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NMR relaxation and exchange in metal–organic frameworks for surface area screening

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ABSTRACT

We describe a robust screening technique that correlates the surface area of metal–organic frameworks to the proton T_2 relaxation behavior of imbibed solvent at low field (13 MHz). In frameworks with small pore sizes (<1 nm) or strong solvent-framework interactions, diffusional exchange between the pore-confined and inter-particle solvent populations remains slow compared to the T_2 of the pore-confined solvent, allowing for a direct porosity analysis of the T_2 spectrum obtained from Laplace inversions. Increases in framework pore-size (>1 nm) lead to corresponding increases in the rate of solvent exchange, as confirmed by T_2 relaxation exchange (REXSY) experiments; increases in the pore size also increases the T_2 of the pore-confined solvent. The combination of these two effects results in comparable rates of relaxation and exchange, which precludes the direct analysis of Laplace inversions. Thus, two- and three-site kinetics models were applied to extract porosity from relaxation decays, thereby improving the utility of the porosity screening tool.

1. Introduction

Metal–organic frameworks are porous crystalline solids consisting of networks of metal clusters or ions connected by organic linkers through coordination bonds. The effectively infinite number of metal–ligand combinations and the modular nature of framework synthesis make high-throughput synthesis an effective optimization tool [1–6], but subsequent characterization of frameworks presents a bottleneck to this workflow. In a previous study we described a porosity-screening technique using nuclear magnetic resonance (NMR) relaxometry. This technique greatly simplified the necessary sample preparation for porosity analysis and reduced the measurement time, thus allowing for faster porosity characterization compared to a typical Brunauer–Emmett–Teller (BET) adsorption experiment [7]. The rate of transverse (T_2) relaxation in a variety of solvent-imbibed metal–organic frameworks and zeolites correlated directly to the two pore-size regimes formed by packed porous particles: nanometer-sized pores belonging to the inherent structure of the framework (pore-confined) and micron-sized voids between the individual crystallites (inter-particle). The clear delineation between the relaxation times of the pore-confined molecules ($\sim 10^{-2}$ to 10^{0} ms) and the inter-particle molecules ($\sim 10^{0}$ to 10^{3} ms) indicated that exchange between the two populations occurred slowly compared to the timescale of relaxation. Thus, the corresponding peak areas for each population, which are proportional to the number of molecules in each population, were directly analyzed to yield an NMR-derived porosity that strongly correlated to the BET surface area.

Direct analysis of the relaxation distributions hinges upon the ability to clearly distinguish the relaxation times of the pore-confined and inter-particle solvent. Diffusional exchange between the two results in relaxation distributions that no longer reflect the size of each population, and in the limiting case of fast exchange, the observed relaxation time is a weighted average of each population's relaxation rates [8–11]. Thus, the limitations of direct analysis depend on the relative magnitudes of the diffusion length and the particle size since solvent molecules that remain within the porous particle during the timescale of the experiment do not exchange with the inter-particle molecules. This direct analysis is also limited by the inherent difference in relaxation times between the pore and inter-particle populations, as well as by the resolution limits of the Laplace inversion algorithm used to deconvolute multi-exponential signals [12]. Given that the relaxation time of pore-confined molecules scales roughly with the pore radius, frameworks with larger pores (>1 nm) would likely exhibit longer pore relaxation times. Furthermore, larger pores

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would decrease the restrictions on diffusion within the framework, resulting in faster exchange. Because of these limitations, the "direct analysis" method was constrained to frameworks with BET surface areas of approximately 1700 m^2/g or less (<1 nm pore sizes). Many important frameworks possess pore sizes greater than 1 nm, since in microporous media (<2 nm pore size), pore volume, porosity, and surface area are proportional to pore size. Thus, the constraint on pore size greatly limits the utility of the technique. Notably, the M_2(dobdc) (MOF-74, $dobdc^{4-}$ = 2,5-dioxido-1,4-benzenedicarboxylate, M = Mg, Ni, Co, Zn) family of frameworks tested in the previous study were also analyzed using the direct analysis method even though they possess pore sizes of ~1.4 nm [13,14]. In these frameworks, strong binding to the high density of open metal sites would greatly hinder diffusion, and thus, the relaxation signals would also exhibit a clear distinction between pore-confined and interparticle solvent.

Here, we describe a second analysis method that allows for the evaluation of high-porosity, large-pore metal organic frameworks and therefore expands the utility of the porosity screening tool. This method accounts for simultaneous relaxation and exchange by using kinetics models to fit the multi-exponential relaxation decays. The fitting results reveal that large-pore frameworks exhibit longer pore relaxation times and faster exchange compared to the frameworks previously tested. Pore volumes derived from these fits correlate strongly with the Langmuir surface area for frameworks up to ~5000 m^2/g, thus allowing for a significant increase in the testing range of the NMR porosity screening tool.

2. Experimental

The compound 4,4″-dihydroxy(1,1′:4′,1″-terphenyl)-3,3″-dicarboxylic acid (H_4dotpdc) was synthesized as detailed in the Supporting information. All other reagents were obtained from commercial vendors and used without further purification. Infrared spectra were obtained on a Perkin-Elmer Spectrum 100 Optica FTIR spectrometer furnished with an attenuated total reflectance accessory. Diffraction data were collected with 0.02° steps using a Bruker AXS D8 Advance diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å), a Göbel mirror, a Lynxeye linear position-sensitive detector, and mounting the following optics: fixed divergence slit (0.6 mm), receiving slit (3 mm), and secondary beam Soller slits (2.5°). The generator was set at 40 kV and 40 mA.

Gas adsorption isotherms were measured using a Micromeritics ASAP 2020 instrument. For standard measurements in ASAP low-pressure glass sample holders, activated samples were transferred under a N_2 atmosphere to preweighed analysis tubes, which were capped with a Transeal. The samples were evacuated on the ASAP until the outgas rate was less than 3 μbar/min. The evacuated analysis tubes containing degassed samples were then carefully transferred to an electronic balance and weighed to determine the mass of sample (typically 100–200 mg). The tube was fitted with an isothermal jacket and transferred back to the analysis port of the gas adsorption instrument. The outgas rate was again confirmed to be less than 3 μbar/min. Langmuir surface areas were determined by measuring N_2 adsorption isotherms in a 77 K liquid N_2 bath and calculated using the Micromeritics software, assuming a value of 16.2 Å^2 for the molecular cross-sectional area of N_2.

2.1. Synthesis of Sc-MIL-100

The compound Sc-MIL-100 was synthesized by following the published procedure [15]. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported.

2.2. Synthesis of Fe-MIL-100

The compound Fe-MIL-100 was synthesized by following the published procedure [16]. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported.

2.3. Synthesis of Al(OH)(bpdc)

The compound Al(OH)(bpdc) was synthesized by following the published procedure [17]. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported.

2.4. Synthesis of MOF-5

The compound MOF-5 was synthesized and activated using a strategy adopted from a previous report [18]. Specifically, H_2bdc (0.66 g, 4.0 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (3.6 g, 12 mmol), and *N*,*N*-diethylformamide (DEF, 100 mL) were combined in a 250-mL Schlenk flask sealed with a rubber septum. The Schlenk flask was heated at 90 °C for 24 h, then placed under N_2, and the reaction solvent was removed via cannula and replaced with anhydrous *N*,*N*-dimethylformamide (DMF) at room temperature. The DMF was exchanged with fresh, anhydrous DMF two further times. The DMF was then exchanged with anhydrous dichloromethane (DCM) at room temperature. The DCM was exchanged with fresh, anhydrous DCM two further times, then the majority of the DCM was removed via cannula. The resulting clear, cubic crystals were activated by heating at 150 °C under vacuum for 24 h. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported.

2.5. Synthesis of Co_2(dotpdc)

The compound Co_2(dotpdc) ($dotpc^{4-}$ = 4,4″-dihydroxy(1,1′:4′,1″-terphenyl)-3,3″-dicarboxylate) was synthesized by following the published procedure. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported [19].

2.6. Framework solvent exchange

Evacuated metal–organic framework samples were imbibed by soaking the framework in DMF overnight. The MOFs were then filtered and dried in a N_2 atmosphere to evaporate excess solvent. Subsequent thermogravimetric analysis (TGA Q50, TA Instruments, New Castle, DE) was used to quantify solvent content of the solvent-filled MOF. Solvent content was determined from the mass loss prior to degradation temperatures for each material. Solvent content was normalized to the dry weight of the MOF sample, and was systematically varied by micropipette addition or thermal evaporation.

2.7. NMR Experiments

^{1}H-NMR relaxation was measured using a 13 MHz Aster Enterprises permanent magnet equipped with a homebuilt probe. This probe consisted of a simple solenoid coil with a diameter of ~8 mm wired to tuning and matching capacitors. A Kea II spectrometer was used for pulse generation and signal acquisition, and all pulse programs were written using a Prospa v3.11 software