

Mieczysław ŻYŁA*, Zenon KŁAPYTA**

MODIFICATION OF SORPTION PROPERTIES OF Ni-MONTMORILLONITE WITH HEXADECYLPYRIDINIUM CATIONS

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Abstract. The paper discusses the effect of hexadecylpyridinium (HDP) cations, adsorbed in various amounts on Ni(II)-montmorillonite, on sorption properties of that mineral. The obtained complexes, in which Ni^{2+} and HDP cations occupy from 0—100% of exchange positions, were subjected to X-ray, IR spectroscopic and sorption investigations. Adsorption of HDP cations up to the 30% occupancy of the exchange positions does not involve changes in the interlayer spacing, $d_{001} = 14.3 \text{ \AA}$, typical of Ni-montmorillonite. When about 59% Ni^{2+} are replaced by HDP cations, mixed-layer structures with one and two layers of organic substance may form. Complete substitution of Ni^{2+} by HDP cations gives rise to a complex in which the organic cations are presumably arranged obliquely to the surface of montmorillonite sheets.

As the content of HDP cations on the exchange position of Ni-montmorillonite increases, its sorption capacity to water and methyl alcohol vapours decreases. A systematic increase in the sorption capacity with respect to benzene vapours has been noted, which indicates that the process of Ni-montmorillonite hydrophobization advances as Ni^{2+} ions are replaced by HDP cations. Argon sorption on the obtained samples of Ni-HDP montmorillonite is not enhanced compared with Ni-montmorillonite. This fact implies that the introduction of HDP cations to the exchange positions does not make the interlayer spaces accessible to argon.

INTRODUCTION

The present paper is a continuation of the studies of surface properties of montmorillonite modified by organic cations. In earlier publications (Gut, Kłapyta 1971; Kłapyta 1974), the mechanism of adsorption of long-

* Institute of Energochemistry of Coal and Physicochemistry of Sorbents, Academy of Mining and Metallurgy, Cracow (Kraków, al. Mickiewicza 30).

** Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy, Cracow (Kraków, al. Mickiewicza 30).

-chain cations on montmorillonite and the mode of their packing in the interlayer spaces were determined. Moreover, sorption properties of modified montmorillonite were studied in order to determine the degree of hydrophobization of its surface (Kłapyta, Fijał, Poreba, Żyła — in press). It has been found that hexadecylpyridinium cations are the most effective for that purpose.

This work aims to define the relationship between the degree of occupancy of the montmorillonite exchange positions by hexadecylpyridinium cations and the sorption properties of the resultant complexes. Modified by organic cations, montmorillonite that contains additionally transitional metal cations shows sometimes most interesting surface, and specifically catalytic, properties (McBride, Mortland 1975). For that reason, Ni-montmorillonite was used in the present investigations.

EXPERIMENTAL

Investigations were carried out on montmorillonite separated from bentonite from the Chmielnik deposit. After converting this montmorillonite into Na-form, the exchange positions were saturated with Ni^{2+} ions using aqueous NiCl_2 solution. Excess salt was washed out in a centrifuge with distilled water until the reaction to Cl^- ion was negative. The exchange capacity of the montmorillonite used was 118.9 mval/100 g.

Four samples containing various proportions of Ni^{2+} and hexadecylpyridinium (HDP) cations on the exchange positions were obtained from Ni-montmorillonite in the following way. Hexadecylpyridinium chloride solutions containing 0.09, 0.25, 0.44, 0.70 and 1.20 mval of HDP cations per gram of montmorillonite were added to aqueous Ni-montmorillonite suspension, and the mixture was stirred for a week. Then the samples were centrifuged and washed with distilled water, and Ni^{2+} content in the solutions was determined using atomic absorption spectroscopy.

The samples thus obtained were subjected to X-ray and infrared spectroscopic analyses, and their sorption properties were determined.

X-ray investigations were carried out in the TUR M-61 diffractometer, using powder preparations and samples sedimented on glass plates. Infrared spectra were recorded in the UR-10 spectrophotometer using KBr disks. Sorption investigations involved measurements of sorption isotherms for vapours of polar (water, methyl alcohol) and nonpolar (benzene, argon) substances. Isotherms for water, methyl alcohol and benzene vapour sorption at 298K were obtained using microburettes for liquids (Lasoń, Żyła 1963) whereas those for argon sorption were determined at 77K in sorption manostats (Ciembroniewicz, Lasoń 1972).

RESULTS

Ion exchange

HDP cations are sorbed by Ni-montmorillonite from aqueous solutions of concentrations of 0.09 — 1.20 mval/g montmorillonite in nearly 100% (Fig. 1). This fact may be accounted for by a considerable size of HDP

cations. As a result of ion-exchange adsorption, complexes containing Ni^{2+} and HDP cations on the exchange position (samples Ni-1 to Ni-5) were obtained from Ni-montmorillonite (sample Ni-0). The organic cations occupy 7, 19, 28, 59 and 100% of exchange positions in samples Ni-1 to Ni-5, respectively.

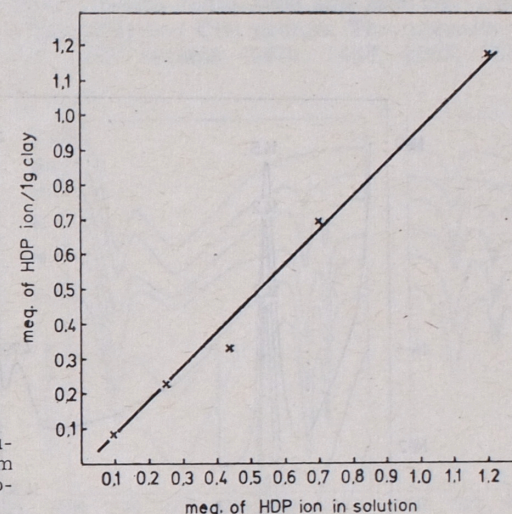


Fig. 1. Isotherm of Ni^{2+} substitution by hexadecylpyridinium (HDP) cations in Ni-montmorillonite

X-ray investigations

The results of X-ray investigations are presented in Figure 2. The diffraction patterns of all the samples show intensive basal reflections of montmorillonite with the d_{hkl} values $\approx 14.5 - 21.3 \text{ \AA}$, and higher-order reflections. When preparing samples for X-ray analyses, all the attempts to obtain complete orientation of montmorillonite plates were a failure, which is evidenced by a small number of 001 reflections and by the presence of 110 reflection (4.49 \AA) (Fig. 2).

On the X-ray diffraction patterns of samples Ni-0 to Ni-3 there are no marked differences in the position of montmorillonite reflections. This indicates that sorption of organic cations up to the point when about 28% of montmorillonite exchange positions are occupied does not produce changes in the interlayer spacings, $d_{001} = 14.3 \text{ \AA}$, typical of Ni-montmorillonite. That spacing also corresponds to one layer of organic cations in the interlayer spaces, lying parallel to the sheet surfaces. In consequence, the X-ray patterns obtained do not yield data permitting to state whether the sorption of HDP cations gives rise to mixed-layer structures. Only in the case of sample Ni-4, the position of basal reflections of montmorillonite suggests the presence of mixed-layer structures with one and two layers of organic cations. Yet, too small a number of 001 reflections does not permit an unequivocal interpretation of the X-ray pattern of that sample. In sample Ni-5, the interlayer spacing of montmorillonite increases to

21.3 Å (Fig. 2). The series of 001 reflections shows that organic cations are uniformly distributed between the layers, so no mixed-layer structure occurs in this case. The spacing $d_{001} = 21.3$ Å corresponds to oblique arrangement of HDP cations with respect to the sheet surfaces, but it may also suggest the presence of three layers of organic substance lying flat on the sheet surfaces (Greenland, Quirk 1962).

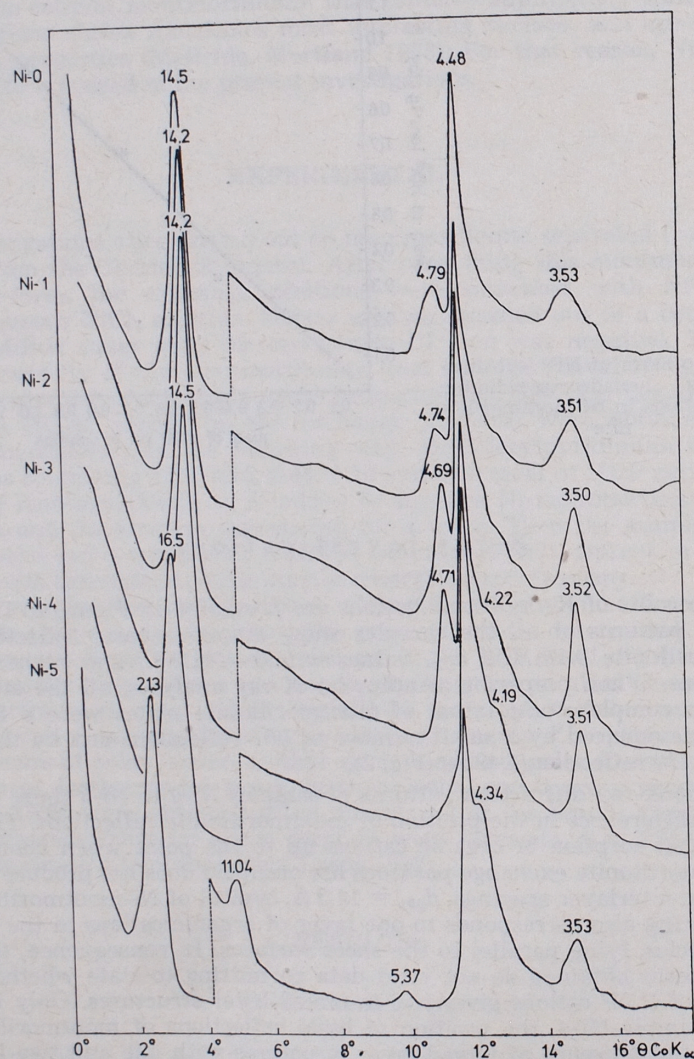


Fig. 2. X-ray diffraction patterns of Ni-montmorillonite (sample Ni-0) and Ni-HDP montmorillonite (samples Ni-1 to Ni-5)

Infrared spectroscopic investigations

Infrared spectra of the complexes studied reveal the presence of absorption bands produced by vibrations of atom groupings in the crystal lattice of montmorillonite and in organic cations (Fig. 3). The gradually increasing content of HDP cations manifests itself in the first place in a higher intensity of the absorption bands about 2850 and 2920 cm^{-1} , due to C—H valence vibrations within CH_2 and CH_3 groups. The intensity of the other bands produced by HDP cations (1470, 1488, 1503, 1635, 3380 cm^{-1}) increases as well.

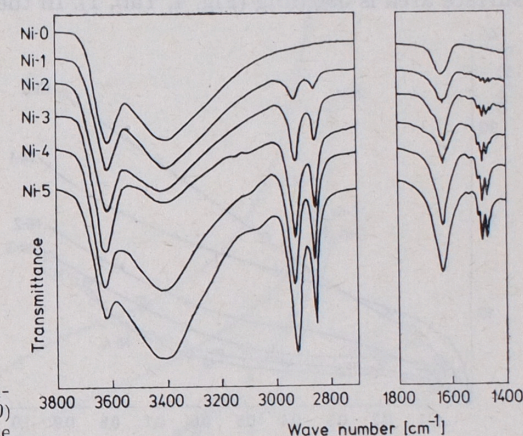


Fig. 3. Infrared spectra of Ni-montmorillonite (sample Ni-0) and Ni-HDP montmorillonite (samples Ni-1 to Ni-5)

The obtained spectra do not permit to determine in all samples the effect of the amount of organic cations on the content of interlayer water in montmorillonite. This is caused by the coincidence of the bands arising from H_2O molecules (1650 and 3430 cm^{-1}) with those produced by vibrations of atom groupings within the organic cations (1635 and 3380 cm^{-1}). Only the spectra of samples Ni-0 to Ni-3 reveal a systematic decrease in the intensity of the absorption band 3430 cm^{-1} , which evidences that the content of interlayer water molecules decreases due to the upsetting of the regular arrangement of H_2O molecules surrounding Ni^{2+} by organic cations (McBride, Mortland 1975). In the other spectra, a higher intensity of the band 3430 cm^{-1} is due to the higher content of HDP cations.

Sorption investigations

The choice of adsorbates used for the analyses was determined by the chemical nature of their molecules as well as by the types of reaction with the adsorbent surface. Water and benzene molecules are sensitive to the chemical nature of the adsorbent surface, the former sorbing mainly on polar, the latter on nonpolar centres. Methyl alcohol adsorption determines to a lesser degree the nature of the adsorbent surface owing to the double character of molecules of that compound, for which hydrophilic

—OH group and hydrophobic —CH₃ radical are responsible. In the case of argon, the adsorption volume permits to define the porous structure of the adsorbent.

From the adsorption isotherms, the BET values for specific surface areas were calculated. They were treated, however, only as indices of sorption capacity in the range of relative pressures $p/p_0 = 0.05 - 0.35$.

The isotherms obtained for water vapour sorption are shown in Fig. 4. According to the BET theory, they are generally type II isotherms. Their sequence depends on the degree of substitution of Ni²⁺ by HDP cations, which is evident from the surface area values. For Ni-montmorillonite the surface area is 390 m²/g (Fig. 4, Tab. 1). In the case of sample Ni-1, a slight

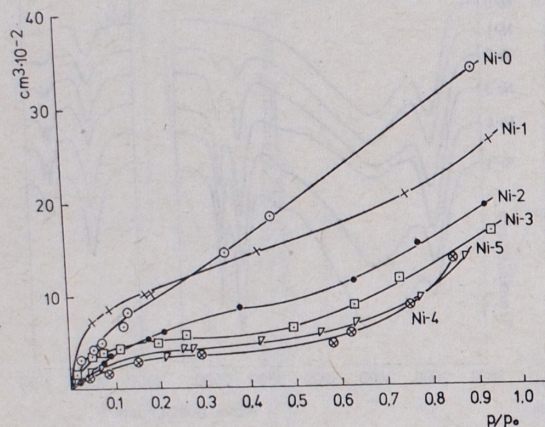


Fig. 4. Isotherms for water vapour adsorption on Ni-montmorillonite and Ni-HDP montmorillonite

increase in sorption capacity may be noted; yet, for p/p_0 higher than 0.3, the sorption isotherm determined for that sample is below the isotherm for sample Ni-0. The sorption capacity of samples Ni-2, Ni-3 and Ni-4 decreases systematically. Complete substitution of Ni²⁺ by organic cations (sample Ni-5) does not result in further decrease of H₂O vapour sorption.

Table 1

Experimental data on sorption properties of Ni-montmorillonite and Ni-HDP-montmorillonite

Sample	% HDP on exchange sites	Surface area (m ² /g)			
		water	methyl alcohol	benzene	argon
Ni-0	0	390.2	441.2	23.2	25.1
Ni-1	7	413.5	296.2	13.3	8.5
Ni-2	19	245.1	178.4	28.2	17.3
Ni-3	28	153.1	117.0	38.4	8.1
Ni-4	59	121.8	113.0	48.0	6.0
Ni-5	100	125.6	169.1	364.3	7.5

The surface area calculated for sample Ni-4, in which about 59% of exchange positions are occupied by HDP cations, is almost identical with that obtained for sample Ni-5.

The systematic diminution of sorption capacity of the samples with respect to water vapour implies that the number of polar centres on the surface of montmorillonite decreases, which is indicative of gradual hydrophobization of that mineral.

The isotherms obtained for CH₃OH vapour sorption (Fig. 5) have a similar shape (type II according to the BET theory) to those determined for

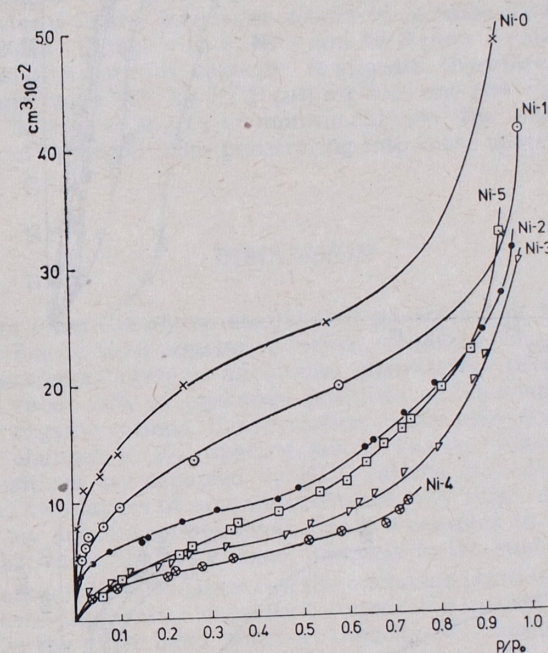


Fig. 5. Isotherms for methyl alcohol vapour adsorption on Ni-montmorillonite and Ni-HDP montmorillonite

water sorption. Ni-montmorillonite shows the greatest sorption capacity whereas gradual substitution of Ni²⁺ by HDP cations results in its decrease from 441 m²/g for the initial sample to 113 m²/g for sample Ni-4. Sample Ni-5 shows a higher sorption capacity than samples Ni-3 and Ni-4. This increase is presumably due to the fact that in sample Ni-5, which is a montmorillonite with the surface completely covered by organic cations, —CH₃ groups are mainly responsible for CH₃OH sorption.

The isotherms determined for benzene vapour sorption (Fig. 6), as well as sorption capacities calculated on their basis (Tab. 1) show certain characteristic features. Sample Ni-0 has the lowest sorption capacity to benzene vapours (23.2 m²/g). This capacity is gradually enhanced as Ni²⁺ are substituted by organic cations, increasing rapidly after all the exchange positions have been occupied by HDP cations (sample Ni-5, 364.3 m²/g).

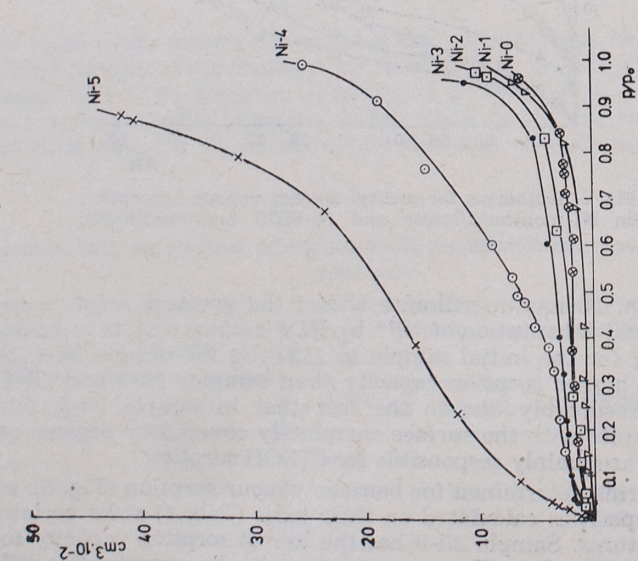


Fig. 6. Isotherms for benzene vapours adsorption on Ni-montmorillonite and Ni-HDP montmorillonite

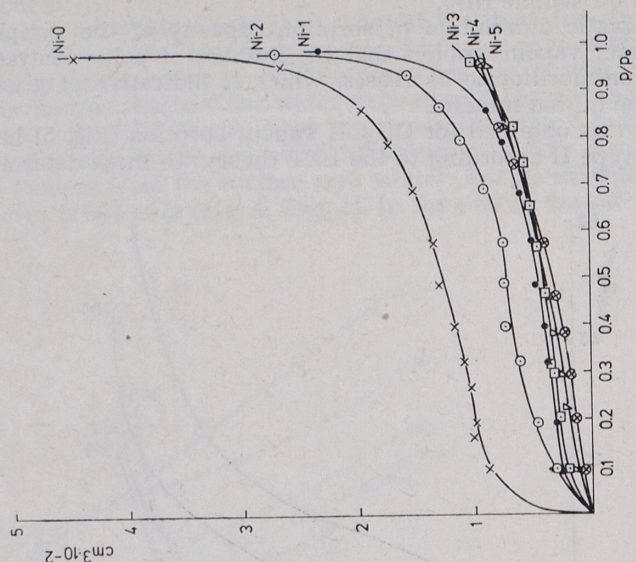


Fig. 7. Isotherms for argon vapour adsorption on Ni-montmorillonite and Ni-HDP montmorillonite

In sample Ni-5, the value for the surface area is almost as high as that calculated from water vapour sorption for initial montmorillonite. Benzene vapour sorption indicates that the surface of montmorillonite becomes markedly hydrophobic as the number of organic cations on the exchange positions increases. In the case of sample Ni-5, an intense reaction between HDP cations and benzene molecules most likely occurs.

The argon sorption isotherms (Fig. 7) indicate that sorption capacity of samples Ni-1 to Ni-4 is lower than that of sample Ni-0. This is particularly pronounced in the case of sample Ni-1 (Tab. 1). Worth noting is a higher capacity of sample Ni-2 compared with sample Ni-1, for which additional pores that formed in the interlayer spaces of montmorillonite are presumably responsible. Samples Ni-3, Ni-4 and Ni-5 show a relatively low and little differentiated sorption capacity. It appears, therefore, that substitution of 30% and more Ni^{2+} by HDP cations does not give rise to additional pores in the interlayer spaces of montmorillonite, the large size of HDP cations preventing argon from penetrating into those spaces.

DISCUSSION

It appears from the above results that adsorption of HDP cations by Ni-montmorillonite from aqueous solutions containing about 7 — 120 mval HDP/g of montmorillonite is an almost quantitative process. Up to the point when about 30% of exchange positions of Ni-montmorillonite are occupied by organic cations, the formation of the complexes studied does not involve changes in d_{001} spacing (about 14.3 Å). When about 59% of exchange positions are occupied by HDP cations, mixed-layer structures with one and two layers of organic substance may form. A 100% substitution of Ni^{2+} by organic cations gives rise to a complex in which the organic cations are most likely arranged obliquely to the surface of sheets.

As the content of HDP cations on the exchange positions of montmorillonite increases, its sorption capacity to water and methyl alcohol vapours decreases. On the other hand, sorption capacity to benzene vapours is enhanced systematically, which suggests that an intense reaction occurs between HDP cations and benzene molecules. Lower sorption capacity of samples modified with organic cations compared with the capacity of Ni-montmorillonite implies that the presence of HDP cations on the exchange positions does not give rise to any significant amount of additional pores in the interlayer spaces.

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Mieczysław ŻYŁA, Zenon KŁAPYTA

МОДИФИКАЦИЯ ВЛАСНОСТИ СОРПЦИЙНЫХ Ni-MONTMORILLONITU PRZY ZASTOSOWANIU KATIONÓW HEKSADECYLOPIRYDINIOWYCH

Streszczenie

W pracy przedstawiono wpływ kationów heksadecylopirydyniowych (HDP), zaadsorbowanych na Ni(II)-montmorillonicie, na własności sorpcyjne tego minerału. Uzyskano kompleksy zawierające Ni^{2+} i HDP w ilościach 0 — 100% pozycji wymiennych. Przeprowadzono dla nich badania rentgenograficzne, spektroskopowe w podczerwieni i sorpcyjne.

Adsorpcja kationów HDP do zawartości około 30% pozycji wymiennych odbywa się z zachowaniem odległości międzypakietowej 14,3 Å typowej dla Ni-montmorillonitu. W przypadku, gdy około 59% Ni^{2+} zastąpionych jest przez kationy HDP, możliwe jest tworzenie się struktur mieszanopakietowych z jedną i dwoma warstwami substancji organicznej. Całkowite zastąpienie Ni^{2+} przez kationy HDP prowadzi do utworzenia kompleksu, w którym kationy organiczne ułożone są prawdopodobnie ukośnie do powierzchni pakietów montmorillonitu.

Wzrost zawartości kationów HDP na pozycjach wymiennych Ni-montmorillonitu powoduje zmniejszenie się chłonności sorpcyjnej tego minerału względem par wody i alkoholu metylowego. Charakterystyczny jest systematyczny wzrost chłonności sorpcyjnej względem par benzenu, co wskazuje na postępujący proces hydrofobizacji Ni-montmorillonitu w miarę wymiany jonowej Ni^{2+} na kationy HDP. Otrzymane próbki Ni-HDP montmorillonitu nie wykazują zwiększonej sorpcji argonu w porównaniu z Ni-montmorillonitem. Świadczy to o tym, że wprowadzenie kationów HDP na pozycje wymienne nie prowadzi do udostępnienia przestrzeni międzypakietowych dla argonu.

OBJAŚNIENIA FIGUR

- Fig. 1. Izoterma wymiany Ni^{2+} na kationy heksadecylopirydyniowe (HDP) w Ni-montmorillonicie
 Fig. 2. Dyfraktogramy rentgenowskie Ni-montmorillonitu (próbka Ni-0) oraz Ni-HDP montmorillonitu (próbki Ni-1 do Ni-5)
 Fig. 3. Spektrogramy w podczerwieni Ni-montmorillonitu (próbka Ni-0) oraz Ni-HDP montmorillonitu (próbki Ni-1 do Ni-5)
 Fig. 4. Izotermy adsorpcji par wody na Ni-montmorillonicie (próbka Ni-0) oraz Ni-HDP montmorillonicie (próbki Ni-1 do Ni-5)

Fig. 5. Izotermy adsorpcji par alkoholu metylowego na Ni-montmorillonicie oraz Ni-HDP montmorillonicie

Fig. 6. Izotermy adsorpcji par benzenu na Ni-montmorillonicie oraz Ni-HDP montmorillonicie

Fig. 7. Izotermy adsorpcji par argonu na Ni-montmorillonicie oraz Ni-HDP montmorillonicie

Мечислав ЖИЛА, Зенон КЛАПЫТА

МОДИФИКАЦИЯ СОРБЦИОННЫХ СВОЙСТВ Ni-MONTMORILLONITA С ИСПОЛЬЗОВАНИЕМ ГЕКСАДЕЦИЛОПИРИДИНИЕВЫХ КАТИОНОВ

Резюме

В работе представлено влияние гексадецилопиридиниевых катионов (ГДП), адсорбированных на Ni(II)-монтмориллоните, на сорбционные свойства этого минерала. Получено комплексы содержащие Ni^{2+} и ГДП в количестве 0 — 100% обменных позиций. На них проведено рентгенографические, инфракрасно-спектроскопические и сорбционные исследования.

Адсорбция катионов ГДП в количестве до около 30% обменных позиций происходит с сохранением межслойных расстояний 14,3 Å, типичных для Ni-монтмориллонита. В случае, когда около 59% Ni замещено катионами ГДП, возможно образование смешанных слоистых структур с одним и двумя слоями органического вещества. Полное замещение Ni^{2+} катионами ГДП ведет к образованию комплекса, в котором органические катионы вероятно расположены диагонально к плоскости слоев монтмориллонита.

Увеличение содержания катионов ГДП на обменных позициях Ni-монтмориллонита вызывает уменьшение сорбционной способности этого минерала по отношению к парам воды и метилового алкоголя. Характерно систематическое увеличение сорбционной способности по отношению к парам бензена, что указывает на прогрессирующий процесс гидрофобизации Ni-монтмориллонита по мере обмена ионов Ni^{2+} на катионах ГДП. Полученные образцы Ni-ГДП монтмориллонита не обнаруживают увеличения сорбции аргона по сравнению с Ni-монтмориллонитом. Это свидетельствует о том, что введение катионов ГДП на обменные позиции не приводят к раскрытию межслойного пространства для аргона.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Изотерма обмена Ni^{2+} на гексадецилопиридиниевые катионы (ГДП) в Ni-монтмориллоните
 Фиг. 2. Дифрактограммы Ni-монтмориллонита (образец Ni-0) и Ni-ГДП монтмориллонита (образец Ni-1 до Ni-5)
 Фиг. 3. ИК-спектры Ni-монтмориллонита (образец Ni-0) и Ni-ГДП монтмориллонита (образец Ni-1 до Ni-5)

- Фиг. 4. Изотермы адсорбции паров воды на Ni-монтмориллоните (образец Ni-0) и на Ni-ГДП монтмориллонита (образцы Ni-1 до Ni-5)
- Фиг. 5. Изотермы адсорбции паров метилового спирта на монтмориллоните и Ni-ГДП монтмориллоните
- Фиг. 6. Изотермы адсорбции паров бензена на Ni-монтмориллоните и Ni-ГДП монтмориллоните
- Фиг. 7. Изотермы адсорбции паров аргона на Ni-монтмориллоните и Ni-ГДП монтмориллоните