Metal–Organic Frameworks

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Generating Reactive MILs: Isocyanate- and Isothiocyanate-Bearing MILs through Postsynthetic Modification**

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Metal–organic frameworks (MOFs) are rapidly becoming one of the most widely studied porous materials.[1,2] This family of hybrid compounds, constructed from inorganic and organic components, exhibit a diverse range of architectures with unprecedented porosity and show promise in applications including gas, liquid and vapor storage, separations, drug delivery, and catalysis.[3,4] Among the many MOFs synthesized, aluminum-based MOFs, developed largely by the group of Férey under the name Material Institut Lavoisier (MIL), exhibit particularly attractive features including high-surface areas, thermal stability, and chemical stability.[5]

An increasingly recognizable advantage of MOF materials, over conventional inorganic porous solids (e.g. zeolites), is the ability to integrate complex chemical functionalities, under mild conditions, onto the organic constituents of the lattice. This strategy, often referred to as postsynthetic modification (PSM), can provide access to porous materials with enhanced properties for specialized applications, such as gas sorption, catalysis, and biomedical uses.[6–17] PSM is generally achieved by using a pre-installed moiety on the precursor ligand that can be coupled with a reactive species in a heterogeneous fashion. Despite much progress in this area, the generation of a highly reactive chemical species as part of the organic strut of the MOF lattice has not been reported to date. Herein, we show that the superior chemical stability of MILs allows for the synthesis of reactive isocyanate and isothiocyanate groups on the organic components of the framework. Under suitable conditions, these reactive groups readily combine with species diffusing through the porous structure, generating new functionalized MILs (Figure 1). To the best of our knowledge, this report is the most extensive study of PSM on MIL materials,[9,18] and several compounds are the first examples of porous materials containing isothiocyanate, thiourea, and thiocarbamate groups. In addition, changes in the pore functionality also results in significant changes in the gas sorption isotherms, with some of the modified materials showing enhanced selectivity for CO_2 uptake.

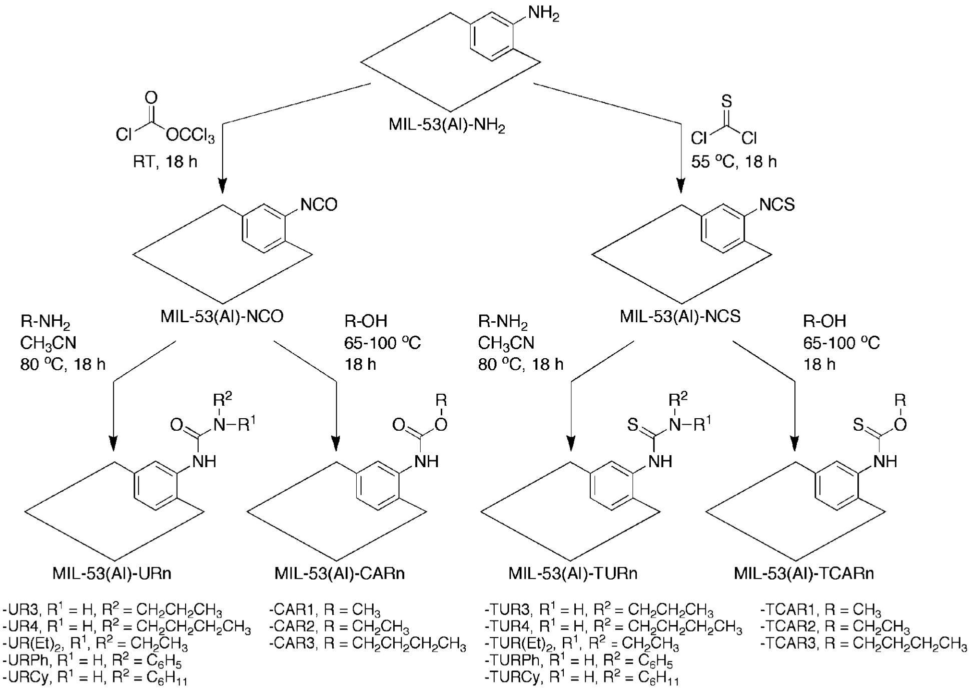

Figure 1. Strategy for the generation of MIL-53 presenting iso(thio)cyanate, (thio)carbamate, and (thio)urea functional groups.

MIL-53(Al)-NH_2 was prepared from the combination of $AlCl_3 \cdot 6H_2O$ with 2-amino-1,4-benzenedicarboxylic acid (NH_2-BDC) and activated using reported conditions.[18] The MIL-53 topology has been widely studied due to its unusual breathing behavior.[5] After activation, MIL-53(Al)-NH_2 was immediately suspended in THF, and either diphosgene or

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thiophosgene (16 and 8 equivalents, respectively) was added and the reaction was allowed to proceed for 18 h (ambient temperature for diphosgene, 55 °C for thiophosgene). After removal of the phosgene reagents by extensive washing with THF, the amine groups of the parent MIL were found to be ca. 90 % converted (see below) to isocyanate and isothiocyanate groups, respectively (Figure 1, designated MIL-53(Al)-NCO and MIL-53(Al)-NCS). The methodology for the conversion of arylamines to iso(thio)cyanates used here is based upon a known solution procedure,[19–22] but no reports on amine-based solids exist. The choice of solvent was found to be critical, as no conversion was observed in other solvents tested including toluene, benzene, DMSO, $CHCl_3$, CH_2Cl_2, and CH_3CN.

The choice of MOF was also important, as attempts with zinc(II)-carboxylate materials, such as IRMOF-3[23] and UMCM-1-NH_2,[8] were unsuccessful. The reaction between amines and phosgene derivatives in THF produces HCl as a byproduct. Hence, reactions performed with the acid- and moisture-sensitive IRMOF-3 or UMCM-1-NH_2 leads to the immediate destruction of the solids, even at room temperature (data not shown). The use of a base, to neutralize the HCl, did not protect these MOFs from degradation.

Infrared spectroscopy (ATR-FTIR) proved a convenient technique for identifying and quantifying the formation of the isocyanate and isothiocyanate groups on MIL-53(Al)-NH_2 (Figure 2). The formation of MIL-53(Al)-NCO was apparent by a very strong, sharp band at 2279 cm^{-1} corresponding to ν_{as}(NCO). Similarly, MIL-53(Al)-NCS exhibits a very strong, broad band (Fermi resonance) centered at 2100 cm^{-1} corresponding to a ν_{as}(NCS) vibration in good agreement with literature values.[24] For both materials, the appearance of these aforementioned bands was concomitant with the loss of a split band centered at 3440 cm^{-1} attributed to the vibration $\nu_{as}(NH_2)$ from the amino groups of the parent MIL-53(Al)-NH_2.

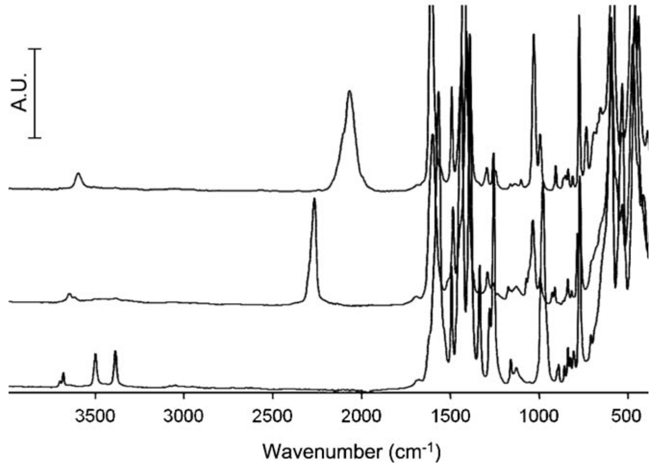

Figure 2. FTIR spectra of MIL-53(Al)-NH_2 (bottom), MIL-53(Al)-NCO (middle), and MIL-53(Al)-NCS (top). Spectra are offset for clarity. Scale bar corresponds to 0.1 absorbance units (A.U.).

The degree of conversion of MIL-53(Al)-NH_2 to MIL-53(Al)-NCO and MIL-53(Al)-NCS was quantified using two approaches: 1) in situ by using ATR-FTIR on intact samples, and 2) in solution using ^1H NMR spectroscopy on digested samples. FTIR is a useful technique for MOF-type solids or other materials to follow structural transformations[25,26] and to quantify adsorbed species.[27,28] In the present case, the percent conversion was determined by comparison of the $\nu_{as}(NH_2)$ band (integrated area) of the starting material and product. In the second approach, the modified materials were digested and the resulting solutions were analyzed by ^1H NMR. Although this digestion method has become common for characterizing PSM on many MOFs,[29–31] it was found to be challenging for the MIL-53(Al) derivatives due to their high chemical stability. However, use of HF in [D_6]DMSO with extensive sonication allowed for essentially complete digestion of most MIL-53(Al) samples. ^1H NMR spectra of modified samples showed a distinct downfield shift of the aromatic resonances associated with the BDC ligand (Figure 3). Electrospray ionization mass spectrometry (ESI-MS) on digested samples (HF in CH_3CN) also confirmed the presence of the expected molecular ions for the NCO-BDC and NCS-BDC ligands (Supporting Information, Figures S1, S2). Both the in situ ATR-FTIR and post-digestion ^1H NMR indicated conversions for MIL-53(Al)-NCO and MIL-53(Al)-NCS of ca. 90 %.

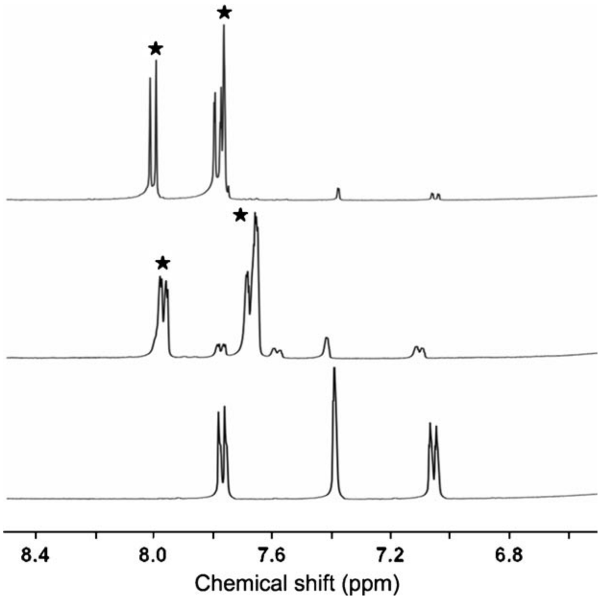

Figure 3. ^1H NMR spectra of MIL-53(Al)-NH_2 (bottom), MIL-53(Al)-NCO (middle), and MIL-53(Al)-NCS (top). Product peaks are marked with stars.

Powder X-ray diffraction (PXRD) confirmed preservation of crystallinity in MIL-53(Al)-NCO and MIL-53(Al)-NCS. Comparison of PXRD patterns with those of MIL-53(Al)-$NH_2(H_2O)$ and MIL-53(Al)-NH_2(as) (as = as synthesized) indicate that MIL-53(Al)-NCO is in a narrow-pore (**np**) configuration, while MIL-53(Al)-NCS is in a large-pore (**lp**) configuration (Figure 4).[18] Thermogravimetric analysis

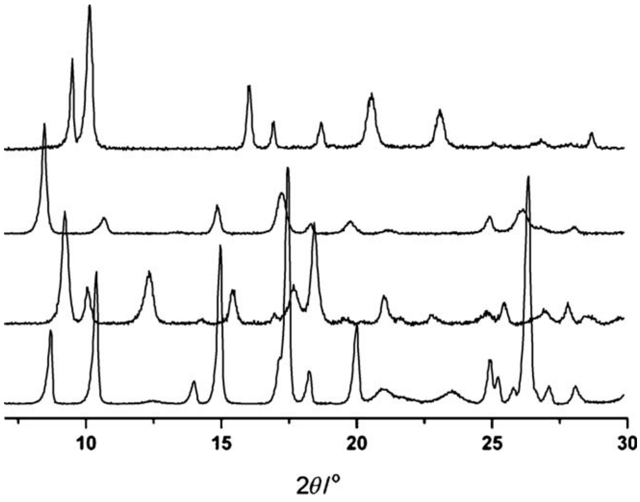

Figure 4. PXRD pattern of (from bottom to top) MIL-53(Al)-NH_2(as) in a **lp** form, MIL-53(Al)-NH_2(H_2O) in a **np** form, MIL-53(Al)-NCO, and MIL-53(Al)-NCS.

(TGA) confirmed that the modified materials possessed good thermal stability (Figure S7, S8).

Having demonstrated that MILs with reactive functional groups could be prepared in good yield, MIL-53(Al)-NCO and MIL-53(Al)-NCS were examined for their ability to react with nucleophilic compounds, thereby performing a multistep reaction on these frameworks.[6,32] MIL-53(Al)-NCO and MIL-53(Al)-NCS were treated with different alcohols (methanol, ethanol, buthanol) to generate carbamate- (MIL-53(Al)-CAR) and thiocarbamate- (MIL-53(Al)-TCAR) modified MILs. The conversions for these transformations ranged from 20% to near quantitative (Table S1). Formation of the carbamates proceeded very efficiently ($>90\%$), while the reactions to form thiocarbamates showed the best yields with the smallest alcohols (ca. 65% with MeOH).[8,33]

ATR-FTIR confirmed the reaction with alcohols; for example, MIL-53(Al)-CAR1 and MIL-53(Al)-TCAR1 (Figure S11) show reductions in the -NCO or -NCS vibrational bands around 2200 cm^{-1} and the formation of new vibrations. Carbamates show a broad band around 3400 cm^{-1} as well as a sharp band at 1690 cm^{-1} assigned to ν_{as}(NH) and ν_{as}(CO) vibrations, respectively. Thiocarbamates also exhibit a band characteristic of the N−H groups, but the ν_{as}(CS) vibration in these materials was obscured by other framework vibrations (band expected at ca. 1500 cm^{-1}). ^{1}H NMR spectroscopy of the digested samples also confirmed transformation to the (thio)carbamate groups (Figure S13, S14, S19). PXRD data showed that the MIL-53(Al)-CAR and MIL-53(Al)-TCAR materials maintained their bulk crystallinity (Figure S17, S18) and revealed that the MILs were in an open configuration after modification regardless of the alcohol used. In the case of MIL-53(Al)-NCS the reaction with alcohols must involve a transition from the **np** to **lp** form of the MIL.

MIL-53(Al)-NCO and MIL-53(Al)-NCS were also exposed to amines to produce urea and thiourea derivatives. Urea-containing MOFs have been reported through other approaches;[6,34,35] however, no reports of thiourea-containing MOFs generated by PSM have been described. MIL-53(Al)-NCO and MIL-53(Al)-NCS were suspended in CH_3CN and treated for 18 h at 80 °C with a variety of amines. The quantity of amine was adapted for each reaction to obtain the best possible yield (Table S1). As with the reaction with alcohols, the reaction of amines with MIL-53(Al)-NCO was higher yielding than with MIL-53(Al)-NCS. Also similar to the reaction with alcohols, yields improved with reduced steric bulk of the amine with the highest yields being achieved with propylamine (the smallest amine used, $>90\%$ with MIL-53(Al)-NCO) and essentially no conversion occurring with the bulkiest reagent cyclohexylamine. Interestingly, as with the reaction of MIL-53(Al)-NH_2 with phosgene reagents, the choice of the solvent, in this case CH_3CN, was critical for promoting the reaction with amines. The reaction of MIL-53(Al)-NCO or MIL-53(Al)-NCS in neat amine or in a solution of the amine in other solvents such as toluene, benzene, THF, DMSO, $CHCl_3$, and CH_2Cl_2 did not proceed (data not shown). Formation of the urea and thiourea products was confirmed using ATR-FTIR, ^{1}H NMR, and ESI-MS as previously described (Supporting Information).[31,33]

The gas sorption properties of different MIL-53(Al) derivatives (-NH_2, -NCO, -NCS) was examined with N_2 (77 K), H_2 (77 K), and CO_2 (196 K). MIL-53(Al) and MIL-53(Al)-NH_2 show a high uptake of CO_2 and N_2 (Figure 5a,b).[36] A slightly lower uptake for MIL-53(Al)-NCO and MIL-53(Al)-NCS was expected due to the larger size of these substituents. However, under the conditions used here, MIL-53(Al)-NCO and MIL-53(Al)-NCS show no uptake of H_2 or N_2, but exhibit a pronounced, stepwise sorption of CO_2 (Figure 5c,d). This surprising finding indicates that, in contrast to MIL-53(Al)-NH_2, MIL-53(Al)-NCO and MIL-53(Al)-NCS show differential adsorption of CO_2 over other gases.[37] The findings here show that changing the pendant group on the lattice can also modulate the pore state and thereby gas sorption, which is consistent with a recent report by Ferey and co-workers on substituted MIL-53(Fe) materials.[38] As clearly shown in Figure 5, the sorption profiles for N_2 and CO_2 vary greatly depending on the BDC ligand pendant group. In short, PSM produces MILs that demonstrate gated sorption for CO_2 that is not observed with either N_2 and H_2. The observed selectivity may be due to stronger interactions between the more polarizable CO_2 molecule and the iso(thio)cyanate groups, which induces opening of the MIL lattice from the narrow pore (**np**) to large pore (**lp**) forms.[37,38]

Using the chemically robust MIL materials a new series of functionalized materials have been produced that could not be obtained with other MOF materials (e.g. zinc carboxylate MOFs) or by traditional solvothermal approaches alone. The generation of functionalized MIL-53(Al) structures by PSM highlights three particularly interesting features: 1) the role of the solvent for suitable modification, 2) the influence of framework functionalization for selective gas sorption, and 3) the first realization of isocyanate-, isothiocyanate-, thiourea-, and thiocarbamate-bearing MOFs. The appropriate choice of solvent is essential for the reactions described here, where the flexibility of the MIL-53(Al) lattice may require the solvent to swell the framework to achieve efficient PSM.

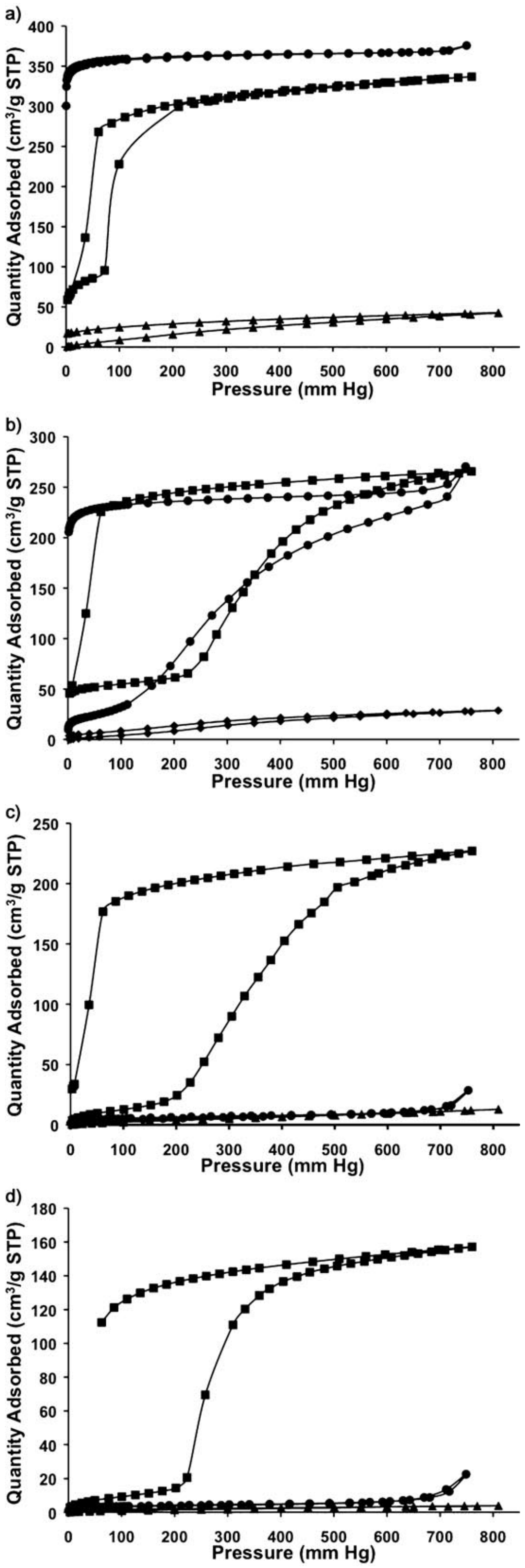

Figure 5. Effect of functionalization on gas sorption behaviors and gas selectivity. N_2 (77 K, ●), H_2 (77 K, ▲), and CO_2 (196 K, ■) sorption isotherms of a) MIL-53(Al), b) MIL-53(Al)-NH_2, c) MIL-53(Al)-NCO, and d) MIL-53(Al)-NCS.

Millange et al. have shown by in situ X-ray diffraction that certain solvents such as acetonitrile and alcohols produce swelling in MIL-53(Fe).[39] This is consistent with the PSM of MIL-53(Al)-NCO and MIL-53(Al)-NCS, which only proceeds effectively in these solvents. Hence, the use of the flexible MIL-53 structure introduces another level of control over PSM in MOFs. Specifically, MIL-53 allows for modulating the accessibility of the interior to PSM by the choice of solvent. This new feature may allow for spatial control (e.g. surface vs. interior)[32] of PSM on MIL-53 structures by the appropriate selection of solvent.

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