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SORPTIVE PROPERTIES OF THERMALLY DECOMPOSED ORGANO-MONTMORILLONITES

Abstract. This paper presents preliminary studies of the sorptive properties of thermally decomposed organo-montmorillonites. Such products were obtained through introducing glycerol molecules into the interlayer spaces of montmorillonite and subsequent heating of the resulting organo-mineral complexes at 623 K, 773 K and 873 K. The process was carried out in an atmosphere of nitrogen and air. Low-temperature argon sorption on the decomposition products was measured over the whole range of relative pressures and at very low pressures. Benzene and water vapour adsorption isotherms were also determined. It has been found that the above modifications give rise to a sorbent that is active towards inert gases and vapours of polar and nonpolar liquids. Maximum sorption capacity was shown by the product obtained at 773 K. The increase in sorption capacity was attributed to changes occurring both in the micro- and mesoporous structures.

INTRODUCTION

The studies of organo-montmorillonite complexes are interesting both from the theoretical and practical points of view. Large-molecular organic substances e.g. methylene blue as well as small molecules of alkyloamines, can be introduced into the interlayer spaces of montmorillonite. As a result of earlier studies or organo--montmorillonites (Żyła, Kłapyta 1976; Kłapyta, Żyła 1977) hydrophobic complexes were obtained that showed lower water vapour sorption and higher benzene sorption.

Due to hydrophobization of clay minerals with aliphatic amine salts it is possible to obtain organo-montmorillonite complexes with increased sorption capacity with respect to argon and benzene and decreased capacity towards water vapour.

The recent studies of sorptive properties of silica gel modified with the decomposition products of higher aliphatic alcohols (Leboda 1980) encouraged the present authors to modify the sorptive properties of montmorillonite with the thermal decomposition products of earlier-absorbed glycerol.

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EXPERIMENTAL AND RESULTS

Sorption investigations

Sorption investigations were preceded by a procedure leading to the preparation of thermally decomposed organo-montmorillonite. Montmorillonite was separated by 24-hour sedimentation from the Milowice bentonite, and then treated with glycerol for 1 hour at the boil. The decomposition process of glycerol was carried out at 623, 773 and 873 K at the fixed air flow. For the resulting pyrolysis products argon adsorption isotherms were determined over the whole range of relative pressures (Fig. 1) and at very low pressures (Fig. 2), using sorption manostat (Ciembroniewicz et al. 1972). Isotherms for benzene (Fig. 3) and water vapour (Fig. 4) adsorption were obtained using microburettes for liquids (Lasoń, Żyła 1963).

From the shape of argon isotherms (Fig. 1) the BET specific surface areas (Brunauer et al. 1938) were calculated for the samples studied. This parameter can be treated as an indicator of changes in sorptive properties occurring during activation. From the resulting data it appears that the pyrolysis product obtained at 773 K shows the highest sorption capacity. Its specific surface area (163.9 m^2/g) is nearly four times greater than that of untreated montmorillonite (41.7 m^2/g). Specific surface areas calculated for thermally decomposed organo-montmorillonites obtained at 623 K and 873 K are smaller, but still greater than the area of pure montmorillonite (Table 1).

Assemblage volume micropores and values of specific surfaces areas

Parameter	Samples			
	F-2	P-623	P-773	P-873
a_o, mm^3/g	11.8	19.9	65.8	31.1
$S_{(Ar)}$, m^2/g	41.7	60.7	163.9	107.5
$S_{(C_6H_6)}$, m^2/g	42.2	84.6	125.6	61.2
$S_{(H_2O)}$, m^2/g	84.7	144.0	197.9	137.1

Argon adsorption measurements in the range of very low pressures allowed the determination of microporosity of the samples studied. The quantity W_o, i.e. the volume of liquid sorbate necessary to fill up the micropores (Table 1), was calculated from the adsorption isotherms (Fig. 2) using the Dubinin-Raduszkiewicz equation (Dubinin 1960). On the basis of this parameter, changes that took place in the microporous structure in response to treatment were estimated. The carbonization of montmorillonite increases the volume of micropores, this increase being nearly sixfold for the samples obtained at 773 K.

The isotherms obtained for benzene and water vapour adsorption determine the effect of modification on the degree of hydrophobization of the surface with respect to "model" polar and nonpolar substances. It has been found that benzene sorption increases for thermally decomposed organo-montmorillonites (Fig. 3). This is presumably due to the deposition of carbon, and maybe of the intermediate decomposition products of glycerol, on the external surfaces and in the interlayer spaces. Maximum sorption was observed for the sample obtained at 773 K. The lowest benzene sorption was noted for the pyrolysis product obtained at 873 K, though it was still higher compared with untreated montmorillonite. Such behaviour has
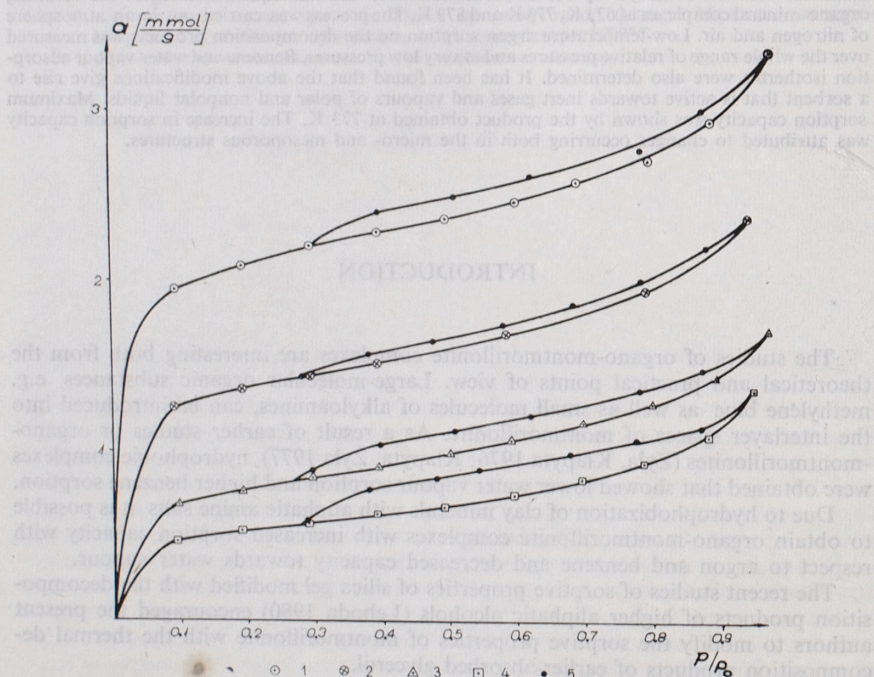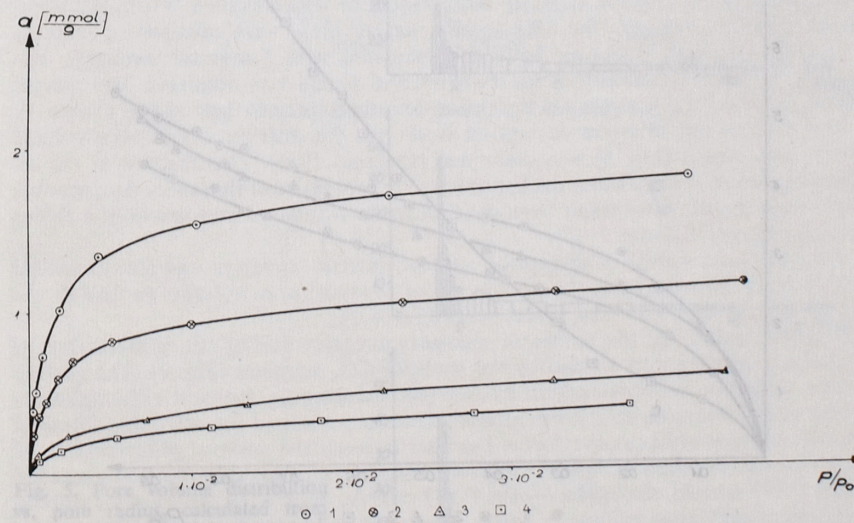

Fig. 1. Argon adsorption and desorption isotherms obtained over the whole range of relative pressures

1 — sample P-773 K, 2 — sample P-873 K, 3 — sample P-623 K, 4 — untreated sample, 5 — desorption isotherm points

Fig. 2. Argon adsorption isotherms obtained for low relative pressures

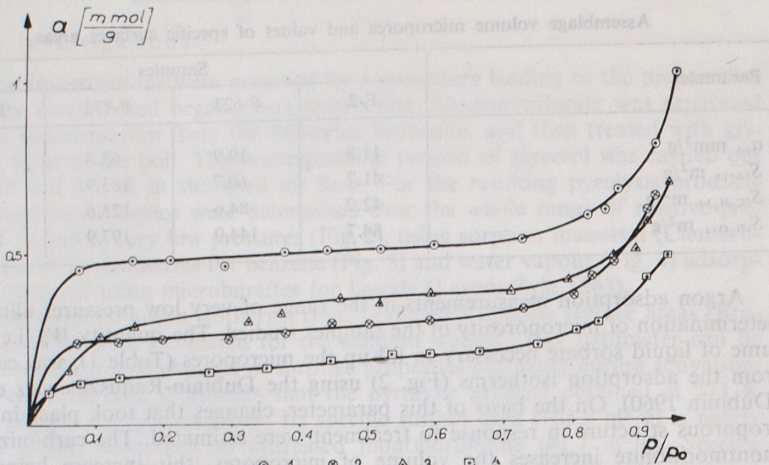1 — P-773 K, 2 — P-873 K, 3 — P-623 K, 4 — untreated sample

Fig. 3. Benzene adsorption isotherms

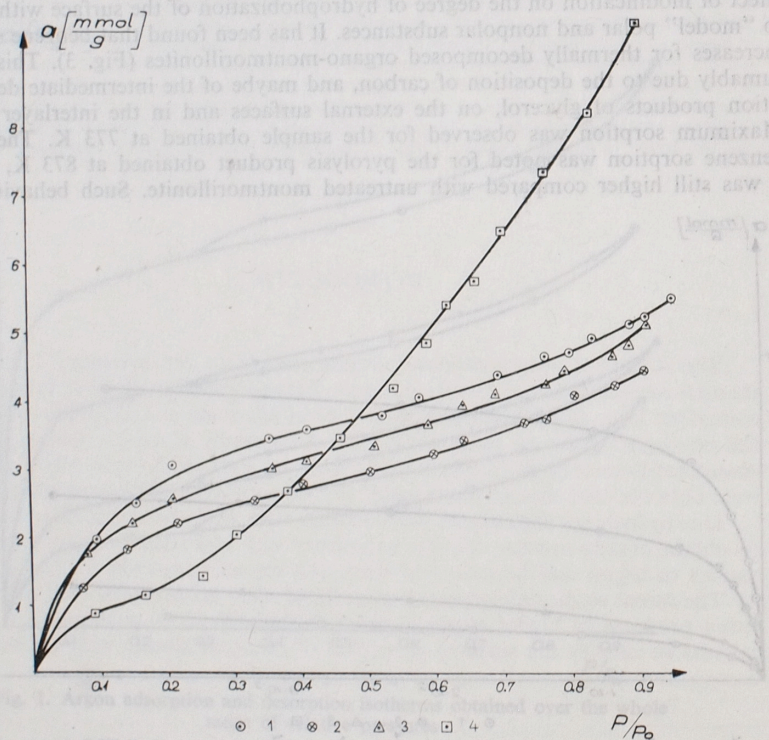*1* — P-773 K, *2* — P-873 K, *3* — P-623 K, *4* — untreated sample

Fig. 4. Water vapour adsorption isotherms

1 — P-773 K, *2* — P-873 K, *3* — P-623 K, *4* — untreated sample

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been attributed to the microporous structure of thermally decomposed organo-
-montmorillonites, which is best developed at 773 K and becomes progressively
degraded with the further rise in temperature. The shape of all the isotherms up to
a relative pressure p/p_o of 0.65 follows that of Langmuir isotherm. Above this pressure
the adsorption curve has an inflexion point and adsorption increases rapidly due
to capillary condensation taking place in this range of pressures.

The shape of water vapour adsorption isotherms (Fig. 4) points to the different
sorption mechanism for untreated and thermally decomposed montmorillonites.
Up to the relative pressure $p/p_o = 0.4$—0.5, the latter show higher sorption. It is
feasible that the decomposition products of glycerol do not block active sorption
centres but cause the layers to part, making the energy centres of the interlayer space
accessible to water molecules. The isotherms obtained for water vapour sorption on
montmorillonites hydrophobized with hexadecylpyridinium hydrochloride ions
(Kłapyta, Żyła 1977), acetic acid anhydride (Bodek, Żyła 1978) and aliphatic amine
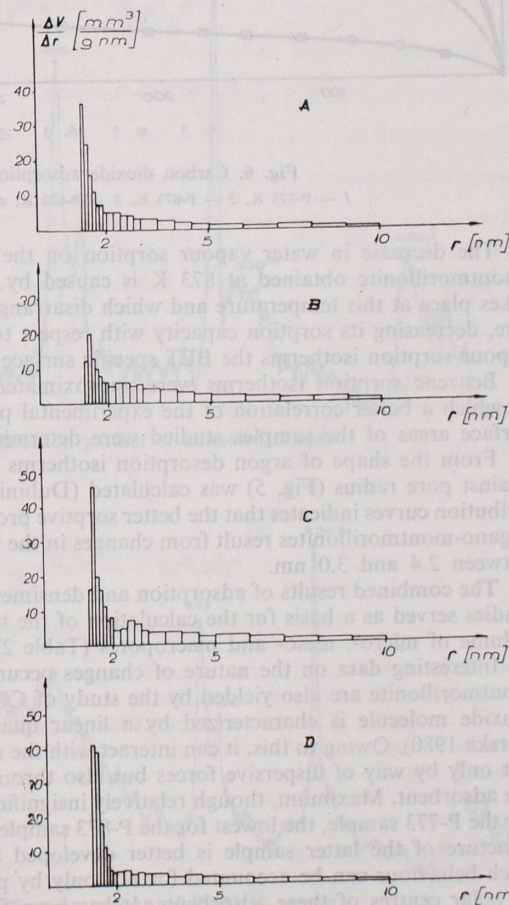salts (Bodek, Żyła 1982) had a similar shape.

Fig. 5. Pore volume distribution
vs. pore radius, calculated from
argon desorption isotherms

A — P-623 K, *B* — P-873 K, *C* — P-773 K,
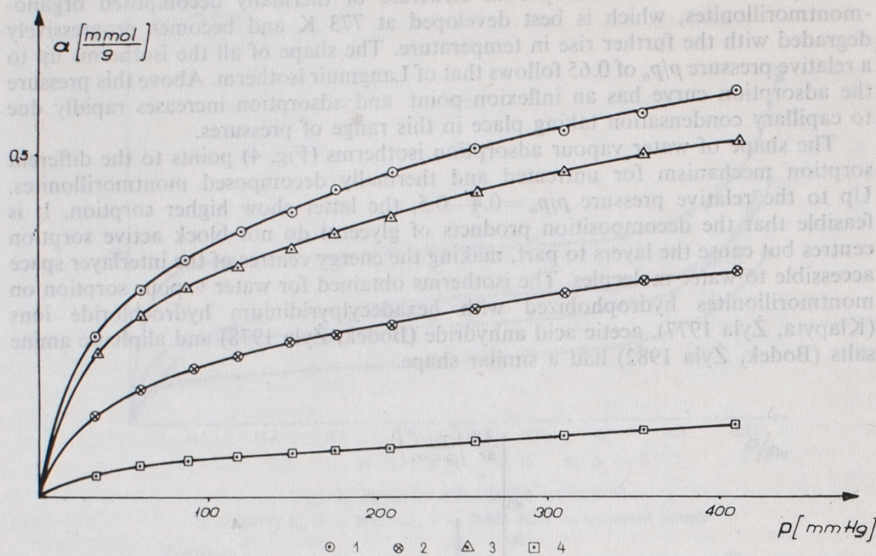*D* — initial sample

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Fig. 6. Carbon dioxide adsorption isotherms

1 — P-773 K, *2* — P-873 K, *3* — P-623 K, *4* — untreated sample

The decrease in water vapour sorption on the thermally decomposed organo-montmorillonite obtained at 873 K is caused by dehydroxylation, which already takes place at this temperature and which disarranges the structure of montmorillonite, decreasing its sorption capacity with respect to water vapour. From the water vapour sorption isotherms the BET specific surface areas were calculated (Table 1).

Benzene sorption isotherms were approximated with Langmuir isotherm, due to which a better correlation of the experimental points was obtained. The specific surface areas of the samples studied were determined from their shape (Table 1).

From the shape of argon desorption isotherms the distribution of pore volume against pore radius (Fig. 5) was calculated (Dubinin 1956). The analysis of the distribution curves indicates that the better sorptive properties of thermally decomposed organo-montmorillonites result from changes in the volume of mesopores of a radius between 2.4 and 3.0 nm.

The combined results of adsorption and densimetric (apparent and true densities) studies served as a basis for the calculation of the total pore volume as well as the volume of micro-, meso- and macropores (Table 2).

Interesting data on the nature of changes occurring during the modification of montmorillonite are also yielded by the study of CO_2 sorption (Fig. 6). The carbon dioxide molecule is characterized by a linear quadrupole moment (Żółcińska-Jezierska 1980). Owing to this, it can interact with the surface of the adsorbents studied not only by way of dispersive forces but also through the surficial polar centres of the adsorbent. Maximum, though relatively insignificant, CO_2 sorption was observed for the P-773 sample, the lowest for the P-873 sample, despite the fact that the porous structure of the latter sample is better developed than that of the P-623 sample. Such behaviour can be accounted for not only by porosity but also by the amount of polar centres of these adsorbents. It has been found that the number of polar

Table 2

Assemblage total volume pores and macro-, meso- and micropores

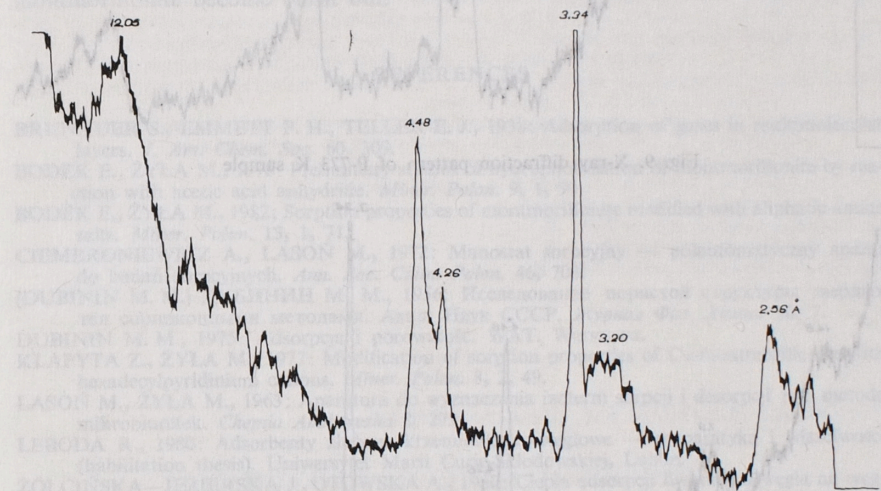| Sample	d_{He} g/cm³	d_{Hg} g/cm³	V_o cm³	micro cm³	meso cm³	macro cm³	ε %
F-2	2.677	2.005	0.125	0.012	0.016	0.097	25.1
P-623	2.633	1.457	0.307	0.020	0.017	0.270	44.7
P-773	2.613	1.303	0.385	0.066	0.023	0.296	50.1
P-873	2.486	1.179	0.446	0.031	0.024	0.391	52.6

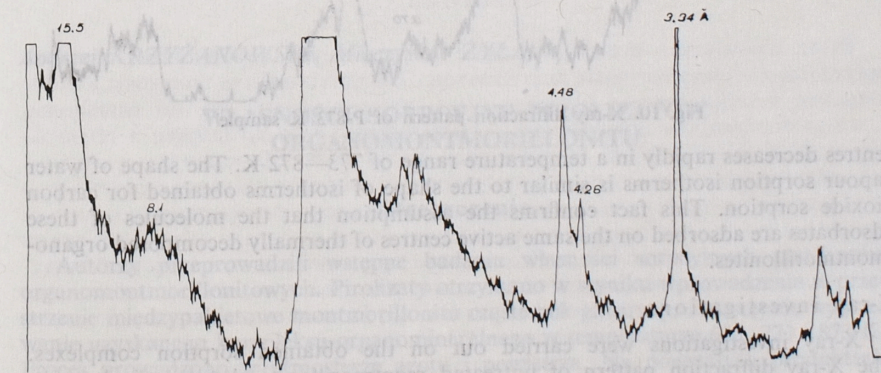Fig. 7. X-ray diffraction pattern of untreated sample

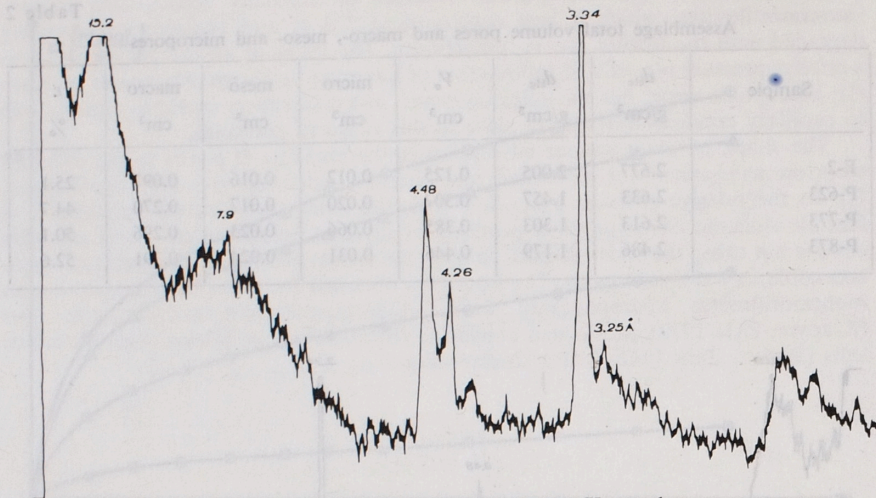Fig. 8. X-ray diffraction pattern of P-623 K sample

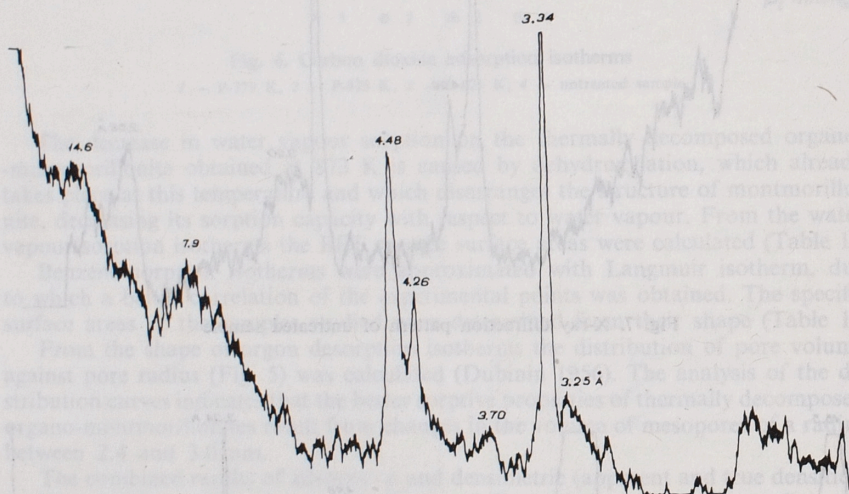Fig. 9. X-ray diffraction pattern of P-773 K sample

Fig. 10. X-ray diffraction pattern of P-873 K sample

centres decreases rapidly in a temperature range of 773—872 K. The shape of water vapour sorption isotherms is similar to the shape of isotherms obtained for carbon dioxide sorption. This fact confirms the assumption that the molecules of these adsorbates are adsorbed on the same active centres of thermally decomposed organo--montmorillonites.

X-ray investigations

X-ray investigations were carried out on the obtained sorption complexes. The X-ray diffraction pattern of untreated montmorillonite shows typical montmorillonite reflections, as well as reflections characteristic of illite. The latter mineral

is subject to co-sedimentation during the separation of montmorillonite from bentonite. A characteristic feature of the Na or Ca-form of montmorillonite is the increase of interlayer spacing d_{001} to 1.77—1.78 nm after saturation with glycerol. Such values of this parameter were noted for glycerol-treated montmorillonite in this study. The reduction in basal spacing, observed in the process of thermal decomposition of organo-montmorillonite, testifies to the decomposition of glycerol present in the structure of this mineral (Figs. 7—10). The sample heated at 623 K shows a shift of d_{001} from 1.78 to 1.55 nm. Higher pyrolysis temperatures cause a further reduction in basal spacing. The values of d_{001} for the P-773 and P-873 samples being 1.52 and 1.46 nm respectively, substantiate this statement. The gradual decrease in basal spacing is presumably due to changes occurring in the organic part of the system. As the pyrolysis temperature is raised, the carbon deposit and possibly the other thermal decomposition products of glycerol present in the interlayer spaces of montmorillonite become burnt out.

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WŁASNOŚCI SORPCYJNE PIROLIZATÓW ORGANOMONTMORILLONITU

Streszczenie

Autorzy przeprowadzili wstępne badania własności sorpcyjnych pirolizatów organomontmorillonitowych. Pirolizaty otrzymano w wyniku wprowadzenia w przestrzenie międzypakietowe montmorillonitu cząsteczek gliceryny, a następnie wygrzewanie uzyskanego kompleksu organomineralnego w temperaturze 623, 773 i 873 K. Proces prowadzono w atmosferze azotu i powietrza. Na powstałych produktach wykonano pomiary niskotemperaturowej sorpcji par argonu w pełnym zakresie

ciśnień względnych i w zakresie bardzo małych ciśnień. Wyznaczono również izotermy adsorpcji par benzenu i wody. Badania wykazują, że zastosowane modyfikacje prowadzą do otrzymania sorbentu aktywnego w stosunku do gazów biernych oraz par cieczy polarnych i apolarnych. Maksymalne własności sorpcyjne przejawia produkt uzyskany w temperaturze 773 K. Wzrost chłonności jest upatrywany w zmianach, zachodzących zarówno w strukturze mikroporowatej, jak i mezoporowatej.

OBJAŚNIENIA FIGUR

Fig. 1. Izotermy adsorpcji i desorpcji par argonu w pełnym zakresie ciśnień względnych
1 — pirolizat P-773 K, *2* — pirolizat P-873 K, *3* — pirolizat P-623 K, *4* — próbka wyjściowa, *5* — punkty izoterm desorpcji

Fig. 2. Izotermy adsorpcji par argonu w zakresie niskich ciśnień względnych
1 — P-773 K, *2* — P-873 K, *3* — P-623 K, *4* — próbka wyjściowa

Fig. 3. Izotermy adsorpcji par benzenu
1 — P-773 K, *2* — P-873 K, *3* — P-623 K, *4* — próbka wyjściowa

Fig. 4. Izotermy adsorpcji par wody
1 — P-773 K, *2* — P-873 K, *3* — próbka wyjściowa

Fig. 5. Rozkład objętości porów w funkcji promienia obliczony z izoterm desorpcji argonu
A — pirolizat 623 K, *B* — pirolizat 873 K, *C* — pirolizat 773 K, *D* — próbka wyjściowa

Fig. 6. Izotermy adsorpcji par dwutlenku węgla
1 — P-773 K, *2* — P-873 K, *3* — P-623 K, *4* — próbka wyjściowa

Fig. 7. Rentgenogram próbki wyjściowej
Fig. 8. Rentgenogram próbki P-623 K
Fig. 9. Rentgenogram próbki P-773 K
Fig. 10. Rentgenogram próbki P-873 K

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СОРБЦИОННЫЕ СВОЙСТВА ПИРОЛИЗАТОВ ОРГАНОМОНТМОРИЛЛОНИТА

Резюме

Были проведены предварительные исследования сорбционных свойств органомонтмориллонитовых пиролизатов. Пиролизаты были получены в итоге введения в межпакетные пространства монтмориллонита частиц глицерина, а затем прогревания полученного органоминерального комплекса в температурах 623 K, 773 K и 873 K. Процесс проводился в атмосфере азота и в воздухе. На образованных продуктах проводились измерения низкотемпературного поглощения паров аргона в полном диапазоне относительного давления и в диапазоне весьма низких давлений. Определены также изотермы адсорбции паров бензола и воды. Обнаружено, что в итоге применяемых модификаций получается сорбент, активен в отношении инертных газов, а также паров полярных и неполярных жидкостей. Максимальные сорбционные свойства проявляет продукт, полученный в температуре 773 K. Увеличение поглощаемости усматривается в происходящих изменениях как в микропористой, так и в мезопористой структурах.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Изотермы адсорбции и десорбции паров аргона в полном диапазоне относительных давлений
1 — пиролизат Р-773 К, *2* — пиролизат Р-873 К, *3* — пиролизат Р-623 К, *4* — исходный образец, *5* — пункты изотерм десорбции

Фиг. 2. Изотермы адсорбции паров аргона в диапазоне низких относительных давлений
1 — Р-773 К, *2* — Р-873 К, *3* — Р-623 К, *4* — исходный образец

Фиг. 3. Изотермы адсорбции паров бензола
1 — Р-773 К, *2* — Р-873 К, *3* — Р-623 К, *4* — исходный образец

Фиг. 4. Изотермы адсорбции паров воды
1 — Р-773 К, *2* — Р-873 К, *3* — исходный образец

Фиг. 5. Распределение объемов поров в функции радиуса, рассчитанное по изотермам десорбции аргона
A — пиролизат 623 К, *B* — пиролизат 873 К, *C* — пиролизат 773 К, *Д* — исходный образец

Фиг. 6. Изотермы адсорбции паров двуокиси углерода
1 — Р-773 К, *2* — Р-873 К, *3* — Р-623 К, *4* — исходный образец

Фиг. 7. Рентгенограмма исходного образца
Фиг. 8. Рентгенограмма образца Р-623 К
Фиг. 9. Рентгенограмма образца Р-773 К
Фиг. 10. Рентгенограмма образца Р-873 К