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SORPTION PROPERTIES OF Mg-FORM OF STILBITE

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Abstract. Sorption properties of stilbite from Strzegom were investigated, in which Ca^{2+} ions had been exchanged for Mg^{2+} . It has been found that sorption capacity of this stilbite with respect to methanol vapours and argon increased significantly. This can be accounted for by the fact that Mg^{2+} ions close the channels of zeolite to a lesser degree than larger Ca^{2+} ions.

INTRODUCTION

Stilbite is monoclinic, $C2/m$, with a chemical formula close to $\text{Na}_2\text{Ca}_4[\text{Al}_{10}\text{Si}_{26}\text{O}_{72}]\cdot 32\text{H}_2\text{O}$. From the related zeolites (heulandite, clinoptilolite, epistilbite, ferrierite, brewsterite) it differs, e.g. in a relatively large size of the cages and channels occurring in the aluminosilicate framework (Galli, Gottardi 1966; Slaughter 1970). X-ray investigations carried out on stilbite by Galli and Gottardi (1966) revealed that channels formed by 10-member silicon-oxygen rings extend in the a -direction. Their smallest diameter is about 4.4 Å. Parallel to c , there extend 8-member ring channels of smaller diameter. On this basis, the cited authors presumed that stilbite may possess some interesting sieve properties. Following their suggestion, the present authors investigated the process of sorption of water methanol, benzene vapours and argon on two natural stilbites, from Strzegom (Poland) and Iceland, in which Ca^{2+} was the main exchange cation (Żyła, Żabiński 1976). It was found that both stilbites showed considerable water vapour sorption, but sorption of the other sorbates was insignificant. This is most likely due to the zeolite channels being partly closed up by large Ca^{2+} and Na^{2+} cations. According to Slaughter (1970), Ca^{2+} ions are located in the centre of the largest part of the channels

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(cages). They are surrounded by water molecules and are not directly bonded to the aluminosilicate framework oxygens.

In order to partly open up the channels of stilbite, large Ca^{2+} ions (ionic radius 0.99 Å) were exchanged for smaller Mg^{2+} ions (0.66 Å), and then the sorption properties of this zeolite were determined again.

EXPERIMENTAL

Investigations were carried out on a stilbite from Strzegom, described earlier by Żabiński (1975). The exchange of Ca^{2+} for Mg^{2+} ions was made by washing the stilbite several times with 2*n* MgCl_2 solution. Excess electrolyte was removed by washing with distilled water in a centrifuge until the reaction for chloride ion was negative.

On the stilbite sample prepared in this way isotherms for water, methanol and argon sorption and desorption were determined. Isotherms for water and methanol vapour sorption were obtained at 298 K using microburettes for liquids (Lasoń, Żyła 1963). Argon isotherms were determined at 77 K using sorption manostats (Ciembroniewicz, Lasoń 1972). The isotherms are presented in Figures 1—4.

RESULTS

Figure 1 shows water vapour sorption and desorption isotherms. The shape of the adsorption isotherm is typical of the BET isotherm II. It is interesting to note that water adsorption is a reversible process. The desorption and adsorption isotherms converge at a relative pressure of about 0.075.

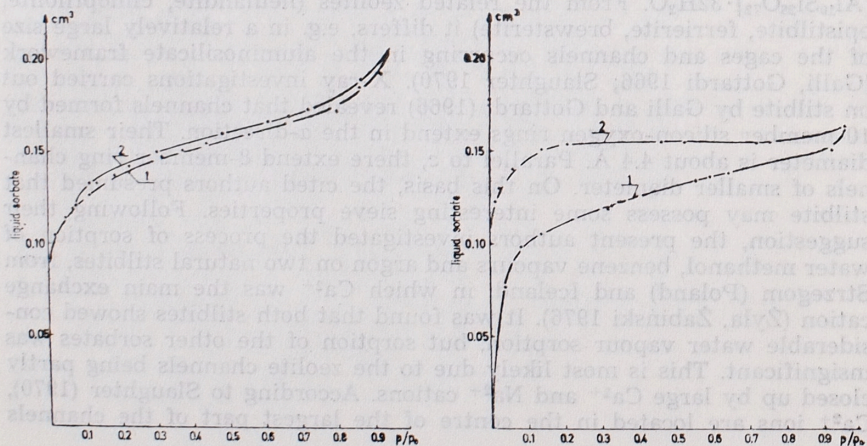


Fig. 1. Adsorption and desorption isotherms of water vapour on Mg-form of stilbite

1 — adsorption, 2 — desorption

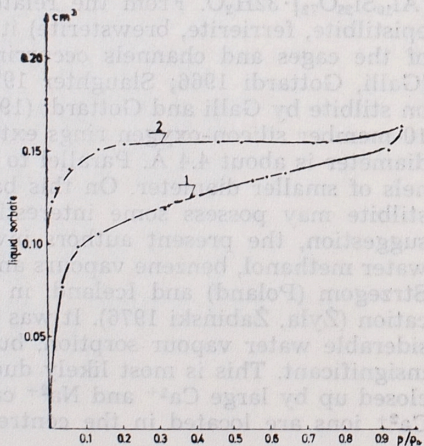


Fig. 2. Adsorption and desorption isotherms of methanol on Mg-form of stilbite

1 — adsorption, 2 — desorption

Figure 2 comprises isotherms for methanol sorption and desorption. It will be noticed that a non-closing hysteresis loop appears on them. The desorption curve at relative pressures $p/p_0 = 0.95-0.20$ is almost parallel to the abscissa, which evidences that desorption of the previously adsorbed methanol molecules does not take place. At relative pressures p/p_0 lower than 0.2, desorption of these molecules begins, but the desorption isotherm has not a single point in common with the adsorption isotherm. Non-closing of the hysteresis loop suggests that a large number of water molecules, bonded in an energetically preferred way, remain in the channels of stilbite.

Worth noting is the shape of the argon adsorption isotherm (Fig. 3). The bulk of argon is adsorbed at low relative pressures, $p/p_0 = 0.005-0.10$. This testifies to a high content of micropores in the porous structure of stilbite, and a very low content of transitional pores and macropores. The desorption isotherm coincides over its whole length with the adsorption isotherm without forming a hysteresis loop. It can be inferred therefore that the micropore system is fairly homogeneous.

A comparison of adsorption isotherms for the three adsorbates used (Fig. 4) illustrates well variations in the sorption capacity of the magnesium form of stilbite, depending on the kinetic diameter of adsorbate molecules. This stilbite shows the highest sorption capacity with respect to water molecules, whose kinetic diameter ranges from 2.20 to 2.80 Å. This capacity is lower with respect to methanol vapours (kinetic diameter of 2.98—3.05 Å), and the lowest with respect to argon atoms (kinetic diameter of 3.83 Å). These observations suggest that the magnesium form of stilbite possesses sieve properties.

Applying the BET equation, V_m values expressed in mmol/g and in cm^3 of liquid sorbate per gram of adsorbent, as well as specific surface areas were calculated from adsorption isotherms (Table 1). To obtain comparative data, the corresponding values for natural (calcium) stilbite are also listed in Table 1. It is evident from these data that sorption capacity of stilbite with respect to methyl alcohol vapours and argon increases markedly after the exchange of Ca^{2+} for Mg^{2+} ions. This fact implies that

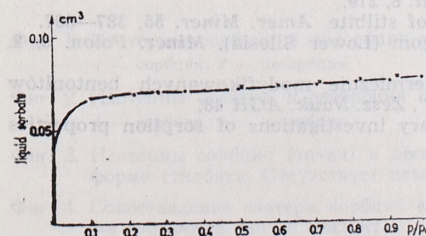


Fig. 3. Adsorption (dots) and desorption (asterisks) isotherms of argon on Mg-form of stilbite. Lack of hysteresis loop

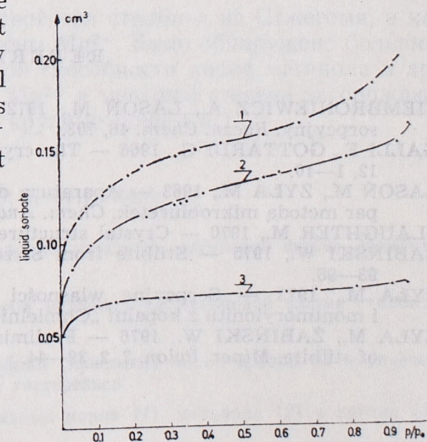


Fig. 4. Comparison of adsorption isotherms of water vapour (1), methanol (2) and argon (3) on Mg-form of stilbite

Table 1

Sorpitive properties of Mg- and Ca-forms of stilbite

Adsorber	Adsorbate								
	water vapour			methanol			argon		
	V_m mmol/g	V_m cm ³ /g	S m ² /g	V_m mmol/g	V_m cm ³ /g	S m ² /g	V_m mmol/g	V_m cm ³ /g	S m ² /g
Mg-form of stilbite	5.56	0.102	358.0	1.99	0.081	216.8	1.89	0.055	188.6
natural stilbite (Ca-form)	6.56	0.119	413.0	0.131	0.0053	14.3	0.051	0.0015	5.1

the pores of this zeolite become accessible even to relatively large molecules or atoms. The enlargement of the aperture of channels may be greater than predicted by simple comparison of the ionic radii of Ca²⁺ (0.99 Å) and Mg²⁺ (0.66 Å) because, as was mentioned earlier in this paper, the Ca²⁺ ions occupy presumably the central position in the channels of stilbite while the Mg²⁺ ions can be located more eccentrically, closer to the channel walls. The marked sorption capacity of stilbite with respect to argon, whose atoms have a kinetic diameter of 3.83 Å, confirms the results of X-ray investigations which revealed a relatively large size of channels in the structure of this zeolite (the smallest diameter in the a-direction is 4.4 Å).

The slight decrease in the sorption capacity with respect to water vapour compared with calcium stilbite may be due to different hydration properties of Ca²⁺ and Mg²⁺ ions. The same was noted when magnesium montmorillonite was compared with its calcium form (Żyła 1972).

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WŁASNOŚCI SORPCYJNE MAGNEZOWEJ FORMY STILBITU

Streszczenie

Zbadano własności sorpcyjne stilbitu ze Strzegomia, w którym uprzednio dokonano wymiany jonów Ca²⁺ na Mg²⁺. Stwierdzono wybitny wzrost chłonności sorpcyjnej par alkoholu metylowego i argonu, co tłumaczyć można tym, iż jony Mg²⁺ w mniejszym stopniu przesłaniają przekrój kanałów zeolitu niż większe od nich jony Ca²⁺.

OBJAŚNIENIA FIGUR

- Fig. 1. Izotermy sorpcji i desorpcji par wody na magnezowej formie stilbitu
1 — sorpcja, 2 — desorpcja
- Fig. 2. Izotermy sorpcji i desorpcji par alkoholu metylowego na magnezowej formie stilbitu
1 — sorpcja, 2 — desorpcja
- Fig. 3. Izotermy sorpcji (punkty) i desorpcji (krzyżyki) par argonu na magnezowej formie stilbitu. Brak pętli histerezy
- Fig. 4. Zestawienie izoterm sorpcji par wody (1), alkoholu metylowego (2) i argonu (3) na magnezowej formie stilbitu

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СОРБЦИОННЫЕ СВОЙСТВА МАГНИЕВОЙ ФОРМЫ СТИЛБИТА

Резюме

Были исследованы сорбционные свойства стилбита из Стжегомья, в котором прежде ионы Ca²⁺ были заменены Mg²⁺. Было обнаружено большое повышение поглощающей сорбционной способности паров метанола и аргона, что объясняется тем, что ионы Mg²⁺ в меньшей степени загромождают сечение каналов цеолита, чем более крупные ионы Ca²⁺.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Fig. 1. Изотермы сорбции и десорбции водяных паров на магниевои форме стилбита
1 — сорбция, 2 — десорбция
- Fig. 2. Изотермы сорбции и десорбции паров метанола на магниевои форме стилбита
1 — сорбция, 2 — десорбция
- Fig. 3. Изотермы сорбции (точки) и десорбции (крестики) паров аргона на магниевои форме стилбита. Отсутствует петля гистерезиса
- Fig. 4. Сопоставление изотерм сорбции водяных паров (1), метанола (2) и аргона (3) на магниевои форме стилбита