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Study of selective adsorption of aromatic compounds from solutions by the flexible MIL-53(Al) metal-organic framework*

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The dynamic method under conditions close to equilibrium was applied to study the liquid-phase adsorption in the Henry region for a series of aromatic compounds on the MIL-53(Al) metal-organic framework at different temperatures. The interpretation of the obtained experimental adsorption data was based on the TOPOS analysis of the structure of the cavities in the MIL-53(Al) framework using the Voronoi—Dirichlet polyhedra concept. It is shown that the adsorption activity of the investigated material under the liquid-phase conditions is governed by a possible expansion of the channels and cavities in the structure and by a breathing effect of the structure caused by the temperature variation. The selectivity of adsorption shown by MIL-53(Al) for a series of the studied compounds is due to the adsorbate—adsorbent π—π-interaction and hydrogen bonding of adsorbate molecules with Brönsted acid sites of the metal-organic framework. High adsorption selectivity of the MIL-53(Al) framework were found for compounds differed in the number of aromatic rings in the molecule and the presence of the methyl substituent, as well as for aromatic hydrocarbons and their sulfur-containing heterocyclic analogs.

Key words: metal-organic frameworks, MIL-53(Al), adsorption, liquid chromatography, temperature dependence, topology.

Many works describing hybrid nanomaterials,[1] among which metal-organic frameworks (MOFs) occupy a special position, have been published in recent years.[2—7] Metal-organic frameworks represent a new type of hybrid organic—inorganic supramolecular materials, whose ordered network is built of electron-donor organic linkers and metal cations.[6,7] The possibility of varying the linker nature favors the preparation of numerous metal-organic frameworks.[8] These structures are characterized by unusually high specific surface areas and pore volumes, the controlled pore size and, as a consequence, the ability to adsorb molecules of various compounds.[5—8] Owing to unique structural and texture characteristics, MOFs are promising functional materials for gas storage and separation,[9,10] heterogeneous catalysis,[11] systems for targeted drug delivery in living organisms,[12] adsorption,[13—15] chromatography,[16—19] and other technological areas.

The promising use of metal-organic frameworks for addressing problems of adsorption separation and chromatography is due to the possibility of purposeful changing selectivity of these materials by the variation of the type of organic linker and, as a consequence, the size and chemistry of pore surfaces.[19,20] The efficiency of MOF application in processes of selective adsorption and separation in the liquid phase is favored by the unimodal pore size distribution and open hydrophobic channels in many frameworks of the system.[12,21] The works published to date on this issue[22—25] provide no information on the mechanism of liquid-phase adsorption on metal-organic frameworks.

The purpose of this work is to reveal the physicochemical regularities of adsorption of a series of aromatic compounds from the liquid phase by the MIL-53(Al) metal-

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organic framework. Many of the chosen adsorbates can hardly be separated on the traditional adsorbents.[26—28] Therefore, it seems interesting to study the selective properties of the MIL-53(Al) framework towards the compounds considered. The metal-organic framework studied as an adsorbent is built of octahedra $AlO_4(OH)_2$ linked by terephthalate ions to form a regular system of elliptic channels.[29] Since the MIL-53(Al) framework has hydrophobic pores formed by aromatic rings[29] and is stable in an aqueous medium,[21] this material can be used in liquid-phase adsorption and HPLC.

Experimental

Synthesis of the metal-organic framework MIL-53(Al). A sample of MIL-53(Al) was synthesized under solvothermal conditions at an autogenic pressure. A solution of $Al(NO_3)_3 \cdot 9H_2O$ (1.30 g, 3.47 mmol) and 1,4-benzenedicarboxylic acid (0.288 g, 1.73 mmol) in deionized water (5 mL) was transferred to an autoclave with a Teflon bush and heated for 72 h at 220 °C. After the end of the reaction, a crystalline precipitate of MIL-53(Al) was separated by centrifugation, washed with deionized water (3×10 mL), and calcined in air (220 °C, 72 h).

Physicochemical properties of the synthesized sample of MIL-53(Al). Prior to physicochemical studies, the MIL-53(Al) sample was additionally activated for 3 h at 440 °C with a heating rate of 3 °C min^{-1}. The activated MIL-53(Al) sample was stored in a drying box.

The XRD powder pattern (Fig. 1) of the studied metal-organic framework MIL-53(Al) was detected with an ARL X´TRA diffractometer (Thermo Fisher Scientific, Switzerland) with the Cu-Kα radiation (λ = 1.54 Å) with a scanning rate of 2 deg min^{-1}. The SEM image (Fig. 2) of the MIL-53(Al) powder was obtained on a JSM-6390A scanning electron microscope (JEOL, USA).

A TG analysis of the MIL-53(Al) sample was carried out on a Jupiter STA 449 F3 instrument (NETZSCH, Germany) under the following conditions: heating from ~20 to 800 °C with a heating rate of 10 °C min^{-1} in an air flow with a flow rate of 100 mL min^{-1}. The corresponding thermogravimetric curve is shown in Fig. 3. The isotherm of low-temperature adsorption—desorption of nitrogen (Fig. 4) for the MIL-53(Al) sample was measured on an Autosorb-1 instrument (Quantachrome Instruments, USA). The specific surface of the adsorbent was formally calculated using the Brunauer—Emmett—Teller (BET) equation (S_{sp}(BET)/$m^2\ g^{-1}$) in the range of relative pressures from 0.05 to 0.3 and using the Langmuir equation (S_{sp}(Langmuir)/$m^2\ g^{-1}$) in a relative pressure range of 0.07—0.2.[30] The size of mesopores in the sample was estimated from the desorption branch of the isotherm in the framework of the Barrett—Joyner—Halenda (BJH) model[30] (r(BJH)/Å), and the micropore size was determined using the Horvath—Kawazoe (HK) model[31] (r(HK)/Å). The characteristics of the porous structure of the studied MIL-53(Al) sample are as follows: S_{sp}(BET) = 1085 $m^2\ g^{-1}$, S_{sp}(Langmuir) = = 1569 $m^2\ g^{-1}$, r(BJH) = 19 Å, and r(HK) = 3.36 Å.

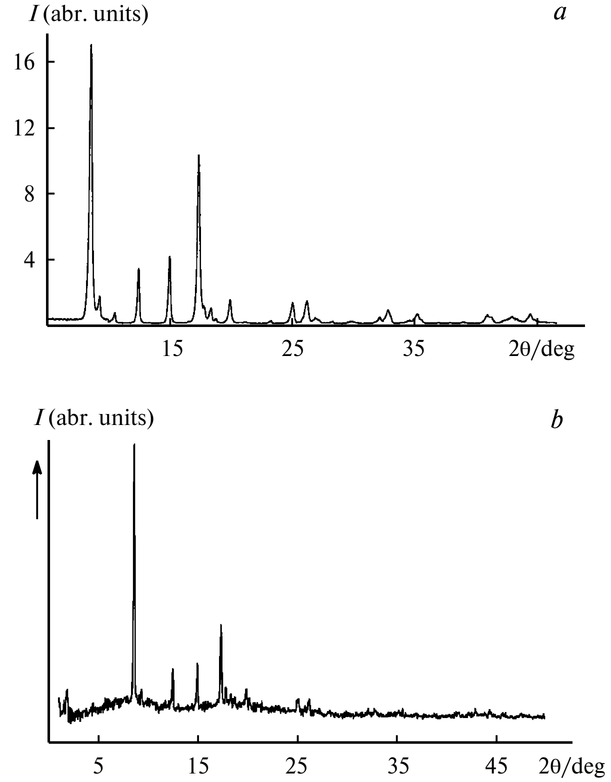


Fig. 1. Comparison of the XRD powder pattern of the samples of the MIL-53(Al) framework (*a*) with that published earlier[29] (*b*).

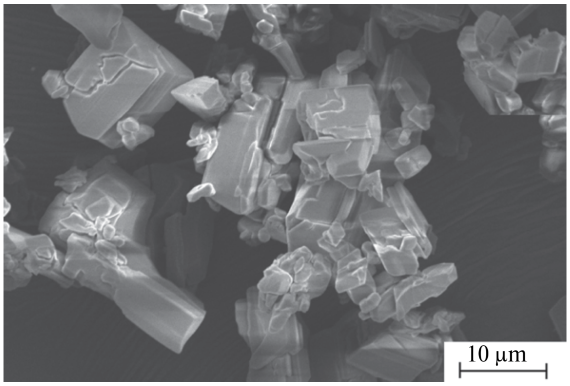


Fig. 2. SEM image of the powdered sample of the MIL-53(Al) metal-organic framework.

Study of adsorption on the metal-organic framework MIL-53(Al). Prior to dynamic adsorption experiments, a dry powdered sample of MIL-53(Al) was placed in a steel chromatographic column (50×4.0 mm), the outlet from which was closed with a porous membrane (frit) mounted by a nipple joint. The MIL-53(Al) sample with an average particle size of 7—8 μm (see Fig. 2) was used as an adsorbent without preliminary isolation of a narrow fraction. Then the inlet to the column was closed with the frit mounted by the nipple joint. The column was connected to a pump of an LC-20AD liquid chromatograph (Shimadzu, Japan) and washed with an H_2O—MeCN (9 : 1) solvent for wetting and compacting of the adsorbent. Then the inlet to the column was opened, an additional amount of the dry powder of MIL-53(Al) was placed into a void formed due to the shrinkage of the adsorbent, and the procedure on adsorbent wetting and compacting was repeated until no adsorbent shrinkage

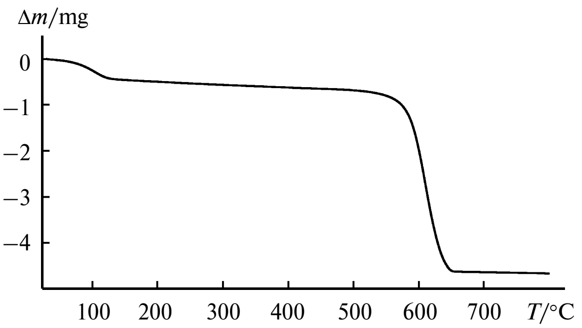


Fig. 3. Thermogravimetric curve for the samples of the MIL-53(Al) metal-organic framework.

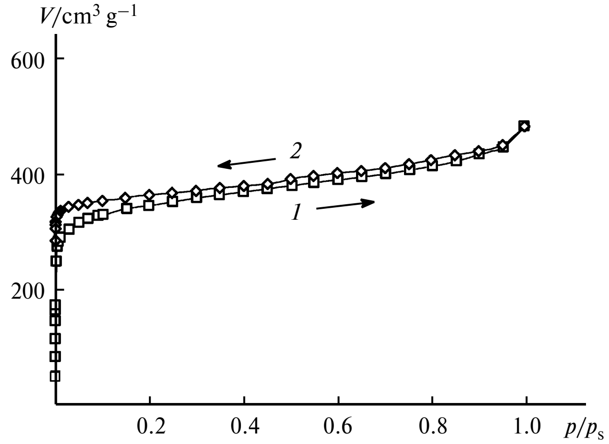
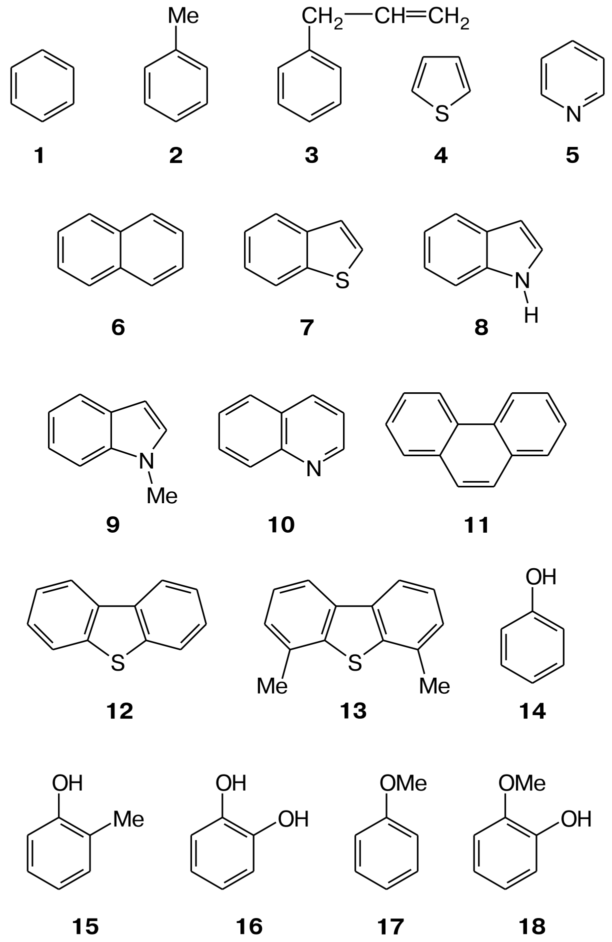


Fig. 4. Isotherm of low-temperature adsorption (*1*)—desorption of nitrogen (*2*) on the sample of the MIL-53(Al) metal-organic framework.

was observed after the next opening of the column. As a result, the solvent volume in the column, the so called "dead" volume, turned out to be $V_M = 350$ μL. The obtained column was characterized by reproducible values of retention times for a series of the studied substances. The pressure at the inlet of the prepared column was 1.4 MPa at 313 K using H_2O—MeCN (1 : 1) as a solvent.

Adsorption of a series of aromatic compounds **1—18** was studied under conditions close to equilibrium by HPLC on a Prominence instrument (Shimadzu, Japan) at temperatures of the column of 313, 323, and 333 K. The components of the solution used to study adsorption were MeCN (HPLC-gradient grade) (Panreac, Spain) and H_2O obtained on a DME-1/B deionization system (BMT, Russia). The binary solvent H_2O—MeCN (1 : 1) was passed through a layer of the MIL-53(Al) adsorbent (weight $g = 0.14265$ g) with a flow rate of 500 μL min^{-1}. All studied aromatic compounds, *viz.*, benzene (**1**), toluene (**2**), allylbenzene (**3**), thiophene (**4**), pyridine (**5**), naphthalene (**6**), benzothiophene (**7**), indole (**8**), 1-methylindole (**9**), quinoline (**10**), phenanthrene (**11**), dibenzothiophene (**12**), 4,6-dimethyldibenzothiophene (**13**), phenol (**14**), *o*-cresol (**15**), pyrocatechol (**16**), anisole (**17**), and guaiacol (**18**), are commercial reagents (Sigma—Aldrich). Solutions of these substance in H_2O—MeCN (1 : 1) were introduced into the flow of the solvent with a Rheodyne dosage valve. Concentration of adsorptives was detected at a wavelength of 254 nm.



The conditions of adsorption experiment were selected in such a way that equilibrium and equilibrium adsorption in the Henry law region were ensured. The absence of changes in the reduced retention time of the adsorbates with the variation of the flow rate of the binary solvent from 50 to 500 μL min^{-1} and the use of solutions of the adsorptives with the concentration <3.3 μmol L^{-1} confirm the assumption that the experiments were carried out under the equilibrium conditions in the Henry law region.[26,32]

Based on the retention volumes of the adsorbates V_R/μL determined taking into account the HPLC data, Henry's constants of adsorption $K_{1,c}$/μL m^{-2} were calculated for the studied aromatic compounds on the MIL-53(Al) samples using the known formula[33]

$$K_{1,c} = (V_R - V_M)S_{sp}{}^{-1}g^{-1},$$

where V_R is the retention volume of the adsorbate (μL), V_M is the dead volume of the column (μL), S_{sp} is the Langmuir specific surface (m^2 g^{-1}), and g is the adsorbent weight (g).

The obtained values of Henry's constant of adsorption at different temperatures are presented in Table 1.

Procedure of crystal-chemical analysis. The values of the surface area S_{VDMP}/Å^2 and volume V_{VDMP}/Å^3 of the Voronoi—Dirichlet molecular polyhedron (VDMP) and the degree of spheric-

Table 1. Henry´s constants of adsorption of aromatic compounds **1**—**10** and **14**—**18** from an H_2O—MeCN solution on the sample of the MIL-53(Al) metal-organic framework at different temperatures of the column

Compound	$K_{1,c}$/μL m^{-2}		
	313 K	323 K	333 K
1	3.2	3.9	4.6
2	17.4	18.6	19.0
3	36.7	40.6	40.9
4	1.8	2.0	2.3
5	2.4	2.6	2.7
6	76.3	79.0	74.9
7	65.1	65.8	60.8
8	14.6	15.3	14.3
9	93.9	90.4	79.0
10	15.0	15.2	13.9
14	1.9	1.7	1.9
15	6.4	6.4	6.2
16	1.3	1.3	1.4
17	7.2	6.9	7.0
18	11.2	10.9	10.9

Table 2. Geometric characteristics of molecules of the studied aromatic compounds **1**—**6**, **8**, and **10**—**18**

Compound	V_{VDMP}/Å^3	S_{VDMP}/Å^2	G3 (arb. units)
1	128.08	154.48	0.0952
2	154.01	178.67	0.0993
3	190.76	211.21	0.1039
4	119.74	144.82	0.0937
5	118.79	144.72	0.0936
6	181.66	205.06	0.1069
8	162.24	188.28	0.1034
10	176.68	199.28	0.1057
11	242.26	257.12	0.1155
12	223.16	241.32	0.1167
13	276.64	289.85	0.1180
14	129.26	158.92	0.0981
15	151.39	180.72	0.1003
16	134.83	166.39	0.1000
17	166.12	190.92	0.1051
18	164.04	192.20	0.1113

ity G3 (arb. units) of molecules of the studied aromatic compounds (Table 2) were calculated using the TOPOS structural topological program packages[34] for crystal structures from the Cambridge Crystallographic Data Centre.[35] An analysis of the structure of cavities in MIL-53(Al) was based on the Voronoi—Dirichlet concept of polyhedra[36] using the TOPOS program package.

Results and Discussion

Physicochemical characteristics of the metal-organic framework MIL-53(Al). The crystalline phase of MIL-53(Al) was identified by the XRD method from the position of the main peaks in the XRD pattern.[37—39] A comparison of the XRD pattern of the synthesized sample (see Fig. 1, *a*) with the earlier published[39] pattern (see Fig. 1, *b*) shows that the sample of MIL-53(Al) corresponds to the variety of the metal-organic framework MIL-53(Al) in which one water molecule is located at the center of each channel.[38,39] This specimen of MIL-53(Al) is characterized by the composition $[\mathrm{Al}(o\text{-}C_6H_4(CO_2)_2)(OH)]\cdot(H_2O)$, and is commonly designated as MIL-53(Al) *lt* (so-called "low temperature form").[38,39]

The SEM image (see Fig. 2) of the synthesized MIL-53(Al) powder shows the presence of microcrystallites, with the size ranging from 1 to 10 μm. Since particles with an average size of 7—8 μm predominate in the studied MIL-53(Al) sample, the latter can be used as an adsorbent for HPLC.

The TG data (see Fig. 3) indicate that the studied material has a high thermal stability and preserves its crystal structure on heating to 550 °C and that even the activated sample contains water. In agreement with the attribution based on the position of the main peaks in the XRD pattern (see Fig. 1), the character of the thermogravimetric curve of the sample of the metal-organic framework (see Fig. 3) confirms its assignment to the MIL-53(Al) *lt* form.[38,39]

Thus, the synthesized metal-organic framework MIL-53(Al) contains pores free of terephthalic acid molecules, which makes it possible to use it as an adsorbent in selective adsorption from the liquid phase.

Analysis of the structure of cavities in the metal-organic framework MIL-53(Al). To study the possibility of adsorption of molecules of the studied compounds by the metal-organic framework MIL-53(Al), it is important to determine the geometric arrangement of the system of voids (cavities and channels) in the crystal structure. The fact is that, the information on the porous structure derived from adsorption methods of measuring porosity in the averaged form is insufficient analyzing the mechanism of adsorption on such supramolecular materials as MIL-53(Al). It is necessary to compare the geometric sizes of the cavities (minimum and maximum sizes of cavities and channels) with dimensions of adsorbate molecules. The comparison makes it possible to establish a possibility of incorporation of these molecules in the cavities and channels and, as a consequence, their adsorption on the crystalline adsorbents, including the metal-organic framework MIL-53(Al). In addition, when analyzing adsorption of molecules on MIL-53(Al), it is necessary to take into account the so-called "breathing" effect,[7,40] that is, possible variations of the pore diameter as the response to the change in the size of adsorbed molecules and to the change in the temperature of the adsorption system.[2,7,40,41]

A powerful method for an analysis of the structure of cavities in crystalline materials is the Voronoi—Dirichlet method of polyhedra,[36] which was used for the analysis of the system of cavities in MIL-53(Al). The construction of the Voronoi—Dirichlet polyhedra for vertices of the atomic Voronoi—Dirichlet polyhedra (centers of cavities) makes it possible to establish specific features of arrangement of the system of cavities (cavities and channels) in the crystal structure. For example, the construction of the Voronoi—Dirichlet polyhedra for cavities of the MIL-53(Al) framework expanded by terephthalic acid molecules using the TOPOS program packages shows that the metal-organic framework with the code [SABVOH] in the database (Table 3) contains parallel channels that can be approximated by elliptic cylinders with sizes of 6.6 and 14.2 Å (Fig. 5). These channels cross-linked by narrower lateral channels ~2.6 Å in diameter (see Fig. 5).

The MIL-53(Al) framework can be simplified and classified according to the known topological types. For this purpose, we plotted the basic network of the framework using the TOPOS structural topological program package.[42] In this network, the sites correspond to aluminum atoms and centers of gravity of terephthalate anions, and the edges correspond to the bonds between them and the bridging μ_2-aqua ligands (Fig. 6). Then, to obtain the basic network, we calculated the topological indices (coordination sequence, point symbol, and vertex symbol) that make it possible to unambiguously identify its topological type. The comparison of the calculated topological indices with those written in the collection of topological types of the TOPOS program package allowed us to establish that the framework can be described by the topology **seh**-4,6-*Imma*.

It follows from the database of these representatives of topological types of the TOPOS (collection TTO) that topology **seh**-4,6-*Imma* can be assigned to 106 crystal structures. Among them are five representatives of MIL-53(Al) and many chemically modified frameworks MIL-53(Al) and MIL-47(V). The latter metal-organic framework has the same topology as that of MIL-53(Al), and the relevant information was deposited at the Cambridge Crystallographic Data Centre.[43] The distinction is only the nature of the central metal atom. The crystallochemical information on seven crystal structures with the MIL-53(Al) framework is presented in Table 3. When molecules of terephthalic acid and water, 1,3,2-benzo-

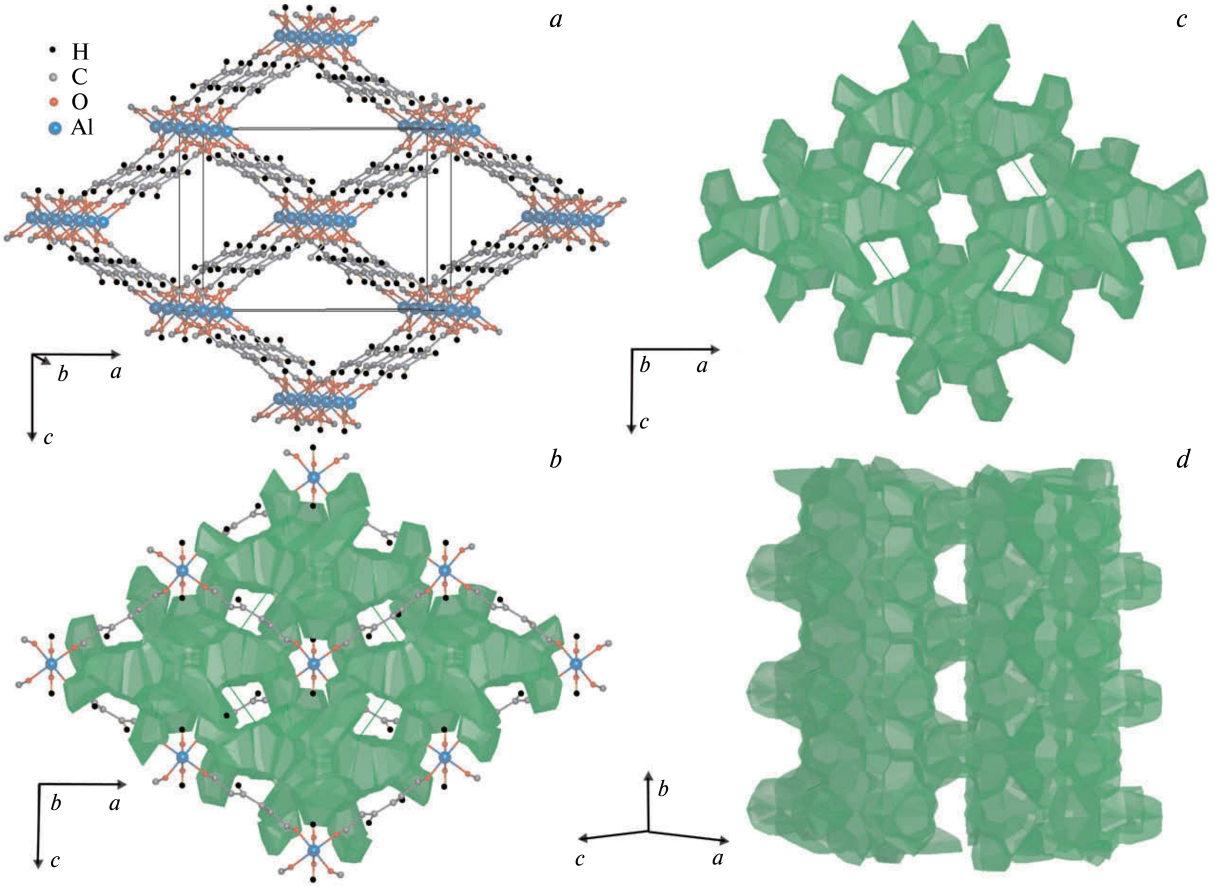


Fig. 5. Fragment of the framework (*a*, *b*) and the system of channels of the framework (*b*—*d*) in the $[Al(o\text{-}C_6H_4(CO_2)_2)(OH)] \cdot$ $\cdot (o\text{-}C_6H_4(COOH)_2)$ [SABVOH] structure.

Note. Figures 5 and 6 are available in full color in the on-line version of the journal (http://www.springerlink.com).

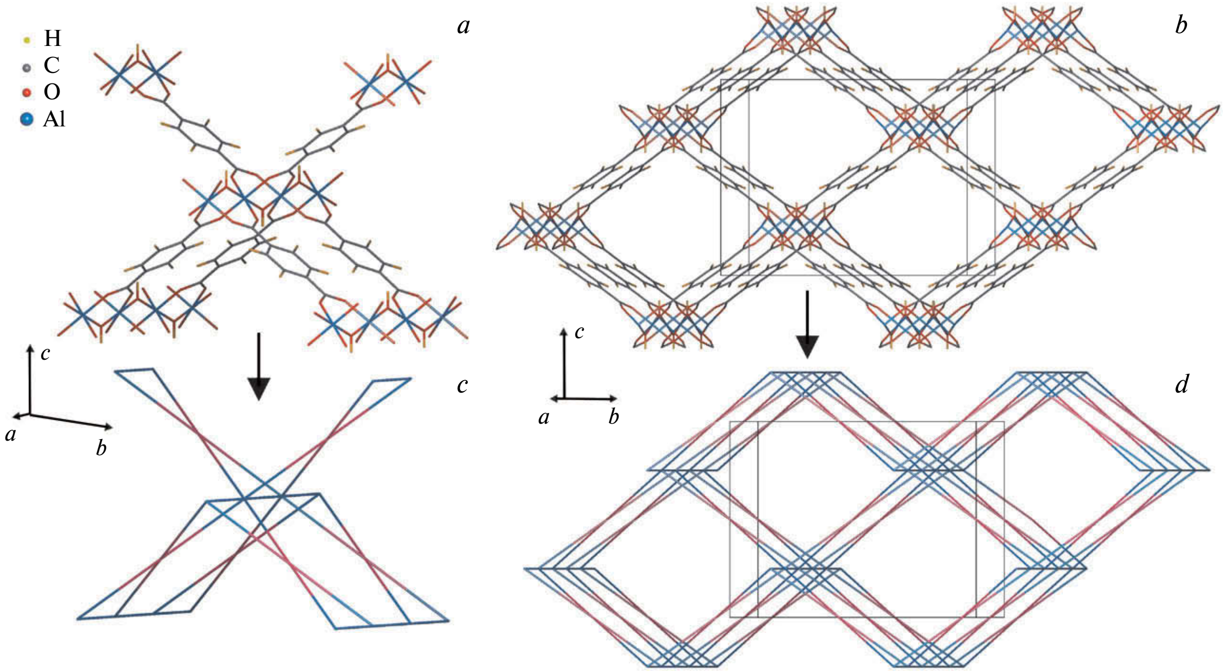


Fig. 6. Fragments of the framework (*a*, *b*) and basis network (*c*, *d*) of the structure $[Al(o-C_6H_4(CO_2)_2)(OH)]$ [Large].

dithiazolyl radical or 5-methyl-1,3,2-benzodithiazolyl radical are incorporated into the pores, the crystal structure of MIL-53(Al) is deformed and takes symmetry *Pnma*, *Cc*, and $P2_1/n$, which somewhat differs from the symmetry of maximally compressed and expanded frameworks ($C2/c$ and *Imma*, respectively).

The sizes of the cavities in the MIL-53(Al) structure respond to compression and expansion of the framework. The compressed metal-organic framework (structure [Narrow] in Table 3) contains broad channels with a dimension of ~16.2×4.4 Å (average diameter 8.4 Å) and narrow channels ~1.8 Å in diameter. The expanded structure of

Table 3. Results of crystallochemical analysis of the crystallographic data on the structure of the MIL-53(Al) metal-organic coordination polymer

Code in database	Compound[a]	Space group	Pore sizes (average pore diameter)/Å	V_{sp} /cm^3 g^{-1}	S_{sp} /m^2 g^{-1}	Guest sizes (average diameter)/Å	V^b/Å^3	
							I	II
SABVOH01[35]	$[Al(o-C_6H_4(CO_2)_2)(OH)] \cdot (o-C_6H_4(COOH)_2)$	*Pnma*	15×5.8 (9.3), 1.8	0.559	4262	4.0×7.6×11 (6.9)	1374.1	182.0
SABVOH[25]	$[Al(o-C_6H_4(CO_2)_2)(OH)] \cdot (o-C_6H_4(COOH)_2)$	*Pnma*	14.2×6.6 (9.7), 2.6	0.615	4160	4.0×7.6×11 (6.9)	1383.1	182.0
SABWAU[25]	$[Al(o-C_6H_4(CO_2)_2)(OH)] \cdot (H_2O)$	*Cc*	17.2×3.6 (7.9), 2.0	0.418	4569	4.0	946.7	28.0
HAFQOW[39]	$[Al(o-C_6H_4(CO_2)_2)(OH)] \cdot$ (*bdta*)	$P2_1/n$	14.4×8.6 (11.1), 2.2	0.610	4105	4.0×7×9.6 (6.4)	1462.4	166.6
HAFQUC[39]	$[Al(o-C_6H_4(CO_2)_2)(OH)] \cdot$ (*mbdta*)	$P2_1/n$	Pores: 10.8×10.8×4.0 (7.8), windows: 4.2, 7×3.6	0.707	5139	4.0×7×10 (6.5)	1499.0	176.6
[Narrow][37]	$[Al(o-C_6H_4(CO_2)_2)(OH)]$	$C2/c$	16.2×4.4 (8.4), 1.8	0.388	4505	—	893.5	—
[Large][37]	$[Al(o-C_6H_4(CO_2)_2)(OH)]$	*Imma*	13.4×6.6 (9.4), 1.8	0.531	3940	—	1423.8	—

[a] Designations: *bdta* is 1,3,2-benzodithiazolyl radical, and *mbdta* is 5-methyl-1,3,2-benzodithiazolyl radical.

[b] The volumes of the unit cell (I) and guest (II) are given.

MIL-53(Al) (structure [Large] in Table 3) has broad channels ~13.4×6.6 Å in size (average diameter 9.4 Å) and narrow channels ~1.8 Å in diameter. According to published data,[6,17,29] the MIL-53(Al) framework contains channels and windows with a diameter of 8.5 Å. An analysis of the results of studying the low-temperature adsorption—desorption of nitrogen using the Horvath—Kawazoe model[31] indicates that the studied sample of MIL-53(Al) contains pores 6.72 Å in diameter, which is well consistent with the earlier published[44] pore sizes for MIL-53(Cr).

Evidently, the diameter of broad channels in MIL-53(Al) is fairly large, and terephthalic acid molecules with an average diameter of 6.9 Å and a volume of 182.0 Å^3 can be incorporated into the channels. Let us consider the results of crystallochemical analysis of cavities of the MIL-53(Al) framework incorporating (see Table 3) water molecules (structure [SABWAU]), terephthalic acid molecules (structure [SABVOH]), 1,3,2-benzodithiazolyl radical (structure [HAFQOW]), and 5-methyl-1,3,2-benzodithiazolyl radical (structure [HAFQUC]). It turned out that the pore volume of the framework in this series increases from 0.418 to 0.707 cm^3 g^{-1} due to the adsorption deformation of the MIL-53(Al) structure caused by the penetration of these molecules into the cavities. The latter value is significantly 33.2% higher than the pore volume (0.531 cm^3 g^{-1}) of the expanded framework (structure [Large] in Table 3). Note that the values of specific pore volume and specific surface determined for the MIL-53(Al) structures taking into account the crystallographic data[35] and presented in Table 3 significantly exceed the corresponding values measured on the basis of adsorption of inert gases (see above). This is due to the fact that the Voronoi—Dirichlet method of polyhedra based on an analysis XRD data takes into account a higher value of the free volume in the structure of the solid than the volume calculated from the data of adsorption measurements of porosity using adsorbate molecules.

Thus, the results of analysis of the structure of the cavities in MIL-53(Al) using the TOPOS program package and preliminary calculations of linear sizes of the adsorbate molecules studied in the present work, whose geometry was optimized by quantum chemical methods, show that the studied aromatic compounds are capable of penetrating into pores of the MIL-53(Al) metal-organic framework.

Dependence of Henry´s constant on the structure of adsorptives. Now we can combine the results of crystallochemical analysis of the cavity structures in the metal-organic framework with the experimental data on adsorption of aromatic compounds from an H_2O—MeCN solution on MIL-53(Al). As can be seen from Table 1, molecules of adsorptives containing two condensed aromatic rings (adsorbates **6**—**10**) are adsorbed on MIL-53(Al) substantially more strongly than analogs with one aromatic ring (adsorptives **1**—**5** and **14**—**18**). Aromatic compounds with three rings in a molecule (adsorptives **11**—**13**) are not desorbed within an appropriate time of HPLC experiment, which indicates an irreversible pattern of adsorption. Thus, it follows from the data in Table 1 that the pores of the adsorbent MIL-53(Al) should be accessible for all studied adsorptives, regardless of the number of aromatic rings in their molecules.

Indeed, the performed preliminary calculations of linear sizes of molecules of the adsorptives studied indicate that the cavities of MIL-53(Al) can incorporate molecules of both mono- and dicyclic aromatic compounds with linear sizes of ~6×4 and 7×5 Å, respectively, and tricyclic adsorbates, whose dimensions (~9×6 Å) are closest to the pore diameter of the metal-organic framework. As a result, these adsorbates can form the maximum number of contacts with the pore "walls," favoring a strong interaction of the pore walls with adsorbed molecules. As shown by the HPLC data, tricyclic adsorbates are adsorbed more strongly on the metal-organic framework than other studied aromatic compounds.

Equal accessibility of cavities in the MIL-53(Al) structure for molecules of mono-, di-, and tricyclic aromatic compounds affects the pattern of the observed dependence of Henry´s constant of adsorption $K_{1,c}$ of the studied substances on the number of aromatic rings in the adsorptive (see Table 1). The value of $K_{1,c}$ increases regularly with an increase in the number of aromatic rings in the molecule, but the increase is noticeably faster than the increase in the volume and surface area of the Voronoi—Dirichlet molecular polyhedron for the studied compounds (see Tables 1 and 2). The both latter parameters determine the ability of adsorbate molecules to participate in the dispersion interaction with hydrophobic cavities of the adsorbent. For example, on going from benzene (adsorbate **1**) to naphthalene (adsorbate **6**), V_{VDMP} and S_{VDMP} increase by a factor of 1.3—1.4, respectively, from 128.08 to 181.66 Å^3 and from 154.48 to 205.06 Å^2, whereas $K_{1,c}$ increases by a factor of ~24: from 3.2 to 76.3 μL m^{-2}. Note that the further same slight increase in V_{VDMP} and S_{VDMP} on going from naphthalene (adsorbate **6**) to phenanthrene (adsorbate **11**) results in irreversible adsorption of the latter on MIL-53(Al). Thus, a substantial increase in $K_{1,c}$ with an increase in the number of condensed rings in the adsorptive molecule is due to two factors. First, weak dispersion adsorbate—adsorbent interactions are enhanced due to an increase in the size of the molecule. Second, as additional aromatic rings appear, the π—π-interactions between the aromatic systems of the adsorbate molecules and terephthalate ions forming "walls" of the hydrophobic cavities in the MIL-53(Al) structure become stronger.[45] An additional argument in favor of the substantial role of π—π-interactions adsorbate—adsorbent in adsorption by the metal-organic framework is a multiple increase in $K_{1,c}$ observed on going from benzene (adsorbate **1**) to allylbenzene (adsorbate **3**). Transition from benzene to allylbenzene, like that from benzene to naphthalene and phenanthrene, produces an increase in $K_{1,c}$ by an order of magnitude (see Table 1) and an insignificant increase in the surface area and volume of the Voronoi—Dirichlet molecular polyhedron (see Table 2). This fact proves that the π—π-interactions are the main factor leading to a stronger adsorption of allylbenzene compared to that of benzene. It cannot be excluded that π—π-interactions adsorbate—adsorbent are not the only reason for a stronger adsorption of di- and tricyclic aromatic compounds compared to that of monocyclic analogs. A compatibility between the shape of the adsorbate molecule and that of the cavity of the MIL-53(Al) metal-organic framework also plays a substantial role.

The methyl radical exerts a strong effect on the adsorption behavior of the studied substances on MIL-53(Al). The introduction of the Me radical into an adsorbate molecule results in a more noticeable increase in $K_{1,c}$ than changes in S_{VDMP} and V_{VDMP} (see Tables 1 and 2). On going from benzene (adsorbate **1**) to toluene (adsorbate **2**), from phenol (adsorbate **14**) to *o*-cresol (adsorbate **15**) and anisole (adsorbate **17**), and from pyrocatechol (adsorbate **16**) to guaiacol (adsorbate **18**), the value of $K_{1,c}$ increases several times (see Table 1). For example, the values of $K_{1,c}$ for toluene is about 5.4 times higher than that of benzene. Probably, such a multiple enhancement of adsorption is due to the appearance of the Me radical in the adsorbate molecule are electron-donor properties of Me, which increase the electron density in the aromatic fragment of the molecules and thus enhance the π—π-interactions adsorbate—adsorbent. In addition, the appearance of the Me radical in the adsorbate molecule evidently favors an increase in the number of intermolecular contacts of the adsorbate with the hydrophobic cavity of the MIL-53(Al) framework, due to which the interaction of the adsorbate molecule with the adsorbent cavity is enhanced.

Intermolecular interactions of adsorbate molecules in solution can explain weak adsorption from an H_2O—MeCN solution on MIL-53(Al) observed for compounds, the molecules of which contain sites able to a stronger specific solvation by the components of an H_2O—MeCN medium (adsorbates **5**, **8**, **10**, and **14**) compared to their closest analogs (adsorbates **1**, **9**, **6**, and **17**, respectively). These interactions decrease the strength of adsorption in the hydrophobic cavities of the metal-organic framework.[46] For example, pyridine (adsorbate **5**) can form a hydrogen bond with the components of solution due to the unshared electron pair of the nitrogen atoms and, this is the reason of a weaker adsorption of pyridine compared to benzene (adsorbate **1**). It should be mentioned that thiophene (adsorbate **7**) is also somewhat weakly adsorbed from an H_2O—MeCN solution compared to benzene (adsorbate **1**) and naphthalene (adsorbate **6**), respectively. In this case, a weaker adsorption of the heterocyclic analogs compared to the corresponding aromatic hydrocarbons is due to the non-specific solvation of molecules of the heterocyclic adsorbates by the components of an H_2O—MeCN solution because of orientational interactions. The data of preliminary quantum chemical calculations indicate that molecules **4** and **7** have dipole moments. In the course of adsorption on MIL-53(Al), aromatic hydrocarbons and their sulfur-containing heterocyclic analogs are separated with a high selectivity, which was not attained for adsorption on the traditional adsorbents[26—28] (see Table 1).

Thus, in the course of adsorption of the studied series of aromatic compounds, the pores of the MIL-53(Al) metal-organic framework are equally accessible for molecules with different sizes; *i.e.*, no exclusion effects are observed in this case. For the adsorption of the studied series of compounds from the polar liquid phase on the MIL-53(Al) metal-organic framework, the determining factor is the ability of the adsorbate molecules to participate in the π—π-interactions with aromatic fragments of hydrophobic cavities of the adsorbent. In addition, the presence of substituents increasing the number of intermolecular contacts with the "walls" of channels and pores or, on the contrary, weakening adsorption due to intermolecular interactions with the components of solution plays an important role.

Temperature effect on Henry´s constant of adsorption of aromatic compounds on the MIL-53(Al) metal-organic framework. Under conditions of the liquid-phase adsorption and HPLC, the temperature increase results, as a rule, in a regular decrease in adsorption interactions on the adsorbent surface.[30,32,47] A minor number of endothermic processes is known in which adsorption is enhanced with temperature. Note that for adsorption by the MIL-53(Al) metal-organic framework the temperature change exerts different effects on Henry´s constant of adsorption $K_{1,c}$ of the studied aromatic compounds (see Table 1). This is due to the fact that the effect of temperature on the strength of adsorption interactions depends on the nature of the adsorbate. An unusual temperature dependence of retention on the MIL-53(Al) adsorbent under the HPLC conditions has been found previously,[48] whereas other researchers[49] established that retention on the considered metal-organic framework is weakened with temperature.

For the adsorbates with one aromatic ring in the molecule (adsorbates **1**—**5**), $K_{1,c}$ increases with temperature. This enhancement of adsorption with temperature is related, most likely, to the expansion of pores[6] in the MIL-53(Al) metal-organic framework due to the "breathing" effect of the structure.[7,40] The compounds, molecules of which contain two condensed aromatic rings (adsorbates **6**—**8** and **10**), are adsorbed somewhat more strongly with the temperature increase from 313 to 323 K, whereas their adsorption is weakened with the further temperature increase to 333 K. A similar behavior of the diaromatic compounds is probably due to the fact that the temperature increase favors trend to desorption.

In these cases, an increase in Henry´s constant with temperature in the course of adsorption of some substances on the MIL-53(Al) metal-organic framework possibly indicates that the adsorption is endothermic. This is associated with the fact that energy consumed by desorption of the solvent exceeds the energy released upon adsorption of hydrophobic molecules. In this case, the driving force of adsorption is evidently an increase in the entropy of the adsorption system observed when solvent molecules are desorbed.

A particular position is occupied by 1-methylindole (adsorbate **9**), which is characterized by a decrease in $K_{1,c}$ with the temperature increase, and phenols (adsorbates **14—18**), the adsorption of which is almost temperature-independent. It can be assumed that some contribution to the adsorption of phenols on MIL-53(Al) is made by the interaction of hydroxyl groups of their molecules with the Brönsted acid sites $AlO_4(OH)_2$ occupying the nodal positions of the network of the metal-organic framework. It is known that the energy of hydrogen bond changes but slightly with temperature and, therefore, adsorption of phenols on the MIL-53(Al) sample is hardly sensitive to a temperature change. The participation of the Brönsted acid sites of the MIL-53(Al) framework in the interaction with the hydroxyl groups of adsorbate molecules is also indicated by the fact that guaiacol (adsorbate **18**) is adsorbed on this sample more strongly than anisole (adsorbate **17**), although a guaiacol molecule contains the hydroxyl group capable of intermolecular interacting with the polar liquid phase.

Thus, the unusual pattern of the temperature dependence of the strength of adsorption interactions of molecules of the studied compounds with the MIL-53(Al) sample characterizes the expansion of the initial system of pores (channels) in the framework existing under the liquid-phase conditions and the appearance of new adsorption sites. In our opinion, this expansion can be due to "swelling" of the framework network[50] in the liquid phase, which is not observed for the MIL-53(Al) structure in the initial activated state.[29] Adsorption of components of an H_2O—MeCN solution leads probably to the expansion of accessible pores (channels) with the temperature change, which favors the adsorption of such bulky molecules as molecules of di- and tricyclic aromatic adsorbates. This assumption is confirmed by the data,[21] according to which the pore size in the MIL-53(Al) structure increases after contact with an aqueous medium at different pH and temperatures. It should be expected that wetting of the metal-organic framework sample on contact with an H_2O—MeCN medium can result in a more significant expansion of pores than that observed upon wetting in pure water, since the hydrophobic cavities of the phenylenecarboxylate frameworks[51] should more efficiently be solvated by MeCN molecules containing the hydrophobic fragment.

The adsorption activity of the metal-organic framework MIL-53(Al) is determined by its elasticity, *i.e.*, the capability of the structure of "breathing" which the temperature change. The accessibility of the system of pores (channels) of this metal-organic framework depends on the temperature of the medium and on the size and form of adsorbates. The adsorption selectivity of MIL-53(Al) towards the studied series of organic compounds is due to π—π-interactions of the aromatic systems of adsorbate molecules with terephthalate ions and the possibility of interaction of the adsorbate molecules with the Brönsted acid sites of the metal-organic framework. The metal-organic framework MIL-53(Al) shows a high adsorption selectivity towards compounds differing in the number of aromatic rings in the molecule, and in the presence of the Me substituent. The selectivity is also shown towards aromatic hydrocarbons and their sulfur-containing heterocyclic analogs. No such selectivity is observed for adsorption on the convertional carbon and polymer materials. Irreversible adsorption on the MIL-53(Al) adsorbent of tricyclic aromatic compounds makes it possible to use this adsorbent, for example, for the decontamination of oil fractions and petroleum products from heavy hardly removable components.

The MIL-53(Al) sample was synthesized at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, the physicochemical and adsorption properties of the metal-organic framework were studied at the Samara State Technical University, and the porous structure of MIL-53(Al) was simulated in terms of the Voronoi—Direchlet concept of polyhedra at the Samara State University.

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