, as a function of the pre-treatment temperature. Immersion heats were measured using water (curve a), methanol (curve b), and cyclohexane (curve c) as immersion liquids. The heats of immersion and respective water losses are listed in Table 1.

As shown in Fig. 1, certain conclusions may be derived as follows.

(1) The water loss increases on raising the pre-treatment temperature. At lower temperatures, below 200 °C, the physically bound water was withdrawn from

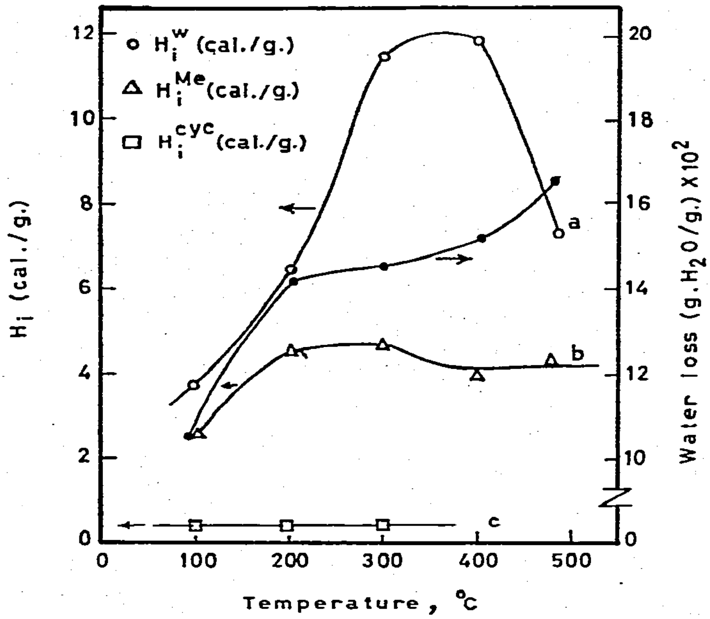

Fig. 1. Variation of the heat of immersion, H_i(cal g^{-1}), and the water loss, (g H_2O g^{-1}), as a function of the pre-treatment temperature.

TABLE 2

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

Sample	*Water loss × 10^2* / *Micropore volume*	$\bar{h}_i^{w\,a}$ *(erg molecule^{-1}) (× 10^{-13})*	$\bar{h}_i^{Me\,a}$ *(erg molecule^{-1}) (× 10^{-13})*	$\bar{h}_i^{cyc\,a}$ *(erg molecule^{-1}) (× 10^{-13})*
CrNaM(100)	524.5	4647.8	3233.5	347.9
(200)	181.2	1979.3	1393.3	129.4
(300)	88.9	1692.5	698.4	63.6
(400)	86.6	1638.7	551.8	
(480)	94.7	1001.0	593.4	

[a] Monolayer equivalents and micropore volumes are listed in ref. 3.

the mordenite structure. However, at relatively higher pre-treatment temperature, the chemically bound water together with the water of hydration of the chromium ions were removed from the zeolitic channels. Figure 1 clearly indicates the presence of a temperature range, 200–300 °C, at which the rate of water loss is relatively small. This temperature range is considered to represent a mixed dehydration of the two mechanisms.

(2) The heat of immersion in water, H_i (cal g^{-1}), increases first with the pre-treatment temperature until it reaches a maximum value between 300 and 400 °C. However, the increase in the pre-treatment temperature above 400 °C results in a sharp decrease in the heat of immersion at 480 °C. This behaviour may be explained as follows: at low pre-treatment temperatures, the heats of immersion increase on increasing the vacated portion of the zeolitic channels until the temperature range 300–400 °C has been reached. Between 300 and 400 °C, the maximum heat of immer-

sion, H_i (cal g^{-1}), was obtained, indicating the possibility of metal cation hydration[5], the filling of the vacated channel structure of the zeolite by water molecules and the onset of the structural collapse begins later. When the pre-treatment temperature exceeded 400 °C, the dehydration of the exchangeable cations was considered to be complete. The dehydrated cations were deposited on the zeolitic walls and as a result, some zeolitic micropores were obstructed. Consequently, immersion heats in water decreased sharply on heating at temperatures above 400 °C, which adds to a measurable extent, to the structural collapse.

(3) The heats of immersion using methanol as wetting liquid, H_i^{Me} (cal g^{-1}), show an early increase with rise in pre-treatment temperature up to 300 °C. Above 300 °C, the immersion heats decrease slightly to an almost constant value in the temperature range 400–480 °C. As indicated in Fig. 1, the early increase in the heats of immersion following the rise in pre-treatment temperature below 300 °C runs parallel with the respective changes in water losses. This indicates that the water molecules were removed from pores which were readily available for methanol immersion. If the pre-treatment temperature exceeds 300 °C, the mordenite structure reflects slightly decreased methanol heats. This decrease in the heat of immersion reaches an almost constant heat of immersion upon heating above 300 °C. The relatively constant heat of immersion, H_i^{Me} (cal g^{-1}), in the range 400–480 °C, significantly reclaims the compensation between the re-uptake of methanol molecules by the metal cations, solvation, which is accompanied by evolution of heat to the surface and the decrease in the heat of immersion as a result of the structural collapse present in this highly dehydrated state above 400 °C.

(4) Using cyclohexane as immersion liquid, the heats of immersion, H_i^{cyc} (cal g^{-1}), show almost the same value over the temperature range studied. This indicates that cyclohexane molecules are accessible only to the external surface of

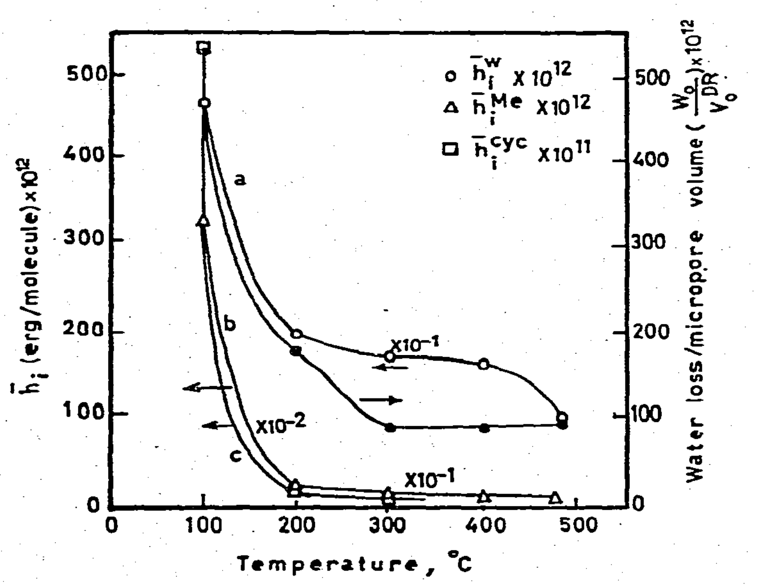

Fig. 2. Variation of the heat of immersion, h_i(erg molecule^{-1}) and the water loss (g H_2O/V_0^{DR}) as a function of the pre-treatment temperature.

the mordenite structure and that the internal pore system is inaccessible to cyclohexane molecules.

Figure 2 shows the variation of the heat of immersion, $\bar{h}_i$ (erg molecule^{-1}), and the water loss per unit micropore volume (W_o/V_m^{DR}) as a function of the pre-treatment temperature. Water heats are shown in curve a, methanol heats in curve b, and cyclohexane heats in curve c. The results shown in Fig. 2 and Table 2 clearly indicate parallel dependence of the heats of immersion of various adsorbates, h_i (erg molecule^{-1}), and the water losses per unit micropore volume on the pre-treatment temperature. This result reflects the opening of the pore system by the removal of water molecules, either by dehydrating the cations or by vacating the canal pore system, before the immersion process, despite the various heat contributions accompanying each process.

The wide differences in the heat of immersion calculated, $\bar{h}_i$ (erg molecule^{-1}), may be attributed to the variable heat contribution involved in the heat of ion hydration[5], filling considerations as a microporous texture[6], and structural collapse of the mordenite pore system.

It was found that the heats of immersion follow the order water > methanol > cyclohexane.

From an earlier communication[1], a distinct heat of ion hydration is revealed as a peak around 200 °C, wherever the smaller sodium ions are present. In the present case, the bigger chromium ions are present and consequently smaller ion hydration effect is revealed; the absence of such a peak for water heats around 200 °C, is taken as sufficient proof for the relatively small contribution of chromium ion hydration.

In Fig. 2(a), the delayed decrease in the heat of immersion, $\bar{h}_i^w$ (erg molecule^{-1}), above 400 °C is related to the outcome of the collapse in the structure which reflects a small hydration dependence on cations and pore structure. This may be due to the limited accessibility towards small water molecules as a pore size effect and/or the blocking of the super micropore by the dehydrated metal cations. The location of water molecules inside these micropores (as a result of immersion) suffers from enhanced mutual repulsions[7].

In conclusion, the heats of immersion reflect and support other adsorptive surface studies, especially if they bear certain significance in energetic characteristics. From these results, almost the same canal pore system was present, with limited heat of ion hydration, and a measurable structural collapse in the pore structure is revealed upon heating at temperatures above 400 °C, which is in agreement with the previous investigations[2, 3].

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