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Sulfation of metal–organic frameworks: Opportunities for acid catalysis and proton conductivity

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ABSTRACT

A new post-functionalization method for metal–organic frameworks (MOFs) has been developed to introduce acidity for catalysis. Upon treatment with a mixture of triflic anhydride and sulfuric acid, chemically stable MOF structures MIL-101(Cr) and MIL-53(Al) can be sulfated, resulting in a Brønsted sulfoxy acid group attached to up to 50% of the aromatic terephthalate linkers of the structure. The sulfated samples have been extensively characterized by solid-state NMR, XANES, and FTIR spectroscopy. The functionalized acidic frameworks show catalytic activity similar to that of acidic polymers like Nafion® display in the esterification of *n*-butanol with acetic acid ($TOF \sim 1\ \mathrm{min}^{-1}$ @ 343 K). Water adsorbs strongly up to 4 molecules per sulfoxy acid group, and an additional 2 molecules are taken up at lower temperatures in the 1-D pore channels of S-MIL-53(Al). The high water content and Brønsted acidity provide the structure S-MIL-53(Al) a high proton conductivity up to moderate temperatures.

1. Introduction

The chemistry of metal–organic frameworks (MOF) has advanced considerably during the last few years. Nowadays, thousands of structures are known [1]. The great topological richness of this new class of materials resulting from the combination of metal ions and organic linkers is without precedent [2].

However, the absence of functionalities other than open metal or weak functional organic sites (e.g., amines) in most of these structures limits to a certain extent their applicability [3,4]. Practical solutions to create functional solids include direct synthesis or post-synthetic functionalization of MOFs [5–7], grafting of active groups on the open metal sites of certain structures [8], and encapsulation of active species [9]. In fact, the incorporation of ligands, including additional functional moieties, is not trivial, since such groups may directly coordinate to the metal ions [10]. One of the current challenges is the development of efficient functionalization methods that can be applied to MOFs without functional organic sites [11] (in many cases, the most stable frameworks), i.e., the direct functionalization of aryl carbons in terephthalate-linked MOFs.

During the last few decades, much effort has been put into the development of super-acidic solid materials such as ion-exchange resins based on sulfonic acid groups [12] or sulfated oxides based on zirconia [13], silica, or alumina [14]. However, the application window of such materials is limited: some exhibit swelling in solvents (polymers) or strong leaching issues (sulfated oxides), while none of them possess a defined porosity. Therefore, the development of nanostructured strongly acidic catalysts is still in the portfolio of materials' researchers.

In principle, MOFs offer a large amount of possibilities for the inclusion of active moieties. Indeed, owing to their hybrid nature, functional groups could be included in such nanostructured materials by applying classical organic chemistry. However, in many cases, the limited chemical stability of MOFs does not allow harsh functionalization conditions, and terephthalate, perhaps the most used ligand in MOF synthesis, is deactivated for electrophilic substitution reactions at its aromatic ring due to the presence of carboxylate groups that diminish the density of electrons in the ring. Traditional sulfonation or sulfation methods [15] are a clear example: MOFs cannot be exposed to high concentrations of sulfuric acid since the framework would be destroyed. In this sense, several groups have tried to include sulfo type of functionalities: Burrows et al. pioneered the incorporation of secondary sulfone moieties by using thiol-tagged linkers followed by a post-synthetic oxidation [16], and Neofotistou et al. used a pre-modified linker already containing secondary sulfones: the ligand 4,4′-bibenzoic

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acid-2,2′-sulfone [17]. This approach, however, does not introduce acid functionality. Along the same line, Britt et al. reported the post-synthetic modification of an amine containing MOF (IRMOF-3) with sultones, resulting in the opening of the sultone ring and the formation of terminal sulfonic acid groups [18]. In spite of the elegance of this method, sultones are among the most hazardous chemicals, forbidden in most developed countries. Unfortunately, no real applications for sulfonate-containing MOFs have seen the light after this research.

In this work, a different approach has been followed. Here, we report a room-temperature, homogeneously activated method to post-synthetically incorporate sulfoxy moieties into non-functional, chemically, and thermally stable MOFs (i.e., MIL-101(Cr) [19] and MIL-53(Al) [20]). Characterization results demonstrate that by treating these stable MOFs with a mixture of sulfuric acid and trifluoromethanesulfonic anhydride (triflic anhydride), sulfoxy acid moieties are covalently bonded to the aryl carbons of the organic linker. The resulting functionalized MOFs (denoted as S-MIL-101(Cr) and S-MIL-53(Al)) show excellent acid catalytic properties and a high proton conductivity.

2. Experimental

2.1. Preparation of catalysts

All chemicals were obtained from Sigma–Aldrich and were used without further purification. MIL-53(Al) and Nafion® R50 (0.5 mm pellets) were also purchased from Sigma–Aldrich, while MIL-101(Cr) was synthesized following the procedure described elsewhere [19].

Stoichiometric sulfation was carried out with sulfuric acid in the presence of trifluoromethanesulfonic anhydride (triflic anhydride, Tf_2O), using nitromethane (CH_3NO_2) as solvent. The used molar ratio was MOF-incorporated terephthalate/H_2SO_4/Tf_2O = 1:1:1.5. The mixture was continuously stirred in a water bath at room temperature. After 60 min, the solid product was filtered off, rinsed with ultrapure water and acetone, soaked in ethanol for 24 h at 343 K, and stored at 160 °C.

2.2. General characterization techniques

Nitrogen sorption at 77 K was measured in a Quantachrome Autosorb-6B unit gas adsorption analyzer. Specific BET surface area was calculated between 0.05 and 0.15 relative pressures and pore volume at 0.95 relative pressure. Water adsorption isotherms were measured using a Quantachrome Aquadyne DVS gravimetric water sorption analyzer. The crystalline structures were analyzed by X-ray diffraction (XRD) using a Bruker-AXS D5005 with Cu Kα radiation. Thermogravimetric analysis (TGA) of the MOFs was performed by means of a Mettler Toledo TGA/SDTA851e, under flowing air (60 ml/min) at a heating rate of 5 K/min up to 873 K.

The carbon and sulfur mass percentages (elemental analysis) in the MOF were measured in a Leco CS induction oven. The samples were burnt in a continuous stream of O_2, while the formed gases were analyzed by IR. The analysis is performed in duplicate after which the average concentration is reported.

The infrared spectra were obtained using a Thermo Nicolet Nexus FTIR spectrometer. The samples (1 mg) were mixed with KBr and pressed into self-supported pellets (50 mg/cm^2). The spectra were taken in the transmission mode in an *in situ* cell equipped with CaF_2 windows. Prior to the measurements, the samples were degassed in vacuum (10^{-5} mbar) at 473 K for 30 min to remove adsorbed molecules.

Solid-state ^{27}Al, ^{13}C, and ^{1}H NMR studies were performed on a Bruker AV-750 spectrometer with a 17.6 T magnetic field, in which these nuclei resonate at 195.46, 188.64, and 750.13 MHz, respectively. A H/X/Y 2.5 mm MAS probe-head and a standard ZrO_2 rotor spun at 20 kHz were used. For the acquisition of ^{27}Al MAS spectra, the RF field frequency, pulse duration, number of scans, and repetition time were 55 kHz, 1.5 μs, 1024 scans, and 1 s, respectively. The corresponding parameters were 78.1 kHz, 3.2 μs, 32 scans, and 1 s for ^{1}H MAS spectra. For ^{1}H to ^{13}C CPMAS with TPPM decoupling, we used 62.5 and 89 kHz RF field frequencies in the ^{13}C and ^{1}H channels, respectively, for cross-polarization (CP). The contact time was 3 ms, and the repetition time was 2 s for 1024 scans. Chemical shift references (0 ppm) are $Al(NO_3)_3$ in aqueous nitric acid solution for ^{27}Al and TMS for ^{1}H and ^{13}C. ^{27}Al spectra were fitted with the DMFIT software package [21] to obtain approximations for quadrupolar coupling constant C_q and asymmetry factor *eta*.

The sulfur K-edge experiments were carried out at beamline X19b, National Synchrotron Light source (NSLS) at Brookhaven National Laboratory (Upton, New York). Powder samples were finely ground to prevent scattering and mounted on 2.5-μm Mylar film to reduce the self-absorption effect that commonly occurs for thick samples with S content higher than 0.3 wt.%. The incident X-ray energy was scanned over the range from 2430 to 2500 eV with a step size of 0.25 eV. Elemental sulfur (99.998%, Sigma–Aldrich, USA) was used as reference. Sample fluorescence was measured using a PIPS (passivated implanted planar silicon) detector (Canberra Industries, CT).

2.3. Proton conductivity

The proton conductivity of the S-MIL-53(Al) pellets was measured by AC impedance spectroscopy, using an Autolab PGSTAT302N over a range of 10–10^7 Hz with controlled voltage. The pellets, pressed at 5 ton/cm^2, ca. 13.5 mm × 0.9 mm thick, were clamped between two pairs of electrodes and placed in a chamber under controlled humidity and temperature. No recording of bare MIL-53(Al) was made as this material could not be pelletized.

The resistance R of the membrane was derived from the low intersection of the high-frequency semicircle on a complex impedance plane with the real Re(Z) axis. The conductivity is calculated using the relationship $\sigma = d/(R \times S)$, where σ is the conductivity in S cm^{-1}, R the measured resistance of the membrane in Ω, d the distance between the two electrodes in cm, and S the contact surface, in cm^2. The σ values reported are an average of at least three measurements.

2.4. Catalytic tests

The esterification of acetic acid and *n*-butanol was performed without solvent using a mixture with a molar ratio acetic acid/*n*-butanol = 1:1. The mixture was introduced in a round-bottom flask while being stirred under reflux. A ratio of 3 g catalyst per mol of acetic acid was used. After recovering the catalyst, it was filtered, stored at 423 K, and reused.

3. Experimental results

3.1. Characterization

3.1.1. XRD, TGA, and adsorption

After treatment of two spatially different MOF structures, MIL-101(Cr) and MIL-53(Al), using stoichiometric amounts of H_2SO_4 for only 60 min, a C/S weight ratio of 6 was determined by elemental analysis for MIL-53(Al). Assuming mono-sulfation, this would correspond to successful sulfation of a 50% of the aromatic