Computer analysis of the nitrogen adsorption process on MIL-53(Al) metal–organic frameworks

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This paper evaluates the effect of different synthesis conditions on the structural properties of the porous metal–organic frameworks MIL-53(Al) produced by the microwave method at different reaction temperatures (120, 150, and 180 °C) and times (30, 180 min). The morphologies, chemical contents and crystal structures of the synthesized samples were determined by the SEM-EDS and XRD methods, respectively. The structural properties of MIL-53(Al)s were analysed according to isotherm data obtained from nitrogen gas adsorption by applying the Brunauer–Emmett–Teller (BET), Langmuir, Dubinin–Radushkevich (DR), t-plot, Barrett–Joyner–Halenda (BJH) and quenched solid density functional theory (QSDFT) methods, as well as the new numerical clustering-based adsorption analysis (LBET) method, which is a unique numerical method that provides advanced assessment for porous structures. The LBET analysis showed that the MIL-53(Al) sample at a reaction temperature of 180 °C for 30 min has the best adsorption properties, with the highest volume of the first adsorbed layer and the highest value of the energy parameter for higher layers. Due to the LBET method, it was possible to evaluate the porous structure of the MIL-53(Al) samples with high precision and reliability, and thus to determine the precise influence of the conditions of their preparation on the formation of their structure. In turn, based on the shapes of the pore size distributions (PSD), the materials analysed have very similar PSD, with only the MIL-35(Al)S1 sample having a significantly lower PSD height. In conclusion, attention was paid to the necessity of complex evaluation of adsorbent properties, taking into account not only their adsorption parameters but also their mechanical and functional properties, as well as production costs and the impact of adsorbent production and utilization on the environment.

1. Introduction

Adsorption is a separation and purification process used in many industries, including chemical, petrochemical, environmental and pharmaceutical. The adsorbent is the key to the adsorption process, and the characteristics of the adsorbent directly determine the performance of any adsorptive separation or purification process and also make an adsorption process unique from other similar processes.

Many papers have reported that surface characteristics of adsorbents, including specific surface area, morphology, porosity, particle size, crystallization, surface state and mechanical stability, obviously influence the adsorptive activity of an adsorbent. The specific surface area, the portion of the total surface available for adsorption, is one of the more critical parameters effecting the adsorption capacities of an adsorbent. Generally, a high surface area of adsorbent provides a higher adsorption capacity than those with less surface area due to the abundance of exchangeable sites. On the other hand, the porosity of an adsorbent is also a determining factor in its surface area value and adsorption capacity. In an adsorption process, while the presence of micropores substantially increases the adsorption capacity, the meso- and macropores of the adsorbent also play an important role in the molecular transport process.

The most commonly used commercial adsorbents are activated carbons, zeolites, activated alumina, silica gel and polymeric adsorbents. Better new adsorbents have been sought in recent years, with the increasing use of adsorption processes in technology, environmental protection, and everyday life, and some of the most promising materials that can be used in these processes are organometallic materials, such as metal–organic frameworks (MOFs). MOFs are a new, very broad group of materials with site-molecular properties, being crystalline and composed of metal ions or ion clusters coordinated with organic ligands, which form porous three-dimensional structures. The large variety of metallic cations and organic ligands used makes it possible to create a huge number of potential structures with different...
geometries and properties. Cations of transition metals are most often used for MOF material synthesis.15,16

The MIL-53 series of MILs (Materials Institute Lavoisier), one of the main groups of MOFs, which are made up of chains of corner-sharing MO4(OH)2 (M = Al3+, Cr3+ and Fe3+) connected by 1,4-benzenedicarboxylate (H2BDC) groups, were first synthesized by Loiseau et al.17 Among them, MIL-53 with aluminium content was remarkable for its high thermal and water stability, even in acidic environments, and offered significant advantages in adsorption and gas separation processes.18–20 One of the interesting abilities of the structure is the large pore (LP)-narrow pore (NP) change depending on the guest molecules in the pores, known as the breathing effect of the MIL-53(Al) structure.

The properties of MOFs, including extremely large specific surfaces, often exceeding 6000 m2 g−1, make MOFs very attractive, especially in the removal of hazardous compounds such as heavy metals from liquid and gaseous streams, the storage and sequestration of gases such as carbon dioxide, methane, and hydrogen, as well as in the separation and purification of gas products, and catalytic processes.21–23 The high specific surface area and adsorption capacity of MOFs determine their performance and application in the aforementioned processes.

In the literature, researchers have usually used three methods for the synthesis of MOFs: solvothermal, electrochemical, and microwave-assisted (MW) methods. The most prevalent approach for MOFs synthesis is the classical solvothermal method, which requires a long reaction at moderate temperatures, i.e., from about 20 to 200 °C for at least 3 days.24,25 Electrochemical methods offer advantages over the solvothermal method due to their reproducibility and potential for precise control over synthesis parameters.16 MW-assisted synthesis is the most prominent option because it is cost-effective and time-saving thanks to homogeneous heating. The fact that water is generally used in this method as a solvent is also an environmental advantage. It was reported that MOFs prepared by the microwave-assisted synthesis method at lower synthesis temperatures and shorter synthesis times than the solvothermal method had smaller particle size and superior adsorption performance.26,27

Even if the same initiators are used, the synthesis conditions, i.e., mixture composition, order of component addition, type of solvent, crystallization time, temperature, etc., significantly impact on the structure and hence the adsorption properties of the same type of MOFs.15,16,25 Still, systematic evaluation of the effect of reaction parameters on surface properties in the production of microwave-assisted MOFs has been insufficiently studied.

Therefore, it is necessary to understand the surface properties of metal–organic frameworks to increase their applicability in adsorption processes. Synthesis temperature and time allow remarkable control over the structure of the material and can be employed in the preparation of new types of porous adsorbent materials.

In this study, surface properties such as surface area, pore size and pore volume of the MIL-53(Al) structure produced by the microwave method at different times and temperatures were examined. We could not find any study in which MOFs were evaluated with LBET and QSDFT models, which provide more reliable information about the surface area, surface energy and also pore structure of the MIL-53(Al) material than classical models. Thus, this study will be a guide in terms of microporous structures, especially MOFs.

2. Materials and methods

2.1. Experimental materials and methods

MIL-53(Al) structures were synthesized by microwave heating at different reaction times and temperatures. For synthesis, 1 mmol of aluminum nitrate nonahydrate (Al(NO3)3·9H2O, Acros Organics, +99%) and 1 mmol of benzene-1,4-dicarboxylic acid (H2BDC, Acros Organics, +99%) were put into a Teflon reactor (100 mL) with 30 mL of ultrapure water and held at 120, 150, and 180 °C for 30 and 180 min in a microwave oven (CEM MARS microwave oven, USA). At the end of the reaction period, the solution reached room temperature and was centrifuged at 10 000 rpm for 10 min. The resulting precipitates were washed three times with hot dimethylformamide (80 °C) (DMF Sigma-Aldrich, for HPLC, ≥ 99.9%) to remove unreacted reagents. It was washed once with methanol to remove DMF. The white precipitates obtained were activated at 300 °C for 72 hours. Fig. 1 displays the production scheme for MIL-53(Al).

Nitrogen adsorption isotherms were measured at −196 °C using a Micromeritics Tristar Orion II 3202 surface area and porosimetry analyzer after a pre-treatment at 200 °C under vacuum for 6 h. The specific surface area values were calculated according to the Langmuir,28 Brunauer– Emmett–Teller (BET),29 Dubinin–Radushkevich (DR),30 and t-plot31 methods. Total pore volume and average pore size were also calculated using the t-plot and Barrett–Joyner–Halenda methods,31 respectively. In addition to these mentioned methods, the LBET method32,33 and QSDFT methods34 were also used for the first time in the structural evaluation of MIL53(Al)s.

Fig. 1 Production scheme for MIL-53(Al).
The characteristics of the produced MIL-53(Al)s were evaluated through scanning electron microscopy-energy dispersive spectrometry (SEM-EDS, ZEISS Supra 55) and X-ray diffraction (XRD, Rigaku Smartlab) analyses. Before the SEM analyses, Pt-Pd coating was applied to the samples to improve the images. X-ray diffraction analyses of MIL-53(Al)s were performed at a 2-theta between 3° and 30° with XRF mode open at 2° min⁻¹ scanning speed with a powder XRD device.

2.2. Analysis methods of MIL-53(Al) MOFs in terms of structural properties

Modern technology and adsorption engineering require more advanced and optimal technological and technical solutions, which determine, among other things, their competitiveness on the market and cost-effectiveness of implementation. These requirements are inextricably connected with the necessity of obtaining effective adsorbents, including MOF materials, and thus it is necessary to precisely select the methods and conditions of their production. However, in order to be able to reliably determine the adsorption properties of these materials, it is necessary to apply appropriate methods of analysis of their structure and adsorption processes taking place on their surface.

The porosity of adsorbents, which is most important for industrial purposes, can be characterized in many different ways, for instance, mercury intrusion porosimetry, helium measurements, and gas adsorption. The most commonly used method is the gas adsorption method (usually N₂, CO₂, and Ar), which is used to obtain information on porous solids’ surface areas and morphological properties. In this method, nitrogen gas is commonly used, and the process is carried out at a temperature of 77 K.

The evolution of the gas–solid adsorption isotherms and the adsorption–desorption hysteresis loops shows that adsorption occurs in the pores in different ways more or less gradually. At an extremely low pressure, firstly the most energetic adsorption sites are occupied in the micropores, the walls of which are close to each other, which increases the adsorption potential, and high adsorption takes place in the micropores, which is called micropore filling. The micropore-filling capacity of an adsorbent can provide information about structural and surface heterogeneity. The size of the micropores is comparable to the adsorbate molecules, and all atoms or molecules of the adsorbent can interact with the adsorbate species. Also, because the main adsorption mechanism in micropores is a pore-filling process, pore volume is the main factor controlling the adsorption. At higher relative pressures, the walls contain a great number of atoms or molecules of adsorbent and single and multilayer adsorption occurs successfully on mesoporous surfaces. Finally, the adsorption proceeds according to the mechanism of capillary condensation of adsorbate molecules in mesopores. For mesopore characterization, specific surface area, pore volume and pore-size or pore-volume distribution are the main parameters. But in macropores, the action of adsorption forces does not occur throughout their void but occurs at a close distance from their walls. Both meso- and macropores play an important role in the transport of adsorbate molecules from the micropore volume. The adsorption mechanism on the macroporous surface, whose specific surface area is quite small, is not different from that on nonporous surfaces. Since capillary condensation does not occur in macropores, adsorption on this surface can generally be neglected. The mesopore and macropore volume distributions can be calculated from the multilayer and condensation stages determined by adsorption isotherms.

There are numerous adsorption isotherm analysis methods for describing the adsorption equilibrium, such as Langmuir, Brunauer–Emmett–Teller (BET), Dubinin–Radushkevich (DR) and t-plot. The Langmuir model is based on the assumption that there is a definite and energetically equivalent number of adsorption sites on the solid surface, adsorbed molecules are not affected by each other and adsorption occurs as a monolayer with the same mechanism. Dubinin and Radushkevich’s (DR) isotherm model is also empirically derived based on the adsorption theory of the monolayer filling of micropores and does not take into account the heterogeneity of the surface. The t-plot method allows for determining the micro- and/or mesoporous volumes and surface area from a gas sorption isotherm without the need to measure the micropore filling portion of the adsorption isotherm at low pressure by comparison with a reference adsorption isotherm of a nonporous material having the same surface chemistry. However, this method cannot always give accurate results for hierarchical porous materials exhibiting both micro- and mesoporosities.

One of the most employed and discussed adsorption isotherm models in the literature is also the Brunauer–Emmett–Teller (BET) model, which basically suggests that the first adsorption layer is formed on active centers located on the adsorbent surface. In addition all adsorption sites on a solid surface are homogeneous in their adsorption energy. It also does not consider the interactions of adsorbed molecules placed at neighboring sites. This model is usually applied for the calculation of BET surface area, \( A_{\text{BET}} \), obtained by analysing the data using the Brunauer–Emmett–Teller (BET) adsorption isotherm equation. Although the BET adsorption isotherm is widely used, it has some inadequacies that cause problems in applications. These reasons can be listed as follows: first, the BET monolayer capacity is problematic due to uneven monolayer formation; second, more than one layer of gas molecules are formed in the multilayer and all of the layers cannot contact with the solid, and thus the BET equation cannot fully describe multilayer formation; and third, pore filling may occur prior to adsorption in micropores and especially sub-micropores at extremely low pressures. High rates of micropore filling capacity result in higher or overestimated surface area values. Despite the inadequacy of its application, it is still widely used for micro- and sub-micropore materials to determine surface area, but should only be used for nonporous or meso- and macropores, including materials. Consequently, to evaluate the performance of the adsorption mechanism, it is necessary to determine its surface energies while determining its structural properties.

In this study, the numerical clustering-based adsorption analysis (LBET) method was applied as an alternative to the problems of the other models mentioned above. This method is based on original mathematical models derived from the basics...
of BET theory, but unlike the BET model, particular emphasis is placed on the heterogeneity of the surface.\textsuperscript{32,33} It is worth emphasizing that the LBET method considers heterogeneity both from the geometrical and energetic points of view. This approach takes into account geometrical and energetic limitations for creating clusters and the adhesive forces in layers higher than the first one. Additionally, the LBET method allows the determination of the size and shape of the adsorbate molecule clusters formed, the adsorption energy distribution (AED), and the reliability and credibility of the obtained results.\textsuperscript{32,33}

In this method, the process of adsorption on a heterogeneous surface is viewed as the clusterisation of adsorbate molecules in highly dispersed space limited by the geometry of the micropores. The clusters are constructed by adding consecutive layers being in equilibrium with the volatile phase. The set of adsorbate molecules, which were adsorbed mainly due to adhesive interactions with the adsorbent matter, is treated as the first layer of adsorption. Joining of further adsorbate molecules is viewed as the second layer of adsorption.\textsuperscript{32,33}

While designing the LBET model, it was formulated by making the following assumptions; each adsorbate molecule can occupy only one adsorption site, each site available on that layer is equally probable to be matched with any adsorbate molecule with no regard to the occupancy of other sites, and each cluster of adsorbate molecules contains a single molecule in the primary adsorption site, and the enlargement of a cluster does not impact the appearance and growth of other clusters.\textsuperscript{32,33}

The group of analytical models of the LBET class is expressed using the following general form:\textsuperscript{32,33}

$$m_a \equiv (1-z) \left\{ \frac{1}{1 + \ln(B_{A1}/B_{A1})} \ln \left( \frac{B_{A1} + \pi}{B_{A1} + \pi} \right) \right\}$$

$$+ d \cdot z (1-z) (1 + \theta_{22})$$

$$+ \frac{1}{1 + \ln(B_{A2}/B_{A2})} \ln \left( \frac{B_{A2} + \pi}{B_{A2} + \pi} \right)$$

$$+ \frac{1}{1 + \ln(B_{A2+d}/B_{A})} \ln \left( \frac{B_{A2+d} + \pi}{B_{A2+d} + \pi} \right)$$

where \( m_a \) is the amount of adsorbate (mmol g\(^{-1}\)), \( m_{ha} \) is the total number of primary sites (mmol g\(^{-1}\)) such that \( m_{ha} = V_{ha}/V_p \), \( V_{ha} \), \( V_p \) being the first adsorption layer capacity (cm\(^3\) g\(^{-1}\)) and \( V_p \) being the molar volume of adsorbate (cm\(^3\) mmol\(^{-1}\)), \( \theta \) is a layer coverage ratio, \( z \) is the relative pressure, \( \pi \) is the geometrical parameter of the porous structure, \( \beta \) is the pore shape parameter such as \( \beta \geq 1 \), \( k \) is the maximum number of layers, \( \theta_{kj} \) is the coverage ratio of the \( j \)-layer at the \( k \)-type cluster calculated according to the formulas, and \( B_{ak} = \exp(Q_{ak}/RT) \) and \( B_{jk} = \exp(Q_{jk}/RT) \), where \( Q_{ak} \) and \( Q_{jk} \) are adsorption energy values for the left and right hand side of the energy distribution, respectively, \( R \) is the molar gas constant and \( T \) is the absolute temperature. The parameter \( B_{jk} \) is defined as follows:\textsuperscript{32,33}

$$B_{jk} \equiv B_A \exp(Q_{jk}/RT) \cdot (Z_{A2+d} - Z_{A}) \cdot (1 - \pi), \quad (2)$$

where \( W_m \) denotes an exponent minimising the approximation error, and \( Q_{cp} \) is the molar adhesion energy in ideal adsorbent–adsorbate contacts [J mol\(^{-1}\)].

The LBET models have five adjusted parameters: the dimensionless energy parameters \( Q_{a}/RT \) and \( B_{C2} \) corresponding to the maximum value of the adsorption energy on the first and subsequent layers, respectively, the volume of the first adsorbed layer \( V_{ha} \) (cm\(^3\) g\(^{-1}\)) interpreted as the volume of space accessible for the first adsorption layer; the geometrical parameter of the porous structure \( x \) determining the height of the adsorbate molecule clusters; the geometrical parameter of the porous structure \( \beta \) determining the width of the adsorbate molecule clusters, which can be adjusted by fitting eqn (1) to the adsorption isotherm, with a chosen variant of the surface energy distribution function.\textsuperscript{32,33}

Fitting the theoretical LBET class adsorption models to the experimental adsorption isotherms was realised using the method of non-linear optimisation with limitations, with using the 30-variant version of the LBET class models in the calculations.\textsuperscript{32,33} The adsorption parameters of the analysed system are assumed to be the values obtained for the best-fitted variant of the LBET model.

The energetical heterogeneity negatively impacts the numerical conditioning of the identification tasks. To solve this problem, a unique fast multivariate method for fitting the LBET models to the empirical adsorption isotherms was used, employed to determine the value of the surface heterogeneity parameter \( h \) and the distribution of adsorption energy on the first adsorbed layer.\textsuperscript{32,33}

Considering that MOFs are microporous structures, it is possible to determine the degree of heterogeneity of the surface and shape of the clusters of adsorbate molecules formed in the pores of the MOF materials and also obtain information about the distribution of adsorption energy on the first adsorbed layer by applying the LBET model. The pore size distributions (PSD) of the MIL-53(Al) samples were determined by using the classic Barrett–Joyner–Halenda (BJH) method\textsuperscript{31} and also the quenched solid density functional theory (QSDFT).\textsuperscript{34} The BJH method is a procedure for calculating pore size distributions based on a model of the adsorbent having cylindrical pores, using the Kelvin equation.\textsuperscript{31} The QSDFT method is a method that takes into consideration surface heterogeneity in one dimension and eliminates the artificial gaps in the pore size distributions.\textsuperscript{34}

For determining the pore size distribution (PSD), nitrogen adsorption isotherm data is evaluated by using thermodynamic models based on the Kelvin equation for the capillary condensation pressure, or semi-empirical treatments are used based on the pore geometry such as Horvath and Kawazoe (HK)\textsuperscript{39} for slit pores, or Saito and Foley (SF) for cylindrical pores.\textsuperscript{40}

Here, besides the classical surface analysis models, mathematical LBET and QSDFT models that correctly interpret the
structural results were applied to the N$_2$ adsorption isotherm data of the MIL-53(Al), a micropore metal organic framework, and the results were discussed.

3. Results

The morphologies and structures of the obtained MIL-53(Al) materials were characterized by SEM, as shown in Fig. 2. The particle size of the materials synthesized with a reaction time of 180 min was below 600 nm and trapezoidal (Fig. 2a–f). Rod-like particles below 100 nm are also seen in Fig. 2a. In Fig. 2c, it can be said that the particle size distribution is relatively homogeneous.

The EDS spectra and the element distributions of the produced MIL-53(Al)s are shown in Fig. 3. Considering the molecular formula of MIL-53(Al) (C$_8$H$_5$AlO$_5$), it can be said that the element distributions are consistent.

The XRD spectra of the MIL-53(Al) structures are shown in Fig. 4. The diffraction patterns of the MIL-53(Al) samples indicate that the materials are well crystalline. The obtained peaks of MIL-53(Al) agree with the literature patterns reported earlier by Loiseau et al.$^{17}$ The differences observed in the diffraction patterns arise from the guest molecules inside the MIL-53(Al) framework.

The structural properties (surface area, pore volume, and pore size) of the synthesized MIL-53(Al) samples at different reaction times (30, 150, and 180 min) for 120 and 180 °C temperature values were evaluated from nitrogen adsorption isotherms, and the obtained data are shown in Fig. 5a and b. It is seen that the MIL-53(Al) surface area values calculated from the BET, Langmuir, DR, and t-plot methods increase with increasing synthesis temperature in all methods. Similarly, the synthesis temperature also increased the micropore volumes of MIL-53(Al) calculated from the t-plot model. However, the increase in synthesis time from 30 to 180 minutes did not cause a significant change in surface area values or pore volumes. As shown in Fig. 5b, the pore sizes of MIL-53(Al) also did not change significantly with the synthesis time and temperature changes. In all experimental conditions, the pore diameters of all MIL-53(Al)s obtained from the BJH model were determined to be 1.84–1.93 nm with a micropore structure.

The surface area values reported in the literature for MIL-53(Al) vary depending on the synthesis conditions and techniques. It has been reported that the theoretical BET surface area for MIL-53(Al) is 1638 m$^2$ g$^{-1}$ and has a microporous structure using various methods and synthesis circumstances. Table 1 summarizes the surface properties reported for MIL-53(Al) using various methods and synthesis circumstances. The
BET surface area values for the synthesized MIL-53(Al) compounds ranged from 819 to 1570 m$^2$ g$^{-1}$. Do et al.\textsuperscript{43} transformed the microporous MIL-53(Al) structure into a hierarchical micromesoporous structure by using structure-directing agents (SDAs). They raised the MIL-53(Al) BET surface area from 950 m$^2$ g$^{-1}$ to 1020 m$^2$ g$^{-1}$ and the total pore volume from 0.508 cm$^3$ g$^{-1}$ to 0.610 cm$^3$ g$^{-1}$ by employing SDA in the synthesis.\textsuperscript{44} Sun et al.\textsuperscript{45} determined a below-average surface area of 961 m$^2$ g$^{-1}$ in

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**Fig. 3** EDS spectra of the produced MIL-53(Al)s at various temperatures and times: (a) 120 °C, 30 min, (b) 150 °C, 30 min, (c) 180 °C, 30 min, (d) 120 °C, 180 min, (e) 150 °C, 180 min, and (f) 180 °C, 180 min.

**Fig. 4** XRD spectra of the produced MIL-53(Al)s at various temperatures and times.
low-temperature microwave-assisted MIL-53(Al) synthesis. However, the 0.80 cm$^3$ g$^{-1}$ pore volume value they determined for MIL-53(Al) is above the average.$^{35}$

Ahadi et al.$^{43}$ achieved very high BET surface area (1538 m$^2$ g$^{-1}$) and total pore volume (0.671 cm$^3$ g$^{-1}$) values in ultrasonic-assisted MIL-53(Al) synthesis. In this study, by using the microwave production method, we achieved a much higher BET surface area of 1281 m$^2$ g$^{-1}$ at 180 °C and 180 minutes for MIL-53(Al), compared to the classical solvothermal production method, which requires a very long production time.

Table 1 briefly shows that different production techniques, synthesis times and temperatures significantly affect the surface properties of MIL-53(Al). The observed different surface features reported for MIL-53, which are generally due to impurities (solvent or precursor ions) in the pores and channels, are effective in their performance in applications.$^{46}$ As the temperature increases, it becomes easier for these contaminants to move away from the structure, and as the empty spaces increase, so do the porosity and surface areas. Therefore, it can be said that the surface areas and pore volumes increase with the increase in temperature from all classic isotherm models (Fig. 5). However, these structural properties do not change significantly with the increase in reaction time from 30 min to 180 min. It shows that a short period, such as 30 minutes, is sufficient to complete the formation of the structure and how advantageous the microwave method is for producing MOF structures in short periods.

The information obtained by classical methods of structure analysis, as shown above, does not give the possibility of an advanced assessment of the influence of reaction time and temperature on the formation of the porous structure of metal–organic frameworks due to the limitations of the mentioned methods and a considerable simplification of the mathematical models of the adsorption process on which they are based. Considerably more information on both the pore structure

Fig. 5 (a) Specific surface area (BET, Langmuir, t-plot, and DR methods) values and (b) pore volume and pore size of the produced MIL-53(Al)s at various temperatures and times.
Table 1  Surface properties of MIL-53(Al) obtained under different synthesis techniques and conditions. Where: ST: solvothermal method, UAST: ultrasonic-assisted solvothermal method, MW: microwave method.

| MIL-53(Al)/L1  | 120 | 180 | 20 | 0.428 | L | 1008.3 | 0.715 | 4.0 | ST(DMF + EtOH + water) | 120 °C, 72 h | 18 |
| MIL-53(Al)/L2  | 150 | 180 | 6  | 0.427 | L | 1050  | 0.675 | 1.75 | ST(DMF) | 120 °C, 72 h | 18 |
| MIL-53(Al)/L3  | 180 | 180 | 16 | 0.424 | L | 1008.3 | 0.715 | 1.74 | ST(DMF) | 120 °C, 72 h | 18 |

As shown by the analysis conducted with the LBET method, the surface of the studied material is characterized by a moderate degree of heterogeneity, which is indicated by the value of the heterogeneity parameter \( h \). The shape of the adsorption energy distribution on the surface of the studied material indicates that there are only pores with practically the same adsorption energy, which allows us to conclude that these pores are the same in the whole material and their size is similar to the size of adsorbed nitrogen molecules. The MIL-53(Al)/S2 sample obtained at 150 °C and a reaction time of 30 min was characterized by a significantly higher value of the \( V_{ha} \) parameter and a lower value of the \( B_c \) energy parameter, which indicates worse adsorption energy conditions for the occurrence of the multilayer adsorption process.

The values of geometrical parameters, similar to those of the previously analysed sample, indicate that only single nitrogen molecules adsorb in the pores of the studied material.

The higher value of the surface heterogeneity parameter \( h \) is noticeable, which indicates that the surface of the tested sample is more heterogeneous than that of the sample obtained at lower temperature, but the difference is not significant.

The next analysed material was the MIL-53(Al)/S3 sample obtained at 180 °C at 30 minutes. This sample is characterized by the highest value of the volume of the first adsorbed layer among all analysed samples and the highest value of the energy parameter for higher layers. The values of the geometrical parameters as well as the shape of the adsorption energy distribution on the surface of the tested sample are identical to the previously discussed MIL-53(Al)/S samples. In order to evaluate the effect of reaction time on the adsorption properties of metal–organic compounds MIL-53(Al), a second series of samples MIL-53(Al)/L was prepared. The samples were obtained similarly to the previously discussed series at temperatures of 120, 150 and 180 °C and the reaction time was 180 min, i.e. six times longer than the previously discussed series MIL-53(Al)/S obtained with an activation time of 30 min. The results of the analyses are also summarized in Fig. 6 and Table 2. Based on the results of analyses carried out with the LBET method, it can be observed that all the samples obtained at the reaction time of 180 minutes are characterized by very similar, practically identical values of the structure parameters, compared to the samples obtained at a much shorter reaction time, i.e. 30 minutes.

As part of the ongoing analyses of the structure of MIL-53(Al) synthesised by microwave heating at different reaction times and temperatures, pore size distributions (PSD) were determined using the QSDFT method based on nitrogen adsorption isotherms. As part of the QSDFT calculations, a cylindrical pore model was selected that approximates well the structure of the materials analysed. Based on the shapes of the pore size distributions obtained (Fig. 7), it was shown that the materials analysed have very similar distributions, with only the MIL-35(Al)/S1 sample having a significantly lower PSD distribution height.

4. Conclusions

As with other porous adsorbents, the surface properties of MOF materials are generally determined with classical isotherm models, such as the BET and Langmuir models. In the evaluations made with these models, MOFs can show different...
surface properties under different production techniques and conditions, even if they are produced with the same precursor materials. MIL-53 is a very porous and flexible material that has the ability to breathe by nature. Although MIL-53 is extensively used in the literature for adsorption, catalysis, separation and drug transport, its surface properties create limitations for some applications. Therefore, more emphasis can be placed on the characterization of surface properties.

Based on our research, the reaction temperature significantly influences the formation of the porous structure of the MIL-53(Al) material in samples obtained at a reaction time of 30 minutes. Namely, a significant increase in the values of the specific surface areas determined by BET, Langmuir, DR, and t-plot and the volume of the first layer calculated by the new numerical clustering-based adsorption analysis (LBET) method was observed with an increase in the production temperature of the MIL-53(Al) samples. The study also observed a positive effect of increasing the reaction temperature from 120 °C to 180 °C, which manifested an increase in both specific surface area and pore volume compared to samples obtained with a
reaction time of 30 min. The results obtained by the LBET method showed that the MIL-53(Al) material with the best adsorption properties analysed in this study was the sample obtained at a reaction temperature equal to 180 °C and a time equal to 30 min. The highest value of the volume of the first adsorbed layer and the highest value of the energy parameter for higher layers were also obtained in the sample MIL-53(Al) obtained for this material.

Popular and widely used activated carbons have many disadvantages, such as heterogeneity of the structure, abrasion of their grains causing dusting of technological installations, energy consumption of the production process and accompanying environmental hazards, as well as high production costs. On the other hand, metal–organic frameworks are known for their unique features, including, among others, unusual flexibility in construction and the phenomenon of respiration, which opens many new possibilities of applications for them and for adsorption processes using them. However, proper selection of the preparation conditions to obtain materials with optimal adsorption properties for a given application requires a precise evaluation of the porous structure of these materials.

Thanks to the universal formulation of mathematical models of the adsorption process implemented in the LBET method, taking into account a wide spectrum of adsorption properties of various materials, it is possible to evaluate the porous structure of metal–organic frameworks with high precision and reliability, and thus to select precisely the conditions of their preparation. As a result, it can be said that reliable results can be achieved with the LBET method in the evaluation of MOF materials with micropore structures such as MIL-53(Al).

Data availability
All data are included in the article.

Author contributions

Conflicts of interest
There are no conflicts to declare.

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