Metal–Organic Frameworks

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Selective Removal of N-Heterocyclic Aromatic Contaminants from Fuels by Lewis Acidic Metal–Organic Frameworks**

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Fossil fuels, such as diesel or gasoline, are blends of aromatic and aliphatic compounds that contain significant levels of heterocyclic aromatic contaminants. These contaminants have to be removed for environmental reasons.[1] One of the most important issues is the presence of sulfur compounds, such as thiophene (TPH), benzothiophene (BT), and dibenzothiophene (DBT) in fuel feeds, which lead to the formation of SO_x exhaust gases and eventually to acid rain. As environmental legislation becomes more stringent on SO_x exhaust levels, it is imperative to keep lowering the sulfur concentrations to currently 10 ppmw S (parts per million by weight of sulfur) or less.[1c,2a] The main industrial process is hydrodesulfurization (HDS) in which sulfur compounds are hydrogenated to hydrocarbons and H_2S over typically a CoMo catalyst.[2] However, nitrogen compounds, such as (substituted) indoles and carbazoles, which are also present in fossil fuels, compete for the active sites on these HDS catalysts, preventing a deep HDS.[3] In the absence of nitrogen compounds, deep HDS can easily produce fuels with sulfur levels well below 10 ppmw, for instance by using the newest generations of materials based on Mo-W-Ni, which can lower sulfur levels to 5 ppmw.[2h] As the eventual aim is to have sulfur-free fuel, even these low concentrations will have to be removed.[2a,h]

A promising way to selectively remove nitrogen contaminants would be adsorption on a microporous material. Efficient purification can be performed by adsorption as long as the interaction between the adsorbate and the adsorbent is relatively strong.[4] A Cu^+Y zeolite has been described as a potential adsorbent for the removal of nitrogen compounds by π complexation, but the maximal capacity at saturation only amounted to 3 mg N per gram of adsorbent, and moreover sulfur compounds are adsorbed as well.[5] An ideal adsorbent for such application should be easy to synthesize, stable in the given feed compositions, possess pores that are large enough to accommodate bulky organic molecules, such as carbazoles, have a sufficient capacity, and be highly selective for nitrogen over sulfur compounds.

Metal–organic frameworks (MOFs) are an emerging class of highly porous materials, formed of inorganic subunits and organic linkers that bear multiple complexing functions (for example, carboxylates, phosphonates, and others), which enables a unique variety of potential interactions inside the pores. To date, they have been successfully used as adsorbents for the capture of greenhouse gases, such as CO_2 and CH_4, and in liquid-phase separations such as those of alkylaromatics and styrene, olefins and paraffins, and for fuel and water purification by adsorption of organic pollutants.[6] Herein, we propose the use of mesoporous metal carboxylates with different topologies and compositions for the selective adsorption of nitrogen contaminants.

These heterocyclic contaminants are found in fuel feeds that are typically aliphatic with a minor aromatic fraction. This system is simulated herein by using a solvent composed of heptane/toluene in a volumetric ratio of 80:20 (labeled hereafter as H/T). Specifically, the adsorptive removal of indole (IND), 2-methylindole (2MI), 1,2-dimethylindole (1,2DMI), carbazole (CBZ), and *N*-methylcarbazole (NMC) as well as of TPH, BT, and DBT has been studied. These molecules are the most important heterocyclic contaminants in fuel feeds.[6h–j] To study the influence of the toluene-containing solvent on the adsorption and on the interaction strength between the host and the adsorbate, the adsorption of the contaminants has also been studied using a toluene/

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heptane mixture in a 80:20 ratio (T/H). A wide variety of MOFs were screened as potential adsorbents, including MOFs with and without coordinatively unsaturated metal sites.

The presence of open metal sites in the pores plays a decisive role in the adsorption from mixtures containing toluene (Table 1). MOFs lacking such sites, for example, MIL-47 ($[V^{IV}O(C_8H_4O_4)]$) or MIL-53 ($[Al^{III}(OH)(C_8H_4O_4)]$) do not show any significant contaminant uptake.[7] This can be explained by competitive adsorption of the abundantly available toluene molecules in the pores of these materials, which lack functional groups that could induce selective adsorption of nitrogenated molecules. In sharp contrast, MIL-100 ($[M_3O(H_2O)_2X(C_6H_3(CO_2)_3)_2]$, M = Al^{3+}, Cr^{3+}, Fe^{3+} X = F, OH)[8a–c] and MIL-101(Cr) ($[Cr_3O(H_2O)_2F(C_6H_4(CO_2)_2)_3]$)[6k] show a strong uptake of nitrogen compounds, while little affinity towards sulfur compounds is observed, especially in T/H. On the other hand, HKUST-1 ($[Cu_3(BTC)_2]$)[8d] and CPO-27 ($[M_2(C_8H_2O_6)(H_2O)_2]$, M = Co^{2+}, Ni^{2+})[8e,f] adsorb both nitrogen and sulfur compounds. Therefore, if nitrogen compounds are to be separated from sulfur compounds, MIL-100 and MIL-101 are promising candidate materials. Even in T/H, they adsorb up to 16 mg of N per g of MOF, which is far more than what is obtained on the reference zeolite Cu^+Y (3 mg N/zeolite Cu^+Y).[5]

Table 1: Maximal uptake values of contaminants obtained from single-compound batch adsorption experiments on various MOFs at 298 K.[a]

		IND	2MI	1,2DMI	NMC	TPH	BT	DBT
MIL-100(Fe)	H/T	36	30	27	19	4	6	7
	T/H	16	–	9	3	1	<1	<1
MIL-100(Cr)	H/T	37	29	27	19	2	7	7
	T/H	16	–	8	3	<1	<1	1
MIL-100(Al)	H/T	34	29	25	17	2	6	6
	T/H	13	–	7	2	<1	1	<1
MIL-101(Cr)	H/T	40	34	25	27	3	5	8
	T/H	14	–	7	4	1	<1	1
$[Cu_3(BTC)_2]$	H/T	22	17	–	4	10	10	12
	T/H	13	–	3	1	5	2	2
CPO-27(Ni)	T/H	11	–	4	1	12	19	20
CPO-27(Co)	T/H	10	–	4	1	13	20	20
MIL-47/MIL-53	H/T	<1	<1	<1	<1	<1	–	<1
	T/H	<1	<1	<1	<1	<1	–	<1

[a] Uptake value given as wt%. 0.15 M initial concentration of contaminants IND, 2MI, 1,2DMI, NMC, TPH, BT, and DBT in either heptane/toluene (H/T, ratio 80:20 v/v) or toluene/ heptane (T/H, 80:20 v/v).

According to Pearson's hard/soft acid/base concept, (substituted) nitrogen bases are intermediate to strong bases, while sulfur compounds tend to be intermediate to soft bases.[9] In line with this concept, a harder base, such as a nitrogen base, interacts preferentially with a hard Lewis acid site, such as Fe^{3+}, Cr^{3+}, or Al^{3+} and also with intermediate Lewis acid sites. In contrast, the softer sulfur compounds prefer to interact with intermediate or soft Lewis acid sites, such as Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Cu^+. This theory fits perfectly with the experimental data reported in Table 1. The fact that there is also a limited uptake of BT and DBT on the MIL-100 and MIL-101 materials in H/T can be explained by the presence of aromatic rings in these adsorbates. Many MOF materials, even without open metal sites, indeed generally prefer aromatic over aliphatic molecules.[6d] As expected, virtually no uptake of sulfur compounds is observed on the MIL-100/MIL-101 group of materials in T/H. Thus, for the selective removal of nitrogen compounds, MOFs containing hard Lewis acid sites are the most promising solids. Therefore, MIL-100(Fe), a cheap, non-toxic, and biodegradable material was further studied.

The role of the hardness or softness of the open coordination sites is further illustrated by the controlled reduction of MIL-100(Fe) under an inert helium atmosphere at 523 K.[10] It was shown previously that increasing the temperature under vacuum or inert atmosphere allows the progressive partial reduction of Fe^{III} metal sites into Fe^{II} coordination sites (approximately 33 %);[10] as a consequence, a stronger interaction with unsaturated organic molecules can occur through a back-donation effect with the Fe^{II} metal sites. Contrary to regular MIL-100(Fe), for which no uptake of BT and DBT is observed out of T/H (Table 1), the partial reduction of the material results in uptakes as high as 9 wt% for BT and 11 wt% for DBT from T/H (Figure 1). Thus, Fe^{II} sites are intermediate Lewis acid sites that interact with sulfur compounds as well. This result not only confirms the idea of interaction between the heteroatoms and the unsaturated metal sites, but also suggests that, depending on the specific pretreatment, MIL-100(Fe) could be used to selectively

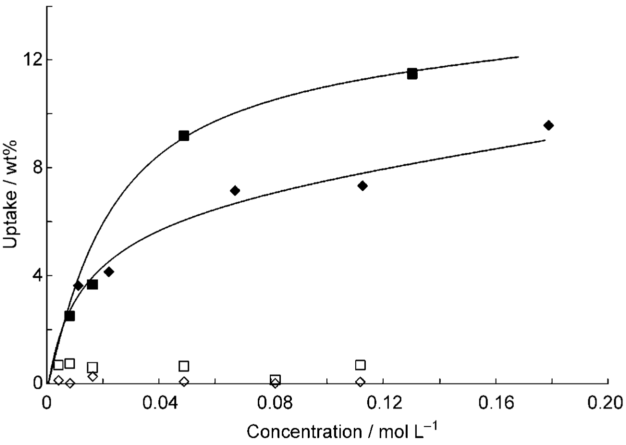

Figure 1. Single-compound adsorption isotherms of benzothiophene (diamonds) and dibenzothiophene (squares) from T/H on MIL-100(Fe) (open symbols) and reduced MIL-100(Fe) (closed symbols) at 298 K.

remove 1) only nitrogen compounds in its as-synthesized, oxidized form, 2) both nitrogen and sulfur compounds in its partially reduced form, and 3) even sulfur compounds that might remain in the feed after removal of the nitrogen compounds and deep HDS.

Table 1 shows not only the strong preference of non-reduced MIL-100(Fe) for nitrogen compounds, but shows also an increase of the maximal uptake levels as the solvent becomes less aromatic in nature. This effect is due to a decreased coadsorption of competing toluene molecules, but also to solubility effects. Indeed, the various nitrogen compounds tested dissolve much better in toluene than in heptane, increasing their tendency to be adsorbed within the porous solid as the liquid phase contains increasing amounts of aliphatics such as heptane.

Solvent composition also affects the initial slopes of the isotherms, which are a good criterion to evaluate the affinity (Table 2).[4] The initial slopes in H/T are much steeper than in T/H, confirming the idea that competing toluene molecules lower the affinity. A high affinity is more desirable in purification applications to efficiently adsorb compounds even at very low concentrations.[4] On the other hand, to facilitate bed regeneration, a solvent should be used that lowers the affinity, with T/H or even pure toluene being obvious candidates.

Table 2: Initial slopes of the single-compound uptake isotherms of contaminants measured on MIL-100(Fe) at 298 K.[a]

	IND	2MI	1,2DMI	CBZ	NMC	TPH	BT	DBT
H/T	8.3	7.0	1.6	8.3	5.1	0.1	0.5	0.7
T/H	4.6	1.9	0.9	1.4	2.4	–	–	–

[a] Slopes given as $\mathrm{L\,mol^{-1}}$ for the contaminants IND, 2MI, 1,2DMI, CBZ, NMC, TPH, BT, and DBT in heptane/toluene (H/T, ratio 80:20 v/v) and toluene/heptane (T/H, 80:20 v/v) at low concentrations (0–0.004 M initial concentration; see the Supporting Information).

The proposed adsorption mechanism implies an interaction between the open metal site of the host and the contaminant. To test this hypothesis, the Mössbauer spectrum of a water-loaded MIL-100(Fe) sample at 298 K is compared with the spectrum obtained from a sample saturated with IND, as IND is the most strongly adsorbed nitrogen compound (Figure 2). Both spectra consist of a set of different quadrupolar components, which are well-defined. The basic building unit of MIL-100(Fe) is a trimer of μ_3-oxo linked $\mathrm{Fe^{III}}$ octahedra. In the spectrum of the water-loaded sample, three main types of Fe octahedral units can indeed be distinguished.[8a] The values of quadrupole shifts of the hydrated sample ($0.27\ \mathrm{mm\,s^{-1}}$, $0.59\ \mathrm{mm\,s^{-1}}$, $0.77\ \mathrm{mm\,s^{-1}}$) correspond to different degrees of distortion as mentioned in literature, with the highest value attributed to the Fe octahedron containing the fluoride anion.[8a] Both other Fe atoms of the μ_3-oxo cluster are generally thought to interact with coordinating water molecules that can be removed upon adequate thermal activation.[8a] The spectrum of an IND-saturated sample shows similar Fe species as the parent hydrated host (quadrupole splittings: $0.27\ \mathrm{mm\,s^{-1}}$, $0.61\ \mathrm{mm\,s^{-1}}$, $0.78\ \mathrm{mm\,s^{-1}}$). This result suggests that IND is affecting the environment of the Fe octahedral units in a similar way as water does. Thus, the free electron pair of indole, like those of water, should be in the vicinity of the available Fe sites, indicating that indole occupies virtually all free ligation sites.

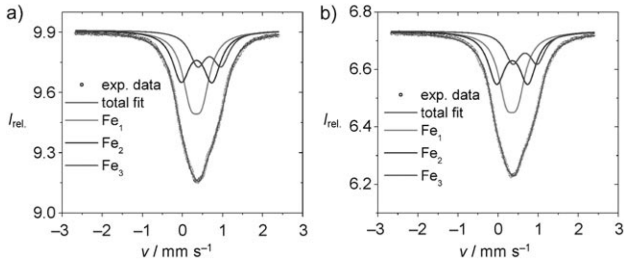

Figure 2. Transmission Mössbauer spectra of a) MIL-100(Fe) saturated with H_2O and b) MIL-100(Fe) saturated with indole recorded at 298 K.

The strong preference for nitrogen compounds and relatively weak affinity for sulfur compounds of the $\mathrm{Fe^{3+}}$ MIL-100 material is also borne out by the integral adsorption enthalpies of the different compounds. To illustrate the host–guest interactions, the adsorption enthalpy was determined using pure heptane as a non-interacting solvent. Microcalorimetric measurements revealed that the integral adsorption enthalpy of IND is the most negative at approximately $-50\ \mathrm{kJ\,mol^{-1}}$ (Figure 3), being much more negative than the one obtained for TPH ($-8\ \mathrm{kJ\,mol^{-1}}$), which is in agreement with a much higher affinity of MIL-100(Fe) for the unsubstituted nitrogen compound compared to the sulfur compound. As expected, a substituted and bulky nitrogenated molecule, such as 1,2DMI or NMC, gives rise to in a less pronounced integral enthalpy of $-12\ \mathrm{kJ\,mol^{-1}}$, as the nitrogen atom becomes less available to interact with the structure. However, the integral enthalpy proves that the adsorption is still in favor of these compounds compared to TPH.

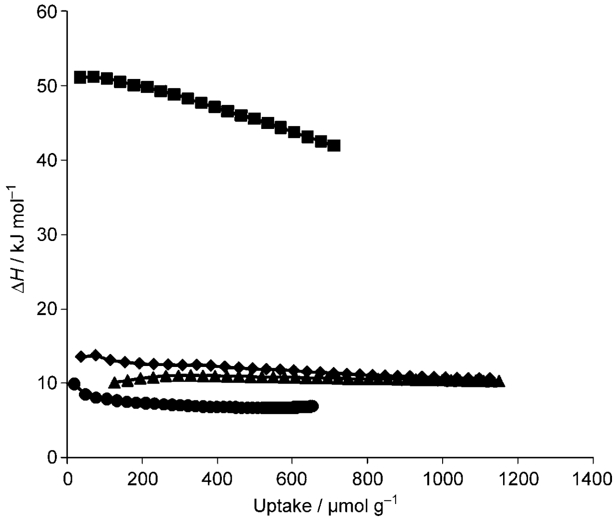

Figure 3. Integral adsorption enthalpies ΔH ($\mathrm{kJ\,mol^{-1}}$) as a function of equilibrium uptake ($\mathrm{\mu mol\,g^{-1}}$) of indole (■), 1,2-dimethylindole (◆), N-methylcarbazole (▲), and thiophene (●) on MIL-100(Fe) measured by microcalorimetry.

Finally, to assess the capability of MIL-100(Fe) in separating nitrogen compounds from their sulfur counterparts, continuous breakthrough experiments have been performed on a column of MIL-100(Fe), using a mixture of H/T containing approximately 1000 ppmw S and 700 ppmw N (Figure 4). Again, nitrogen compounds are preferred over sulfur compounds (Table 1). The initial 2 mL that eluted from the column after the dead volume contain no detectable concentration of heterocyclic contaminants (<2 ppmw S and <0.1 ppmw N). This results in 2 mL of ready-to-use purified fuel with sulfur levels lower than those obtained by deep HDS using the best current catalyst. After 2 mL, both sulfur compounds BT and DBT are eluting simultaneously, confirming the weak affinity of the host for these compounds. In the next 6 mL interval, fuel contaminated with only sulfur compounds is obtained, which can be directly sent to the deep HDS process, as no nitrogen is present in this feed. Then, the more complex nitrogen compounds, such as 1,2DMI and NMC, are eluted, and IND is retained the longest on the column, eluting only after 12 mL. This underpins the idea that the interaction between the host and IND is more pronounced compared to the interaction with a substituted nitrogen compound such as NMC or 1,2DMI, as was also inferred from the integral adsorption enthalpies. In any case, the breakthrough profile shows that even the more complex substituted nitrogen compounds can be efficiently adsorbed out of a hydrocarbon feed.

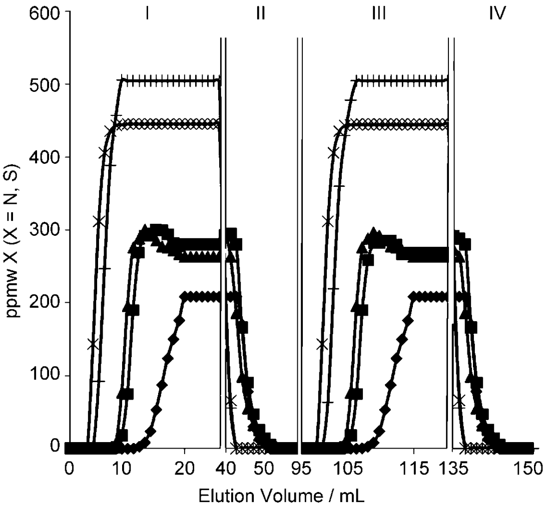

Figure 4. Breakthrough experiment at 298 K on a MIL-100(Fe) column at 298 K with a solution of 0.011 M indole (◆), 0.011 M 1,2-dimethylcarbazole (■), 0.014 M N-methylcarbazole (▲), 0.009 M benzothiophene (×), and 0.009 M dibenzothiophene (+) dissolved in H/T (a total of 950 ppmw S and 750 ppmw N). All curves are corrected for the dead volume. Sections I and III: adsorption of the mixtures; sections II and IV: the final part of the regeneration in pure toluene. Between adsorption and desorption, the column was flushed with pure toluene (13.5 mL; 10 mL of which is dead volume); between desorption and adsorption, the column is flushed with pure H/T to be regenerated (40 mL; not shown).

Regeneration of the column was achieved by flushing the column with pure toluene to obtain an effluent stream that contains less than 0.1 ppmw N and 2 ppmw S (zones III and IV in Figure 4), although thermal regeneration can also be achieved by flushing the bed material with N_2 at 383 K during 3 h. After this regeneration, the column is flushed with pure H/T before a second cycle is started. As the second cycle results in similar breakthrough profiles (see Supporting Information), it can be concluded that this material can be fully regenerated and reused in multiple cycles.

To summarize, it has been demonstrated that mesoporous MOFs containing trimers of metal octahedra with Lewis acid sites are suitable adsorbents for selective removal of the nitrogen compounds in fuel feeds, whereas sulfur compounds are hardly adsorbed. Based on the hard/soft acid/base concept, the potential of new materials can be predicted for this separation. The composition of the solvent has a strong impact on the adsorption and separation as it coadsorbs, but even then MOFs are capable of performing the desired purifications, and they can be fairly easy regenerated. This work clearly demonstrates the large potential of MOFs for liquid-phase adsorption applications.

Experimental Section

MOFs were synthesized according to literature procedures.[8] Batch experiments were performed in small vials loaded with adsorbent. A 5 cm stainless steel column placed in an HPLC apparatus was used for pulse and breakthrough experiments. Microcalorimetry has been performed on TAM III calorimeter (TA Instruments). Mössbauer spectroscopy was performed using a conventional constant-acceleration spectrometer; the ^{57}Co(Rh) source had a nominal activity of 96.7 MBq. Procedures for the syntheses, experimental methods, and calculations can be found in the Supporting Information.

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