Microwave-assisted synthesis of mesoporous metal-organic framework NH_2—MIL-101(Al)

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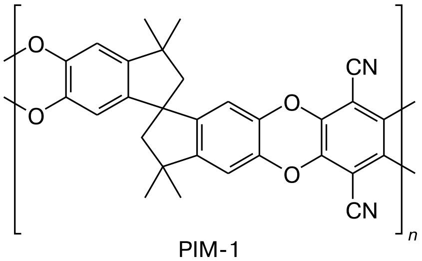
The possibility of formation of the mixed matrix membranes NH_2—MIL-101(Al) under the conditions of microwave activation of the reaction mixture at atmospheric pressure is studied. Microwave irradiation affects the morphology and crystallite size and significantly shortens the synthesis time (from tens of hours to 10—30 min). The obtained samples of NH_2—MIL-101(Al) with a crystallite size of 100 nm were used as nanofillers for polymer matrix based on the PIM-1 polymer with intrinsic microporosity for the preparation of hybrid membrane materials. Gas permeability for a series of gases was measured on the synthesized membranes.

Key words: metal-organic frameworks, mesopores, nanoparticles, morphology, microwave activation, mixed matrix membranes, nanofiller, gas permeability.

There is the increased research interest in hybrid membrane materials (MMM, mixed matrix membranes) that represent nanoparticles of porous solid substances incorporated into polymer matrices.[1] A correct choice of polymer matrix and introduced nanofiller is very important to achieve a necessary gas permeability of these materials. Metal-organic framework (MOF) structures are promising fillers for MMM membranes, since they have a number of advantages over other inorganic fillers (zeolites).[1—3] The family of MOFs includes nanoporous coordination polymers with three-dimensional framework in which ions of small metal clusters are joined by polydentate organic linkers.[4—8] MOFs are unique among many framework structures in that they have high specific surface area and developed pore system with the shape and size controlled by the variation of the coordination number of metal ions and the nature of organic linkers.[9] Linkers with various functions in the structure of metal-organic frameworks can favor a strong interaction of MOF with the polymer matrix. This prevents the formation of microcavities between the nanofiller and organic phase that can lead to a decreased selectivity in the separation of gases.[3,10] It has recently been shown[11] that the introduction of the zeolite-like imidazolate framework ZIF-8 into polymer with intrinsic microporosity PIM-1 significantly improves permeability and selectivity of gas separation.

The size of MOF crystallites is the key parameter determining their physical properties, such as rheology and external surface of these materials.[12] Compared to their macroscopic analogs MOF nanoparticles show increased values of external surface area. A combination of the high specific internal and external surface areas can substantially improve the sorption and separation properties of MOF nanocrystals.



PIM-1

Structures with nanosized crystallites can serve as MMM membrane fillers. It is therefore important addressing the problem of preparation of membrane materials of this type to develop new reliable methods for the synthesis of MOF nanoparticles. It is known[13] that the most efficient methods for the preparation of nanocrystals of metal-organic frameworks is hydro/solvothermal synthesis under the conditions of microwave activation of the reaction mixture. It was established[14] that the rate of nucleation and the rate of crystal growth of the metal-organic frameworks increase under microwave irradiation.

Examples for the microwave-assisted synthesis of nanosized MOFs known from the literature are restricted

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by the solvothermal method under elevated autogenic pressure.[15] The preparation of iron-containing frameworks MIL-88(Fe), NH_2—MIL-88 (see Ref. 16) and NH_2—MIL-101(Fe) (see Ref. 17) are the only examples for the microwave-assisted synthesis under atmospheric pressure.

In this work, we studied the possibility of the synthesis in a microwave field of nanocrystals of the mesoporous framework NH_2—MIL-101(A) modified by amino groups under atmospheric pressure.

The metal-organic framework structure NH_2—MIL-101(Al) consists of supertetrahedral building units including three-dimensional octahedral clusters [Al_3O] connected by 2-amino-1,4-benzenedicarboxylate linkers.[18] The zeolite-like topology ("extended" topology MTN) and mesocavities of different sizes (29 and 34 Å) accessible for the adsorbate combined with high thermal and chemical stability (above 380 °C in air) provide prospects of NH_2—MIL-101(Al) as a promising material for the use in gas adsorption and separation. The presence of the amino group in the organic linker NH_2—MIL-101(Al) favors the enhancement of compatibility of a nanofiller with a polymer matrix when preparing membrane materials of the MMM type based on this framework. This improves their gas separation properties of membrane materials.

Nanocrystals of the mesoporous framework NH_2—MIL-101(Al) synthesized under microwave irradiation were used as nanofillers for the preparation of the MMM membranes based on the PIM-1 polymer (Fig. 1). The gas permeability of the synthesized MMM was measured using a set of gases.

Experimental

Synthesis of metal-organic framework NH_2—MIL-101(Al) ($Al_3O(DMF)(ABDC)_3$). The framework NH_2—MIL-101(Al) was synthesized using two methods: (1) solvothermal method using a known procedure[18] under autogenic pressure and (2) under the conditions of microwave activation of the reaction mixture according to a dedicated method of synthesis under atmospheric pressure.

Solvothermal synthesis. A solution of $AlCl_3 \cdot 6H_2O$ (0.51 g) and 2-aminobenzene-1,4-dicarboxylic acid (ABDC, $HO_2CC_6H_3NH_2CO_2H$, 0.56 g, 3.1 mmol) in DMF was placed in an autoclave with a Teflon vessel and heated for 72 h at 130 °C. The formed crystalline yellow precipitate was separated on a centrifuge and washed with DMF (3×10 mL) and acetone (3×10 mL). Then the crystalline product was treated with boiling methanol (20 mL) with stirring (24 h), isolated on a centrifuge, and activated by evacuation (7 h, 130 °C, $1 \cdot 10^{-2}$ Torr).

Synthesis of NH_2—MIL-101(Al) under microwave activation (heating) of the reaction mixture. 2-Aminobenzene-1,4-dicarboxylic acid (0.56 g, 3.1 mmol) and aluminum chloride ($AlCl_3 \cdot 6H_2O$, 0.51 g) in DMF (40 mL) were mixed and placed in an ampule of a microwave resonator (working frequency 6 GHz, power 12 W, 130 °C, 20 min). The formed crystalline yellow precipitate was separated on a centrifuge and washed with DMF (3×10 mL) and acetone (3×10 mL). Then the crystalline product was treated with boiling methanol (20 mL) with stirring (24 h), separated on a centrifuge, and activated by evacuation (7 h, 60 °C, $1 \cdot 10^{-2}$ Torr).

Physicochemical studies of the synthesized samples of the metal-organic framework NH_2—MIL-101(Al). Nitrogen was used as a gas-adsorbate in the measurements of the specific surface area of the synthesized NH_2—MIL-101(Al) samples. The specific surface area (BET) was determined by the volumetric method.[19]

The powder diffraction pattern of the NH_2—MIL-101(Al) sample obtained by the microwave method was measured on an Empyrean diffractometer (Cu-Kα radiation, Ni filter) in the Bragg—Brentano geometry in the angle range $2\theta = 1—11°$.

The microstructure of the synthesized samples was studied by scanning electron microscopy with field emission (FE-SEM) on a Hitachi SU8000 electron microscope. The images were detected in the secondary electron detection mode at an accelerating voltage of 2 kV and a working distance of 5—6 mm. The morphology of the samples was studied implying a correction to the surface effects of conducting layer sputtering.[20] Prior to recording, a powdered sample was placed on a copper grid with a diameter of 3 mm held in a special holder. The microstructure of the sample was studied by scanning transmission electron

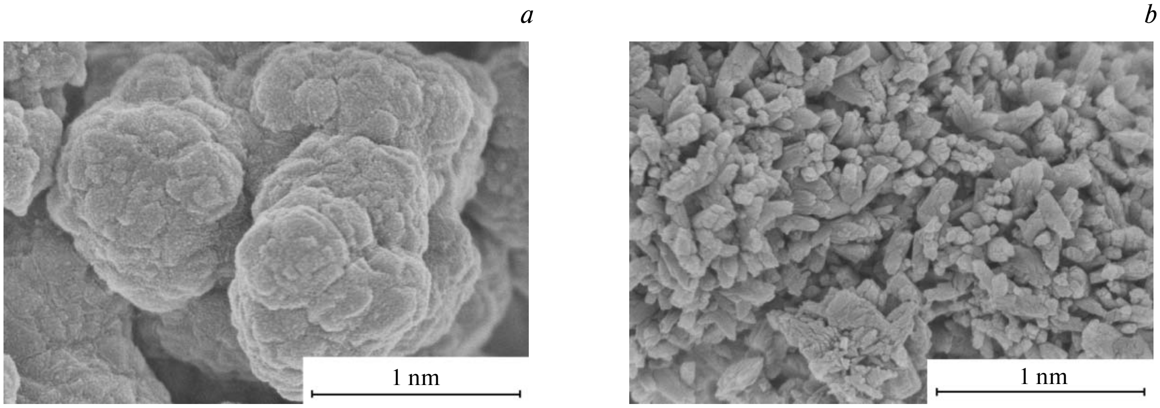

Fig. 1. SEM images of the NH_2—MIL-101(Al) samples synthesized by the solvothermal method (*a*) and under microwave activation conditions (*b*).

Table 1. Permeability coefficients of gases for the hybrid MMM membranes PIM-1/NH_2—MIL-101(Al) (MIL)

Sample	He	H_2	O_2	N_2	CO_2	CH_4
PIM-1	840	1870	820	270	6020	540
PIM-1 (EtOH)[a]	2040	4850	2570	840	14960	1270
PIM—MIL (100 : 30)[b]	1180	2470	1010	350	6720	690
PIM—MIL (EtOH) (100 : 30)[c]	1740	3660	1780	660	11210	1140

[a] Polymer PIM-1 treated with ethanol.

[b] Hybrid MMM membrane PIM-1/NH_2—MIL-101(Al) with the weight ratio of the polymer matrix to nanofiller equal to 100 : 30.

[c] Hybrid MMM membrane PIM-1/NH_2—MIL-101(Al) (weight ratio of the polymer matrix to nanofiller 100 : 30) treated with ethanol.

microscopy with field emission (FE-STEM) on a Hitachi SU8000 electron microscope. The images were registered in passed electron detection mode (light field mode) at an accelerating voltage of 30 kV.

Procedure of preparation of membranes of the MMM type (mixed matrix membranes) and determination of gas permeability. For membrane preparation, a powder of NH_2—MIL-101(Al) (0.04 g) obtained in experiment (Table 1) was suspended in chloroform for 12 h. Polymer PIM-1 (0.4 g) was dissolved in anhydrous chloroform (5 mL). The combined solution was stirred and subjected to ultrasonication in an ultrasonic bath (Scientific Laboratory Services) for 15 min and transferred to a Teflon vessel. The vessel with a solution of NH_2—MIL-101(Al) and polymer PIM-1 was kept for 72 h in a drying box *in vacuo* to remove chloroform.

Then the gas permeability of the synthesized membranes based on the nanosized samples of the NH_2—MIL-101(Al) framework was determined. The values of permeability coefficients of the membranes were obtained by chromatography.[21] Experiments were carried out at the pressure under the membrane up to 0.016 Torr.

Results and Discussion

It is mentioned in the literature that the source of Al^{3+} ions (aluminum chloride) and solvent (DMF) play the key role in the formation of the pure crystalline phase of the mesoporous framework NH_2—MIL-101(Al).[18] The developed method of microwave-assisted synthesis under atmospheric pressure makes it possible to shorten the reaction time to 20 min. The formation of crystalline yellow precipitate is observed in 5 min after the beginning of the reaction as the synthesis temperature reached 120—125 °C. In this case, the reaction time is substantially shorter than the duration of the synthesis (6 h) performed according to the known procedure of microwave synthesis implying an enhanced autogenic pressure.[18]

Physicochemical studies of the synthesized NH_2—MIL-101(Al) samples. The morphology of the NH_2—MIL-101(Al) samples synthesized using the indicated approaches is presented in the SEM images (see Fig. 1). The average size of microcrystallites of the octahedral shape of the sample synthesized under the solvothermal conditions is ~2—3 μm (see Fig. 1, *a*). The main feature of the NH_2—MIL-101(Al) sample synthesized according to the dedicated procedure under the microwave activation of the reaction mixture that it is composed of prismatic crystallites ~50—100 nm in size and these crystals are characterized by a uniform particle-size distribution (see Fig. 1, *b*).

The results of X-ray phase studies show that the pure phase NH_2—MIL-101(Al) is formed under the found conditions of microwave-assisted synthesis (Fig. 2). To confirm that the crystal structure of this sample has the architecture MIL-101, we refined the structure using the MRIA program[22] by the Pauli method.[23] According to the refinement, all peaks observed in the powder diffraction pattern are assigned to the cubic space group *Fd*-3*m* with the cell parameter a = 87.75(5) Å. These results are well consistent with the crystalline lattice parameters presented in the literature (cubic cell *Fd*-3*m*, a = 87.536(27) Å).[18]

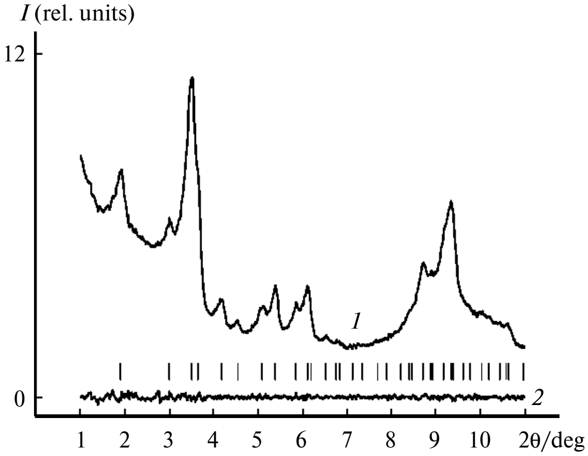

Fig. 2. Results of the Pauli refinement of the powder diffraction pattern of the microwave-assisted sample under the assumption of cubic cell in the space group *Fd*-3*m* (227): *1*, experimental curve; *2*, difference between the experimental and calculated curves by the refinement results. The calculated positions of reflections are designated by vertical sections.

Table 2. Selectivity of gas permeability for the hybrid MMM membranes PIM-1/NH_2—MIL-101(Al)

Sample	O_2/N_2	CO_2/O_2	CO_2/CH_4	H_2/N_2	H_2/CH_4	He/N_2
PIM-1	3.0	7.3	11.1	6.9	3.5	3.1
PIM-1 (EtOH)	3.1	5.8	11.8	5.8	3.8	2.4
PIM—MIL (100 : 30)	2.9	6.7	9.7	7.1	3.6	3.4
PIM—MIL (EtOH) (100 : 30)	2.7	6.3	9.8	5.5	3.2	2.6

The measured specific surface area for the NH_2—MIL-101(Al) sample synthesized in the microwave field (2095 $m^2 g^{-1}$) coincides with that published[18] for the samples prepared by the solvothermal synthesis (2100 $m^2 g^{-1}$).

Measurement of gas permeability using the membrane material containing nanocrystals NH_2—MIL-101(Al). The samples of the mesoporous framework NH_2—MIL-101(Al) with the crystallite size in the nanorange (up to 100 nm) prepared under the microwave activation of the reaction mixture using a dedicated procedure were used as fillers for the polymer matrix PIM-1 to prepare hybrid membrane materials of the MMM type. The composite based on NH_2—MIL-101(Al) nanocrystals was re-dissolved under the action of ultrasound for the preparation of films from stable dispersions.

The results of studies of gas permeability using the synthesized materials of the MMM type are presented in Tables 1 and 2 along with data for the pure polymer PIM-1, and the effect of the ethanolic treatment of the samples can also be traced.

The data obtained on measuring the permeability of the synthesized MMM membranes toward a series of gases (H_2, He, O_2, N_2, CO_2, CH_4) (see Table 1) indicate an increase in the permeability upon the introduction of a nanofiller as nanoparticles of the mesoporous amino-modified framework NH_2—MIL-101(Al). The highest values of permeability coefficients for all samples were registered for carbon dioxide. This results are predictable, since high values of $P(CO_2)$ are a sequence of high solubility coefficients of this gas in all polymers. It can be assumed that the increase in the permeability is accompanied by an increase in the free volume and diffusion and solubility coefficients of the gases in the considered system. The earlier known phenomenon of increasing permeability due to the treatment of the samples with alcohol was substantiated. It follows from the data in Table 2 that the selectivity of gas separation when using the NH_2—MIL-101(Al) nanofiller increases in the case of gas pairs H_2/N_2, H_2/CH_4, and He/N_2 (for the initial MMM samples). In the most cases, including gas pairs O_2/N_2 and CO_2/CH_4, the selectivity decreases with an increasing permeability (see Table 2). In this way a usual "compensation" relationship between these parameters in the polymers is displayed. The decrease in the permeability of the samples containing a nanofiller after the ethanolic treatment is an unexpected result. This phenomenon requires additional studies.

Thus, using microwave irradiation (microwave activation of the reaction mixture) nanocrystals of the mesoporous amino-modified framework NH_2—MIL-101(Al) were obtained as prisms with the average size up to ~100 nm with the sufficiently uniform particle-size distribution. The procedure proposed for the synthesis made it possible to substantially reduce the time of formation of the pure phase NH_2—MIL-101(Al) (from 6 h to 20—30 min).

As far as it is known from the literature, this is the shortest time of crystallization of samples of the metal-organic framework NH_2—MIL-101(Al). The NH_2—MIL-101(Al) sample obtained by microwave irradiation demonstrates the same high specific surface area as the "solvothermal" sample of this framework.

Due to a small size, nanocrystals of the mesoporous NH_2—MIL-101(Al) framework synthesized under the microwave activation conditions were used as fillers for polymer matrices of different natures. Thus prepared MMM matrices demonstrate a high level of permeability with respect to a series of gases.

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