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Thermodynamic Characteristics of the Adsorption of Organic Molecules on Modified MCM-41 Adsorbents

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Abstract—The adsorption of a number of organic molecules on samples of MCM-41 adsorbent modified with dichloromethylphenylsilane and subsequently treated with sulfuric acid (MDCS) and *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride (MNM) is studied. Specific retention volumes equal to the Henry constant are determined by means of inverse gas chromatography at infinite dilution. The thermodynamic characteristics of adsorption, the dispersive and specific components of the Helmholtz energy of adsorption, and the increment of the methyl group to the heat of adsorption are calculated. It is shown that the grafting of aminosilane and phenylsilane groups enhances the forces of dispersion and reduces specific interactions. A greater drop in polarity is observed for MDCS than for MNM, due to the stronger polarity of amoinosilane; the enthalpy factor makes the main contribution to the adsorption of organic compounds on the investigated adsorbents. It is found that the MNM sample is capable of the irreversible adsorption of alcohols.

Keywords: MCM-41, specific retention volume, sorption thermodynamic functions, polarity, inverse gas chromatography, dichloromethylphenylsilane, amination

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INTRODUCTION

Developing adsorbents with specific properties is one of the main problems of modern surface chemistry. Highly-ordered silica gels developed by Mobil Research and known as MCM-41, synthesized from micelles of some surfactants via the formation of associates with hexagonal symmetry and subsequent hydrolysis of tertarethoxysilane, are of particular interest [1, 2]. Depending on the conditions of synthesis, the samples have narrow size distributions of pores with diameter in the range of 15 to 100 Å [3] and high specific surface areas [4, 5], leading to wide application of the MCM-41 adsorbents in microconcentration devices, catalysis, and medicine [6–10].

Varying the adsorbents' polarity by modifying its surface with different functional groups is of interest in expanding the area of MCM-41 application. The adsorption of organic compounds by MCM-41 after silylation with dichloromethylphenylsilane and subsequent treatment with sulfuric acid, and after modification with *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride, is studied in this work.

EXPERIMENTAL

MCM-41 silica gel with a specific surface area of 1250 m^2/g and pore sizes of around 33 Å (Clariant, formerly Süd-Chemie, Germany) was used as our initial adsorbent. The silylation of MCM-41 with dichloromethylphenylsilane (DCMPS) and its subsequent sulfonation with sulfuric acid were performed as described in [11, 12]. The obtained sample was labeled MDCS. Modification with *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride (TMTMAC) in the form of a 50% solution in methanol (ABCR Company, Germany) was conducted using the scheme shown in Fig. 1 [12–14].

Samples of MCM-41 composite with grafted quaternary amino groups were synthesized by adding TMTMAC to a suspension of MCM-41. Prior to modification, MCM-41 was activated at 130°C for 12 h in a nitrogen flow. Activated MCM-41 ($m = 1.0$ g) was dispersed in 50 mL of solvent with the subsequent addition of 1 mL of TMTMAC. The mixture was stirred at room temperature for 4 h. Its products were then washed with 100 mL of methanol and 100 mL of *n*-hexane. The solvents were removed by drying at 60°C for 4 h. The modified material is referred to below as MNM. The specific surface area of the inves-

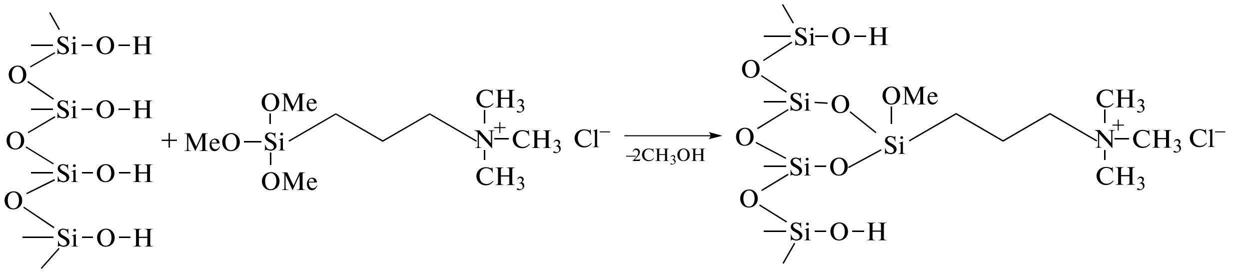

Fig. 1. Scheme of the synthesis of the MNM sample (the modification of MCM-41 with *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride).

tigated samples, determined from the data of low-temperature nitrogen adsorption/desorption at 77 K, was 1000–1100 m^2/g [13, 14].

The adsorption properties of the MCM-41 composites were studied on an upgraded Tsvet 500M gas chromatograph equipped with a flame-ionization detector. A steel column 300 mm long with an internal diameter of 3 mm was used. The flow rate of the nitrogen carrier gas, measured at the outlet of the cold column using a bubble flowmeter, was 10 mL/min. The temperature was varied from 150 to 170°C for MDCS and from 140 to 170°C for MNM. The temperature in the column thermostat, measured over the thermostat volume by an independent multimeter, was maintained with an accuracy of 1 K. All of the samples were preliminarily conditioned in a flow of carrier gas at a temperature of 170°C for 10 h. The selection of the maximum operating temperature was determined by the thermal stability of the investigated samples. Normal alkanes (C_5–C_9), isooctane, cyclohexane, benzene, toluene, ethyl acetate, ethanol, and *n*-propanol were used as adsorbates.

Using the experimentally determined values of the retention time (t_R, s), the specific retention volumes ($V^0_{g(T)}$, mL/g) were calculated with the formula

$$V^0_{g(T)} = \frac{j(t_R - t_D)F_C}{W_a}\frac{T}{T_c}\left(1 - \frac{p_{\text{water}}}{p_{\text{atm}}}\right), \tag{1}$$

where *j* is the James–Martin coefficient; t_M is the dead retention time, s; F_C is the carrier gas flow rate, mL/s; W_a is the weight of the adsorbent in the column, g; T is the temperature at which the carrier gas flow rate is measured, K; T_c is the column's temperature, K; p_{water} is the partial pressure of water vapor at the temperature at which the carrier gas flow rate is measured, Torr; and p_{atm} is the atmospheric pressure, Torr.

The desorption branches of the peaks of different heights overlapped each other, and the specific retention volume values did not depend on the carrier gas flow rate. This allowed us to consider the experimental conditions as quasiequilibrium, and the Henry constants of adsorption/desorption interaction as equal to the specific retention volumes at the column temperature. The concentration of the adsorbate in the gas phase was 1 μmol/mL, and the concentration of the adsorbate in the adsorbed state was 1 μmol/g (the standard states of the materials).

Using the formula

$$\ln V^o_{g(T)} = -\frac{\Delta U}{RT} + \frac{\Delta S}{R} + 1, \tag{2}$$

changes in molar adsorption internal energy and entropy $-\Delta U$ and $-\Delta S$, expressed in kJ/mol and J/(mol K), respectively, were calculated from the dependence of $\ln V^0_{g(T)}$ on $1/T$. The molar Helmholtz energy in kJ/mol was calculated using the formula

$$\Delta F = -RT\ln V^0_{g(T)} + RT. \tag{3}$$

The error in determining the ΔF value did not exceed 3%. The contributions from dispersion and specific interactions to the ΔF value of adsorption were estimated according to Dong, using the linear dependence of the adsorption energy of alkanes on their polarizability [15, 16]. It was assumed that only dispersion (nonspecific) interactions were involved on the interaction between alkanes and the adsorbent's surface. The energy of nonspecific interactions (ΔF^{disp}, kJ/mol) of the other molecules was considered to be equal to the energy of the adsorption of hypothetical alkane with the same polarizability. The energy of specific interactions (ΔF^{spec}, kJ/mol) was calculated from the difference between the total adsorption energy and the energy of nonspecific interactions. The ΔF^{disp} value the dispersion interactions between the adsorbate molecules and the adsorbent's surface, while the ΔF^{spec} value characterized the induction, orientation, and donor–acceptor interactions.

The P' parameter expressed by the formula [17, 18]

$$P' = \frac{\sum_{i=1}^{n}\left(\frac{\Delta F_i^{\text{spec}}}{\Delta F_i}\right)}{n} \times 100\% - P_{\text{GCB}}, \tag{4}$$

where n is the number of adsorbates and P_{GCB} is the provisional chromatographic polarity of graphitized

Table 1. Specific retention volumes ($V^0_{g(T)}$, mL/g) on the investigated adsorbents at 170°C

Adsorbate	MDCS	MNM	MCM-41
n-Pentane	24	26	–
n-Hexane	37	56	19
n-Heptane	73	124	47
n-Octane	127	213	105
n-Nonane	252	417	239
Isooctane	82	134	–
Cyclohexane	46	42	13
Benzene	66	157	65
Toluene	105	312	160
Ethyl acetate	329	542	201
Ethanol	95	–	107
n-Propanol	131	–	131

carbon black, was used as a nominal value characterizing the polarity of the studied adsorbents.

RESULTS AND DISCUSSION

The values of the specific retention volumes on the studied adsorbents are compared to those of the initial MCM-41 in Table 1. As can be seen, $V^0_{g(T)}$ for alkanes grow upon transitioning from MCM-41 to MDCS and assumes its maximum values for MNM. The retention parameters of benzene on the MCM-41 and MDCS adsorbents are comparable, while the retention volume of toluene on MDCS is less than on MCM-41. With MNM, the retention volume values for all the adsorbates are 2–3 times higher than for the other materials. This can be explained by a reduction in pore size, due to the grafting of functional groups. The distance between molecules and pore walls in smaller micropores is shorter, increasing the strength of dispersion interactions. This effect is more strongly pronounced for MNM due to the larger functional group, and thus a greater reduction in pore size.

The strong retention of alcohols with considerable smearing of peaks, particularly of the peak desorption branches (the tail), is observed on the MDCS sample prepared by modifying MCM-41 with dichloromethylphenylsilane and its subsequent treatment with sulfuric acid. We were able to reliably determine the retention times only for ethanol and *n*-propanol. With MNM, the strong retention and smearing of peaks in the region of infinite dilution did not allow us to determine the retention time of any alcohols on chromatographic columns packed with the investigated sorbent.

The values of the dispersion and specific components of the ΔF parameter of adsorption on the investigated adsorbents at a temperature of 170°C, relative to those for the initial MCM-41, are given in Table 2. The dispersion component on both of the investigated adsorbents was larger than on the initial MCM-41. This was also due to in the reduction in pore size after modification. As with the retention volumes, the maximum $-\Delta F^{\text{disp}}$ values for the investigated materials were observed for MNM (3–4 kJ/mol higher than for the initial sorbent).

The specific component of the ΔF parameter for MNM is higher than for MDCS (MCM-41 with grafted dichloromethylphenylsilane groups and subsequent treatment with sulfuric acid) but lower than for MCM-41. We may assume that the drop in surface polarity after amination with TMTMAC is relatively small. This is due to the capacity of the nitrogen atom in the trimethylammonium group for strong specific interactions, especially via the donor–acceptor mechanism. The MNM surface is thus capable of strong

Table 2. Dispersion and specific components of the Helmholtz energy (kJ/mol) of adsorption on the investigated adsorbents at 170°C

Adsorbate	MDCS		MNM		MCM-41	
	$-\Delta F^{\text{disp}}$	$-\Delta F^{\text{spec}}$	$-\Delta F^{\text{disp}}$	$-\Delta F^{\text{spec}}$	$-\Delta F^{\text{disp}}$	$-\Delta F^{\text{spec}}$
Benzene	15.0	4.1	15.5	6.8	11.7	8.4
Toluene	17.3	3.5	18.5	6.3	15.3	8.8
Ethyl acetate	14.1	10.9	14.2	12.1	10.2	14.4
Ethanol	9.2	11.2	–	–	2.6	19.4
n-Propanol	11.4	10.2	–	–	6.0	17.0
P'	13		20		31	

Table 3. Molar changes in internal energy (ΔU, kJ/mol) and entropy (ΔS, J/(mol K)), and linear correlation factors

Adsorbate	MDCS			MNM		
	$-\Delta U$	$-\Delta S$	r	$-\Delta U$	$-\Delta S$	r
n-Pentane	21	20	0.9999	27	34	0.9763
n-Hexane	34	47	0.9932	34	43	0.9805
n-Heptane	37	48	0.9699	46	64	0.9736
n-Octane	60	98	0.9965	50	77	0.9772
n-Nonane	67	108	0.9984	57	87	0.9999
Isooctane	48	72	0.9944	52	76	0.9934
Cyclohexane	41	63	0.9977	37	52	0.9959
Benzene	28	28	0.9983	37	41	0.9941
Toluene	42	56	0.9958	58	80	0.9963

specific interactions and can be considered to be more polar in comparison to MDCS.

Analysis of the adsorption thermodynamic characteristics given in Table 3 shows that the ΔU and ΔS values of the adsorption of alkanes on MDCS and MNM differ in their directions: the adsorption thermodynamic characteristics are higher for low-boiling hydrocarbons on MNM and for high-boiling hydrocarbons on MDCS. This tendency is due to the different adsorption energy increments of the methyl groups. The increment of the methyl groups of alkanes with respect to the heat of adsorption is 7.5 kJ/mol on MNM and 11.8 kJ/mol on MDCS, confirming the higher hidrophobicity of MDCS, relative to MNM. For arenes, the heat of adsorption on MNM is higher than on MDCS, testifying to MNM's capacity for stronger specific interactions. The enthalpy–entropy compensation plot is shown in Fig. 2. As can be seen from the obtained data, the positions of the adsorbate points for both adsorbents shift to the enthalpy axis. This means that the enthalpy factor predominates over the entropy factor.

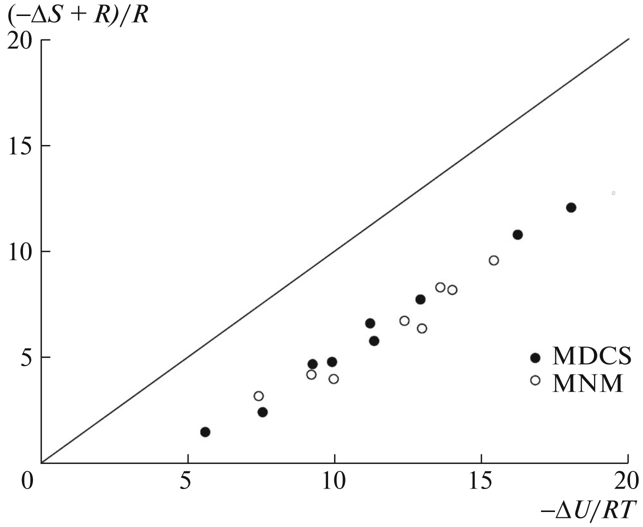

Fig. 2. Plot of the enthalpy–entropy compensation for the studied adsorbents.

CONCLUSIONS

As a result of silylating MCM-41 adsorbent with dichloromethylphenylsilane and subsequent treatment with sulfuric acid, the adsorbent's capacity for dispersion interactions increases while its capacity for specific interactions declines, resulting in a general reduction in polarity. The MCM-41 sample modified with *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride was also less polar than the initial sample. In light of the data obtained for the series of four modified samples in [17], MDCS and methylated MCM-41 show the lowest polarity, while MNM displays the highest polarity.

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REFERENCES

1. J. S. Beck, J. C. Vartuli, W. J. Roth, et al., J. Am. Chem. Soc. **114**, 10834 (1992). doi 10.1021/ja00053a020
2. C. T. Kresge, M. E. Leonowicz, W. J. Roth, et al., Nature **359**, 710 (1992). doi 10.1038/359710a0
3. R. Glaeser, R. Roesky, T. Boger, et al., in *Progress in Zeolite and Microporous Materials* (Elsevier, Amsterdam, 1997), Vol. 105, p. 695.
4. E. I. Shkolnikov, E. V. Sidorova, A. O. Malakhov, et al., Adsorption **17**, 911 (2011). doi 10.1007/s10450-011-9368-9
5. S. I. Karpov, F. Ressner, V. F. Selemenev, N. A. Belanova, and O. O. Krizhanovskaya, Russ. J. Phys. Chem. A **87**, 1888 (2013). doi 10.1134/S0036024413110125
6. J. Choma, M. Kloske, M. Jaroniec, et al., Adsorption **10**, 195 (2004).
7. P. A. Russo, M. M. L. R. Carrott, and P. J. M. Carrott, Adsorption **14**, 367 (2008).
8. S. Z. Qiao, S. K. Bhatia, and D. Nicholson, Langmuir **20**, 389 (2004).
9. Y. Chen, X. Shi, B. A. Han, et al., J. Nanosci. Nanotechnol. **12**, 7239 (2012).
10. R. L. Lavall, S. Ferrari, C. Tomasi, et al., Electrochim. Acta **60**, 359 (2012). doi 10.1016/j.electacta.2011.11.073
11. S. I. Karpov, F. Roessner, and V. F. Selemenev, J. Porous Mater. **23**, 497 (2016). doi 10.1007/s10934-015-0103-x

12. E. V. Borodina, F. Ressner, S. I. Karpov, and V. F. Selemenev, RF Patent No. 2438780 (2010).
13. E. V. Borodina, S. I. Karpov, V. F. Selemenev, et al., Microporous Mesoporous Mater. **203**, 224 (2015). doi 10.1016/j.micromeso.2014.10.009
14. E. V. Borodina, F. Roessner, S. I. Karpov, and V. F. Selemenev, Nanotechnol. Russ. **5**, 808 (2010). doi 10.1134/S1995078010110091
15. J. H. Park, Y. K. Lee, and J.-B. Donnet, Chromatografia **33**, 154 (1992).
16. S. Dong, M. Brendle, and J.-B. Donnet, Chromatografia **28**, 469 (1989).
17. D. A. Sukhareva, V. Yu. Gus'kov, S. I. Karpov, F. Kh. Kudasheva, F. Roessner, and E. V. Borodina, Russ. J. Phys. Chem. A **90**, 470 (2016). doi 10.1134/S0036024416020291
18. V. Yu. Gus'kov, Yu. Yu. Gainullina, S. P. Ivanov, and F. Kh. Kudasheva, J. Chromatogr., A **1356**, 230 (2014). doi 10.1016/j.chroma.2014.06.045

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