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Surface thermodynamics and Lewis acid-base properties of metal-organic framework Crystals by Inverse gas chromatography at infinite dilution



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ABSTRACT

In this study, the surface thermodynamic properties and more particularly, the dispersive component γ_s^d of the surface energy of crystals of a Zr-based MOF, UiO-66 (Zr₆O₄(OH)₄(BDC)₆; BDC = benzene 1,4-dicarboxylic acid), the specific interactions, and their acid-base constants were determined by using different molecular models and inverse gas chromatography methods. The determination of γ_s^d of the UiO-66 surface was obtained by using several models such as Dorris-Gray and those based on the Fowkes relation by applying the various molecular models giving the surface areas of n-alkanes and polar organic molecules. Six models were used: Kiselev, spherical, geometric, Van der Waals, Redlich-Kwong, and cylindrical models. The obtained results were corrected by using our model taking into account the thermal effect on the surface areas of molecules. A linear equation was obtained between γ_s^d and the temperature.

The specific free energy, enthalpy and entropy of adsorption of polar molecules, as well as the acid and base constants of UiO-66 particles were determined with an excellent precision.

It was also proved that the UiO-66 surface exhibited an amphoteric acid-base character with stronger acidity. The linear variations of the specific free energy of interaction as a function of the temperature allowed to obtain the specific surface enthalpy and entropy of adsorption, as well as the acid and base constants of UiO-66 by using ten different models and methods. The best results were obtained by using our model that gave the more precise values of the acid constant $K_A = 0.57$, the base constant $K_D = 0.18$ of the MOF particles and the ratio $K_A/K_D = 3.14$ clearly proving a strong acid character of the UiO-66 surface.

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1. Introduction

The study of surface energy is of significant importance in the industrial fields that encompass inter-particulate interactions such as catalytic processes, coating, wetting, dispersion of particles in liquid, powder handling, and many other applications [1].

The surface properties of a crystal are crucial to the understanding and design of materials for many applications. For instance, technologies such as fuel cells and industrial chemical manufacturing require the use of catalysts to accelerate chemical reactions, which is fundamentally a surface-driven process [1–9]. Surface effects are especially important in nanomaterials, where relatively large surface area to volume ratios lead to properties that differ significantly from the bulk material [10–14]. For example, the nanoscale stability of metastable polymorphs is determined from the competition between surface and bulk energy of the nanoparticle [15–18].

Surface energy is composed of two main components, namely the dispersive interactions, caused by long forces like van der Waals forces, and the specific or polar interactions, caused by the acid-base interactions [19–39]. Inverse gas chromatography (IGC)

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is usually used to measure the surface energy of solids where both polar and non-polar solvents are passed through a column packed with the solid under study at very low concentrations [19]. IGC technique was first used by Conder and Young in the 1970s [20-21] and was more developed during the last forty years by characterizing the physicochemical and specific properties of many solid materials [23-26]. The retention volume of a series of alkanes is determined to obtain the dispersive surface energy, while the specific free energies are obtained by determining the retention volumes of polar solvents [19]. The net retention time t_n is the key thermodynamic parameter determined by IGC allowing the full scanning of the surface properties of solid surfaces. Given the fact that a change in the surface energy can result in a change in the bulk properties of the solid material, the understanding of the surface energy becomes essential especially for newly discovered porous materials with high potential of application in many fields.

Recently, metal-organic frameworks (MOFs) have emerged as a new class of hybrid crystalline porous materials [2,3]. MOFs are composed of two main building blocks, the metal cluster and the organic linker, which can be selected from a wide variety of choices yielding a great flexibility in the design of the nanoporous and crystalline structures of MOFs [4]. Since their discovery, MOFs have been extensively employed in many applications due to their interesting properties which include their very large surface area, highly porous and crystalline structure, as well as their ease of design [5–7]. These properties have made these new materials very interesting in various applications such as gas storage [8], gas separation [9], chemical detection [10], water purification [11], and catalysis. [12] Although MOFs proved to outperform other porous materials, such as zeolites, in many applications, its main drawback in the pathway of industrial application was its chemical stability. This is why a lot of research focused on synthesizing new structures that exhibit high chemical stability and could be used in a wide variety of applications. Consequently, the discovery of the Zr-based secondary building unit, $Zr_6O_4(OH)_4(CO_2)_{12}$, found in UiO-66 $(Zr_6O_4(OH)_4(BDC)_6; BDC = benzene-1,4-dicarboxylic acid,$ Fig. 1), was considered as a breakthrough in MOF development as it demonstrated high chemical and thermal stability compared to other MOFs structures and opened doors to MOFs application in fields that were previously not possible [40]. Alongside the many variations of UiO-66 structures and characteristics that could be obtained through the conventional materials engineering methods such as functionalizing the organic linker and introducing guest molecules into the porous network of the MOFs, Zr-MOFs are known to be tunable through defects engineering [41]. UiO-66 MOFs have shown the ability to retain their crystalline nature and structure integrity even in the presence of a high defect density, which are usually caused by a missing linker or a missing cluster. The reason behind the interest in these defects is the fact that they allow the creation of high surface area structures of more open active metal sites which increase their activity in certain applications such as adsorption, separation and catalysis [17]. This had led to the development of many synthesis procedures that cause the intentional introduction of defects in UiO-66 structures, to tune the properties of MOFs for a specific application. One of the most famous defect engineering methods is the modulation synthesis during which an acid is added to the synthesis mixture of the MOF and competes with the organic linker on the binding sites within the Zr cluster, favoring thus the creation of defects (Fig. 1) [42]. Despite the great potential of these Zr-MOFs in a significant number of applications, and despite the interest in understanding the changes in its characteristics following a change in its defect density, there have not been much research on MOF's surface energy. Gutierrez et al. [43] studied the role of the structure of three isoreticular metal-organic frameworks (IR-MOFs) on their adsorption behavior by using IGC technique to eval-

uate different thermodynamic parameters of adsorption of some organic molecules on these materials. The dispersive component of the surface free energy of the adsorbent was determined with the help of n-alkanes and Dorris-Gray formula. The specific interaction parameters for the IRMOFs were also calculated [43] taking into account their variations as a function of the projection of the molecule probe, the dipolar moment and the polarizability deformation some polar. The inverse chromatography method was also used by Münch et al. [44] to quantify the systematic changes in the interaction of a series of related unbranched aliphatic analytes (C2-C10) with HKUST-1 ((Hong Kong University of Science and Technology, CuBTC, MOF-199)). They determined the interfacial energy contributions of the intrinsic surface of the porous material based on the method proposed by Dorris and Gray and the work of adhesion by observing a very low dielectric constant of the used material. The acid base interactions of HKUST-1 were determined by Münch et al. [45] by considering the Fowkes method and supposing the surface areas of organic molecules constant as well as the dispersive component of the surface tension of n-alkanes and polar molecules.

The results obtained by Gutierrez et al. [43] and Münch et al. [44,45] cannot be considered as quantitative, because of the extreme dependency of the surface areas of methylene group, n-alkanes and polar molecules on the temperature as it was proved in previous studies [19,28,39].

Duerinck et al. [46] characterized the adsorption properties of UiO-66 type MOFs by determining adsorption parameters of organic molecules (alkanes, alkenes, and aromatics of the linear, branched, and cyclic types) on four different UiO-66 materials (UiO-66, UiO-66-Me, UiO-66-Me2, UiO-66-NO2) using pulse gas chromatography in the temperature range 433–573 K. The adsorption enthalpy, Henry constants, and entropic factors were determined by proving the effect of methyl and nitro groups on the selectivity of UiO-66. However, the dispersive energy, specific interactions acid base surface properties of these materials were not studied. The investigation of the physicochemical properties such as the thermodynamic surface parameters and the Lewis acid and base constants is very important in the pathway of understanding these novel structures properties in order to fully explore their potential.

In this paper, UiO-66 was synthesized using modulation synthesis to induce the formation of defects, and was then fully characterized using Powder X-ray Diffraction (PXRD), Thermogravimetric Analysis (TGA), Brunauer-Emmett-Teller (BET) surface area analysis, and Scanning Electron Microscopy (SEM). The fully characterized MOFs particles were then employed as a stationary phase for the inverse gas chromatographic separation of various analytes (e.g. benzene, toluene, acetonitrile, chloroform, dichloromethane and ether) of different modes of interaction with the MOF particles. By using IGC methods, it was possible to determine the surface thermodynamic properties of the MOFs, especially, the dispersive and non-dispersive thermodynamic surface parameters and to quantify the Lewis acid and base constants of UiO-66. IGC at infinite dilution was used to quantify the surface properties of adsorption of polar and non-polar molecules on UiO-66 structures and the effect of defects density on its surface properties, by taking into account the effect of the temperature on the surface areas of n-alkanes and polar molecules and on the surface properties of Ui0-66

2. Methodology

2.1. Materials

In this study, the chemicals purchased were used directly without further purification. Zirconium chloride (ZrCl₄, 98%), tereph-



Fig. 1. Crystal structure of UiO-66 and its defected form (a), PXRD patterns of the synthesized UiO-66 and the simulated UiO-66 (b) and SEM images of UiO-66 synthesized in this study (c).

thalic acid (C_6H_4 (CO_2H)₂, 99%), formic acid (CH_2O_2 , 99%) and acetic acid ($C_2H_4O_2$, 99%) were obtained from Acros Organics. The n-alkanes (pentane, hexane, heptane, and octane), and the polar solvents (N, N-dimethylformamide, DMF, dichloromethane, DCM, chloroform, benzene, toluene, ether, acetonitrile and tetrahydrofuran, THF) at highly pure grade (99%) were purchased from Fisher Scientific.

2.2. General synthesis procedure of the UiO-66-based MOFs

With some modifications, UiO-66 was synthesized under conditions similar to those reported in the literature [39,40]. In this study, the metal source used was ZrCl₄ and the organic linker was terephthalic acid. Briefly, in a 500 ml autoclavable reagent bottle, 795 mg of ZrCl₄ (3.4 mmol) and 566 mg of terephthalic acid (3.4 mmol) were dissolved with 250 ml of DMF by sonication at room temperature after the addition of 15 ml of acetic acid to the mixture. The obtained mixture was placed in a preheated oven at 120 °C for 21 h. After 21 h, the bottle was removed from the oven and was left to cool to room temperature. The content of the bottle was then transferred to a falcon tube and the white precipitate obtained was collected by centrifugation. The obtained MOF was washed with two solvents: first, four times with approximately 60 ml DMF, and then four times with approximately 60 ml DCM. For each solvent, during the first three washes, the MOF were allowed to settle in each wash for 3 h, but in the last wash, the MOFs were soaked in the fresh solvent overnight. Then, UiO-66 was dried in a vacuum oven at 150 °C overnight for thermal activation.

2.3. Structural characterization of UiO-66-based MOFs

The synthesized UiO-66 was fully characterized using powder X- ray diffraction (PXRD), scanning electron microscopy (SEM), N₂ sorption measurements and thermogravimetric analysis (TGA). For the PXRD analysis, the patterns were recorded with an advanced Bruker D8 X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany, operating at 40 kV and current 40 mA, range 2θ : 5 – 50°, increment: 0.01°) using Cu K α radiation (λ = 1.5418Å). Approximately 60 mg of activated UiO-66 was placed in a glass sample holder with a circular cavity in the middle to place the sample in. A spatula was used to spread and flatten the sample. Then, for measurement, the sample was fixed in place.

For SEM imaging, an aluminum SEM sample stub was covered with a conductive carbon tape and a very small amount of the required MOF sample was spread on it. Then, the sample was coated with a very thin layer of gold (almost 20 nm) before being placed in the MIRA3 Tescan electron microscope for imaging.

Prior to N₂ sorption measurements, vacuum degassing was first carried out at 150 °C for 7 h. Then, a second degassing under a flow of nitrogen was conducted at 150 °C overnight in a BET cell. The cell was then placed in the measurement unit of the Micrometrics Gemini VII 2390p surface area analyzer. The N₂ sorption was performed at 77 K.

For the TGA analysis, a microbalance was used to weigh about 6 mg of the UiO-66 tested which was placed in a platinum crucible. Then, the crucible was inserted in the autosampler of the Netzsch TG 209 F1 Libra TGA apparatus. The thermal stability of the sample was evaluated under air flow from a temperature of 30 °C up to 1000 °C at a heating rate of 10 K/min. TGA curve was

normalized to 100% for its final weight loss and it was used to calculate the defect number following a well-established method in the literature [47,48].

2.4. Methods of inverse gas chromatography

2.4.1. Retention volume, dispersive and non-dispersive parameters of adsorption

The value of the net retention volume Vn [29-31] of the adsorption of organic solvents on a solid substrate (with a mass m and a specific surface s) contained in the chromatographic column was obtained during the experiments. The net retention volume Vn was calculated from Eq. (1):

$$Vn = jDc(tR - t0)$$
(1)

By using the experimental values of the retention time t_R of the probe, the zero retention reference time t_0 measured with a nonadsorbing probe such as methane, the corrected flow rate D_c and the correction factor j taking into account the compression of the gas [20]. D_c and j are respectively given by Eqs. (2) and (3):

$$D_{c} = D_{m} \frac{T_{c}}{T_{a}} \frac{\eta(T_{c})}{\eta(T_{a})}$$
⁽²⁾

$$j = \frac{3}{2} \frac{\left(\frac{\Delta P + P_0}{P_0}\right)^2 - 1}{\left(\frac{\Delta P + P_0}{P_0}\right)^3 - 1}$$
(3)

where D_m is the measured flow rate, T_c the column temperature, T_a the room temperature, h(T) the gas viscosity at temperature T, P_0 the atmospheric pressure and ΔP the pressure variation.

On Tables SI1 to SI11, we gave the experimental values of the net retention time, atmospheric pressure, room temperature and their uncertainties relative to n-alkanes and polar solvents adsorbed on UiO-66 surface for different temperatures (from 220 °C to 270 °C).

The thermodynamic calculations led to the standard free energy ΔG_i^0 of adsorption of the probe (Eq. (3)):

$$\Delta G^{0} = -RT \ln V_{n} + C(T) \tag{3}$$

where R is the ideal gas constant, T the absolute temperature and C(T) a constant depending on the reference state of adsorption [22] given by the following relation:

$$C(T) = RTln\left(\frac{P_0}{sm\pi_0}\right)$$

Two reference states were used to determine the standard free enthalpy of adsorption. Considering $T_0 = 0$ °C and $P_0 = 1.013 \times 10^5$ Pa, Kemball and Rideal reference state [49] supposed $\pi_0 = 6.08 \times 10^{-5}$ N m⁻¹, whereas, De Boer et al. reference state [50] proposed $\pi_0 = 3.38 \times 10^{-5}$ N m⁻¹.

From the retention time value, the free enthalpy of adsorption $(-\Delta G^0)$ of the probe can be obtained, which is equal to the sum of its dispersive $(-\Delta G^d)$ and specific $(-\Delta G^{sp})$, or non-dispersive, contributions (Eq. (4)):

$$\Delta G^0 = \Delta G^d + \Delta G^{sp} = -RT ln V_n + C(T) \tag{4}$$

Many methods proposing the determination of the specific free energy of adsorption of polar solvents were used in literature [23– 30]. They can also be used to evaluate the polar or acid-base interactions of adsorbed molecules on the solid substrates and, then, separate the dispersive (or London) and polar (or specific) contributions. Three important IGC methods are selected, and they are presented in the next sections.

2.4.2. Vapor pressure method

One of the most famous IGC methods was proposed by Saint-Flour and Papirer [25,26]. They represented the variations of RTInVn as a function of the logarithm of the vapor pressure of probes adsorbed on the solid surface, RTInVn = $f(\log P_0)$. They obtained for a homologous series of n-alkanes, a straight line, named alkane straight line with Eq. (5):

$$RT \ln Vn(n - alkane) = m \log P_0(n - alkane) + n$$
(5)

where m and n are constants depending of the solid surface nature.

The specific free energy of adsorption $(-\Delta G^{sp})$ of a polar molecule is given by (Eq. (6)):

$$(-\Delta G^{sp})(polarmolecule) = RT lnVn(polarmolecule) - mlogP0(polarmolecule) - n$$
(6)

The specific enthalpy $(-\Delta H^{sp})$ and entropy $(-\Delta S^{sp})$ of polar solvents were obtained from the variations of $(-\Delta G^{sp})$ of polar molecule as a function of the temperature. The acid and base constants of the solid in Lewis terms are obtained from the values of $(-\Delta H^{sp})$.

2.4.3. Method of deformation polarizability

Donnet et al. [30] used the deformation polarizability α_0 of organic solvents as a thermodynamic parameter in order to separate the London dispersive forces and specific interactions between the solid and the polar solvent. They used the representation of *RTlnVn* versus $(hv_L)^{1/2} \alpha_{0, l}$ of the liquid solvent, where v_L is the electronic frequency of the probe and h the Planck's constant. They proposed the following relation [31]:

$$RT \ln V n = K (h v_s)^{1/2} \alpha_{0,s} \left[(h v_L)^{1/2} \alpha_{0,l} \right] + Cst$$
(7)

Where v_s is the electronic frequency of the solid, $\alpha_{0, s}$ is its polarizability, and K is a constant depending on the permittivity of the vacuum and the distance between the adsorbed probe and the solid surface. The straight line obtained by the representation of $RTInVn = f[(hv_l)^{1/2} \alpha_{0, L}]$ for n-alkanes allowed to deduce the specific free enthalpy of adsorption $(-\Delta G^{sp})$ of a polar molecule on the solid and therefore $(-\Delta H^{sp})$ and $(-\Delta S^{sp})$.

2.4.4. Method of topological index

Brendlé and Papirer [32] used the topological index χ_T of molecules and represented the function $RTlnVn = f(\chi_T)$ of n-alkanes, polar molecules, branched alkanes, and cycloalkanes. This method also allowed the determination of the specific interactions and the acid and base constants of solid surfaces.

The three previous methods led to the determination of the specific free energy $(-\Delta G^{sp})(T)$ of the polar molecules and therefore to the specific enthalpy $(-\Delta H^{sp})$ and entropy $(-\Delta S^{sp})$ of adsorption through Eq. (8):

$$(-\Delta G^{sp})(T) = (-\Delta H) - T(-\Delta S^{sp})$$
(8)

In the case where ΔH_a^{sp} and ΔS_a^{sp} do not depend on the temperature. If they do, the variations of such thermodynamic parameters as a function of temperature should be taken into account.

2.4.5. Method of the dispersive component of the surface energy

The evaluation of the dispersive component γ_s^d of the surface energy of a solid used Fowkes relation [35]:

$$\left(-\Delta G^{0}\right) = 2\mathcal{N}a\left(\gamma_{l}^{d}\gamma_{s}^{d}\right)^{1/2} + Cst$$
(9)

Where \mathcal{N} is Avogadro's number, a is the surface area of one adsorbed molecule on the solid, and γ_l^d and γ_s^d are the dispersive components of the surface tension of the probe and of the solid respectively [36].

The Fowkes relation for non-specific interactions is only valid for lower dielectric constant of the studied solid surface [44]. In this paper, the used UiO-66 material exhibited a dielectric constant equal to 1.95 [50–53] and this justified the applicability of the Fowkes approach.

This method could determine, a priori, both the specific free enthalpy of adsorption and the dispersive component of the surface energy of the solid particles.

However, this method cannot be used due to the important effect of the temperature on the surface area that cannot be known with accuracy. On the other hand, for higher temperature (greater than 450 K), the value of γ_l^d cannot be determined. These reasons lead to inaccurate estimation of the values of γ_s^d of the solid and the specific free enthalpy of adsorption of polar molecules on the solid substrates [28,38,39,54].

Dorris and Gray [36] proposed relation (10) derived from relation (9):

$$\gamma_{s}^{d} = \frac{\left[RTln\left[\frac{V_{n}\left(C_{n+1}H_{2(n+2)}\right)}{V_{n}\left(C_{n}H_{2(n+1)}\right)}\right]\right]^{2}}{4\mathcal{N}^{2} a_{-CH2-}^{2} \gamma_{-CH2-}}$$
(10)

Where $C_nH_{2(n+1)}$ and $C_nH_{2(n+1)}$ represent the general formula of two consecutive n-alkanes; while $V_n(C_nH_{2(n+1)})$ and $V_n(C_{n+1}H_{2(n+2)})$ indicate their retention volumes. Supposing the surface area of methylene group a_{-CH2-} equal to 6 Å², the surface energy of -CH2- group γ_{-CH2-} is given by the relation (11):

$$\gamma_{-CH2-} = 52.603 - 0.058 T(TinK; \gamma_{-CH2-}inmJ/m2)$$
(11)

The same difficulty remains present with Dorris-Gray method. The value 6 Å² for the surface area of methylene group a_{-CH2-} is supposed constant for all the temperatures. In fact, Hamieh et al. [19,28,38,39,54] proved that the surface area of organic molecules extremely depends on the temperature by studying the adsorption of n-alkanes and polar solvents on polyethylene (PE) and polyte-trafluoroethylene (PTFE) surfaces. Therefore, the effect of the thermal energy on the methylene group surface area and on the dispersive surface energy must be taken into account when using the Dorris-Gray expression.

2.4.6. Determination of the acid and base constants of a solid substrate

The acid K_A and base K_D constants of a solid can be determined by the means of the following equation [25,26,33,34]:

$$\left(-\Delta H^{Sp}\right) = K_A D N + K_D A N \tag{12}$$

where DN and AN are the donor and acceptor numbers of electrons of the various probes.

The curve of $\frac{-\Delta H^{5p}}{AN}$ versus $\frac{DN}{AN}$ gives in general a straight line of slope K_A and intercept K_D .

2.4.7. Inverse gas chromatograph conditions

The IGC measurements were performed on a DELSI GC 121 FB chromatograph equipped with a flame ionization detector by using dried nitrogen as a carrier gas. The column was filled by 207 mg of dried UiO-66 powder. The packed column was then preconditioned (at 280 °C and under a nitrogen flow rate) overnight to remove any residual solvent left in the packing material. The gas flow rate was optimized at 20 mL/min. The temperatures of injector and detector were fixed at 200 °C. To satisfy the infinite dilution, each probe was injected with 1 μ L Hamilton syringes. The column temperatures were 220 to 270 °C, varied in 5 °C steps. The first order retention time was determined for all measurements. Every injection was repeated three times, and the average retention time, t_R, was used for the calculation. The standard deviation was less than 1% in all measurements. The net retention volume was calculated by using the classical thermodynamic relations.

2.4.8. The specific free enthalpy of adsorption

The standard free enthalpy of adsorption $(-\Delta G^0)$ of the probes on UiO-66 surface was determined by using the two reference states of Kemball and Rideal [49] and De Boer et al. [50] and the specific parameters were obtained by using the various molecular and thermal models by varying the temperature from 220 to 270 °C.

From the retention time values, the free enthalpy of adsorption $(-\Delta G^0)$ of the probe can be obtained. In the case of polar molecules, the specific free enthalpy $(-\Delta G^{sp})$ of the adsorption of such molecules on the solid substrate can be easily calculated from the straight line of n-alkanes by subtracting the dispersive contribution from the total free enthalpy.

3. Results and discussion

3.1. Structural characterization of UiO-66 particles

The PXRD pattern of the synthesized UiO-66 was recorded and the results are shown in Fig. 1 which reveals narrow and sharp peaks that are in complete agreement with the calculated pattern of UiO-66.

Furthermore, no additional peaks were observed, as evidenced in the indexed peaks of the as synthesized sample, which reflects the high crystallinity and phase purity of this MOF.

The morphology and the size of the UiO-66 crystals are investigated using SEM and the results are displayed in Fig. 1. The images reveal that UiO-66 sample is pure and the crystals exhibit homogeneous truncated octahedral shape.

The thermal stability of UiO-66 is examined using the thermogravimetric analysis (TGA) where the mass of a UiO-66 sample is continuously monitored in an oven with an increasing temperature in the presence of air. In order to estimate the defect number in UiO-66 structure, TGA curve was normalized to 100% for the final weight loss. This method is well-established in the literature for defects number calculation. The TGA curve is presented in Fig. 2a and it shows the evolution of the mass of sample with a temperature starting from 30 °C to 1000 °C. Three phases of weight loss could be distinguished. The first weight loss occurs approximately between 35 °C and 100 °C, where the water adsorbed on the surface of the MOF is volatilized. The second weight loss corresponds to the vaporization of unreacted species and remaining DMF in the pores between 100 °C and 300 °C. The third major weight loss in the TGA curve is attributed to the destruction of the framework of the MOF by the combustion of the organic linker. The weight loss attributed to the linker is the one that occurs above the temperature T_{link}, of 400 °C. The TGA curve allows us to calculate the defect number based on the published method [7,47], and it was found to be 1.2, which is in agreement with the modulated synthesis method employed in the production of UiO-66 crystals in this studv.

The nitrogen sorption isotherm of the synthesized MOF is shown in Fig. 2b.

The isotherm is of type I which is consistent with the microporous nature of MOFs and depicting a monolayer adsorption on their surface. The textural properties such as Brunauer–Emmett–Teller (BET) surface areas and pore volume of the synthesized UiO-66 are calculated from the nitrogen isotherm to be 988 m²/g and 0.512 cm³/g respectively. These numbers are in the same values range of the reported ones in the literature [7,40,47,48].

3.2. Surface properties of UiO-66 surface by IGC

3.2.1. The dispersive component of the surface energy

The dispersive component of the surface energy of UiO-66 was determined by using Dorris-Gray method, Fowkes relation, and the



Fig. 2. Normalized TGA curve of UiO-66 crystals under air atmosphere (a), Nitrogen adsorption and desorption isotherms of the UiO-66 at 77 K (b).



Fig. 3. Variations of the dispersive component of the surface energy $\gamma_s^d (mJ/m^2)$ of UiO-66 as a function of the temperature T (K) using different methods and models.

methods proposed by Hamieh et al. [19,28,38,39] taking into account the molecular models of n-alkanes and polar molecules as well as the variations of the surface area as a function of the temperature.

The dispersive component γ_s^d (*T*) of the surface energy of UiO-66 at fixed temperature was calculated by using 9 molecular and thermal models.

Fig. 3 shows the variations of γ_s^d (*T*) of UiO-66 surface against the temperature by using the above mentioned methods. It is clear in Fig. 3 that the slopes of all models are negative proving the decrease of γ_s^d (T) of UiO-66 surface when the temperature increases. Additionally, the straight lines of the spherical and Dorris-Gray-Hamieh models are significantly above the other curves showing that there is a divergence between the $\gamma_s^d(T)$ values obtained by the various models. The effect of the change in temperature on the surface area of the probes indeed affected the values of the dispersive energy of materials. The conventional model proposed by Kiselev which is largely used in literature, resulted in inaccurate values since, upon the change in the molecular model used, different γ_s^d (*T*) values were obtained. Moreover, the thermal model proposed by Hamieh [39] resulted in more accurate estimation. As previously mentioned, Hamieh et al. [19,38,39,54] proved the dependency of the molecular surface areas of organic molecules on the dispersive component of the surface energy and gave the various expressions of the surface areas, an (T) of nalkanes as a function of the temperature T. The general form was given by:

$$a_n(T) = \lambda_n T + \beta_n \tag{13}$$

where λ_n is the dilatation rate and β_n the surface area of n-alkanes at 0 K.

These findings implied the use of the new values of the surface area of the probes depending on the temperature to determine the accurate values of γ_s^d (*T*).

The variations of $\gamma_s^d(T)$ are linear for all molecular models (Table 1). A general equation was obtained with an excellent linear regression coefficient:

$$\gamma_s^d(T) = aT + b \tag{14}$$

where $a = \frac{d\gamma_s^d}{dT}$ and $b = \gamma_s^d (T = 0K)$ that can be experimentally obtained.

Table 1 showed that there is an important difference between the values of $\frac{d\gamma_s^d}{d\tau}$ and $\gamma_s^d(0K)$ obtained by the different models.

In Fig. 4a, we plotted the values of $\frac{d\gamma_s^d}{dT}$ and $\gamma_s^d(0K)$ for the different used models. The highest values of $\gamma_s^d(0K)$ and $\frac{d\gamma_s^d}{dT}$ (in absolute value) are obtained successively for models taking into account the thermal effect such as Redlich-Kwong model and our models. The deviation of the spherical model is certainly due to the fact of the overestimation of the surface area of the molecules.

In order to show the difference between the different models used in a clearer way, the values of the dispersive component of the surface energy of UiO-66 were depicted in Fig. 4b at five temperatures using the various models taking into account the effect of the temperature on the surface area of the solvent molecules.

It could be seen when observing Figs. 3-4 and Table 1 that the used models could be classified into two categories. The first group comprises the conventional molecular models such as geometric, Dorris-Gray, cylindrical, VDW, Kiselev models, which underestimate the values of the surface areas of organic molecules, in addition to the spherical model, which gives an overestimation of these surface areas. The second group is composed of Redlich-Kwong model, Dorris-Gray relation and our approach which take into account the effect of the thermal agitation on the surface areas of molecules a (T). The best results were obtained when using our model [39] that determined the different relations of the surface areas a (T) as a function of the temperature and therefore obtained the variations of the dispersive surface energy as a function of the temperature. The accurate expression of $\gamma_s^d(T)$ of UiO-66 surface given by Hamieh is the following (Eqn. (15)):

$$\gamma_s^d(T) = -0.444T + 190.86\tag{15}$$

Table 1

Equations $\gamma_s^d(T)$ of UiO-66 surface for various molecular models of n-alkanes, the dispersive surface entropy ε_s^d , the extrapolated values $\gamma_s^d(T = 0K)$ and the regression coefficient R² obtained by using the different molecular models.

Molecular model	$\gamma_s^d(T)$ (in mJ/m ²)	$\frac{d\gamma_s^d}{dT}$ (in mJ m ^{- 2} K ^{- 1})	$\gamma_s^d(T=0K)~({\rm in}~mJ/m^2)$	Regression coefficient
Geometric	$\gamma_{\rm s}^{\rm d}({\rm T}) = -0.098 \ T + 56.71$	-0.098	56.71	0.9980
Dorris-Gray	$\gamma_{\rm s}^{\rm d}({\rm T}) = -0.139 \ T + 86.68$	-0.139	86.68	1.0000
Cylindrical	$\gamma_{\rm s}^{\rm d}({\rm T}) = -0.163 \ T + 84.63$	-0.163	84.63	0.9990
VDW	$\gamma_{\rm s}^{\rm d}({\rm T}) = -0.175 \ T + 87.15$	-0.175	87.15	0.9996
Kiselev	$\gamma_{\rm s}^{\rm d}({\rm T}) = -0.180 \ T + 89.97$	-0.180	89.97	0.9995
Redlich-Kwong	$\gamma_{\rm s}^{\rm d}({\rm T}) = -0.286 \ T + 142.14$	-0.286	142.14	0.9996
Hamieh model	$\gamma_{\rm s}^{\rm d}({\rm T}) = -0.444 {\rm x} + 190.86$	-0.444	190.86	0.9932
Dorris-Gray-Hamieh	$\gamma_{\rm s}^{\rm d}({\rm T}) = -0.502 \ T + 235.74$	-0.502	235.74	0.9982
Spherical	$\gamma_s^d(T) = -0.6014T + 279.23$	-0.601	279.23	1.0000





Fig. 4. Values of $\gamma_s^d(0K)$ and $\frac{d\gamma_s^d}{dT}$ of UiO-66 (a), and values of the dispersive component of the surface energy γ_s^d (mJ/m^2) of UiO-66 at five temperatures (b), using the various models.

3.2.2. Thermodynamic measurements of differential heat and entropy change of adsorption

The experimental determination by IGC technique of the retention volume of the probes adsorbed on UiO-66 is employed to evaluate the differential heat ΔH_a^0 and the entropy change of ad-



Fig. 5. Variations of lnV_n as a function of 1000/T of different organic molecules adsorbed by UiO-66.

sorption ΔS_a^0 of the probe. The Eqs. (16) and (17) were used:

$$\Delta H_a^0 = -R \frac{\partial \left(ln V_n \right)}{\partial \left(\frac{1}{T} \right)} \tag{16}$$

$$\Delta S_a^0 = -\left(\frac{\partial \left(RT\ln V\right)}{\partial T}\right) \tag{17}$$

Fig. 5 shows the obtained straight lines of lnV_n as a function of (1/T) for the various organic molecules adsorbed on the solid surface.

The different straight lines can be represented by the Eq. (18):

$$lnV_n = \alpha \left(\frac{1}{T}\right) + \beta \tag{18}$$

where α and β are constants depending on the probe nature. ΔH_a^0 and ΔS_a^0 can be estimated using Eq. (19):

$$\Delta H_a^0 = -R\alpha; \ \Delta S_a^0 = -R\beta \tag{19}$$

By using relations (10)-(13) and the data from Fig. 6, the values of the differential heat and the standard entropy change of adsorption can be obtained. The results are given in Table 2.

The differential heat and the standard entropy change of adsorption of n-alkanes seemed to be correlated with an excellent linear relation represented as follows (eqn. (20)):

$$\Delta H_a^0(kJ/mol) = 702.1, \ \Delta S_a^0(kJ/mol) + 7.142; \ R^2 = 0.9994$$
(20)

On the other hand, the values of $(-\Delta H_a^0)$ of n-alkanes increase from 56.560 to 70.981 kJ/mol and that of $(-\Delta S_a^0)$ of the probe increase from 90.6 to 111.1 J/mol when the carbon atom number n_C increases. Linear relations (21) and (22) were obtained as a function of n_C for n-alkanes:

$$\left(-\Delta H_a^0\right)(kJ/mol) = 4.719n_C + 32.396\tag{21}$$

Table 2

Values of $\Delta H^0_a(kJ/mol)$, $\Delta S^0_a(J K^{-1} mol^{-1})$ and the expressions of $\Delta G^0_a(T)$ (kJ/mol) of different polar and n-alkane molecules adsorbed on UiO-66 surface.

Molecules	$\Delta H_a^0 ~(kJ/mol)$	$\Delta S^0_a~(J~K^{-1}~mol^{-1})$	$\Delta G^0_a(T)~(kJ/mol)$
Pentane	-56.560	-90.6	$-56.559{+}9.1\times10^{-2}{\rm T}$
Hexane	-60.403	-96.2	$-60.403 + 9.6 \times 10^{-2} \text{ T}$
Heptane	-64.325	-102.1	$-64.325{+}10.2 \times 10^{-2} \text{ T}$
Octane	-70.981	-111.1	$-70.981{+}11 \times 10^{-2} T$
Dichloromethane	-62.793	-85.7	$-62.793 + 8.6 \times 10^{-2} \text{ T}$
Chloroform	-59.069	-85.8	$-59.069 + 8.6 \times 10^{-2} \text{ T}$
THF	-68.484	-129.1	$-68.484{+}12.9 \times 10^{-2} \text{ T}$
Ether	-59.835	-125.9	$-59.835 + 12.6 \times 10^{-2} \text{ T}$
Acetonitrile	-85.451	-142.5	$-85.451{+}14.3 \times 10^{-2} \text{ T}$
Toluene	-70.801	-78.5	$-70.801{+}7.9 \times 10^{-2} \text{ T}$
Benzene	-67.832	-105.3	$-67.832{+}10.5 \times 10^{-2} \text{ T}$



Fig. 6. Evolution of the differential enthalpy of adsorption as a function of the carbon atom number of n-alkanes and polar molecules $(\Delta H_a^0 = f(n_c))$.

$$\left(-\Delta S_a^0\right)\left(JK^{-1} \ mol^{-1}\right) = 6.72n_{\rm C} + 56.29\tag{22}$$

This increase is due to the increase in the boiling points of nalkanes and to the stronger interaction between the solute and UiO-66 surface.

For the polar molecules, we can classify the differential enthalpy by increasing order:

Chloroform \approx Dichloromethane < Benzene < Toluene < Ether < Acetonitrile < Tetrahydrofuran

The above order strongly depends on the interaction force of adsorption and affinity of polar probes on the solid surface of UiO-66. It is necessary to separate the two polar and non-polar contributions of the enthalpy of adsorption. The variations of the differential enthalpy of adsorption as a function of the carbon atom number of the organic molecules are plotted in When considering Fig. 6, the Eqs. (14) and (15), and the values of polar probes from Table 2, the polar and non-polar contributions of every molecule could be calculated, and the results are shown in Table 3.

The values of polar contributions of the enthalpy of adsorption $(-\Delta H_a^{pol.})$ can be classified for the polar probes in increasing order:

Toluene < Benzene < Ether < Tetrahydrofuran < Chloroform

< *Dichloromethane* < *Acetonitrile*

This classification is perfectly in line with the order obtained with the relative polarity (R.P.) of the above polar molecules. We obtained a perfect linear correlation between $(-\Delta H_a^{pol.})$ and R.P. of

Iddle 2									
Values	of	polar	$(\Delta H_a^{\text{pol.}})$	and	non-polar	$(\Delta H_a^{non-pol.})$	enthalpies	of	different
probes	ads	orbed	on UiO-6	6 par	ticle surface	e.			

Probes	$\Delta H_a^{\text{pol.}}(kJ/mol)$	$\Delta H_a^{non-pol.}(kJ/mol)$	$\Delta H^0_a(kJ/mol)$
Pentane	0	-56.560	-56.560
Hexane	0	-60.403	-60.403
Heptane	0	-64.325	-64.325
Octane	0	-70.981	-70.981
Dichloromethane	-25.678	-37.115	-62.793
Chloroform	-21.954	-37.115	-59.069
Tetrahydrofuran	-17.213	-51.271	-68.484
Ether	-8.564	-51.271	-59.835
Acetonitrile	-43.618	-41.833	-85.451
Toluene	-5.374	-65.427	-70.801
Benzene	-7.124	-60.708	-67.832



Fig. 7. Variations of the differential enthalpy of different organic molecules adsorbed by UiO-66 as a function of their relative polarity.

polar probes (Fig. 7). The linear relationship can be described as:

$$\left(-\Delta H_a^{pol.}\right)(kJ/mol) = 102.33 \times R.P. - 4.329, R^2 = 0.9958$$
 (23)

Therefore, the value of the polar differential enthalpy of adsorption depends not only on the solid material nature but also on the affinity and polarity of the polar molecules adsorbed by UiO-66 crystals. The values of the specific enthalpy of adsorption also proved that the used MOF, UiO-66, has an amphoteric acid-base character with an acid predominance.

Table 4

Linear expressions of the specific free enthalpy $(\Delta G_a^{sp}(T)) = y$ of adsorption of CH_2Cl_2 , chloroform, diethyl ether and THF on UiO-66 catalyst as a function of the temperature T by using the various models.

Vapor pressure $y = -0.0081T + 7.317$ $y = -0.0094T + 5.893$ $y = -0.0323T + 28.191$ $y = -0.0365T + 28.191$ Deformation polarizability $y = -0.0021T + 5.539$ $y = -0.0011T + 7.727$ $y = -0.0608T + 45.741$ $y = -0.0409T + 24.191$		CH ₂ Cl ₂	Chloroform	Diethyl ether	THF
Topological index $y = -0.0119T + 16.072$ $y = -0.079T + 13.155$ $y = -0.0399T + 33.863$ $y = -0.0376T + 23.863$ Kiselev $y = -0.0230T + 18.395$ $y = -0.0226T + 17.889$ $y = -0.0328T + 27.537$ $y = -0.0643T + 57.537$ Spherical $y = -0.0106T + 11.698$ $y = -0.0090T + 9.831$ $y = -0.0498T + 35.462$ $y = -0.0498T + 35.462$ Geometric $y = -0.0121T + 13.331$ $y = 0.01850T + 2.736$ $y = -0.0352T + 29.071$ $y = -0.0630T + 39.577$ VDW $y = -0.0072T + 10.158$ $y = -0.0636T + 30.327$ $y = -0.0374T + 22.105$ $y = -0.0475T + 34.577$ Redlich-Kwong $y = -0.0069T + 10.084$ $y = -0.0633T + 30.24$ $y = -0.0373T + 22.101$ $y = -0.0893T + 44.5775$ Ulmirical $y = -0.0142T + 14.708$ $y = -0.0331T + 21.07$ $y = -0.0277T + 18.580$ $y = -0.0753T + 54.5775$	Vapor pressure Deformation polarizability Topological index Kiselev Spherical Geometric VDW Redlich-Kwong Cylindrical	y = -0.0081T + 7.317 y = -0.0021T + 5.539 y = -0.0119T + 16.072 y = -0.0230T + 18.395 y = -0.0106T + 11.698 y = -0.0121T + 13.331 y = -0.0072T + 10.158 y = -0.0142T + 14.708 y = -0.0142T + 14.708	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	y = -0.0365T + 21.262 y = -0.0409T + 24.018 y = -0.0376T + 21.753 y = -0.0643T + 57.46 y = -0.0498T + 35.462 y = -0.0630T + 39.241 y = -0.0475T + 34.814 y = -0.0893T + 44.450 y = -0.0753T + 54.630

Table 5

Linear expressions of the specific free enthalpy $(\Delta G_a^{sp}(T)) = y$ of adsorption of acetonitrile, toluene and benzene on UiO-66 catalyst as a function of the temperature T by using the various models.

	Model or method	Acetonitrile	Toluene	Benzene
Vapor pressure $y = -0.0424 T + 22.724$ $y = -0.005 T + 3.609$ $y = -0.003 T + 3.174$ Deformation polarizability $y = -0.0849 T + 49.862$ $y = -0.0056 T + 6.200$ $y = -0.0042 T + 2.395$ Topological index $y = -0.0849 T + 49.864$ $y = -0.0026 T + 6.200$ $y = -0.0042 T + 2.395$ Kiselev $y = -0.0303 T + 14.866$ $y = -0.0200 T + 9.905$ $y = -0.0012 T + 3.500$ Spherical $y = -0.0932 T + 47.097$ $y = -0.0115 T + 5.003$ $y = -0.0112 T + 4.512$ Geometric $y = -0.0565 T + 30.363$ $y = -0.0068 T + 3.383$ $y = -0.0063 T + 2.346$ VDW $y = -0.0565 T + 30.363$ $y = -0.0068 T + 3.383$ $y = -0.0063 T + 2.346$ Redlich-Kwong $y = -0.0723 T + 37.971$ $y = -0.0123 T + 7.919$ $y = -0.0063 T + 2.346$ Lyindrical $y = -0.0723 T + 37.971$ $y = -0.0121 T + 7.600$ $y = -0.0005 T + 3.120$ Hamieh model $y = -0.0055 T + 39.197$ $y = -0.0121 T + 7.600$ $y = -0.0005 T + 0.821$	Vapor pressure Deformation polarizability Topological index Kiselev Spherical Geometric VDW Redlich-Kwong Cylindrical Hamieh model	y = -0.0424 T + 22.724 y = -0.0849 T + 49.862 y = -0.0684 T + 40.644 y = -0.0303 T + 14.866 y = -0.0932 T + 47.097 y = -0.0681 T + 36.339 y = -0.0566 T + 30.363 y = -0.0566 T + 30.363 y = -0.0723 T + 37.971 y = -0.0065 T + 39.197	y = -0.005 T + 3.609 y = -0.0056 T + 6.200 y = -0.0021 T + 6.600 y = -0.0200 T + 9.905 y = -0.0115 T + 5.003 y = -0.0034 T + 1.311 y = -0.0068 T + 3.383 y = -0.0068 T + 3.379 y = -0.0139 T + 7.919 y = -0.0121 T + 7.600	y = -0.0003 T + 3.174 y = -0.0042 T + 2.395 y = -0.0012 T + 2.395 y = -0.0021 T + 3.500 y = -0.0112 T + 4.512 y = 0.0032 T + 1.980 y = -0.0063 T + 2.346 y = -0.0063 T + 3.120 y = -0.005 T + 3.120

3.2.3. Determination of the specific free energy and acid-base properties of UiO-66 particles

Using the different methods mentioned above (the vapor pressure [25,26], deformation polarizability [31], topological index methods [32] and molecular and thermal models [38,39,54]), the specific free energy ($\Delta G_a^{sp}(T)$) of the various polar solvents adsorbed on UiO-66 surface were determined as a function of the temperature T, and the results are depicted in Tables SI12 – SI23.

Afterwards, the obtained data was used to extract a linear correlation between the specific free enthalpy $(\Delta G_a^{sp}(T))$ and the time relative to the various polar molecules by using the different IGC models and methods, and the results are depicted in Tables 4 and 5.

Tables 4,5 and SI 1–12 clearly show that the different methods used in IGC at infinite dilution to characterize the solid surfaces did not give identical values of $(\Delta G_a^{sp}(T))$ no matter the chosen polar probes and temperatures. In some cases, the obtained values are, for one chosen method, three times higher than for the other methods.

In order to clarify the difference between the various chromatographic methods and models, Figs. 8a and 8b show the variations of ΔG_a^{sp} of the polar solvents such as dichloromethane and tetrahydrofuran respectively, as a function of the temperature.

The obtained results further confirm our previsions on the significant differences in the values of the specific free enthalpy obtained by the various methods. Indeed, there is no universal method that can be used by IGC technique for an accurate determination of the specific surface properties of solid particles. However, our approach, and since it takes into account the effect of temperature, gave the more accurate specific values followed by the methods of the topological index, the vapor pressure and the deformation polarizability.

3.2.4. Enthalpic acid base constants

For all used probes and the different IGC methods, a linear variation of $(\Delta G_a^{sp}(T) \text{ as a function of the temperature was obtained})$ (Tables 4 and 5). This allowed to determine the specific enthalpy $(-\Delta H_a^{sp})$ and entropy of adsorption $(-\Delta S_a^{sp})$ of the various polar solvents adsorbed on the UiO-66 surface for the different molecular models and IGC methods. These results were reported in Tables SI 13 and SI 14.

The results depicted in the two Tables SI 13 and SI 14 showed an important deviation between the obtained results of specific enthalpy and entropy of adsorption from IGC method or model to other models and methods showing the difficulties to choose a particular method that gives the most accurate results. The values of the specific enthalpy and entropy of adsorption depend on the nature of the method utilized. Consequently, it appears difficult to prefer a method over another. However, it seems that the more accurate method is that based on the thermal effect followed by the vapor pressure and topological index.

In order to determine the acid base constants of UiO-66 surface, it is convenient to plot the variations of $(\frac{-\Delta H_a^{Sp}}{AN'})$ and $(\frac{-\Delta S_a^{Sp}}{AN'})$ as a function of $(\frac{DN'}{AN'})$ for the different methods and models (Figs. 9a and 9b). The straight lines (in dark) represent the average results of all the used methods.

The values of the enthalpic acid base constants K_A and K_D and entropic acid base parameters ω_A and ω_D for the different IGC methods are summarized in the Table 6. The values obtained by taking the average of these IGC methods are also inserted in Table 6.

Table 6 showed very acidic UiO-66 surface which is 3 times more acidic than basic in Lewis terms when using our model relative to the thermal effect and the ratio acidity/basicity decreased to 1.8 for the other molecular models and IGC methods, excepted for the vapor pressure method where we found a ratio equal to 2. our model gave an acidic constant $K_A = 0.57$ and a smaller basic constant $K_D = 0.18$. These results confirm the acidic nature of this framework which was employed as acid heterogeneous catalyst for esterification reaction [7,47]. The strong Lewis acidity of this MOF is induced by the defected nature of its structure as evidenced by the TGA analysis (1.2 missing linkers per cluster).







Fig. 8. Variations of ΔG_a^{sp} as a function of the temperature in the case of THF (a) and DCM (b) adsorbed on UiO-66 surface by using the different IGC models and methods.

Table 6
Values of the enthalpic acid base constants K_A and K_D (unitless) and the entropic acid base con-
stants $\omega_{\rm A}$ and $\omega_{\rm D}$ (unitless) of UIO-66 catalyst and their acid base ratios for the different used
molecular models and IGC methods.

Models and IGC methods	K _A	K _D	K_A/K_D	ω_{A}	$\omega_{ m D}$	$\omega_{\rm A}/\omega_{\rm D}$
Kiselev	0.63	0.35	1.80	7.1×10^{-4}	$4.6~\times~10^{-4}$	1.53
Spherical	0.59	0.41	1.43	9.3×10^{-4}	6.2×10^{-4}	1.49
Geometric	0.44	0.23	1.93	6.9×10^{-4}	3.5×10^{-4}	2.01
VDW	0.49	0.26	1.91	7.3×10^{-4}	4.4×10^{-4}	1.66
Redlich-Kwong	0.48	0.27	1.80	9.6×10^{-4}	6.4×10^{-4}	1.50
Cylindrical	0.58	0.34	1.73	8.1×10^{-4}	5.2×10^{-4}	1.57
Vapor pressure	0.32	0.16	1.96	3.8×10^{-4}	3.1×10^{-4}	1.24
Deformation polarizability	0.50	0.30	1.67	6.9×10^{-4}	9.0×10^{-5}	7.63
Topological index	0.38	0.21	1.81	4.6×10^{-4}	3.8×10^{-4}	1.20
Hamieh model	0.57	0.18	3.14	5.2×10^{-4}	3.5×10^{-4}	1.48
Global average	0.50	0.27	1.84	6.9×10^{-4}	$4.2~\times~10^{-4}$	1.65



Fig. 9. Variations of $\left(\frac{-AR_{2}^{2}}{AN^{2}}\right)$ (a) and $\left(\frac{-AR_{2}^{2}}{AN^{2}}\right)$ (b) as a function of $\left(\frac{DN}{AN^{2}}\right)$ for different molecular models and IGC methods.

The superiority of our model results from the use of the effect of the temperature on the surface areas of adsorbed molecules. All other methods used constant values of the parameter descriptors for all polar molecules independently from the temperature. The vapor pressure method only used the variation of the vapor pressure of polar solvents as a function of the temperature. The last method with our model describes more accurately the acid base constants of solid surfaces and considers the effect of the temperature on the different thermodynamic properties of the solid substrates.

In conclusion, all used models and IGC methods gave more acid surface than basic for UiO-66 surface. The result obtained by this study confirmed other results obtained by many authors [47,48,55] on the acidic behavior of this MOF.

3.2.5. Specific statistical probability of interaction

In order to understand the thermodynamic behavior of the used MOF, the specific statistical probability of interaction \mathcal{P}_a^{sp} between the probes and the UiO-66 was studied. The following thermodynamic relation was used (Eqn. (24)):

$$\Delta S_a^{sp} = Rln \ \mathcal{P}_a^{sp}, \text{ where, } \mathcal{P}_a^{sp} = \frac{\Omega_f}{\Omega_i}$$
(24)

Where Ω_f and Ω_i are the respective numbers of the final and initial microstates of the system.

On Figure SI 1, we plotted the specific statistical probability \mathcal{P}_a^{sp} of interaction of the various polar molecules adsorbed on the solid particles by applying the different models and IGC methods. Results of Figure SI 1 showed larger values of the specific statistical

probability for THF, diethyl ether, toluene and acetonitrile whatever the used model or method. It seems that the specific interaction is smaller in the case of benzene, DCM and chloroform due to the strong acidic character of the MOF.

The obtained results allowed to classify the different probes by decreasing order of specific statistical probability of interaction as follows:

Tetrahydrofuran > *diethyl ether* > *acetonitrile* > *toluene*

> dichloromethane > chloroform > benzene

These interesting results appear similar to those obtained in previous study on silica particles [19] that proved also a near classification:

Tetrahydrofuran > diethyl ether > ethyl acetate > acetone

> benzene.

In both cases, it was proved a strong acid character of the solid particles due to the larger value of the specific probability of interaction with basic probes and weaker values with acid molecules.

4. Conclusion

Different models and methods of inverse gas chromatography at infinite dilution were used to determine the dispersive energy and the superficial acid base properties in Lewis terms of UiO-66. The specific thermodynamic properties of interaction of polar model molecules were determined by using different IGC methods and models.

Seven molecular models of the surface areas of organic molecules or ethylene group were used to determine the dispersive component γ_s^d of the surface energy of UiO-66 particle surface: Dorris-Gray, Kiselev, Van der Waals, Redlich-Kwong, geometric, cylindrical, spherical and our models. Based on the important effect of the temperature on the surface area of molecules adsorbed on solid substrates, this present study proved the Hamieh thermal model gave the more accurate values of the dispersive surface energy of UiO-66 surface as a function of the temperature. All other molecular models supposed that the surface area of the solvents is constant even when the temperature varies. This was contradicted by Hamieh works that gave the variations of the surface area a (T) of molecules as a function of the temperature.

The values of the thermodynamic variables such as the specific free enthalpy ΔG_a^{sp} , enthalpy and entropy of adsorption of polar molecules on the MOF surface, as well as the acid-base constants were determined by using the various molecules models and the other IGC methods respectively based on the vapor pressure, topological index or deformation polarizability concepts. The accurate results were obtained by using our model because it takes into account the thermal effect on the surface area of molecules. The enthalpic and entropic acid base constants were determined proving the strong acidity of UiO-66 which was also confirmed by the defected nature of the framework. These results showed an excellent separation between enthalpic and entropic acid base constants of the used UiO-66.

A perfect linear correlation between the polar enthalpy of adsorption $(-\Delta H_a^{pol.})$ and the relative polarity (R.P.) of polar probes was obtained. The specific statistical probability of interaction Ω_a^{sp} between polar molecules and UiO-66 particles was also determined. We proved that the specific statistical probability of interaction is the highest for tetrahydrofuran and diethyl ether compared to the other polar molecules.

Compliance with ethical standards

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Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Declaration of Competing Interest

Author declare that there is no conflict of interest.

Supplementary materials

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CRediT authorship contribution statement

Tayssir Hamieh: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing. **Ali-Ahmad:** Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Asmaa Jrad:** Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Thibault Roques-Carmes:** Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Supervision, Validation, Writing – original draft. **Mohamad Hmadeh:** Conceptualization, Formal analysis, Investigation, Supervision, Validation, Writing – original draft. **Joumana Toufaily:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Resources, Validation, Writing – original draft.

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