Synthesis and adsorption properties of ZIF-76 isomorphs

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Abstract :

ZIF-76, $\text{Zn}(\text{Im})_x(5\text{-ClbIm})_y$ (Im=imidazolate, 5-ClbIm=5-chlorobenzimidazolate), is, among the known ZIF structures, one of the few materials that combine a relatively large pore aperture with a large pore volume. Moreover, it is thermally stable up to 400 °C and can be stored under ambient atmosphere without undergoing a measurable degradation. ZIF-76, therefore, appears to be an interesting material for applications in adsorption and separation. The published synthesis protocol leads to very low yields and is, thus, not applicable on a larger scale [1]. In this work, we have succeeded in preparing ZIF-76 in suitable yields by changing the solvent and adding NaOH to the synthesis mixture. The addition of the base increases the yield and leads to smaller crystal sizes, by favoring nucleation over crystal growth. By using the same synthesis strategy, four new isomorphs of ZIF-76 were obtained, with different substituents on the benzimidazole ligand (Me, Br and NO_2) and different metal sources (Co and Zn). All the samples were tested in the adsorption and separation of CO_2/CH_4 in order to highlight the influence of the linker and of the metal center on the adsorption/separation properties.

KEYWORDS: MOF, ZIF, LTA, benzimidazole, carbon dioxide

1. INTRODUCTION

In the last years, the Metal-Organic Frameworks (MOFs) have received a lot of attention because of their large porosity, and structural diversity [2-4]. It has been shown that these compounds are good candidates for adsorption and catalytic processes [5-7]. The hybrid nature of the materials fuelled expectations that it will be possible to discover new behaviours in separation and catalysis. But the hybrid character of these compounds, which is at the

origin of their structural diversity, also implies that the thermal stability of this class of materials is limited. Only a minority of the known MOFs maintain their structure at temperatures above 300 °C.

The Zeolitic Imidazolate Frameworks (ZIFs) constitute a new subfamily of MOFs [1,8]. ZIFs are synthesised from imidazolate ligands coordinated to bivalent metal cations, usually Zn^{2+} or Co^{2+} . The M-Im-M angle (M = metal) is similar to the Si-O-Si angle observed in zeolites. The nature and the size of ligands (imidazolate and/or benzimidazolate) lead to ZIFs with zeolite topology, but with bigger pores than their inorganic analogues. The resulting structures are in general very stable: some of ZIFs are thermally stable up to 400 °C [1,9,10]. ZIF-76 is one of the most interesting structures published by the Yaghi's group. ZIF-76 is composed of zinc and a mixture of imidazole (Im) and 5-chlorobenzimidazole (5-ClbIm) as ligands. The resulting structure displays **LTA** topology, but with bigger pores than those of related non-hybrid zeolitic materials (Figure 1).

Application of the ZIF-76 synthesis protocol described by Yaghi's group using a larger amount of reactants gives a low yield. In order to obtain gram scale quantities of ZIF-76 for adsorption and separation measurements, we first had to optimize the synthesis procedure on a small scale. To improve the yield of the synthesis, we investigated several parameters such as the solvent mixture, the duration, the temperature and the addition of a base as a catalyst. An obvious role of a base in the synthesis of ZIF/MOF materials is the deprotonation of the organic ligand [11]. Bases are often employed in the room temperature synthesis of ZIFs/MOFs. The addition of a base was recognized as an opportunity to accelerate the synthesis, obtain high yields and crystals in the nanometer size range, which is more attractive for most applications [12]. However, several studies of the synthesis of MOF-5 show that materials prepared by the base route at room temperature possess a lower crystallinity and more defects compared to MOF-5 samples prepared under solvothermal conditions [13,14].

In this work, we investigate in detail the influence of adding a base to the synthesis mixture of ZIF materials. We highlight the link between basicity, duration of synthesis and morphology of the final product, using a solvothermal synthesis route. After optimization of the synthesis protocol, we describe the preparation of several isomorphs of the ZIF-76 (**LTA**) involving imidazole (Im) and derivatives of benzimidazole (5-XbIm where X is either a chloro, bromo, methyl or nitro group) as organic linker and zinc or cobalt as metal node. All these materials were then tested in the adsorption and separation of CO₂/CH₄ in order to evaluate the influence of the ligand and of the metal center on the interaction between adsorbate and framework [15-17].

2. EXPERIMENTAL SECTION

Reactants and solvents

All the reactants and solvents were used without further purification. The metal sources, cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98.0%) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99.0%) were purchased from Alfa Aesar. Organic compounds were supplied by Sigma Aldrich for imidazole (Im, 99.5%), 5-chlorobenzimidazole (5-ClbIm, 96.0%), 5-methylbenzimidazole (5-MebIm, 98%), by Maybridge for 5-bromobenzimidazole (5-BrbIm, 97.0%) or by Acros Organics for 5-nitrobenzimidazole (5-NibIm, 98.0%). The solvents, N,N-dimethylformamide (DMF, 99.0%) and N,N-diethylformamide (DEF, 99.0%) were provided by Alfa Aesar.

Synthesis

Initial synthesis conditions for the preparation of ZIF-76 are given in the literature by Yaghi's group: 2.25×10^{-5} mol imidazole (Im) and 1.13×10^{-5} mol 5-chlorobenzimidazole (5-ClbIm) were mixed together in 0.3 ml of DMF [1]. 1.12×10^{-5} mol of zinc nitrate was added

to this solution. A vial of 0.5 ml was loaded with the mixture and was heated in an oven at 65 °C for 5 days.

The above-mentioned literature protocol was optimized by modifying the reaction parameters : temperature, duration, concentration of the reactants, nature of solvent and concentration of the base. The different synthesis conditions are compiled in Table 1. As it will be explained in detail in the results section, the optimal synthesis conditions are those of entry 10 in Table 1: 17.25×10^{-4} mol imidazole (Im) and 8.66×10^{-4} mol 5-chlorobenzimidazole were mixed in 743×10^{-4} mol of DMF and 516×10^{-4} mol of DEF. 8.59×10^{-4} mol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to this solution. In the optimized protocol, 12.96×10^{-4} mol of a solution of NaOH (2.5 mol/L) were added in addition. All the syntheses were performed in 23 ml polypropylene containers, which were heated in an oven at 90 °C for 5 days. The yields were calculated by dividing the mass of desolvated (guest free) materials by the theoretical mass of product, calculated from the amount of metal precursor.

For the preparation of modified ZIF-76 materials, $\text{Zn}(\text{Im})(5\text{-MebIm})$, $\text{Zn}(\text{Im})(5\text{-BrbIm})$, $\text{Zn}(\text{Im})(5\text{-NibIm})$, $\text{Co}(\text{Im})(5\text{-ClbIm})$, the reaction conditions were the same as in the optimized protocol mentioned above. Either 5-ClbIm was substituted by one of the other ligands or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Characterization

XRD, SEM, NMR and thermal analysis

All samples were characterized by X-ray diffraction using a STOE STADI-P diffractometer equipped with a curved monochromator Ge(111) and a linear position sensitive detector in the 3-50° (2 θ) range on transmission $\text{CuK}\alpha 1$ ($\lambda=0.15406$ nm).

Morphology and size of the crystals were determined by scanning electron microscopy using a Philips XL 30 microscope equipped with a field electron gun.

Thermogravimetric measurements were performed on a Netzsch TG 209 F1 Iris apparatus with a heating rate of 5 °C/min from room temperature to 800 °C.

¹H NMR spectra were carried out on a Bruker 400 UltraShield™ by using tetramethylsilane as standard. Typically, around 3 mg of ZIF-76 materials are digested in a solution of DCl/D₂O 35 % wt dispersed in DMSO-d₆.

Adsorption and separation measurements

N₂ isotherms were recorded at 77 K on a Micromeritics ASAP 2420 apparatus, after degassing at 250 °C for 12 h. The specific surface area was deduced from the BET model, in the pressure range of $P/P^\circ = 0.002-0.05$. The pore volume was determined by the t-plot method. Isotherms of CO₂ and CH₄ were performed on a Rubotherm magnetic suspension balance. In a typical adsorption experiment, about 1 - 2 g of sample was placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and the sample is heated under high vacuum to 240 °C for 3 h. The CO₂ and CH₄ isotherms were then recorded at 30 °C. Helium was used to determine the volume of sample and sample holder, which is necessary to correct the measured apparent mass for buoyancy effects.

The separation of CO₂ and CH₄ was evaluated by breakthrough measurements. 1.5 - 2 g of powder sample were placed in a stainless steel column with an inner diameter of 7 mm and a length of 10 cm, which was placed in furnace. The sample was heated in a flow of 0.5 NL/h He to 240 °C and kept at this temperature for 3 h before cooling down to 30 °C. The breakthrough experiment was started by switching from He to an equimolar gas mixture of CO₂/CH₄. The breakthrough was followed by a mass spectrometer [18]. The adsorbed quantities Q_{ads} were calculated by a mass balance. The CO₂/CH₄ selectivity S was obtained from the equation $S = (Q_{\text{CO}_2}/p_{\text{CO}_2})/(Q_{\text{CH}_4}/p_{\text{CH}_4})$.

3. RESULTS

Optimization of the synthesis of ZIF-76

Table 1 summarizes the synthesis conditions which were tested in order to optimize the synthesis of ZIF-76. The XRD patterns of the products are shown in the supporting information files (S1). In order to investigate the influence of the nature of solvent on the crystallinity, two syntheses were carried out (samples 1 and 2): the first one using DMF as unique solvent and the second one using a mixture of DMF/DEF (1:1; V:V). The resulting XRD patterns are shown in Figure 2. Sample 2, which was synthesised in a mixture of DMF/DEF, appears more crystalline than sample 1, prepared in DMF. However, the yield remains low: 20.5 % and 14.5 % for samples 1 and 2 respectively.

In order to determine the roles of the temperature and of the concentration of reactants, the results for synthesis runs 2 to 5 have to be examined. The four syntheses were performed in a mixture of DMF/DEF (1:1; V:V). The reactant concentrations were either those used by Yaghi's group or twice higher. The temperature was either 70 or 90 °C. A comparison of runs 2 and 4 (respective yields: 14.5 % and 37.2 %) as well as runs 3 and 5 (respective yields: 0.0 % and 27.5 %), indicates that the best yields are obtained at the higher temperature (90 °C) and at the lower reactant concentration. A high dilution of the reactants is, however, undesirable for syntheses at medium/large scale because it increases the required reactor volume.

In order to increase the yield at high reactant concentration, we investigated the influence of increasing the duration of the synthesis and of adding a base to the synthesis mixture. Two series of four syntheses (runs 5 to 8 and runs 9 to 12) were prepared with the same reactant concentration (twice higher than proposed by Yaghi's group) at 90 °C, but two different durations (5 or 30 d). The basicity of the solution was modulated by adding a

solution of NaOH (2.5 mol/L). The amount of base, expressed as the ratio B/L (base/ligand), i.e. the number of moles of NaOH divided by the total number of moles of imidazole ligands (Im+ClbIm), was fixed at 0, 0.5, 1 and 2. The ratios B/L = 1 and 2 led to a product with a low crystallinity (B/L = 1) or a product that was not pure (B/L = 2), see Figure 3. It is, therefore, preferable to limit the addition of NaOH to a value of B/L = 0.5.

The yield of the synthesis without NaOH (synthesis 5 and 9) increases with time from 27.5% (5 days) to 73% (30 days). The yield of the analogue synthesis with a ratio of B/L = 0.5 increases from 50.6 % after 5 days to 71.9 % after 30 days. The addition of a base increases the yield of the synthesis by a factor of 1.8 after 5 days. The positive effect of the base on the yield disappears at longer synthesis duration (30 d).

To be sure that NaOH does not recrystallize in the pore of the ZIF-76, the products of syntheses 9 and 10 were analysed by N₂ adsorption measurements. The isotherms of the two materials are very close. The pore volume of compounds synthesized with and without addition of NaOH is 0.59 and 0.56 mL/g, respectively. Therefore, the addition of NaOH does not influence the porosity of the materials.

The morphologies of ZIF-76 materials were investigated by SEM (see Figure 4; more SEM pictures are shown in the supporting information S2). The SEM pictures confirmed that the addition of a large quantity of base (B/L = 1 and 2) induced the formation of impurities (see the zooms for samples 11 and 12 in Figure 4 c and d). Table 2 reports the average values of the crystal size observed after 5 and 30 days (full crystal size distributions are given in the supporting information). The crystals synthesised without any addition of NaOH (B/L = 0) are much bigger than the others. Moreover, we observe a strong crystal growth between 5 and 30 days in the absence of NaOH, but no clear evolution of the crystal size with time when NaOH is present.

Synthesis and characterization of new isomorphs of ZIF-76

A main characteristic of hybrid materials is the possibility to tune the composition of materials by changing the metal source or the organic functional group without any modification of the topology of the framework. We used our optimized protocol of synthesis in order to obtain several isomorphs of ZIF-76, using two different metal sources (zinc or cobalt) and three new benzimidazole ligands containing a bromo, methyl or nitro group in position 5. The materials were analysed by XRD and compared to the experimental and theoretical patterns of ZIF-76 (see Figure 5). The XRD patterns of the isomorphous structures are very close to the original pattern of ZIF-76. XRD reveals that all the compounds crystallize in the same space group with similar unit cell parameters.

According to the thermal analysis shown in Figure 6, the isomorphs are stable to 400 °C under helium atmosphere, except for ZIF-76 synthesised with 5-nitrobenzimidazole. This high thermal stability allows a direct activation of the compound by heating to 250 °C for 6 hours without any prior solvent exchange. The ZIF-76 synthesised with 5-nitrobenzimidazole is air sensitive. It loses crystallinity already at a temperature of 90 °C. Due to the poor thermal stability of this material, the activation procedure is particular. The as made compound was immediately immersed in methanol after filtration and heated at 65°C for two weeks before activation at 90°C.

The ratio between imidazole and the substituted benzimidazole ligand was obtained by NMR measurements (Figure 7 and Table 3) for each material. In all cases, the Im/XbIm ratio is lower than the value of 3 that was reported by Yaghi's group. Curiously, the Im/XbIm ratio decreases when the size of the organic functional group increases. Steric effects cannot explain this trend. In spite of the beneficial influence of DEF in the synthesis of ZIF materials, NMR indicates that DEF is not present in the pores of the ZIF-76 isomorphs, while DMF is, with the exception of ZIF-76-NibIm. The absence of DMF in the porosity of the ZIF-76

synthesized with 5-nitrobenzimidazole confirms that the solvent exchange by methanol was very efficient.

The compounds were analyzed by nitrogen adsorption in order to evaluate the porosity of all isomorphs. All nitrogen isotherms are of type I. The specific surface areas and pore volumes are summarized in Table 4. Except for the isomorph based on 5-NibIm, all materials possess a specific surface area above $1000 \text{ m}^2\cdot\text{g}^{-1}$. We assume that the low porosity of the $\text{Zn}(\text{Im})_{1.05}(5\text{-NibIm})_{0.95}$ is due to a partial destruction of the framework because contact of the sample with moisture could not be entirely avoided. It is, however, possible that a different orientation of the nitrobenzimidazole ligand also contributes to the loss of pore volume.

Adsorption and separation results of CO_2 and CH_4

The five isomorphous materials were tested in the adsorption and separation of CO_2/CH_4 . The adsorption isotherms of CO_2 and CH_4 at 303 K are shown in Figure 8 (a zoom on the low pressure part of the isotherms is shown in the supporting information S3). The high pressure part of the isotherm is governed by the available pore volume, while the initial slope depends on the specific surface area and the affinity between adsorbate and adsorbent [19]. All the isomorphs have a lower CO_2 uptake than the "parent" $\text{Zn}(\text{Im})_{1.25}(5\text{-ClbIm})_{0.75}$ material. Since pore volume, surface and affinity change at the same time, it is not straightforward to identify a clear trend within the group of substituents chloro, bromo and methyl. We can, however, perceive in Figure 8 that the material synthesized with 5-NibIm has a higher initial slope than expected from its surface area. The high polarity of the NO_2 functional group induces a strong interaction between the ZIF-76 network and CO_2 molecules and, therefore, leads to an isotherm that is more concave.

The adsorption of CH₄, on the other hand, is only governed by non specific interactions. Therefore, the NO₂ functional group does not have an apparent influence on the concavity of the CH₄ isotherm (as compared to chloro, bromo or methyl).

It is possible to estimate the co-adsorption selectivity of a CO₂/CH₄ mixture from the Henry constants (the initial slopes) of the respective single component isotherms. These values are given in Table 4. A direct measurement of co-adsorption selectivity by, for example, a breakthrough experiment is, however, more reliable. Figure 9 shows, as an example, the breakthrough curve of an equimolar CO₂/CH₄ mixture over the parent Zn(Im)_{1.25}(5-ClbIm)_{0.75}. The curve of CH₄ exhibits a characteristic "roll-up", due to replacement of adsorbed CH₄ by CO₂, when the adsorption front of CO₂ advances through the column. The CO₂/CH₄ selectivities obtained from the breakthrough experiments are summarized in the Table 4. They agree fairly well with the ratios of the Henry constants. The substitution of chloro by bromo or methyl in the benzimidazole ligand or the replacement of Zn by Co as the metal node does not have a measurable impact on the separation selectivity. Only the nitrobenzimidazole ligand leads to a significantly higher selectivity than the parent sample.

4. DISCUSSION

The role of solvent and base in the synthesis of ZIF-76

In MOF/ZIF synthesis, it is commonly admitted that the solvent is not only to dissolve the reactants; it can also serve as a structure directing agent [11]. In the synthesis of the ZIF-76, the addition of a second solvent (DEF) increases the crystallinity of the final material. Surprisingly, NMR analyses show that hardly any DEF is present in the porosity of the materials, which excludes a structure directing role. We suspect that the role of DEF is to slow down the kinetics of crystallization (the yield in DEF mixtures is lower), maybe because

it solubilizes the reactants less well, thereby improving the quality of the crystals that are formed.

Many synthesis protocols of MOF/ZIF materials use a base to promote the reaction (usually at room temperature). In our case, the main role of the base is to deprotonate the imidazole ligands. This favors the bond formation between metal cation and imidazolate and thereby favors nucleation. As a consequence, the imidazole nutrients are consumed more quickly, the yield at short synthesis times increases and small crystals are obtained. The addition of a controlled quantity of NaOH allows to double the reactant concentration and to obtain a satisfactory yield in five days. Moreover, this optimized protocol could be scaled up to a volume of 1 L without any loss of yield or crystallinity and could be extended to the synthesis of several isomorphs of ZIF-76.

Stability of the ZIF-76 isomorphs

Except for the material synthesized using 5-NibIm, all the isomorphs display a high porosity and good thermal stability. The high thermal stability allows to easily activate the materials without prior solvent exchange. In the case of the ZIF-76-NibIm, a solvent exchange of the DMF by MeOH allows to completely remove DMF of the porosity and makes it possible to activate material in spite of its low thermal stability. The low thermal stability of the ZIF-76 with 5-NibIm could be explained by the pK_a of the ligand. The higher the electrophilicity of the organic group is, the lower is the pK_a of the ligand and, consequently, the metal-imidazolate bond becomes weaker. 5-NibIm exhibits the lowest pK_a of the ligands used in this study (pK_a (5-NibIm) = 4.17, pK_a (5-ClbIm) = 4.86, pK_a (5-MebIm) = 5.81) {Brown, 2006 128 /id;Brown, 2006 129 /id}.

Discussion of the adsorption behavior of ZIF-76 isomorphs

Organic ligands with highly polar functional groups considerably increase the interactions between framework and CO₂ molecules but not with CH₄. ZIF-76 materials

prepared with chloro, methyl and bromo groups show a similar selectivity of 2.5 ± 0.2 . This value is characteristic of nonpolar adsorbents, like activated carbons or a dealuminated zeolite Y {Wilson, 1983 125 /id; Ritter, 1987 126 /id; Buss, 1998 127 /id}. Only the ZIF-76 material synthesized with 5-NibIm is more selective for the CO_2/CH_4 separation. The high polarity induced by the NO_2 functional group specifically increases the interaction between the CO_2 molecules and the ZIF-76 framework, but does not affect the adsorption of CH_4 . As a consequence, the selectivity of this isomorph is nearly 3 times higher than for the other ZIF-76 samples. Our results are in line with data published by Yaghi et al. who tested several isomorphs of ZIF materials with GME topology using benzimidazole ligands substituted by chloro, methyl, bromo, nitro or hydrogen moieties [16]. The results show that the addition of chloro, methyl or bromo functional groups does not influence the CO_2/CH_4 selectivity; only the nitro group could increase the CO_2/CH_4 selectivity. However, we mentioned above that the use of the nitro group decreases the pKa of the benzimidazole ligand and decreases the stability of the material. An amino-substituted benzimidazole could be an attractive alternative because it combines a high polarity with a high pKa of the ligand (pKa of 5-aminobenzimidazole = 6.11), and, therefore, according to our theory, a higher stability of the ZIF framework [15,20]. The positive effect of amino-functionalization of MIL-53(Al) type material on the CO_2/CH_4 separation was already shown by Couck et al. [25]. Our future work will aim to synthesize the ZIF-76 isomorph built from 5-aminobenzimidazole and to evaluate its separation properties.

Our results further show that choice of the transition metal center (Zn^{2+} or Co^{2+}) does not change the separation selectivity of the material. The metal center is too distant from the adsorbate to have an influence on the CO_2 adsorption. This result was already predicted by Monte Carlo simulations [26].

5. CONCLUSIONS

In this paper, we present an optimized procedure to obtain ZIF-76 and four new isomorphs of ZIF-76 in high yield and a short synthesis time. The key is the addition of the base NaOH to the mixture, which increases the yield and accelerates the crystal formation. The base promotes the nucleation phase and inhibits crystal growth. Crystals obtained by the above-described protocol are 50 to 200 times smaller than those obtained without the addition of any base.

In the separation of CO₂/CH₄, only the isomorph synthesized with the 5-nitrobenzimidazole presents an improved selectivity. This is attributed to its strong polarity. Unfortunately, this is accompanied by a weak stability of the material, presumably caused by the low pK_a of 5-nitrobenzimidazole. A better compromise between selectivity and stability could probably be achieved by using imidazole ligands with polar, but more basic substituents, for example 5-aminobenzimidazole. Finally, adsorption and separation tests of CO₂ and CH₄ show that the metal source (cobalt or zinc) does not have a significant influence on the adsorption properties.

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Figure Captions

Figure 1 : representation of the structure of ZIF-76 with LTA topology

Figure 2 : XRD patterns of the ZIF-76 materials synthesized in DMF (sample 1, blue), DMF/DEF (sample 2, red) and simulated (black)

Figure 3 : XRD patterns of ZIF-76 materials synthesized with different quantities of base.

Figure 4 : SEM pictures of ZIF-76 synthesised with different B/L ratios : a/ 0, b / 0.5, c/ 1 and d/ 2.

Figure 5 : XRD patterns of new isomorphs of ZIF-76 and the original structure of ZIF-76 compared with the simulated pattern

Figure 6 : TGA of ZIF-76 isomorphs

Figure 7 : ^1H NMR spectra of ZIF-76 isomorphs $\text{M}(\text{Im})_x(\text{XbIm})_y$ after digestion

Figure 8 : a) CO_2 and b) CH_4 isotherms of adsorption of ZIF-76 isomorphs

Figure 9 : Breakthrough curves of CO_2 and CH_4 on ZIF-76 ($\text{Zn}(\text{Im})_{1.25}(\text{5-ClbIm})_{0.75}$) at 30° and 1 bar.

Figures

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Figure 2 : XRD patterns of the ZIF-76 materials synthesized in DMF (sample 1, blue), DMF/DEF (sample 2, red) and simulated (black)

Figure 3 : XRD patterns of ZIF-76 materials synthesized with different quantities of base.

Figure 4 : SEM pictures of ZIF-76 synthesised with different B/L ratios : a/ 0, b / 0.5, c/ 1 and d/ 2.

Figure 5 : XRD patterns of new isomorphs of ZIF-76 and the original structure of ZIF-76 compared with the simulated pattern

Figure 6 : TGA of ZIF-76 isomorphs

Figure 7 : ^1H NMR spectra of ZIF-76 isomorphs $\text{M}(\text{Im})_x(\text{XbIM})_y$ after digestion

Figure 8 : a) CO₂ and b) CH₄ isotherms of adsorption of ZIF-76 isomorphs: Zn(Im)_{1.25}(5-ClbIm)_{0.75} full diamonds; Co(Im)_{1.3}(5-ClbIm)_{0.7} open diamonds; Zn(Im)_{1.2}(5-BrbIm)_{0.8} circles; Zn(Im)_{1.1}(5-MebIm)_{0.9} squares; Zn(Im)_{1.05}(5-NibIm)_{0.95} triangles.

Figure 9 : Breakthrough curves of CO₂ and CH₄ on ZIF-76 (Zn(Im)_{1.25}(5-ClbIm)_{0.75}) at 30° and 1 bar.

TABLES

Table 1. Summary of the different synthesis conditions of ZIF-76 applied in this work

Run	Temperature (°C)	Duration (days)	n Im ^a (10 ⁻⁴ moles)	n 5-ClbIm ^b (10 ⁻⁴ moles)	n Zn(NO ₃) ₂ (10 ⁻⁴ moles)	n DMF (10 ⁻⁴ moles)	n DEF (10 ⁻⁴ moles)	n NaOH (10 ⁻⁴ moles)
1	70	5	8.63	4.33	4.29	1485	0	0
2	70	5	8.63	4.33	4.29	743	516	0
3	70	5	17.25	8.66	8.59	743	516	0
4	90	5	8.63	4.33	4.29	743	516	0
5	90	5	17.25	8.66	8.59	743	516	0
6	90	5	17.25	8.66	8.59	743	516	12.96
7	90	5	17.25	8.66	8.59	743	516	25.91
8	90	5	17.25	8.66	8.59	743	516	51.83
9	90	30	17.25	8.66	8.59	743	516	0
10	90	30	17.25	8.66	8.59	743	516	12.96
11	90	30	17.25	8.66	8.59	743	516	25.91
12	90	30	17.25	8.66	8.59	743	516	51.83

^a Im =imidazole, b ClbIM = chlorobenzimidazole

Table 2. Crystal size as function of the quantity of NaOH used in the synthesis.

Run	Synthesis time (days)	$\frac{n_{\text{NaOH}}}{n_{\text{Imidazoles}}}$	Average crystal size (μm)
5	5	0	57.0
6	5	0.5	1.2
9	30	0	232.0
10	30	0.5	0.8

Table 3. Composition of the ZIF-76 isomorphs deduced from NMR analysis

Metal source	Ligand 1	Ligand 2	Formula of the materials	Im/XbIm
Zn(NO ₃) ₂ .6H ₂ O	Im	5-ClbIm	Zn(Im) _{1.25} (5-ClbIM) _{0.75} (DMF) _{1.5} (DEF) _{0.02}	1.7
Co(NO ₃) ₂ .6H ₂ O	Im	5-ClbIm	Co(Im) _{1.3} (5-ClbIM) _{0.7} (DMF) _{1.4}	1.8
Zn(NO ₃) ₂ .6H ₂ O	Im	5-BrbIm	Zn(Im) _{1.2} (5-BrbIM) _{0.8} (DMF) _{0.9} (DEF) _{0.03}	1.4
Zn(NO ₃) ₂ .6H ₂ O	Im	5-MebIm	Zn(Im) _{1.1} (5-MebIM) _{0.9} (DMF) _{0.54} (DEF) _{0.11}	1.2
Zn(NO ₃) ₂ .6H ₂ O	Im	5-NibIm	Zn(Im) _{1.05} (5-NibIM) _{0.95}	1.1

Table 4. Adsorption properties of the ZIF-76 isomorphs: BET surface area, micropore volume, Henry constants of CO₂ and CH₄ at 303 K, ratio of the Henry constants and CO₂/CH₄ selectivity obtained from breakthrough curves.

Materials	S_{BET} $\text{m}^2\cdot\text{g}^{-1}$	V_{μ} $\text{cm}^3\cdot\text{g}^{-1}$	$K_{\text{Henry CO}_2}$ $\text{mmol}\cdot\text{g}^{-1}\cdot\text{bar}^{-1}$	$K_{\text{Henry CH}_4}$ $\text{mmol}\cdot\text{g}^{-1}\cdot\text{bar}^{-1}$	$K_{\text{Henry CO}_2} / K_{\text{Henry CH}_4}$	Selectivity $\text{CO}_2 / \text{CH}_4$
$\text{Zn}(\text{Im})_{1.25}(5\text{-ClbIM})_{0.75}$	1561	0.60	1.52	0.75	2.0	2.3
$\text{Co}(\text{Im})_{1.3}(5\text{-ClbIM})_{0.7}$	1097	0.42	1.13	0.52	2.2	2.4
$\text{Zn}(\text{Im})_{1.2}(5\text{-BrbIM})_{0.8}$	1050	0.40	0.97	0.69	1.4	2.7
$\text{Zn}(\text{Im})_{1.1}(5\text{-MebIM})_{0.9}$	1536	0.58	1.18	0.67	1.8	2.4
$\text{Zn}(\text{Im})_{1.05}(5\text{-NibIM})_{0.95}$	850	0.32	0.98	0.18	5.5	6.5