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N/S-Heterocyclic Contaminant Removal from Fuels by the Mesoporous Metal–Organic Framework MIL-100: The Role of the Metal Ion

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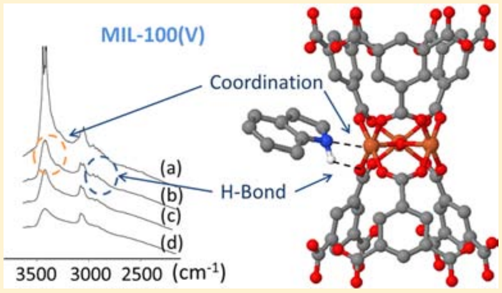
Ⓢ *Supporting Information*



ABSTRACT: The influence of the metal ion in the mesoporous metal trimesate MIL-100(Al^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}) on the adsorptive removal of N/S-heterocyclic molecules from fuels has been investigated by combining isotherms for adsorption from a model fuel solution with microcalorimetric and IR spectroscopic characterizations. The results show a clear influence of the different metals (Al, Fe, Cr, V) on the affinity for the heterocyclic compounds, on the integral adsorption enthalpies, and on the uptake capacities. Among several factors, the availability of coordinatively unsaturated sites and the presence of basic sites next to the coordinative vacancies are important factors contributing to the observed affinity differences for N-heterocyclic compounds. These trends were deduced from IR spectroscopic observation of adsorbed indole molecules, which can be chemisorbed coordinatively or by formation of hydrogen bonded species. On the basis of our results we are able to propose an optimized adsorbent for the deep and selective removal of nitrogen contaminants out of fuel feeds, namely MIL-100(V).

1. INTRODUCTION

The removal of sulfur and nitrogen heterocyclic compounds from fuels is a topical challenge, given the increasing restrictions on the sulfur and nitrogen contents of fuels from either fossil or renewable origin.[1−3] The removal of thiophenic compounds from fuels is important to prevent the formation of acid rain, as the combustion of sulfur compounds results in SO_x. Additionally, the combustion of nitrogen compounds leads to the formation of NO_x species. Both groups of exhaust compounds are responsible for smog and global warming.[4] From a production point of view, the removal of S-compounds from petroleum requires an effective hydrodesulphurization (HDS) technology, which will also prevent serious downstream corrosion issues caused by derived N/S-oxyacids.[5]

In the EU, the sulfur concentration has gradually been legally restricted down to 10 mg S/kg of gasoline or diesel.[6] Ideally, HDS is capable of meeting these requirements by removing the sulfur compounds via hydrogenation over a solid Co−Mo or Ni−Mo catalyst.[7] However, the presence of nitrogen compounds in fuel feeds can prevent the catalyst to efficiently hydrogenate the S-compounds to H_2S and hydrocarbons, by irreversible poisoning of the active sites.[8,9] As a result, the selective removal of the nitrogen contaminants seems a prerequisite for meeting the imposed regulations on sulfur contents in fuels.

Several adsorbents have been proposed over the years for either N- or S-compounds, including Cu(I)/Ag(I) exchanged zeolites,[10,11] metal oxides such as Al_2O_3,[12] supported metals like Ni/SiO_2−Al_2O_3,[13] active carbon,[12,13] ion-exchange resins,[14] and metal−organic frameworks (MOFs).[1,2,15,16] The latter are highly porous hybrid crystalline solids, and some MOFs have shown especially promising results as selective adsorbents for fuel contaminants.[2,16] Maes *et al.*[1] reported a high adsorption selectivity for nitrogen contaminants on the mesoporous iron(III) trimesate MIL-100(Fe) and the chromium(III)

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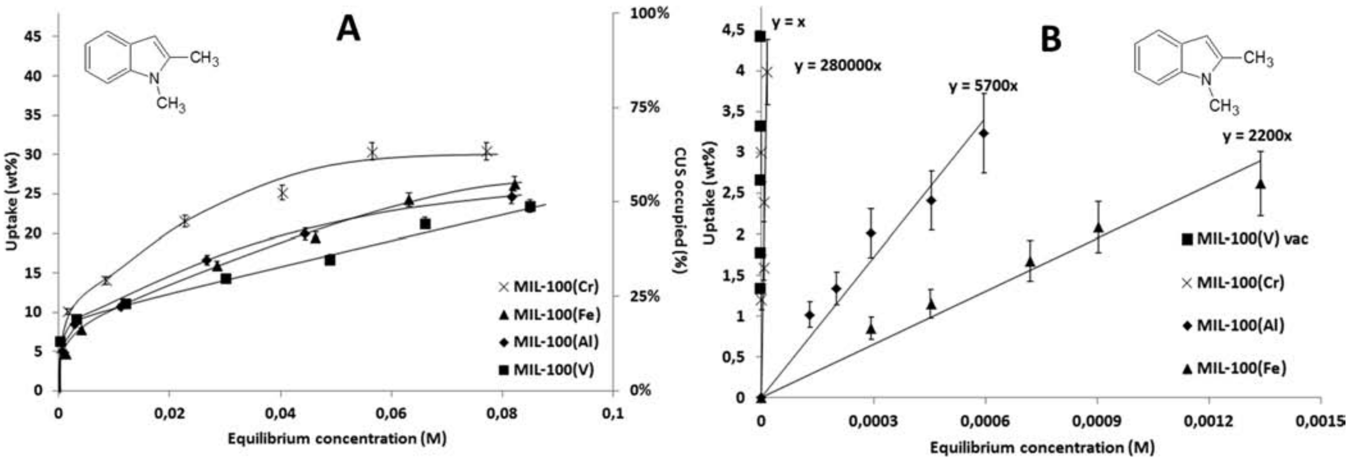

Figure 1. Isotherms for single-compound adsorption of 1,2-dimethylindole from heptane on MIL-100(Cr) (×), MIL-100(Fe) (▲), MIL-100(Al) (◆), and MIL-100(V) (■) at 298 K: (A) full concentration range, (B) low concentration domain.

terephthalate MIL-101(Cr). Both MOFs contain accessible Lewis acid metal sites, which may play a crucial role in the selective adsorption through coordination with the heteroatom. In particular, MIL-100(Fe) seems to be an excellent candidate as a selective adsorbent, reaching an uptake of 16 mg N/g MOF.[1] MIL-100 solids exhibit a cubic-zeotype mesoporous structure, based on trimers of metal(III) octahedra (Fe,[17] Al,[18] Cr,[19] V,[20] Sc,[21] Tb[22]) and trimesate anions, with a very important porosity (S_{BET} up to 2400 m^2/g, $V_{\mathrm{p}} \sim 1.2$ cm^3 /g) associated with two types of mesocages (2.5 and 2.9 nm) accessible through microporous windows (~0.47 × 0.55 nm and 0.86 nm). Considering these results and in view of the existence of isostructural MIL-100 materials, one could rationally expect that by modifying the nature of the metal (e.g., Fe, Cr, Al, or V), the interaction between S- and N-heterocycles and the open metal sites of MIL-100 will change. It has already been shown that the adsorption affinity and capacity of porous materials can be greatly altered by using different metals.[1,2,22−25] This was illustrated by Wade et al. for CO_2 adsorption on isostructural M_3BTC_2 MOFs (M = Cr, Cu, Mo, Ru, Ni);[23] they recorded very large adsorption enthalpy differences of >10 kJ mol^{-1} between the Ni and Mo materials. Bearing this example in mind, the present paper studies in detail the influence of the metal on the N/S-heterocycles separation, through a detailed study of the nature of the interaction between S- and particularly N-heterocycles and open coordination sites in MIL-100(Fe, Cr, Al, V) type MOFs.

2. EXPERIMENTAL SECTION

Materials Preparation. MIL-100(Fe) was prepared according to a modified literature procedure[17] by mixing metallic iron (8.0 mmol, 0.45 g), 1,3,5-benzenetricarboxylic acid or trimesic acid (5.4 mmol, 1.13 g), HF (16 mmol, 3.2 mL of a 5 M solution), and HNO_3 (4.8 mmol, 4.8 mL of a 1 M solution) in deionized water (40 mL) and heating the mixture at 433 K for 24 h in a Teflon-lined autoclave. The light-orange solid product was recovered by filtration and washed with deionized water. In order to decrease the amount of residual trimesic acid, a treatment in hot deionized water was applied, with 1 g of MIL-100(Fe) in 350 mL of water at 353 K, followed by extraction in hot ethanol at 333 K for 3 h.

MIL-100(Al) was synthesized according to the literature procedure[18] by mixing $Al(NO_3)_3 \cdot 9H_2O$ (4.66 mmol, 1.74 g), trimethyl 1,3,5-trimesate (3.11 mmol, 0.78 g), and HNO_3 4 M (6.2 mmol, 1.55 mL) in deionized water (25.2 mL) and heating the mixture in a 85 mL Teflon-lined Parr autoclave for 12 h in an oven at 433 K. The initial pH was adjusted to 0.57 using HNO_3; the final pH measured was 1.77. The resulting yellowish powdered sample was collected by filtration, abundantly washed with water, and dried at room temperature.

MIL-100(Cr) was synthesized according to the procedure of Férey *et al.*[19] Metallic chromium (10 mmol, 0.52 g) was dispersed in an aqueous solution of 5 M HF (20 mmol, 4 mL). After addition of trimesic acid (6.7 mmol, 1.41 g) and H_2O (48 mL), the mixture was heated in a hydrothermal bomb at 493 K for 11 h, kept at this temperature during 48 h, and then cooled in 22 h to room temperature. The resulting green powder was washed with deionized water and acetone, and dried in air.

MIL-100(V) was synthesized according to the literature procedure.[20] The vanadium trimesate was hydrothermally synthesized under autogenous pressure from a mixture of VCl_3 (4 mmol, 0.628 g) and trimethyl 1,3,5-trimesate (2.4 mmol, 0.51 g) in 5 mL of H_2O. The synthesis was carried out in a Teflon-lined 23 mL Parr autoclave at 493 K for 72 h. The product was retained by filtration as a greenish powder and washed with hot ethanol in order to remove the unreacted ligand (either in its esterified or hydrolyzed form). Finally it was washed with deionized water and dried at 373 K under air.

N_2 adsorption−desorption isotherms were recorded at 77 K after dehydration under vacuum at 423 K for 12 h using a Micromeritics Tristar 3000 instrument. The specific surface areas were evaluated using the Brunauer−Emmett−Teller (BET) method in the P/P_0 range 0.05−0.2. The BET surface areas for MIL-100(Al), MIL-100(Cr), MIL-100(Fe), and MIL-100(V)vac were 2175, 2030, 2230, and 2133 m^2/g, respectively.

Batch Adsorption. Liquid phase batch adsorption experiments were carried out at 298 K in 1.8 mL glass vials filled with 0.025 g of adsorbent and 1.8 mL of a heptane solution contaminated with either nitrogen or sulfur compounds following a literature procedure.[1] Uptakes were directly calculated from gas chromatography (GC) output data. In a standard procedure, the materials MIL-100(Al, Cr, Fe, V) were pretreated at 423 K in an oven overnight under atmospheric conditions; the material MIL-100(V) was also pretreated under vacuum (<10^{-5} Pa) at 423 K for 12 h, and is then denoted as MIL-100(V)vac. Adsorption isotherms were constructed by plotting the uptake, in weight %, versus the residual concentration in solution. The initial slopes of the isotherms were determined by fitting a straight line through the first data points including the origin. These data points were obtained using diluted mixtures containing less than 0.004 M of heterocycles.

Microcalorimetry. In each experiment, 0.025 g of sample was placed in a stainless steel ampule and activated under air or vacuum for 12 h. A thermal treatment at 423 K was used for MIL-100(Al), MIL-100(Cr), MIL-100(Fe) in air while for MIL-100(V) the treatment took place under vacuum. After activation, 800 μL of heptane was added through a septum, and the ampule with the stirred suspension was loaded into the TAM III calorimeter (TA Instruments). An ampule with only the solvent was used as a reference. In the isothermal titration calorimetry (ITC), the liquid titrant (adsorbate) is added to the reaction ampule using a motor driven syringe pump via a fine cannula, and the heat flow is measured versus time until equilibrium is reached for each step. A total volume of 200 μL was added in steps of 10 μL. The integrated heats correspond to the adsorption and dilution phenomena ($Q_{measured} = Q_{adsorption} + Q_{dilution}$). In order to subtract the heat change due to dilution, an experiment without the sample is performed using the same conditions. For each injection, the corresponding equilibrium concentration was determined from adsorption isotherms determined on samples activated in identical conditions.

IR Spectroscopy. MIL-100 samples were pretreated at 423 K at atmospheric pressure or under vacuum (for MIL-100(V)vac), and were loaded with indole in heptane. After elimination of most the heptane by heating at 323 K, the sample was pressed as a pellet and introduced into the IR cell. The samples were outgassed under secondary vacuum at increasing temperatures. Transmission IR spectra were recorded, at 4 cm^{-1} resolution, on a Nicolet Nexus spectrometer equipped with an extended KBr beam splitting device and a MCT cryo-detector.

3. RESULTS AND DISCUSSION

Adsorption Isotherms. First, adsorption isotherms were recorded for thiophene (THP), indole (IND), and 1,2-dimethylindole (1,2-DMI) out of heptane for all MIL-100 materials (Figures 1, S1, and S2), pretreated under air. These are representative compounds for the heterocycles typically present in fuels. To evaluate the uptake capacity of the materials for the respective adsorbates, the number of molecules adsorbed per unit cell (UC) at the highest tested concentration is presented in Table 1. For 1,2-dimethylindole and thiophene, the highest tested concentrations correspond to a plateau in the adsorption isotherm, at which saturation can be assumed (Figures 1 and S2). The latter is not the case for indole, as we are limited by its maximum solubility in heptane (15 g/L). Nevertheless, clear differences in indole uptake can be seen for the MIL-100 MOFs based on different metals. The uptake on MIL-100(Fe) is about twice as high as that on MIL-100(V) (670 vs 370 mol/UC). Considering the chemical formula ($[M_3O(H_2O)_2X(C_6H_3(CO_2)_3)_2]$, M = Al^{3+}, Cr^{3+}, Fe^{3+},V^{3+}; X = F, OH, Cl, NO_3), removal of two water molecules generates two coordinatively unsaturated sites (CUS) per M_3O metal trimer.[17,26,27] Each UC contains 272 metal trimers, with theoretically 544 CUS/UC. Comparing this value with the numbers of adsorbed indole molecules, only MIL-100(V) would not have all CUS occupied at high loading. In MIL-100(Fe) and MIL-100(Al), the number of adsorbed molecules is significantly larger than the number of available open metal sites, indicating that, besides the adsorption on CUS, which are obvious adsorption sites, there must also be adsorption at secondary sites. Even if the latter have likely a lower indole affinity than the CUS, the poor solvation of indole by heptane is a strong driving force for the indole molecules to leave the solvent and be adsorbed in the MIL-100 cages, where they can experience various other interactions, like van der Waals interactions. While the capacity differences between the Fe, Cr, and Al MOFs are not significant, a much smaller number of molecules is present in MIL-100(V) at the highest concentration offered, with only 69% of the available CUS occupied (Table 1).

Table 1. Number of Molecules per Unit Cell at Saturation in the Adsorption Isotherms with All MOFs Pretreated at 423 K under 1 atm of Air

mol/UC (% of CUS)[a]	IND	1,2-DMI	THP
MIL-100(Al)	670 (124%)	240 (45%)	160 (29%)
MIL-100(Cr)	560 (103%)	340 (63%)	140 (25%)
MIL-100(Fe)	670 (124%)	300 (56%)	180 (32%)
MIL-100(V)	370 (69%)	290 (54%)	80 (15%)

[a] Fraction of CUS occupied at saturation.

This result could be related to the pretreatment under air, resulting in the presence of residual free trimesic acid occupying some of the pore volume, as previously reported,[20] which lowers the indole uptake capacity.

With the slightly larger adsorbate 1,2-dimethylindole, the capacity differences between the metals are less pronounced. MIL-100(Cr) has the highest number of molecules per UC and a corresponding CUS occupation of 63%. The adsorption isotherms (Figure 1) show that the uptake has an inflection point around 10 wt % uptake, corresponding to ~25% of the CUS; after this the uptake only gradually increases. This indicates that not all CUS are equally available for adsorbates. While the initial affinity of the metal-oxoclusters for 1,2-dimethylindole seems very high, subsequent adsorption of more 1,2-dimethylindole molecules on the trimeric clusters is considerably more difficult. One could suggest that the adsorption of this bulky adsorbate on a CUS decreases the accessibility of neighboring CUS, leading to a decreased uptake. For all materials, the results are in reasonable agreement with an occupation at saturation of around 50% of the CUS, which indicates that an average occupation of one CUS per trimer leads to a decreased availability of the other CUS.

The preference of MIL-100(Al, Cr, Fe, V) to adsorb nitrogen compounds over sulfur compounds is already evidenced by the number of molecules adsorbed per unit cell in Table 1. Although the molecular size of thiophene is much smaller than that of indole, only 130−180 molecules are adsorbed per UC at saturation, corresponding to less than $^1/_3$ of the CUS. These results are in accordance with Pearson's hard and soft acids and bases (HSAB) concept.[28] Nitrogen compounds like indole and 1,2-dimethylindole are intermediate to hard bases, while thiophene is a soft base. According to the HSAB-concept, the soft base thiophene does not interact well with the hard Lewis acids present in MIL-100, like Al^{3+}, Cr^{3+}, Fe^{3+}, and V^{3+}. Hence the HSAB-concept explains the low average affinity of the CUS for thiophene.

Not only is the capacity of an adsorbent important, but also a high affinity at low concentrations is essential for successful removal of contaminants in purification processes.[7] The affinity of the MIL-100 adsorbents was compared by looking at the initial slopes of the isotherms (Figure 1, S3, and S4 and Table 2). MIL-100(V) exhibits a very high affinity for the nitrogen compounds, while MIL-100(Al) has weaker affinity. The initial slope for indole uptake on MIL-100(V) indicates a 35% higher affinity than for MIL-100(Cr), a three times higher affinity than for MIL-100(Fe) and even a 14 times higher affinity than for MIL-100(Al). Even though the heteroatom may be less accessible because of steric hindrance in 1,2-dimethylindole than in indole, MIL-100(V), MIL-100(Al), and MIL-100(Cr) have a higher affinity for 1,2-dimethylindole than for indole. This observation seems to be in agreement with additional weak interactions, typically van der Waals interactions through the methyl groups of 1,2-dimethylindole. Furthermore, the weak initial slopes for thiophene confirm the idea that hard Lewis acid metal sites do not interact well with soft bases such

Table 2. Initial Slopes of the Single Compound Uptake Isotherms of Contaminants Measured at 298 K in Heptane on MIL-100(Al, Cr, Fe, V)[a]

	IND	1,2-DMI	THP
MIL-100(Al)	3900	5700	67
MIL-100(Cr)	41 000	280 000	105
MIL-100(Fe)	19 000	2200	114
MIL-100(V)	55 000	∞	47

[a] Slopes given in L mol^{-1} for the contaminants indole, 1,2-dimethylindole, and thiophene in heptane at low concentrations (0–0.004 M) with regression coefficients >0.99.

as thiophene.[28] The highest affinity for thiophene is obtained for MIL-100(Fe), while the lowest affinity is obtained for MIL-100(V).

These results indicate that MIL-100(Fe), which was proposed in previous studies,[1] is not the best option for the selective removal of nitrogen compounds, as it has a rather favorable affinity for the sulfur compounds (≈100 L mol^{-1}). Using a material with a lower affinity for the sulfur compounds, like MIL-100(V), could increase the performance of the adsorbent.[1,7] Therefore, further adsorption studies were performed using the MIL-100(V) solid pretreated in different conditions (at 423 K under atmospheric pressure or under vacuum).

Performance of MIL-100(V) as an Adsorbent. A crucial observation for MIL-100(V) is the dependency of the uptake of the compounds on the pretreatment. If the material is pretreated under high vacuum (10^{-5} Pa) at 423 K for 5 h, an increase in indole uptake can be observed in comparison with the standard pretreatment under air (Table 3). In order to understand the dependency of the uptake on the pretreatment conditions, we compare in Figure 2 the FTIR spectra of the MIL-100(V) sample first pretreated at 423 K under 1 bar of air (spectrum a) or under vacuum (spectrum b), and subsequently loaded with indole.

Table 3. Adsorption Characteristics (Loading at Saturation; Affinity at Low Concentration) of MIL-100(V) Pretreated at 1 atm (Air) or under High Vacuum (10^{-5} Pa) at 423 K

pretreatment	INDI	1,2-DM	THP
	Molecules/UC (CUS%)[a]		
air	370 (69%)	290 (54%)	80 (15%)
vac	630 (116%)	300 (56%)	99 (18%)
	Affinity (L mol^{-1})		
air	55 000	∞	47
vac	120 000	∞	73

[a] Fraction of CUS occupied at saturation.

The reference spectrum of solid indole (trace c) displays a well-defined band at 3410 cm^{-1} (ν(NH) mode) and several bands at lower wavenumbers (1246, 1090, 1060 cm^{-1}). It is clear that all these bands are present in the spectrum of the sample pretreated under vacuum (Figure 2b). By contrast, they are not clearly discerned when the sample is pretreated under air (Figure 2a). In such case, the spectrum displays very broad bands between 2500–3500 cm^{-1} and 1100–1300 cm^{-1} previously assigned to residual free trimesic acid.[20] Thus, the pretreatment of MIL-100(V) under vacuum at 423 K removes most of the trimesic acid present as impurities in the sample, allowing the further adsorption of indole. In further experiments the pretreatment of MIL-100(V) is performed under high vacuum (10^{-5} Pa), in order to completely remove the trimesic acid from the pores and make full use of the available CUS. When comparing the results for MIL-100(V)vac with the other MIL-100 materials, the indole capacity is similar irrespective of the metal, which is not surprising when considering the similar measured surface areas, in agreement with a similar number of accessible CUS.

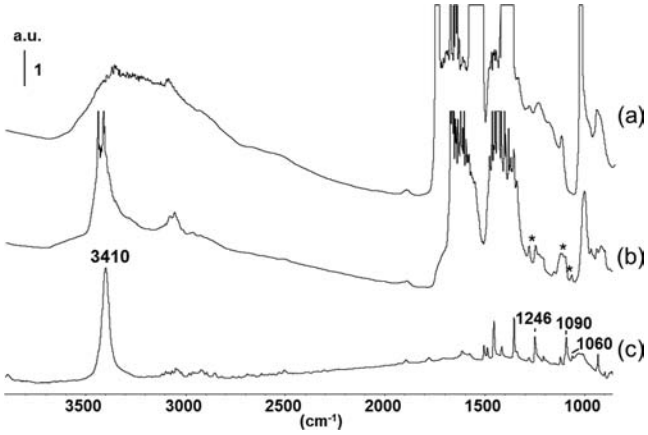

Figure 2. FTIR spectra of MIL-100(V) loaded with indole after pretreatment at 423 K under air atmosphere (spectrum a) or under vacuum (spectrum b) and of solid indole deposited on silicon wafer (spectrum c). The asterisks in part b indicate some characteristic bands of indole adsorbed on MIL-100(V).

The capacity of the material was further evaluated in a recycling experiment for MIL-100(V)vac. As shown in Figure S8, a full regeneration was possible after washing the material with pure toluene. Successive runs give 26.4, 27.5, and 24.1 ± 2 wt % uptake, indicating that the capacity was not altered during three adsorption runs. Despite the high affinity of the material for N-heterocycles, the integrity of the crystalline structure is not altered during adsorption–desorption cycles, as confirmed by X-ray powder diffraction after the recycling experiment (Figure S9). Furthermore, the stability of the MIL-100(V)vac was also evaluated by quantification of the constitutive linker (trimesic acid) released into the medium; no trimesate release was observed, at a limit of detection <0.1 μg mL^{-1}, or less than 0.1% of the total number of linkers.

Adsorption Calorimetry. In a next step, the integral adsorption enthalpies were recorded for the different compounds on each material (Figure 3). First, the adsorption enthalpies confirm the preferential uptake of nitrogen versus sulfur compounds. Moreover, comparing the initial slopes of the isotherms for the nitrogen compounds with the calorimetric results shows that the order of preference of the materials is in correct qualitative agreement with the values of the integral adsorption enthalpies (Table 4). This proves that the preferences, as observed in the isotherms, are largely based on enthalpic differences for interaction with the sites in the MIL-100 MOFs, even if one must also consider that, in a solvent-filled adsorbent, entropic effects of molecule packing in the cages can play an important role,[29] even for the first heterocyclic adsorbates entering the pores.

In general, the integral adsorption enthalpies decrease more or less strongly with the loading of the adsorbents, which lines up very well with the observation of Figure 1a that all isotherms are initially quite steep, but display pronounced leveling off at higher concentrations of adsorbate. When comparing results for

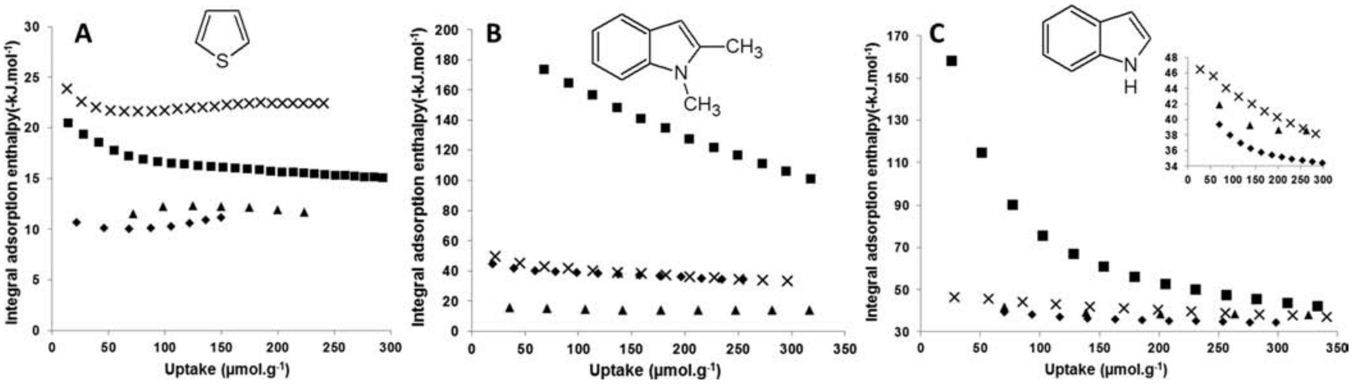

Figure 3. Integral adsorption enthalpies ΔH (−kJ mol^{-1}) as a function of equilibrium uptake (μmol g^{-1}) of thiophene (A), 1,2-dimethylindole (B), and indole (C) from heptane on MIL-100(Cr) (×), MIL-100(Fe) (▲), MIL-100(Al) (♦), and MIL-100(V)vac (■).

Table 4. Comparison of the Initial Slopes in the Isotherms and the Initial Integral Adsorption Enthalpies (−kJ mol^{-1}) for the MIL-100 Materials with Different Metals

IND	slopes	V > Cr > Fe > Al
	−ΔH	V (158) > Cr (46) > Fe (42) > Al (41)
1,2-DMI	slopes	V > Cr > Al > Fe
	−ΔH	V (198) > Cr (49) > Al (44) > Fe (15)
THP	slopes	Fe ~ Cr > V > Al
	−ΔH	Cr (24) > V (20) > Fe (12) > Al (11)

1,2-dimethylindole with those for indole, the remarkable increases in the initial slopes for MIL-100(V), MIL-100(Al), and MIL-100(Cr) are confirmed by the higher obtained adsorption enthalpies (Table 4 and Figure 3). Note that the adsorption enthalpy of 1,2-dimethylindole on MIL-100(Fe) is surprisingly low compared to the other MIL-100s.

For thiophene a quite different situation is observed (Table 4). In comparison with the other materials, MIL-100(Fe) has a higher initial slope than expected on the basis of the integral adsorption enthalpies. Generally, the enthalpies (Cr > V > Fe > Al) do not at all allow us to predict the affinities, as expressed by the initial isotherm slopes (Fe ~ Cr > Al > V). This suggests that not only the heat of adsorption but also entropic effects control the preference for adsorption of the sulfur compound. The enthalpies are also considerably smaller for the S-compounds than for the N-heterocycles.

It seems that the factors determining the affinities of the materials for thiophene are not easy to unravel. Therefore, our further efforts were focused on understanding the interaction of a N-heterocycle like indole with the CUS in MIL-100 materials.

FTIR Observation of Adsorbed Probe Molecules. In order to understand the binding mode of some of these heterocycles on the CUS, IR spectroscopy was applied. The MIL-100 materials exhibit strong carboxylate vibrations in the 1600−1350 cm^{-1} range, preventing the observation of the relevant sensitive bands of adsorbed thiophene, which are expected near 1400 cm^{-1}.[30] Therefore, the study was limited to the understanding of the high affinity of MIL-100 for N-heterocycles. The presence of a highly sensitive N−H vibration in indole makes this molecule a very good model adsorbate. In contrast, the absence of this ν(NH) band in 1,2-dimethylindole limits its characterization by FTIR. Nevertheless, a straightforward extrapolation of the indole results to 1,2-dimethylindole will be given in the general discussion.

MIL-100(Al), MIL-100(Fe), and MIL-100(V) were impregnated with indole prior to insertion in the IR cell. In the case of MIL-100(Cr), the strong affinity of this material for water, the low temperature of activation before indole impregnation, and the exposure of the impregnated sample to ambient atmosphere for making the pellet prevented the analysis of the spectra of the adsorbed species, in particular after heating at increasing temperature. For the other three MIL-100 materials, it was attempted to discriminate between physisorbed and chem-

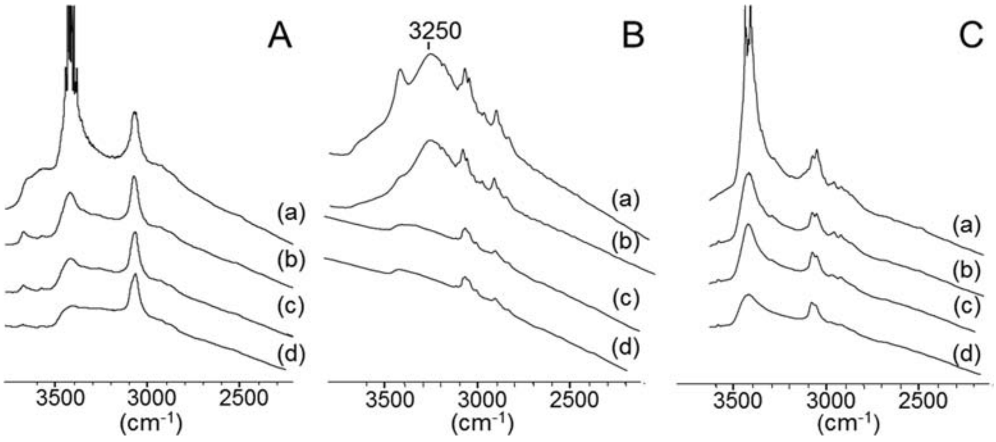

Figure 4. FTIR spectra of MIL-100 after impregnation with indole in heptane and outgassing at 323, 373, 423, and 473 K (spectra a−d, respectively): (A) spectra for MIL-100(Al), (B) for MIL-100(Fe), and (C) for MIL-100(V)vac.

isorbed indole species. Physisorbed indole quickly desorbs under vacuum, and its infrared spectrum is quite similar to that of solid indole. Two types of chemisorbed species can be considered: (1) coordinated species in which the lone pair on the indole nitrogen atom interacts with the Lewis acid sites, and (2) hydrogen bonded species, with the N−H group involved in a hydrogen bond with a putative basic site. Infrared spectroscopy is highly suitable to detect the latter species since the ν(NH) vibration is quite intense and very sensitive to formation of hydrogen donor−acceptor complexes. By contrast, the formation of coordinated species is not expected to significantly affect the ν(NH) band. Thus, the relative thermal stability of such species in comparison with merely physisorbed indole will serve as evidence for the formation of coordinated species.

In the 3700−2400 cm^{-1} region, the spectra of the activated MIL-100 samples display a strong band near 3080 cm^{-1} assigned to the ν(CH) vibrations of the trimesate entities. Figure 4 shows spectra of MIL-100 samples impregnated with indole and evacuated at 323, 373, 423, and 473 K. In the case of MIL-100(Al) (Figure 4A), the main ν(NH) band at 3400 cm^{-1}, which is prominent in the spectrum after evacuation at 323 K, strongly decreases in intensity after progressive evacuation at 373−473 K. The initial intensity decrease is certainly due to the removal of physisorbed species since the ν(NH) frequency is that of solid indole molecules. The species remaining at 373 K, and particularly those left at 423 K, also present a similar ν(NH) band at the same wavenumber, suggesting that their persistence results from the formation of coordinated species. In the case of MIL-100(Fe) (Figure 4B), the very weak band left at 3400 cm^{-1} after evacuation at 373 K provides evidence for near-complete desorption of physisorbed species. Supplementary bands are detected at about 3250 cm^{-1} (broad) and 2900 cm^{-1} (sharp). Their frequency and the fact that they persist under evacuation at 373 K show that they are characteristic for chemisorbed indole species in which the N−H bond seems involved in the binding. Finally, the spectra recorded for MIL-100(V) evacuated at different temperatures (Figure 4C) resemble well those observed for MIL-100(Al), but the residual intensity at 3400 cm^{-1} is much stronger at the respective evacuation temperatures, by comparison with the internal reference of the ν(CH) trimesate bands. Additionally, some well-defined extra bands appear between 3100 and 2800 cm^{-1}.

In order to zoom on the nature of the noncoordinated species formed on the MIL-100 samples, the spectra of species persisting after evacuation at 423 K were subtracted from those at 373 K, at which temperature most of the physisorbed species have desorbed (Figure 5). It is clear that, in the case of MIL-100(Al), no band is detected in the 3100−2800 cm^{-1} region, which proves that the N−H bond of indole is unaffected. Hence, the indole binding on MIL-100(Al) seems to be of a purely coordinative nature. The spectra of indole on MIL-100(Fe) and MIL-100(V) are more complex, indicating that the N−H mode is affected by the chemisorption. The occurrence of bands below 3300 cm^{-1} could be related to coordinated indole species that are also hydrogen-bonded to an adjacent basic center by the NH group. The stronger the interaction, the lower the ν(NH) frequency is.

Moreover, when strong interactions occur, the ν(NH) massif is complex due to the presence of many submaxima at lower wavenumbers resulting from Fermi resonance phenomena.[31] The multiplicity of weak bands below 3200 cm^{-1} in the spectrum of MIL-100(V) (Figure 5) suggests the formation of a small number of indole species both coordinated on CUS and hydrogen-bonded to basic sites. The basic centers could result from the presence of vanadyl oxygen (V═O), with vanadium in the +4 state. The existence of such vanadyl groups has previously been revealed by IR spectroscopy through a ν(V═O) mode situated at 1018 cm^{-1} (Figure S5) and has been supported by a previous study related to NO adsorption.[20] The use of CO_2 as probe molecules on vanadyl phosphate compounds has shown that the vanadyl entities can act as either as electron acceptor center (Lewis acid sites) or as electron donor centers (basic sites).[32] The nature of the chemisorbed species formed on MIL-100(Fe) is still unclear; experiments using pyrrole are in progress to specify the type of interaction that occurs. Whatever the precise interaction, Figure 4B shows that it is weak since most of the species desorb between 373 and 423 K.

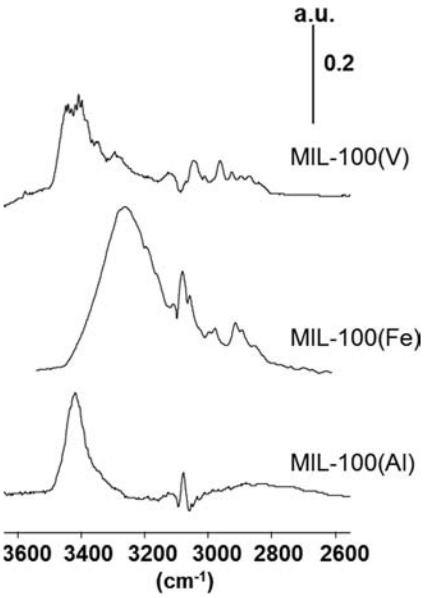

Figure 5. Spectra of adsorbed species persisting on MIL-100 after outgassing at 423 K, subtracted from spectra at 373 K.

4. GENERAL DISCUSSION

Calorimetric data for indole show that the adsorption enthalpies at low loadings follow for the different metals the same order as the initial slopes in the isotherms. They decrease as follows: V > Cr > Fe > Al. The infrared spectra reveal the formation of coordinated species on all materials. In addition, on MIL-100(V), one also detects a small fraction of coordinated indole species that are also hydrogen bonded to adjacent basic sites. As MIL-100(V) contains predominantly V^{3+}, but also a few percent of V^{4+} in vanadyl groups, it is logical to suppose that the basic oxygen atoms of the vanadyl groups may be involved in the formation of hydrogen bonded species.

While indole can be bound on MIL-100(V) via H-bonding, this is impossible for 1,2-dimethylindole. Despite the absence of the N−H group, the initial integral adsorption enthalpy of 1,2-dimethylindole on MIL-100(V) is even higher (−198 kJ mol^{-1}) than that of indole, as also expressed in an almost infinitely steep isotherm. Therefore, we deduce that for MIL-100(V) mainly coordinated species have to be considered to explain the results relative to indole adsorption. Such species are characterized by an infrared ν(NH) band at 3400 cm^{-1} which persists under vacuum at low temperature. Their stability under evacuation even at higher temperatures reflects the strength of the coordination. For MIL-100(Fe) (Figure 4B), contribution of such coordinated species is negligible; the strongest chemisorption in MIL-100(V)vac seems due to coordinative binding of indole, as is clear from the persistence of the 3400 cm^{-1} IR band at 423 and even 473 K (Figure 5).

While adsorption of 1,2-dimethylindole cannot be followed in IR by a similar sensitive vibration like the υ(NH) of indole, straightforward extrapolation of the results of indole to 1,2-dimethylindole gives sound trends. As MIL-100(Fe) poorly binds the N-heterocycles via the coordinative mechanism, there is no preferred binding mechanism left for 1,2-dimethylindole, and this perfectly agrees with the changed affinity order (Fe > Al for indole, vs Al > Fe for dimethylindole) and the very low adsorption enthalpy for 1,2-dimethylindole on MIL-100(Fe) (less than -20 kJ mol^{-1}). At the other extreme, the proposal that MIL-100(V)vac strongly binds indole via a coordinative mechanism is confirmed by the 1,2-dimethylindole result: despite the absence of N−H bonds, binding of 1,2-dimethylindole on MIL-100(V)vac is even stronger than that of indole. The extra methyl groups clearly provides increased electron density in the lone pair, resulting in a stronger coordinative binding on the CUS of MIL-100(V)vac.

It is of particular interest to compare these trends with the reported data on Lewis acid strength of CUS in MIL-100 materials. Different orders have been reported using various probes.[15,33] Using acetonitrile as a probe, the increase of the υ(CN) frequency reflects the polarizing power of the Lewis acid center, giving the following order:

$$Al^{3+} > V^{3+} > Cr^{3+} > Fe^{3+}$$

Using adsorbed CO at 100 K, the order is somewhat different:

$$Cr^{3+} > V^{3+} > Al^{3+} > Fe^{3+}$$

In either case, Fe^{3+} possesses the weakest Lewis acidity, and this perfectly matches with the observed lack of stable indole-Fe^{3+} coordination complexes in MIL-100(Fe). Despite its reported Lewis acidity, e.g., using acetonitrile as a probe, Al^{3+} in MIL-100(Al) has the lowest affinity for indole, both in the calorimetry and in the adsorption isotherms. It must be noted that indole is a large molecule with considerable polarizibility; hence as a base, it may interact in a less favorable way with the hard Lewis acid center Al^{3+} than with transition metals like V^{3+} or Cr^{3+}.

5. CONCLUSION

In our initial study on N/S heterocycle adsorption on MOFs, MIL-100(Fe) seemed an excellent candidate adsorbent.[1] However, the performance of this material is clearly surpassed by MIL-100(V)vac in several respects: (1) the material possesses a very high affinity for all N-heterocycles, which is due to an enthalpic, coordinative interaction with the CUS; (2) the selectivity of the adsorption is high for N-heterocycles with or without N−H bonds, as exemplified by indole and 1,2-dimethylindole, respectively; (3) the material preserves its capacity and selectivity over several cycles, implying that full regeneration is possible, and (4) the high adsorption enthalpy can be advantageously exploited to stimulate desorption by mild heating; (5) if properly pretreated, the capacity of the V-material can be as high as that of the other MIL-100 materials. The detailed mechanistic study has revealed that for N-heterocycle adsorption on MIL-100 materials, the interaction is enthalpic through coordination on CUS.

ASSOCIATED CONTENT

Supporting Information

Extra figures, HPLC analysis, PXRD patterns, elemental analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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