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PRELIMINARY STUDIES OF CARBON OXIDE SORPTION ON
MONTMORILLONITE WITH ALKALI INTERLAYER CATIONS

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A b s t r a c t. Studies have been made of CO adsorption on montmorillonite possessing exchange interlayer cations of metals of the first and second groups of the periodic table. It has been found that the cationic radius affects the sorption of this adsorbate, this effect being insignificant for cations of the first group and somewhat greater for those of the second group. The sorption properties have been compared with the results of earlier studies of argon and methyl alcohol adsorption.

INTRODUCTION

Carbon oxide is an interesting adsorbate capable of extending our knowledge of the chemical properties and structure of montmorillonite. A carbon oxide molecule shows the asymmetric distribution of charge, it is readily polarizable and therefore responsive to the action of the strong electrostatic field surrounding the cations. It performs the function of both a weak donor and acceptor of π -electrons, which results in that carbon oxide molecules form specific bonds with the transition group cations. Three different configurations are possible in the system metallic cation-carbon oxide molecules /Angell, Schaffer, 1966/:

a. A configuration of the type presented in Fig. 1a. K is an interlayer cation linked to a surface oxygen atom. Linkages of this type can also be formed during adsorption on metal oxides /Fig. 1b/.

b. A $/CO/^{+}$ cation /Fig. 1c/.

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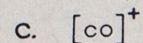
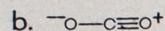
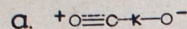


Fig. 1. Three possible configurations in the system: adsorbate surface - carbon oxide molecule /detailed explanations in the text/

As a result of CO adsorption on zeolites with different exchangeable cations, a displacement of the frequency of the carbon-oxygen band in the IR spectrum is visible. This displacement depends on the cation-generated electrostatic field acting on the carbon oxide molecule /Rabo *et al.*, 1966/. Under the influence of the electrostatic field, electrons from the carbon atom orbital with a free pair of electrons can be displaced towards the cations. This process is similar to the first stage of formation of the $\sigma - \pi$ bond present in metal carbonyls.

It is conceivable /Zecchina *et al.*, 1975/ that CO sorption on exchangeable cations located on the surface of a zeolite, in the "windows" of cubo-octahedral cages, can be accomplished by several ways. An illustrative case is provided by CO sorption on surface Cr^{3+} ions, which can yield four different-configurations:

- 1/ one cation is linearly linked to one CO molecule /Fig. 2a/,
- 2/ one cation is linked to two CO molecules /Fig. 2b/,
- 3/ two cations are linked to three CO molecules /Fig. 2c/,
- 4/ two cations are linked to four CO molecules /Fig. 2d/.

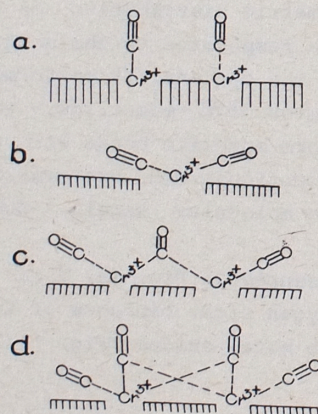


Fig. 2. CO adsorption on surface Cr^{3+} ions /detailed explanations in the text/

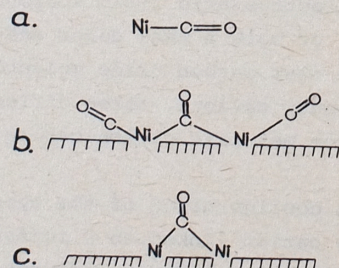


Fig. 3. CO adsorption on the surface of nickel /detailed explanations in the text/

Carbon oxide is sorbed in a similar way on the surface of nickel:
1/ the first one is an equivalent of the first chromium-carbon oxide bond /Fig. 3a/,

2/ the second configuration corresponds to the third linkage between the chromium-cation and carbon oxide /Fig. 3b/,

3/ the third one has no equivalent in the chromium cation-carbon oxide linkage /Fig. 3c/.

EXPERIMENTAL

Adsorption investigations were carried out on montmorillonite isolated from the Milowice bentonite by sedimentation in aqueous medium. The $< 1 \mu m$ fraction obtained in this way was converted into the hydrogen form. This montmorillonite served as a starting material for the introduction of other cations into the interlayer spaces. The substitution of hydronium ion for the required cation was accomplished through treatment with aqueous solution of NH_4Cl , $NaCl$, KCl , $MgCl$, $CaCl_2$ and $BaCl_2$. Then the sample was washed with distilled water until the reaction for chloride ion was negative. Isotherms for spec-pure carbon

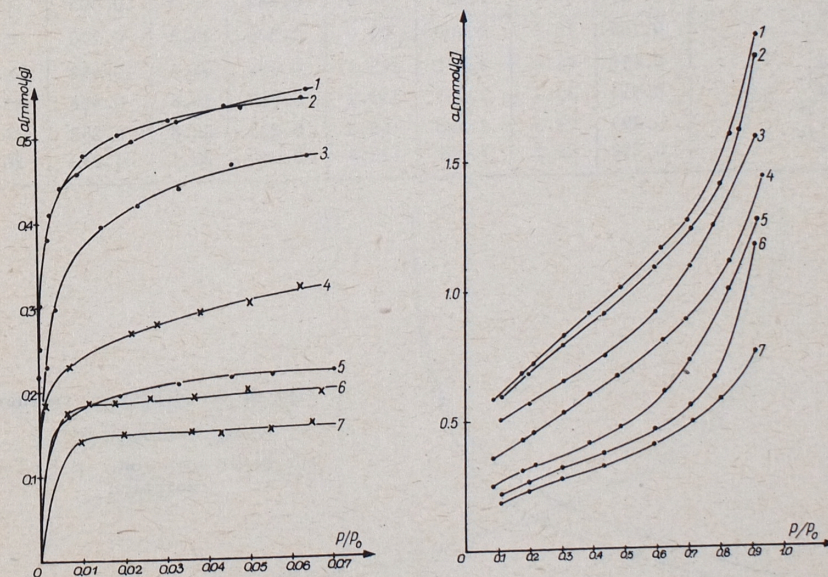


Fig. 4. Low-pressure CO adsorption isotherms on montmorillonites with alkali interlayer cations

1 - NH_4^+ , 2 - Ca^{2+} , 3 - Mg^{2+} , 4 - Na^+ , 5 - K^+ , 6 - Sr^{2+} , 7 - Ba^{2+} -montmorillonite

Fig. 5. CO adsorption isotherms on montmorillonites with alkali interlayer cations

1 - NH_4^+ , 2 - Ca^{2+} , 3 - Mg^{2+} , 4 - Na^+ , 5 - K^+ , 6 - Sr^{2+} , 7 - Ba^{2+} -montmorillonite

oxide adsorption on the different cation-exchanged forms of montmorillonite were obtained at 77.5 K using sorption manostats/Ciembroniewicz, Lasoń, 1972/. Prior to measurements, the samples were outgassed at 397 K down to a pressure of $1.33 \cdot 10^{-7}$ Pa. The resulting sorption equilibria curves are presented in Figures 4 and 5.

The isotherms were determined over two ranges of relative pressures: up to $0.07 p/p_0$ /Fig. 4/, and $0.05 - 0.975 p/p_0$ /Fig. 5/. The sequence of isotherms, reflecting sorption capacity, is the same in both cases. From the parts of isotherms lying in the range of relative pressures $p/p_0 = 0.05 - 0.35$ the BET values for V_m and then specific surface areas S were calculated. These values, together with ones determined from argon and methyl alcohol sorption, are listed in Table 1. The cal-

Table 1
 V_m /mmol/g/ and S_{BET} /m²/g/ values determined from adsorption isotherms

Montmorillonite	Ar		CH ₃ OH		CO		CO after second sorption	
	V_m	S	V_m	S	V_m	S	V_m	S
NH ₄ ⁺	0.702	70.2	1.587	173.9	0.581	56.7	0.585	57.0
Na ⁺	0.327	32.7	1.407	152.8	0.382	37.3	0.305	29.8
K ⁺	0.165	16.5	0.900	98.2	0.300	29.3	0.270	26.3
Mg ²⁺	0.458	45.8	3.272	365.9	0.454	44.3	0.452	44.1
Ca ²⁺	0.334	33.4	2.935	320.2	0.560	54.6	0.566	55.2
Sr ²⁺	0.293	29.3	1.543	168.3	0.234	22.8	0.252	24.6
Ba ²⁺	0.252	25.2	1.269	138.4	0.206	20.1	0.210	20.5

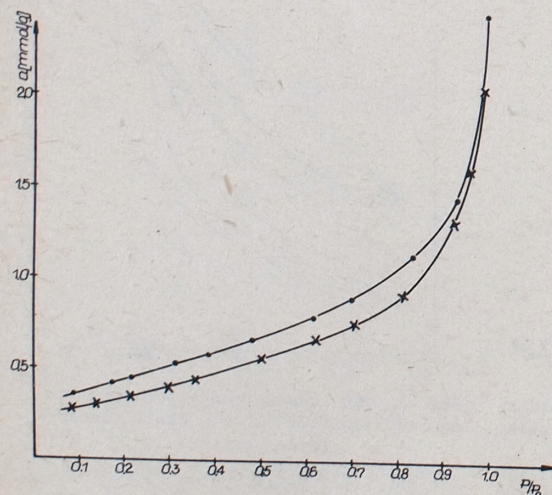


Fig. 6. CO adsorption isotherms on Na⁺-montmorillonite
-- first sorption, x - second sorption

culations took into account the molecular area of a carbon oxide molecule $\omega = 0.162 \text{ nm}^2$ determined from Emmet's formula. In order to ascertain the stability of the CO-montmorillonite bond, the samples after sorption were outgassed at room temperature down to a pressure of $1.33 \cdot 10^{-7}$ Pa, whereupon sorption measurements were repeated /Figs. 6-8/ and the V_m and S_{BET} values calculated again. These values are also given in Table 1 and compared with those calculated for the first sorption.

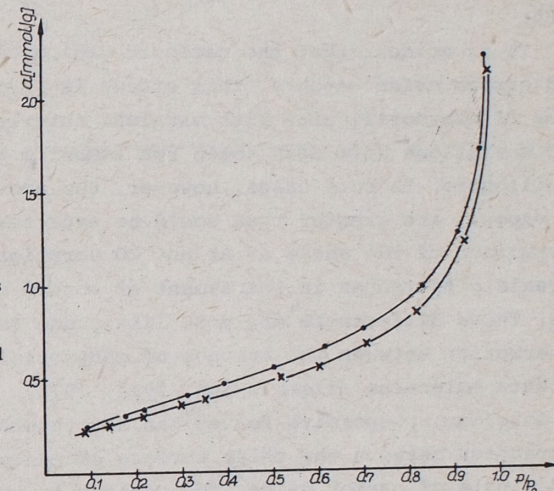


Fig. 7. CO adsorption isotherms on K⁺-montmorillonite
-- first sorption, x - second sorption

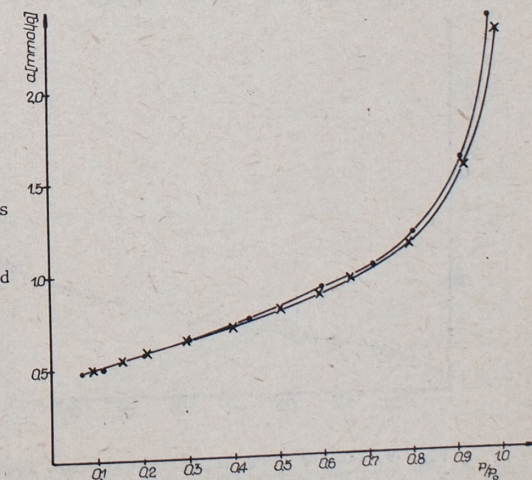


Fig. 8. CO adsorption isotherms on Mg²⁺-montmorillonite
-- first sorption, x - second sorption

From the shape of the isotherms obtained it appears that the bonding of CO molecules to the surface of montmorillonite is effected by chemisorption. The slope of the isotherm is steep in the range of relative pressures $p/p_0 = 0.05 - 0.1$, becoming flat only at higher pressure values. Condensation occurs at a relative pressure higher than 0.85.

It is evident that the cationic radius affects the amount of sorbed carbon oxide vapours. This effect is particularly pronounced in the case of montmorillonite with bivalent interlayer cations, although marked deviations have been noted for ammonium and calcium forms of montmorillonite. In both cases, however, the amounts of sorbed carbon oxide vapours are greater than could be expected from the ionic radii. A comparison of the shape of Ar and CO sorption isotherms [Fig. 9-12/ reveals differences in the amount of sorbed vapours of these adsorbates. These differences are most likely due to the different nature of interaction between the surface of montmorillonite and respective adsorbate molecules [Ziętkiewicz, Żyła, 1976/]. In the case of carbon oxide sorption, dispersive forces can act together with the forces of attraction between the polar surface of montmorillonite and the induced dipole of carbon oxide. The changes in the shape of isotherms are particularly pronounced for the sodium and calcium forms of montmorillonite, whilst for the magnesium and barium forms the differences are insignificant. A comparison of the shape of carbon oxide and methyl

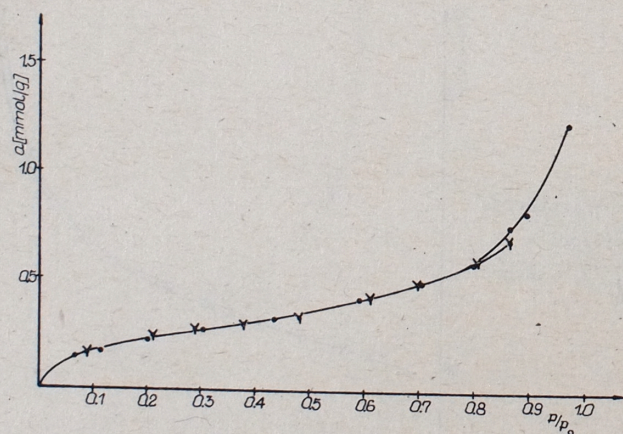


Fig. 9. CO /•/ and Ar /Y/ adsorption isotherms on Ba²⁺-montmorillonite

Fig. 10. CO /•/ and Ar /Y/ adsorption isotherms on Mg²⁺-montmorillonite

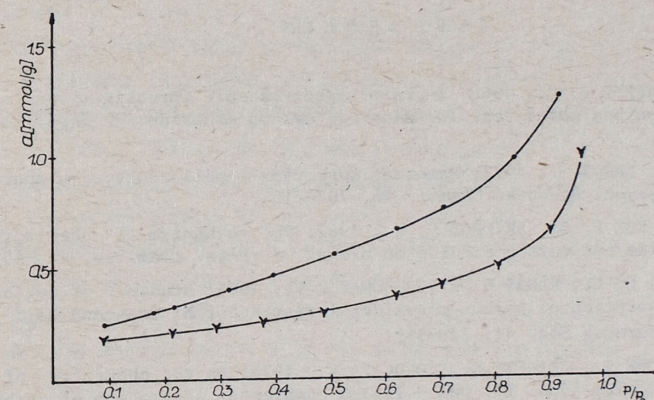
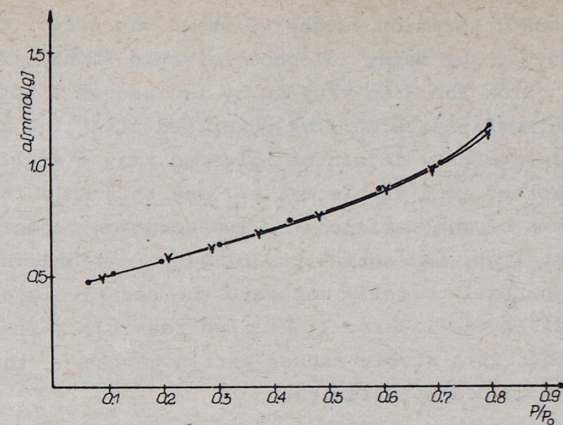
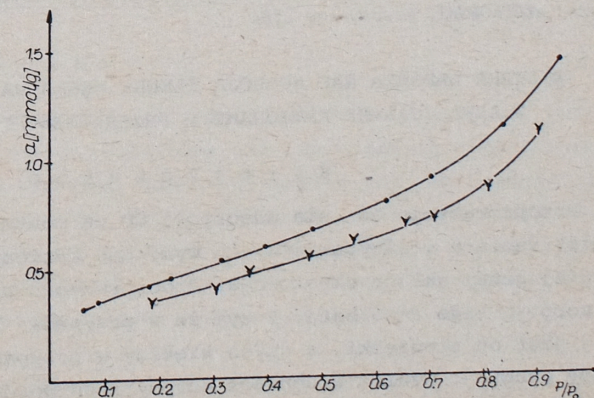


Fig. 11. CO /•/ and Ar /Y/ adsorption isotherms on K⁺-montmorillonite

Fig. 12. CO /•/ and Ar /Y/ adsorption isotherms on Na⁺-montmorillonite



alcohol sorption isotherms shows the effect of the stable dipole moment of the methyl alcohol molecule /Table 1/.

From the data yielded by the second sorption of carbon oxide on montmorillonite samples outgassed after the first sorption prior to measurements, it can be inferred that a small part of carbon oxide is adsorbed in a stable manner, and this only in the sodium and potassium forms of montmorillonite. The sorption capacity indices /Table 1/ suggest that, in contrast to bivalent cations, sodium and potassium cations fail to fully saturate the negatively charged surface of montmorillonite layers. It is also feasible that the carbon oxide being sorbed in a stable manner partly blocks up the access to the pore system in montmorillonite.

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WSTĘPNE BADANIA NAD SORPCJĄ TLENKU WĘGLA NA MONTMORILLONICIE Z ALKALICZNYMI KATIONAMI W PRZESTRZENI MIĘDZYPAKIETOWEJ

Streszczenie

Przeprowadzono badania adsorpcji CO na montmorillonicie mającym w przestrzeniach międzypakietowych wymienne kationy metali pierwszej i drugiej grupy układu okresowego. Zaobserwowano wpływ promienia kationu na sorpcję tego adsorbentu, z tym że w przypadku kationów grupy pierwszej jest on niewielki, a nieco większy w przypadku kationów metali drugiej grupy. Wyniki własności sorpcyjnych porównano z wynikami przeprowadzonych wcześniej badań adsorpcji argonu i alkoholu metylowego.

OBJAŚNIENIA DO FIGUR

- Fig. 1. Trzy możliwe konfiguracje w układzie powierzchnia adsorbentu - cząsteczka tlenku węgla /szczegółowe objaśnienia w tekście/
- Fig. 2. Sorpcja CO na powierzchniowych jonach Cr^{3+} /szczegółowe objaśnienia w tekście/
- Fig. 3. Sorpcja CO na powierzchni niklu /szczegółowe objaśnienia w tekście/
- Fig. 4. Niskociśnieniowe izotermy adsorpcji CO na montmorillonitach modyfikowanych alkalicznymi kationami
1 - NH_4^+ , 2 - Ca^{2+} , 3 - Mg^{2+} , 4 - Na^+ , 5 - K^+ , 6 - Sr^{2+} , 7 - Ba^{2+} -montmorillonit
- Fig. 5. Izotermy sorpcji CO na montmorillonitach modyfikowanych alkalicznymi kationami
1 - NH_4^+ , 2 - Ca^{2+} , 3 - Mg^{2+} , 4 - Na^+ , 5 - K^+ , 6 - Sr^{2+} , 7 - Ba^{2+} -montmorillonit
- Fig. 6. Izotermy sorpcji CO na Na^+ -montmorillonicie
· - pierwsza sorpcja CO, x - wtórna sorpcja CO
- Fig. 7. Izotermy sorpcji CO na K^+ -montmorillonicie
· - pierwsza sorpcja CO, x - wtórna sorpcja CO
- Fig. 8. Izotermy sorpcji CO na Mg^{2+} -montmorillonicie
· - pierwsza sorpcja CO, x - wtórna sorpcja CO
- Fig. 9. Izotermy sorpcji CO /·/ i Ar /Y/ na Ba^{2+} -montmorillonicie
- Fig. 10. Izotermy sorpcji CO /·/ i Ar /Y/ na Mg^{2+} -montmorillonicie
- Fig. 11. Izotermy sorpcji CO /·/ i Ar /Y/ na K^+ -montmorillonicie
- Fig. 12. Izotermy sorpcji CO /·/ i Ar /Y/ na Na^+ -montmorillonicie

Андрей ВЛОДКОВСКИ, Мечислав ЖИЛА

ПРЕДВАРИТЕЛЬНЫЕ ИССЛЕДОВАНИЯ СОРБЦИИ ОКСИ УГЛЕРОДА НА МОНТМОРИЛЛОНИТЕ СО ЩЕЛОЧНЫМИ МЕЖПАКЕТНЫМИ КАТИОНАМИ

Резюме

Были проведены исследования адсорбции CO на монтмориллоните, имеющим в межпакетном пространстве обменные катионы металлов первой и второй группы периодической системы. Замечено влияние радиуса катиона на сорбцию этого адсорбента, с тем, что в случае катионов первой группы он небольшой, а несколько больший в случае катионов металлов второй группы. Результаты сорбционных свойств сравнивались с результатами проведенных ранее исследований адсорбции аргона и метилового спирта.

ОБЪЯСНЕНИЕ ФИГУР

- Фиг. 1. Три возможные конфигурации в системе поверхность адсорбента-молекула окиси углерода /подробное объяснение в тексте/

Фиг. 2. Сорбция CO на поверхностных ионах Cr^{+3} /подробное объяснение в тексте/

Фиг. 3. Сорбция CO на поверхности никеля /подробное объяснение в тексте/

Фиг. 4. Изотермы низкого давления адсорбции на монтмориллонитах модифицированных щелочными катионами

1 - NH_4^+ , 2 - Ca^{2+} , 3 - Mg^{2+} , 4 - Na^+ , 5 - K^+ , 6 - Sr^{2+} , 7 - Ba^{2+} монтмориллонит

Фиг. 5. Изотермы сорбции CO на монтмориллонитах модифицированных щелочными катионами

1 - NH_4^+ , 2 - Ca^{2+} , 3 - Mg^{2+} , 4 - Na^+ , 5 - K^+ , 6 - Sr^{2+} , 7 - Ba^{2+} - монтмориллонит

Фиг. 6. Изотермы сорбции CO на Na^+ - монтмориллоните

. - первичная сорбция CO, x - вторичная сорбция CO

Фиг. 7. Изотермы сорбции CO на K^+ - монтмориллоните

. - первичная сорбция CO, x - вторичная сорбция CO

Фиг. 8. Изотермы сорбции CO на Mg^{2+} - монтмориллоните

. - первичная сорбция CO, x - вторичная сорбция CO

Фиг. 9. Изотермы сорбции CO /. / и Ag/Y/ на Ba^{2+} - монтмориллоните

Фиг. 10. Изотермы сорбции CO /. / и Ag/Y/ на Mg^{2+} - монтмориллоните

Фиг. 11. Изотермы сорбции CO /. / и Ag/Y/ на K^+ - монтмориллоните

Фиг. 12. Изотермы сорбции CO /. / и Ag/Y/ на Na^+ - монтмориллоните