Thermochimica Acta, 27 (1978) 177–188
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

PHYSICO-CHEMICAL STUDIES ON CATION-EXCHANGED MORDENITES. II. SURFACE PROPERTIES

R. SH. MIKHAIL, S. A. ABO-EL-ENEIN AND H. A. EL-WAKIL*
Department of Chemistry, Faculty of Science, Ain Shams University, Cairo (Egypt)
(Received 7 November 1977)

ABSTRACT

The adsorption of nitrogen, water vapour, methanol and cyclohexane vapours on the synthetic sodium mordenite and its transition metal exchanged forms were studied in order to elucidate the microstructural characteristics of these samples. The results obtained indicate that the major part of the total pore system, mainly the intracrystalline pore system, is inaccessible to various adsorbates to variable extents depending on their molecular size. Cyclohexane adsorbate was found to measure only the external (inter-crystalline) pore system.

INTRODUCTION

The knowledge of the sorptive properties of the synthetic sodium mordenite and its transition metal exchanged forms are of prime importance in elucidating their microstructural characteristics which are related to their activity and to their selectivity in catalytic reactions.

The intra- and intercrystalline sorption of a great number of representative molecules using different techniques were reported in the literature[1–8]. These studies suggest[2] a framework of natural mordenite probably consisting of 8-membered rings with diameter 4.2 Å, but the proposed crystal structure of mordenite as given by Meier[9] indicates rings of ~7 Å in diameter, and that the stacking faults are not the cause of their molecular sieve character[1].

In this investigation, the adsorption isotherms of nitrogen, water, methanol, and cyclohexane vapours on the different mordenite samples were studied in order to investigate the influence of the geometry and character of the canal pore system of these samples on the adsorption of these molecules of various sizes and polarities.

---

* Present address: Basic Science Department, Faculty of Petroleum and Mining Engineering, Suez Canal University, Suez, Egypt.

EXPERIMENTAL

The apparatus used for determining the adsorption isotherms of nitrogen at liquid nitrogen temperature was a conventional volumetric one[10]. The mordenite samples were pre-outgassed at a pressure as low as 10^{-5} mm Hg in the temperature range 100–480°C. The samples were kept for a period of 3 h at the desired temperature prior to any adsorption run.

The adsorption of water vapour at 35°C was measured using a conventional gravimetric apparatus containing a number of silica spring adsorption balances of McBain–Bakr type[11].

The adsorption isotherms of methanol and cyclohexane vapours at 35°C were determined by means of a conventional volumetric apparatus similar in type to that described by Razouk and Salem[12]. Each adsorbent was thoroughly outgassed in situ at 480°C for a period of 3 h at a pressure as low as 10^{-5} mm Hg before carrying out the experiment.

The materials used in this investigation are the synthetic sodium mordenite and its transition metal (Cr^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) exchanged forms. Detailed information regarding the method of preparation and the proposed chemical formulae of all investigated samples are described in an earlier publication[13].

RESULTS AND DISCUSSION

Adsorption of nitrogen

The surface properties of these mordenite samples were determined using nitrogen gas as an adsorbate. The adsorption isotherms of nitrogen at liquid nitrogen temperature (−195.8°C) on the various mordenite samples pre-outgassed at different temperatures were determined (cf. Fig. 1).

All the adsorption isotherms obtained were found to belong to type I of Brunauer's classification[10]; they are initially very steep and exhibit plateaus covering almost the whole range of the equilibrium relative vapour pressure of the adsorbate.

From these adsorption isotherms the monolayer equivalent values could be calculated by applying the Dubinin–Radushkevich equation[14–16] which is based on the Polani potential theory of adsorption. Figure 2 is a representative case for the Dubinin–Radushkevich plots.

The monolayer equivalent values obtained by the DR method were found to agree within ± 4% with the results obtained by applying the Génot analytical method[17]. The latter provides a direct standard method of detecting the monolayer point on the isotherm.

The monolayer equivalents as well as the pore volumes for the various mordenite samples obtained from nitrogen adsorption at −195.8°C, pre-outgassed at different temperatures, are given in Table I. From this Table some interesting characteristics were drawn and could be summarized as follows.

(i) The monolayer equivalent values showed a sharp increase with the pre-out-

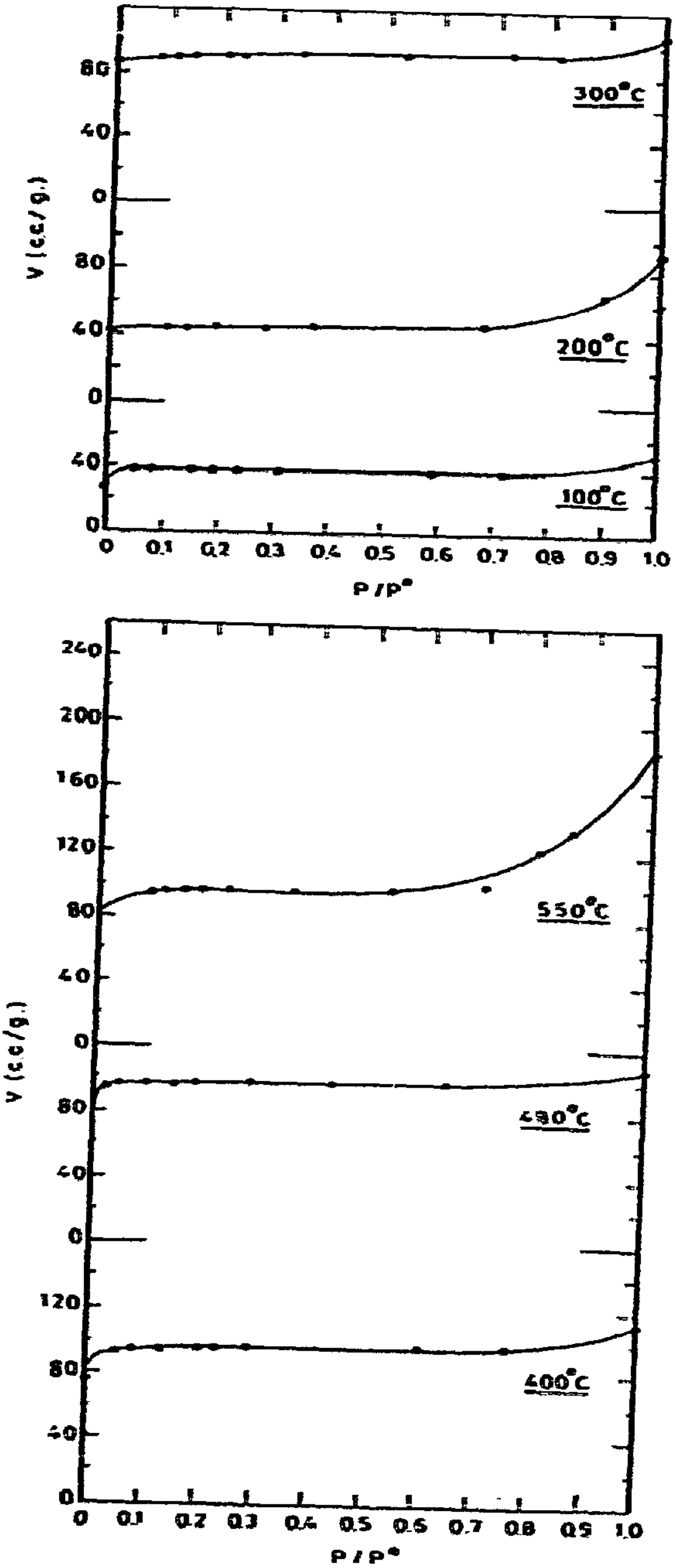

Fig. 1. Adsorption isotherms of nitrogen on the original (Na–M) pre-outgassed at various temperatures.

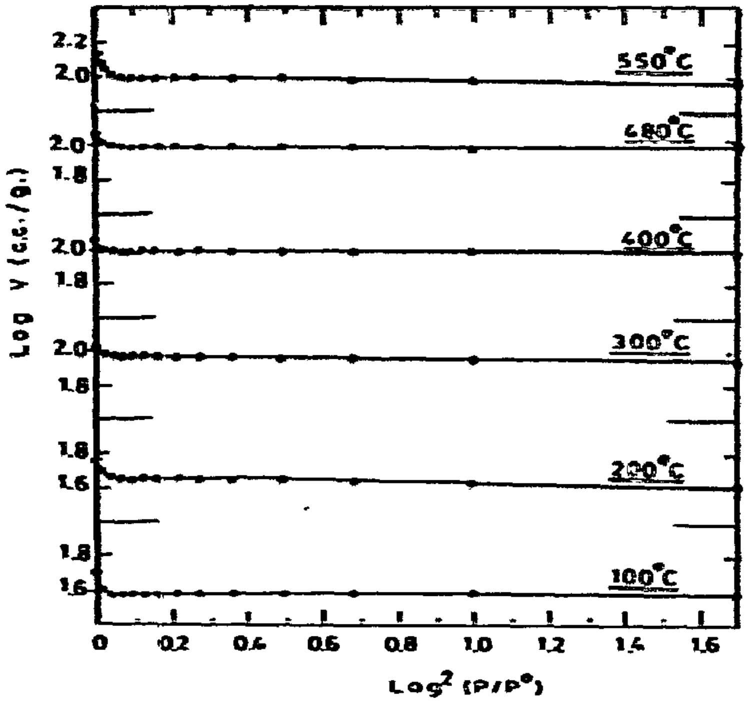

Fig. 2. Dubinin–Radushkevich plots of nitrogen adsorption on the original (Na–M) pre-outgassed at various temperatures.

TABLE I

THE MONOLAYER EQUIVALENTS AND THE TOTAL PORE VOLUMES FOR THE VARIOUS MORDENITE SAMPLES PRE-OUTGASSED AT VARIOUS TEMPERATURES (°C) (FROM NITROGEN ADSORPTION)

Sample	*V_m (molecules/g × 10^{20})*						*V_p (ml/g)*					
	100	*200*	*300*	*400*	*480*	*550*	*100*	*200*	*300*	*400*	*480*	*550*
Na–M	10.22	12.28	25.08	26.26	26.26	26.26	0.078	0.140	0.161	0.176	0.170	0.289
CrNa–M	0.34	13.47	28.13	30.15	30.15		0.022	0.088	0.183	0.179	0.250	
MnNa–M	0.41	19.46	25.08	28.81	29.29		0.013	0.150	0.186	0.173	0.170	
CoNa–M	1.02	16.57	22.35	24.79	30.15		0.013	0.112	0.158	0.164	0.204	
NiNa–M	0.89	25.08	26.26	27.49	28.81		0.032	0.161	0.162	0.169	0.186	
CuNa–M	0.44	26.26	30.15	30.15	30.15		0.027	0.170	0.197	0.203	0.198	

gassing temperature up to 300°C, and this was followed by a gradual increase until the range 400–480°C (cf. Fig. 3). This could be attributed to the successive removal of physically then chemically bound water molecules from the mordenite structure.

(ii) The successive removal of intracrystalline zeolitic water from the pores goes parallel with increasing the adsorption capacity. Accordingly the temperature range 400–480°C can be regarded as the optimum temperature range for activating the mordenite catalysts. At this temperature range, almost all the intracrystalline zeolitic water was removed.

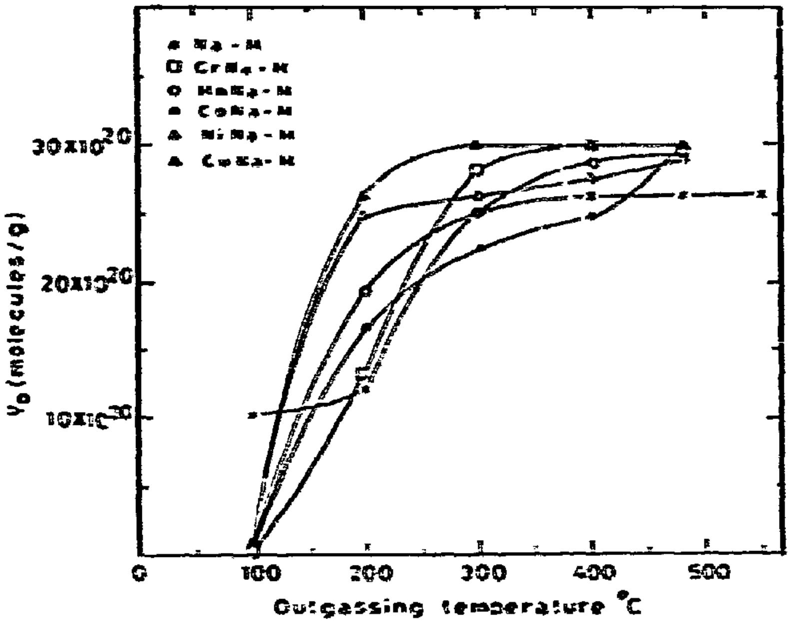

Fig. 3. The monolayer equivalents of various mordenite samples as a function of outgassing temperature.

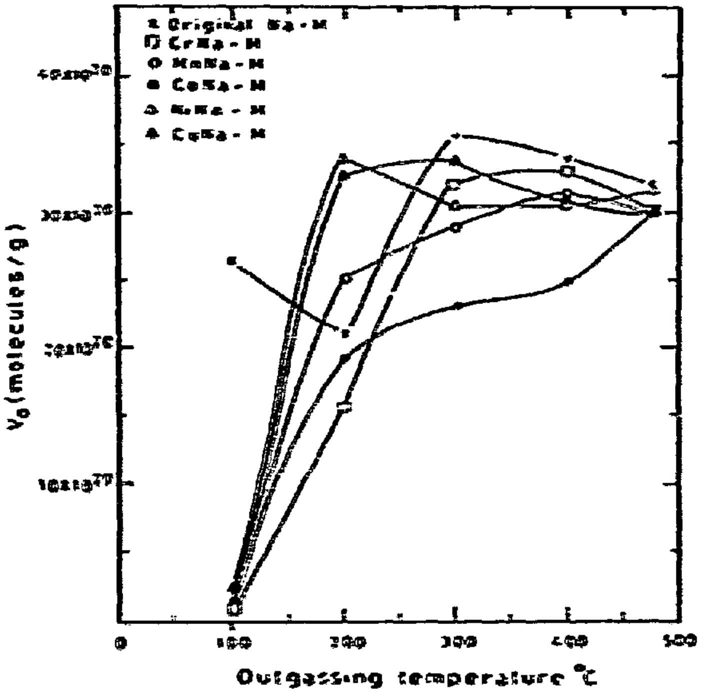

Fig. 4. Monolayer equivalents corrected for complete water loss at various outgassing temperatures.

(iii) When the monolayer equivalent values were corrected for complete dehydration of the various samples heated at different temperatures, the relationship shown in Fig. 4 was obtained; from this Fig. it is clear that by drying at 100°C the cation-exchanged forms of mordenite show a certain degree of inaccessibility of the nitrogen molecules towards the total pore system, reflecting thus extremely small monolayer equivalent values. At intermediate outgassing temperatures, the accessibility of nitrogen molecules towards the pore system increases as a result of further dehydration and opening of the pore system. However, outgassing at a high temperature leads to a partial collapse in the structure of the submicropores present leading to a decrease in the monolayer equivalents measured by nitrogen molecules. The extent of collapse in the structure is appreciable for the (Na-M) sample and becomes smaller in the cation-exchanged forms. The cation-exchanged forms tend to have the same characteristic values when outgassed at a temperature as high as 480 °C. The two opposing mechanisms, namely the dehydration, and the partial collapse of the narrower pores at high temperatures, lead to the appearance of the maxima shown in Fig. 4.

Adsorption of water vapour

The adsorption isotherms of water vapour on the original synthetic sodium mordenite (Na-M), and its transition metal exchanged forms, (CrNa-M, CoNa-M, NiNa-M, and CuNa-M), are given in Fig. 5. All these isotherms are of the rectangular

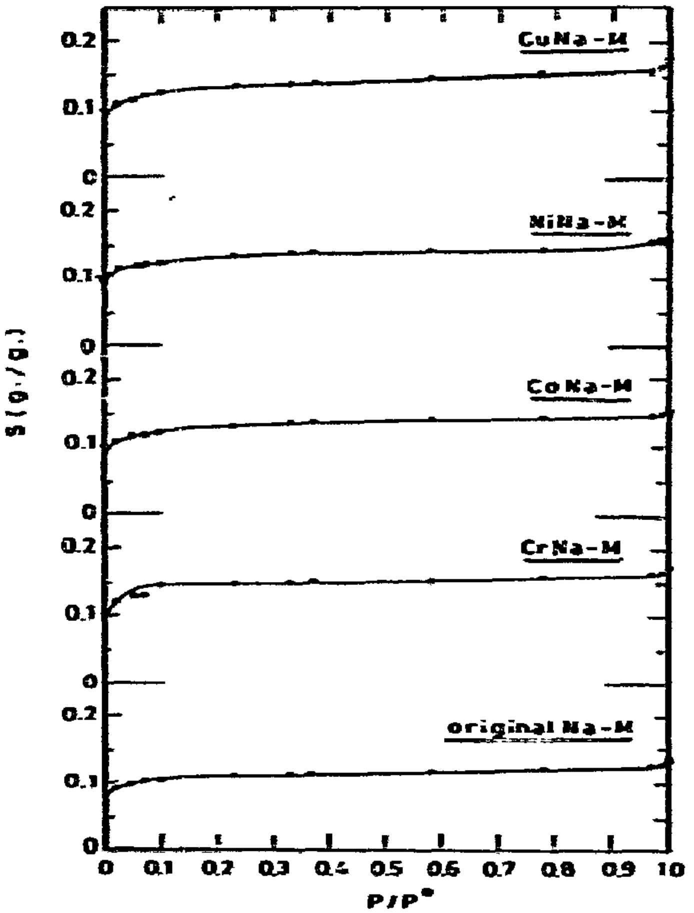

Fig. 5. Adsorption isotherms of water vapour on the various mordenite samples at 35 °C.

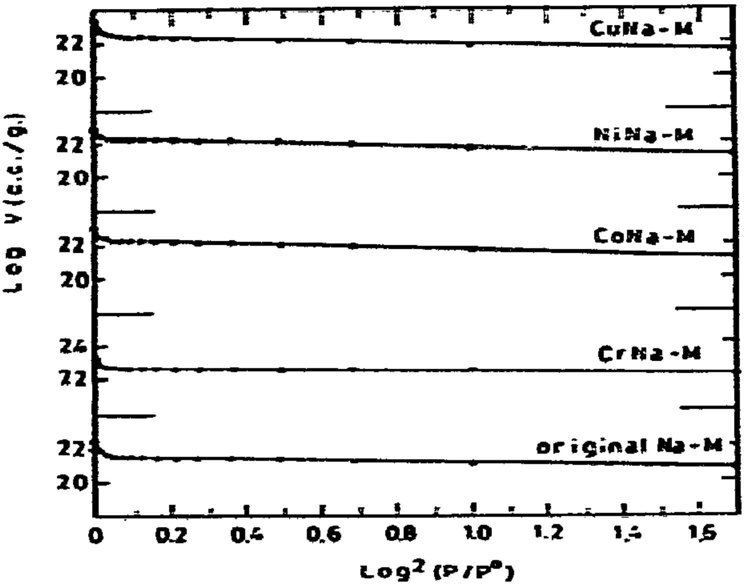

Fig. 6. Dubinin-Radushkevich plots of water vapour adsorption on the various mordenite samples.

TABLE 2

THE MONOLAYER EQUIVALENTS AND THE TOTAL PORE VOLUMES FOR THE SYNTHETIC SODIUM MORDENITE AND ITS TRANSITION METAL CATIONIC FORMS FROM WATER VAPOUR ADSORPTION AT 35°C

Sample	V_m			V_p		
	cc/g	*ml/g*	*molecules/g* $(\times 10^{20})$	*cc/g*	*ml/g*	*molecules/g* $(\times 10^{20})$
Na-M	141.3	0.114	37.96	164.5	0.133	44.20
CrNa-M	182.0	0.147	48.90	206.6	0.167	55.51
CoNa-M	169.8	0.137	45.63	189.2	0.153	50.84
NiNa-M	173.8	0.141	46.70	194.2	0.157	52.18
CuNa-M	173.8	0.141	46.70	211.5	0.171	56.83

shape and belong to type I of Brunauer's classification[10]. The Dubinin-Radushkevich method[14-16] was applied to estimate the monolayer equivalents, which for typical I isotherm are close to the saturation values of the isotherms. The Dubinin-Radushkevich plots of water vapour adsorption on the various investigated samples are given in Fig. 6, whilst the monolayer equivalent values as well as the total pore volumes are given in Table 2.

From the results summarized in Table 2, it is evident that the monolayer equivalents estimated from water adsorption, $V_m^{H_2O}$ (molecules/g), are higher than those determined using nitrogen; $V_m^{N_2}$ (molecules/g). These differences are mainly attributed to the following factors.

(i) The smaller size of water molecules in comparison with nitrogen allows a single pore to accommodate a larger number of the former molecules.

(ii) The polarized mordenite surface facilitates the adsorption of strongly polar molecules such as water rather than of weekly polar molecules such as nitrogen (only quadripole character is involved).

In addition, the values of the monolayer equivalent obtained from water vapour adsorption on the various cation-exchanged forms are higher than that of the unexchanged mordenite. This reflects the specific interaction between the water molecules and the exchanged cations. Such interaction includes the contribution of polarized mordenite surface, as affected by the exchanged cation, towards the polar water molecules.

On the other hand, the total pore volumes measured by water $V_p^{H_2O}$ (ml/g), are lower than those measured by nitrogen, $V_p^{N_2}$ (ml/g)[15]. This is presumably due to the adsorption being mainly restricted to a monomolecular layer on the elliptical channel

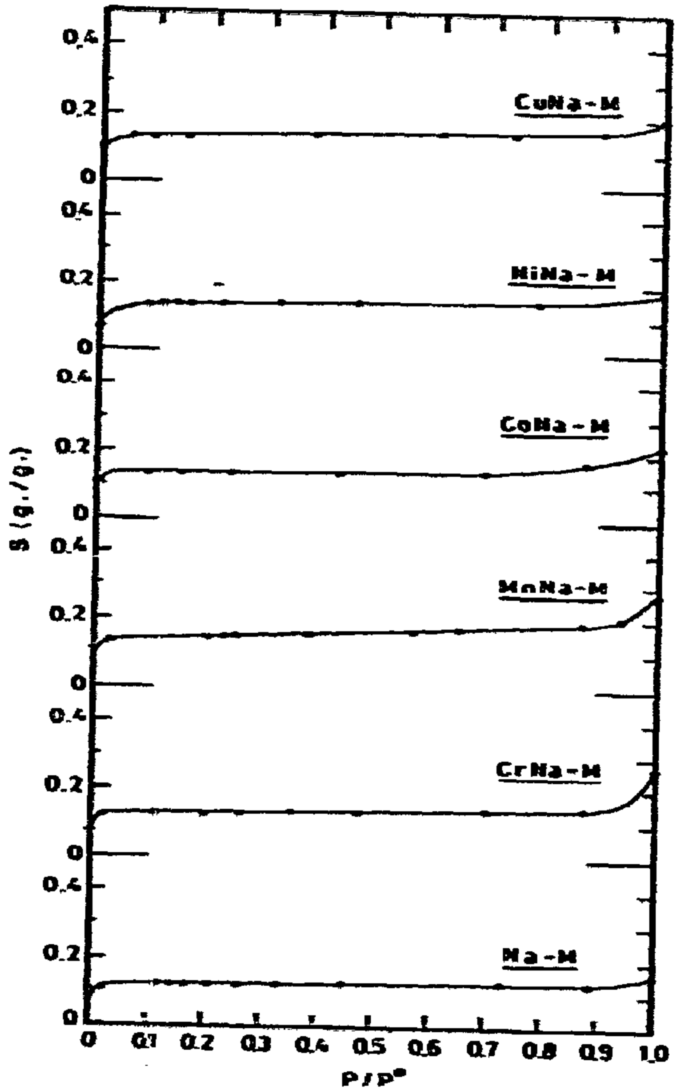

Fig. 7. Adsorption isotherms of methanol on the various mordenite samples at 35°C.

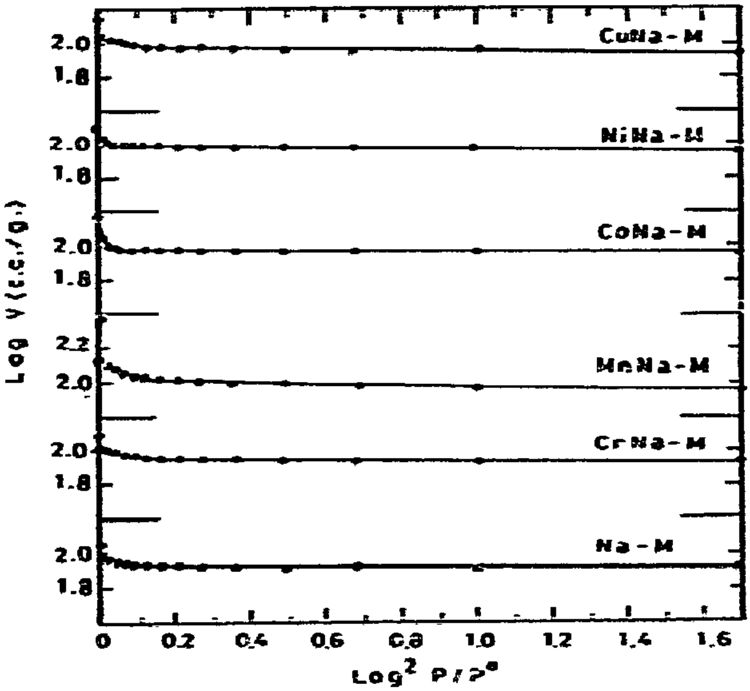

Fig. 8. Dubinin-Radushkevich plots of methanol adsorption on the various mordenite samples.

TABLE 3

THE MONOLAYER EQUIVALENTS AND THE TOTAL PORE VOLUMES FOR THE SYNTHETIC SODIUM MORDENITE AND ITS TRANSITION METAL CATIONIC FORMS FROM METHANOL ADSORPTION AT 35°C

Sample	V_m			V_p		
	cc/g	*ml/g*	*molecules/g* (× 10^{20})	*cc/g*	*ml/g*	*molecules/g* (× 10^{20})
Na-M	83.18	0.150	22.35	111.36	0.201	29.92
CrNa-M	87.10	0.157	23.40	188.92	0.341	50.76
MnNa-M	102.30	0.185	27.49	192.24	0.347	51.65
CoNa-M	93.33	0.168	25.08	150.14	0.271	40.34
NiNa-M	96.61	0.174	25.96	123.55	0.223	33.20
CuNa-M	93.33	0.168	25.08	124.10	0.224	33.35

walls, accordingly bigger adsorbate molecules as nitrogen will occupy a larger fraction of the channel pore volume than the smaller water molecules.

Adsorption of methanol

The adsorption isotherms of methanol vapour on the various samples investigated are shown in Fig. 7. All the isotherms are of type I of Brunauer's classification[10]. The Dubinin-Radushkevich plots of methanol adsorption are shown in Fig. 8. The monolayer equivalent values and total pore volumes are given in Table 3.

The results summarized in Table 3 indicate that for various investigated samples, the monolayer equivalent values measured using methanol as an adsorbate, $V_p^{CH_3OH}$ (molecules/g), are lower than those measured by both water and nitrogen. On the other hand, it is interesting to report that the values of the total pore volumes measured by methanol $V_p^{CH_3OH}$ (ml/g) for the various mordenite samples are found to be higher than those measured by both water and nitrogen. Again this result confirms the conclusion that a single pore can accommodate a larger number of smaller adsorbate molecules.

In the light of the results described above, the Dubinin–Radushkevich monolayer equivalents, V_0 (molecules/g), measured by the various adsorbate molecules decrease in the order $V_0^{H_2O} > V_0^{N_2} > V_0^{CH_3OH}$, whilst the total pore volumes, V_p (ml/g) increase in the order $V_p^{H_2O} < V_p^{N_2} < V_p^{CH_3OH}$.

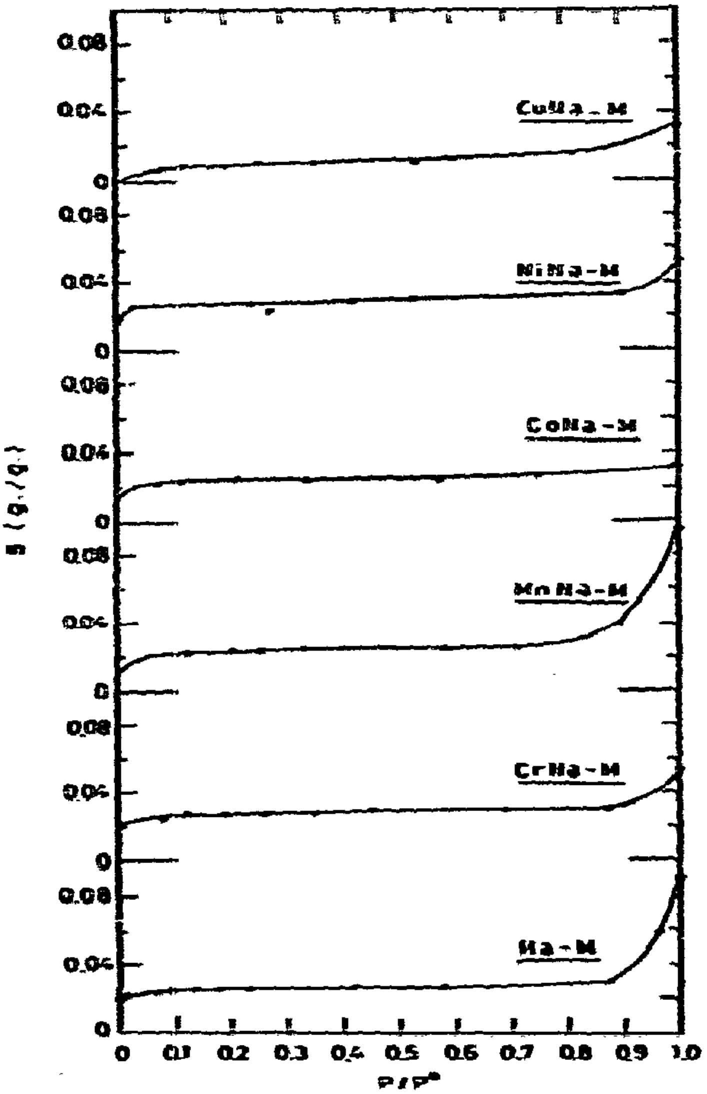

Fig. 9. Adsorption of cyclohexane on the various mordenite samples at 35°C.

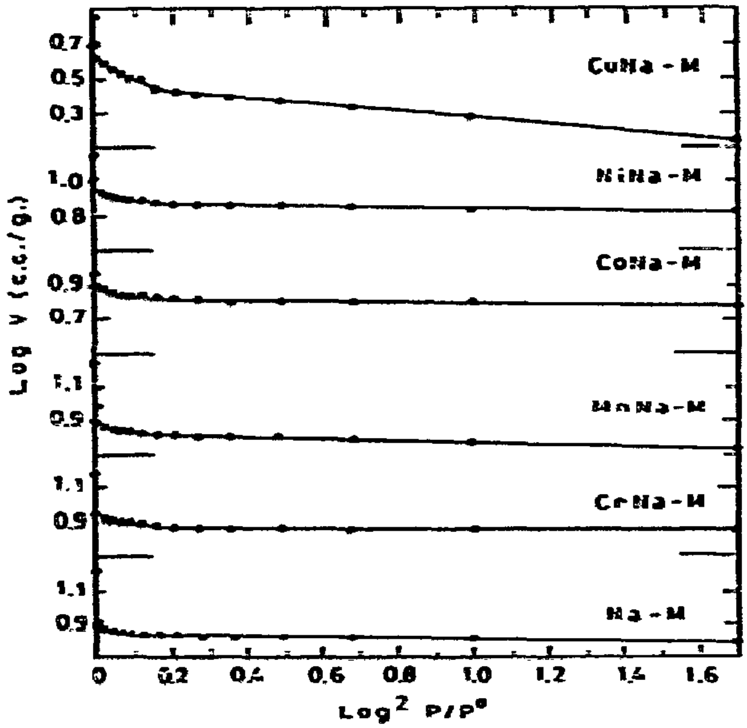

Fig. 10. Dubinin-Radushkevich plots of cyclohexane adsorption on the various mordenite samples.

TABLE 4

THE MONOLAYER EQUIVALENTS AND THE TOTAL PORE VOLUMES FOR THE SYNTHETIC SODIUM MORDENITE AND ITS TRANSITION METAL EXCHANGED FORMS FROM CYCLOHEXANE ADSORPTION AT 35 °C

Sample	V_m			V_p		
	cc/g	*ml/g*	*molecules/g* $(\times 10^{20})$	*cc/g*	*ml/g*	*molecules/g* $(\times 10^{20})$
Na-M	6.76	0.033	1.82	24.46	0.118	6.57
CrNa-M	7.41	0.036	1.99	14.72	0.071	3.96
MnNa-M	6.61	0.032	1.78	25.91	0.125	6.96
CoNa-M	6.61	0.032	1.78	9.12	0.044	2.45
NiNa-M	7.59	0.037	2.04	14.72	0.071	3.96
CuNa-M	3.02	0.015	0.81	8.71	0.042	2.34

Adsorption of cyclohexane

The results of the adsorption measurements of cyclohexane vapour on the various samples investigated are given in Fig. 9, whilst the Dubinin-Radushkevich plots are given in Fig. 10. The Dubinin-Radushkevich monolayer equivalent values, as well as the total pore volumes, both are expressed in cc/g, and molecules/g are given in Table 4.

The results given in Table 4 indicate that the monolayer equivalent values as well as the total pore volumes measured by cyclohexane are appreciably lower than those measured by the other three adsorbates, namely, water, nitrogen and methanol. Also it was noticed that the monolayer equivalent measured by cyclohexane is the same for all investigated samples (1.8–2.0 × 10^{20} molecules/g) except the CuNa–M sample which possesses a cyclohexane monolayer equivalent of 0.8 × 10^{20} molecules/g.

Evidently, cyclohexane can measure only the monolayer equivalents and the pore volumes of the external pore system (intercrystalline pores) and is therefore excluded from the major part of the total pore system.

REFERENCES

1 R. M. Barrer and D. L. Peterson, *Proc. Soc. London, Ser. A,* (1353) 280, (1964) 466.
2 V. J. Frilette and M. R. Rubin, *J. Catal.,* 4(2) (1965) 310.
3 V. T. Bykov and N. E. Shcherbatyuk, *Kinet. Catal. (U.S.S.R.),* 9(2) (1968) 447.
4 I. A. Belitskii, *Eksp. Issled. Mineral.* (1965) 92.
5 Y. Nishimura and H. Takahashi, *Kolloid. Z. Z. Polym.,* 245(1) (1971) 415.
6 D. W. Breck and R. W. Grose, *Adv. Chem. Ser.,* (1973) 121. (Mol. Sieves Int. Conf., 3rd) 319–29.
7 B. A. Baran, I. M. Balen'kaya and M. M. Dubinin, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.,* 1 (1974) 24.
8 T. Takaishi, A. Yusa, Y. Ogino and S. Ozawa, *J. Chem. Soc., Farad. Trans.,* 1 (1974) 24.
9 W. M. Meier, *Z. Kristallogr.,* 115 (1961) 439.
10 P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.,* 59 (1937) 1553.
11 J. W. McBain and A. M. Bakr, *J. Am. Chem. Soc.,* 48 (1926) 690.
12 R. I. Razouk and A. S. Salem, *J. Phys. Colloid Chem.,* 52 (1948) 1205.
13 S. A. Abo-El-Enein, R. Sh. Mikhail and H. A. El-Wakil, *Thermochim. Acta,* accepted for publication.
14 M. M. Dubinin and E. D. Zaverina, *Zh. Fiz. Khim.,* 23 (1949) 1129.
15 L. V. Radushkevich, *Zh. Fiz. Khim.,* 23 (1949) 1410.
16 M. M. Dubinin, *Chem. Rev.,* 50 (1960) 235.
17 B. Genot, *J. Colloid Interface Sci.,* 50 (1975) 413.