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ZEOLITIC PROPERTIES OF MIXED HEXACYANOFERRATES/II/: ADSORPTION ISOTHERMS AND DIFFERENTIAL HEATS OF ADSORPTION OF WATER VAPOUR

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The series of mixed hexacyanoferrates $M_2Zn_3[Fe/CN/_6]_2.xH_2O$ ($M = K^+, Na^+, Cs^+$) present zeolitic properties. The adsorption water vapour isotherms were determined by TG at 303 K. The differential heats of adsorption of water vapour were measured by microcalorimetry; the molar integral entropy of the sorbed phase was calculated. The data obtained show that (i) the H_2O-sorbent interactions are very weak at the beginning of cavity filling, whereas the sorbed molecules exhibit the same mobility as in the vapour phase; (ii) during the filling, the H_2O-H_2O interactions increase up to a maximum; (iii) close to total filling, the adsorption phenomenon is comparable to a vapour-liquid transition and the sorbed phase has the same molar entropy as that of the liquid phase.

The zeolitic properties of mixed hexacyanoferrates synthetized in our laboratory have been studied, and their adsorption compared with that of the classical zeolites.

In this study, the water vapour adsorption isotherms were determined for three mixed hexacyanoferrates, together with the differential heats of adsorption by microcalorimetry.

Experimental

Preparation

Following the method of Vlasselaer et al. [1], the mixed hexacyanoferrate/II/ of zinc and potassium (product I) was prepared by dropwise mixing of molar solutions of potassium hexacyanoferrate(II) and zinc sulphate (volume ratio, 1/4). After 7 days the slurry was centrifuged and washed with distilled water. It was then dried for 7 days at 343 K.

The mixed hexacyanoferrate of zinc and sodium (product II) was prepared following the procedure used by Kamura et al. [2].

The hexacyanoferrates of this series are ion-exchangers. The mixed hexacyanoferrate of zinc and caesium (product III) was prepared by exchanging completely the K^+ in product I for Cs^+.

The three products are white powders. On analysis [3], their formulae were in accordance with those expected: $M_2Zn_3[Fe/CN/_6]_2.xH_2O$, x depending on the hydration state of the product.

Structure

Single crystals of product I were prepared and their structure characterized [4]. It consists of a three-dimensional framework of octahedra (FeC_6) and tetrahedra (ZnN_4) linked by CN groups. In this framework, large ellipsoidal cavities appear with dimensions of a = 5.1 Å, b = 12.7 Å and c = 8.3 Å. Each cavity is linked to six other cavities by means of six ellipsoidal windows, whose axes measure 5.2 Å and 2.9 Å. There are two K^+ ions in each cavity; these neutralize the electrical charge. The water molecules present do not influence this structure.

The cavity dimensions allowed calculation of a free volume of 260 $Å^3$ per unit cell, provided that the occupied volume of K^+ is known.

We can predict that products II and III have the same crystal structure since only the exchanged ions are different.

The characteristics shown below give the zeolite-like properties to these products.

Thermal stability and adsorption properties

The thermal stability of product I was studied by DTA, TG and X-ray analysis [5]. It remains stable up to 523 K. Adsorption and desorption of water is reversible in this temperature range, without alteration of the crystal structure. The anhydrous products are stable [6].

The desorbed water can be substituted by permanent gases (N_2, CO_2, CO) or light hydrocarbons (C_2H_6, C_3H_8, C_4H_{10}, C_2H_4) [6]. The free volume of the cavities is wholly occupied by the guest molecules when the vapour pressure is reached.

Adsorption water vapour isotherms

The adsorption water vapour isotherms were determined by TG, at 303 K and up to the vapour pressure. The samples (about 0.1 g) were dehydrated first by pumping and heating up to a convenient temperature depending on their thermal stability. The experimental results are shown in Fig. 1, where the amounts adsorbed are given in gram per gram of dehydrated material. The adsorption and desorption isotherms coincide perfectly and resemble the type I of Brunauer et al. [7].

The adsorption capacities, i.e. the volumes W_0, were determined by means of the point A method [8], and are shown in Table 1.

The volume W_0 is usually considered to be wholly occupied by the sorbe phase at the pressure corresponding to this point. Knowledge of this volume W_0 allows calculation of the number of H_2O molecules (n) per cavity. The value of W_0 determined experimentally for product I coincides perfectly with the volume resulting from the crystallographic parameters.

Table 1 Adsorption capacities

	$K_2Zn_3[Fe(CN)_6]_2$	$Na_2Zn_3[Fe(CN)_6]_2$	$Cs_2Zn_3[Fe(CN)_6]_2$
W_o, cm^3.g^{-1}	0.215	0.245	0.128
$n.H_2O$ molecules/ cavity	8.4	8.8	6.3

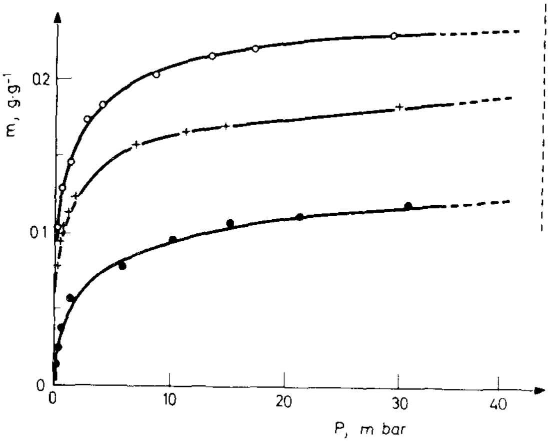

Figure 1 Adsorption water vapour isotherms for $M_2Zn_3[Fe(CN)_6]_2$
o M = Na^+
+ M = K^+
● M = Cs^+

Differential heats of adsorption

The differential heats of adsorption of water vapour were determined by calorimetry, by means of a differential microcalorimeter. The heat quantity ΔQ was measured as a function of the number of moles adsorbed, Δn. The amount adsorbed was calculated from the known pressures in the calorimeter before and after adsorption and from the previous adsorption isotherms.

Before adsorption, the samples were activated following the same procedure as in TG.

The ratio $\Delta Q/\Delta n$ is closer to the differential heat of adsorption dQ/dn as Δn is smaller. Δn was smaller than 10^{-3} mol per gram of dehydrated material, that is less than 10 per cent of the adsorption capacity. The order of magnitude of ΔQ was less than 10 J.

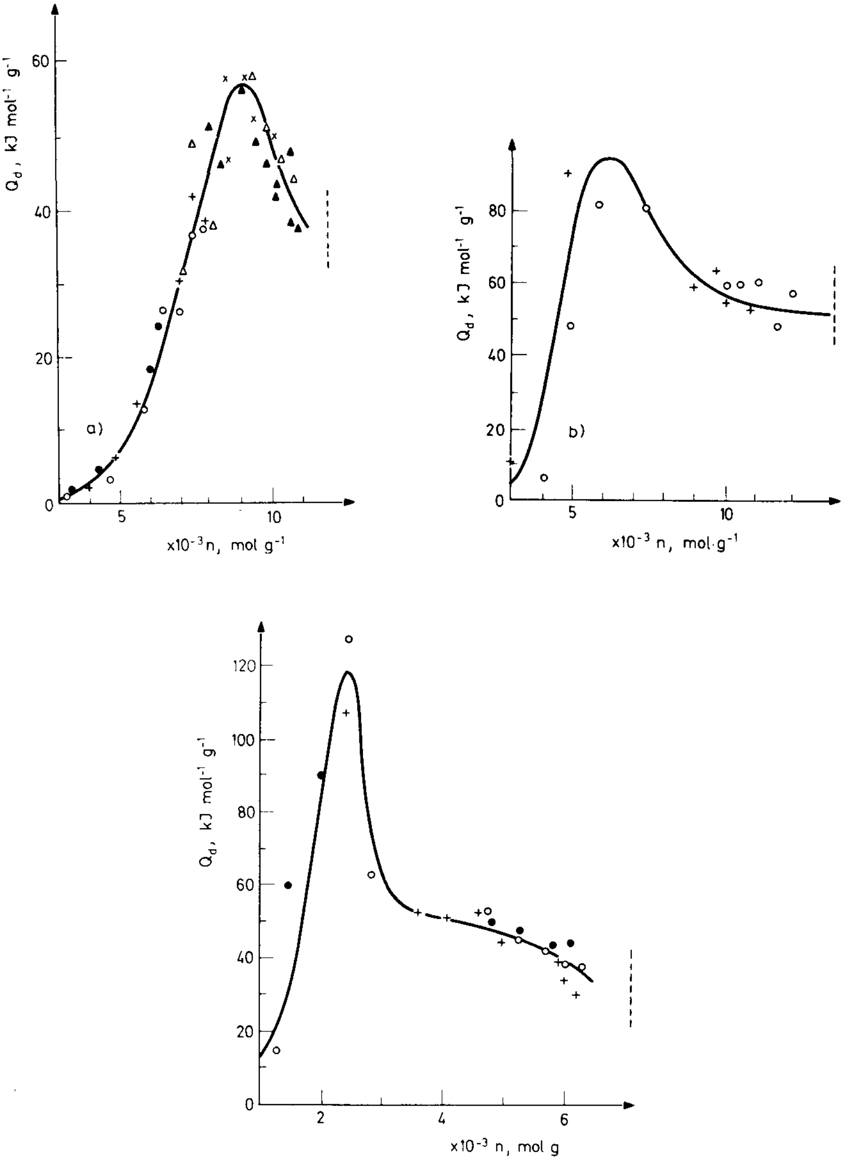

Figure 2 Differential heat of adsorption of water vapour on $M_2Zn_3[Fe(CN)_6]_2$

2a : $M = K^+$

2b : $M = Na^+$

2c : $M = Cs^+$

o, ●, +, x, △, ▲ = different experiments

The experimental results are shown in Fig. 2. The three curves present the same features. For the initial sorbed molecules the differential heat is very small. It then increases, rises to a maximum and reaches a constant value close to the heat of liquefaction of water.

Results

Molar integral entropy of sorbed phase

The molar integral entropy of the sorbed phase S_a can be calculated [9] from the following relationship:

$$S_a = \frac{1}{n} \int_0^n \bar{S}_a \, dn$$

n is the number of sorbed moles, and $\bar{S}_a$ is the molar differential entropy:

$$\bar{S}_a = S_g - \frac{q_{st}}{T}$$

S_g is the molar entropy of the vapour. In experimenting with a differential calorimeter system according to an isothermal process at temperature T, isosteric heat q_{st} can be calculated from the experimental values of the differential heat q_D:

$$q_{st} = q_D + RT$$

if we assume ideal behaviour of the vapour; R is the gas constant.

S_a is calculated by graphical integration of the area under the $\bar{S}_a$ vs. n curves (Fig. 3).

The integral entropy of the sorbed phase, $\bar{S}_a$, decreases continuously from S_G, the molar entropy of the corresponding vapour, to S_L, the molar entropy of the liquid.

Discussion

The variations in the differential heat of adsorption and the variations in the integral entropy of the sorbed phase with the number of adsorbed moles lead to the same conclusions. The H_2O-sorbent interactions are very weak at the beginning of cavity filling, whereas the entropy shows that the sorbed molecules have the same mobility as in the vapour phase.

In contrast, with zeolites, water adsorption occurs with strong interactions between the H_2O and the solid for the initial sorbed molecules [10].

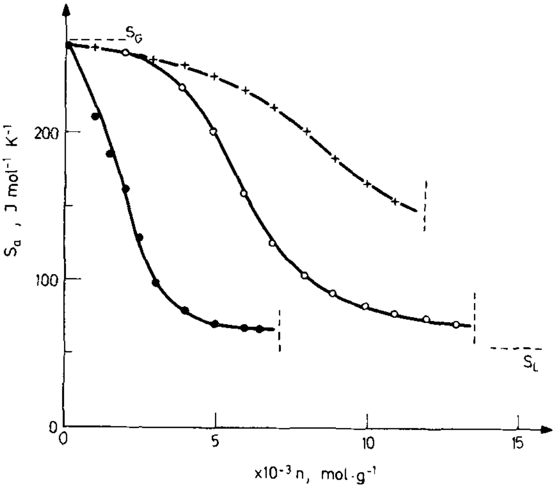

Figure 3 Molar integral entropy of sorbed phase: H_2O-$M_2Zn_3[Fe(CN)_6]_2$
+ M = K^+
o M = Na^+
● M = Cs^+
S_G = molar entropy of vapour phase
S_L = molar entropy of liquid phase

During the filling, the H_2O-H_2O interactions increase up to a maximum. The values taken by the differential heat then indicate that the adsorption phenomenon present the characteristics of a vapour-liquid transition. This deduction conforms with the value of the molar entropy of the sorbed phase, which is equal to that of the liquid phase.

Finally, the adsorption behaviour of the ferrocyanides compares favourably with that of zeolites.

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Zusammenfassung – Die Serie der gemischten Hexacyanoferrate $M_2Zn_3[Fe(CN)_6]_2 \cdot x\ H_2O$ ($M = K^+, Na^+, Cs^+$) weist zeolithische Eigenschaften auf. Die Wasserdampfadsorptionsisothermen wurden mittels TGA bei 303 K bestimmt. Die differentiellen Wärmen der Adsorption von Wasserdampf wurden mittels Mikrokalorimetrie experimentell bestimmt; die molare integrale Entropie der sorbierten Phase wurde berechnet.

Die erhaltenen Daten zeigen dass:

(i) zu Beginn des Auffüllens der Hohlräume die Wasser-Sorbent-Wechselwirkung sehr schwach ist, wobei die sorbierten Moleküle die gleiche Beweglichkeit wie in der Dampfphase aufweisen;

(ii) die Wasser-Wasser-Wechselwirkung während des Prozesses der Hohlraumauffüllung ein Maximum erreicht;

(iii) nahe der vollständigen Hohlraumauffüllung das Adsorptionsphänomen mit dem Dampf-Flüssigkeits-Übergang vergleichbar ist und die molare Entropie der sorbierten Phase gleich der der flüssigen Phase ist.

Резюме – Ряд смешанных гексацианоферратов $M_2Zn_3[Fe(CN)_6]_2 \cdot x H_2O$ ($M = K^+, Na^+, Cs^+$) обладают свойствами цеолитов. Методом ТГА определены адсорбционные изотермы паров воды при 303 К. Микрокалориметрией измерены дифференциальные теплоты адсорбции паров воды. Вычислена молярная интегральная энтропия сорбированной фазы. Полученные данные показали, что взаимодействия типа H_2O – сорбент очень слабы в самом начале полостей наполнения, в то время как сорбированные молекулы обладают такой же подвижностью как и в газообразной фазе. В течении наполнения, взаимодействия типа H_2O–H_2O увеличиваются до максимума. Близко к полному наполнению адсорбционное явление сравнимо с переходом типа пар – жидкость и сорбированная фаза имеет такую же молярную энтропию как и одна из жидких фаз.