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Adsorption−Desorption Induced Structural Changes of Cu-MOF Evidenced by Solid State NMR and EPR Spectroscopy

Yijiao Jiang,† Jun Huang,‡ Besnik Kasumaj,† Gunnar Jeschke,† Michael Hunger,‡ Tamas Mallat,†
and Alfons Baiker*,†

Department of Chemistry and Applied Bioscience, ETH Zürich, Hönggerberg, HCI, 8093 Zürich, Switzerland, and Institute of Chemical Technology, University of Stuttgart, 70550 Stuttgart, Germany

Received November 12, 2008; E-mail: alfons.baiker@chem.ethz.ch

Porous metal−organic frameworks (MOFs) are promising materials for gas storage, separation, and catalysis.[1] To some extent, their unique properties can be attributed to their structural flexibility, which affords them a predominant capability to response to external stimuli.[2] Recently, intensive efforts have been made to demonstrate that the robust MOFs act as sponges upon evacuation/inclusion of physisorbed guests, whereas their crystallinity still remains.[3] As promising catalysts in green chemistry, MOFs possess properties of both homogeneous and heterogeneous catalysts so that they can exhibit high catalytic performance and also easily be separated from reactants and products. Solid-catalyzed heterogeneous reactions generally are initiated by adsorption of reactants on the active sites, followed by surface reaction and desorption steps. The active sites are regenerated upon desorption of products from the surface. A crucial question to be addressed is whether the above surface processes can affect the structure of the MOF materials. To the best of our knowledge, such chemisorption−desorption induced local structural changes of MOFs have not been evidenced so far, and understanding of such phenomena may be crucial for properly assessing the potential of MOFs for technical applications.

Chemisorption of probe molecules in porous MOFs, which results in formation of chemical bond or change of interaction strength between guest molecules and host framework, is considered as a direct approach to study their structural flexibility. High resolution MAS NMR spectroscopy is very sensitive for the local structure of adsorbates and surface sites and provides more detailed separation and assignment of signals,[4] while continuous-wave (CW) EPR is well suited for characterizing the coordination environment of transition metal sites.[5] In this communication, for the first time, MAS NMR combined with EPR spectroscopy gives direct experimental evidence for the flexible structure of MOFs during adsorption−desorption of probe molecules.

The two-dimensional grid $Cu(bpy)(H_2O)_2(BF_4)_2(bpy)$ [Cu-MOF] (bpy = 4,4′-bipyridine) sheets comprise hydrogen-bonded bpy and bpy coordinated at equatorial positions of a Jahn−Teller elongated Cu(II) coordination octahedron. This provides some flexibility in bond cleavage or inclusion.[6a] The Cu-MOF exhibits volume expansion (6.66%) during CO_2 adsorption at a pressure of 101 kPa.[7c] In this work, Cu-MOF was selected as a model to study the structural flexibility induced by adsorption−desorption of probe molecules.

The Cu-MOF was prepared according to the literature[6b] and vacuumed at 373 K under a pressure below 10^{-2} mbar for 12 h (see Supporting Information, SI). As shown in Figure 1a, boron atoms in the Cu-MOF caused a narrow signal at *ca.* −2.0 ppm, which corresponds to tetrahedral coordination. In comparison with free BF_4^- anions,[4b] the polarizing effect of Cu(II) species on the BF_4^- anions is responsible for the decrease of the nuclear shielding resulting in a weak low-field shift of the signal. Upon adsorption of CH_3OH on the Cu-MOF (*ca.* 2.0 CH_3OH per Cu (II) atom), the ^{11}B NMR signal was shifted to −4.9 ppm corresponding to a high-field shift of $\Delta\delta_{11B} = -2.9$ ppm (see Figure 1b). It indicates that the interaction of the Cu(II) species and fluorine in tetrafluoroborate became weaker due to chemisorption of CH_3OH on these active sites, which shifts the ^{11}B MAS NMR signal to a higher magnetic field. Interestingly, when this sample was degassed (0.1 mbar, rt, 20 min) to partially remove the adsorbed CH_3OH, the ^{11}B signal in Figure 1c was reversibly shifted back to the same resonance position ($\delta_{11B} = -2.0$ ppm) as in the original material shown in Figure 1a. It was reported that MOFs exhibited structural flexibility in gas storage under high pressure.[3,7] Here, the structural change in Cu-MOF was obviously detected even upon loading/removing of a few mbar probe molecules.

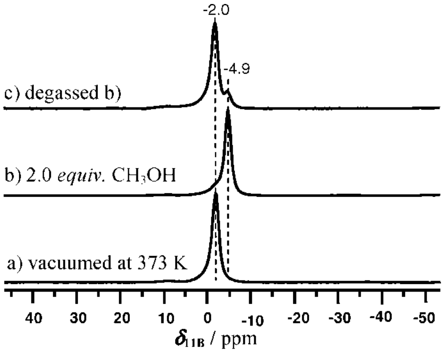

Figure 1. ^{11}B MAS NMR spectra of Cu-MOF vacuumed at 373 K (a), after loading with 2.0 equiv of CH_3OH (b) and degassed sample b (c).

After loading of *ca.* 0.5 CH_3CN per Cu(II) atom on the Cu-MOF (Figure 2a), a new signal appeared at −5.8 ppm corresponding to $\Delta\delta_{11B} = -3.8$ ppm, which was accompanied by a decrease of the ^{11}B signal at −2.0 ppm (Figure 2b). Upon loading of *ca.* 2.0 CH_3CN per Cu(II) atom, the signal at −2.0 ppm totally moved to −5.8 ppm, indicating that virtually all Cu(II) sites interacted with CH_3CN. This finding clearly shows that the structural flexibility is directly caused by chemisorption at Cu(II) sites: the more Cu(II) sites interact with probe molecules, the more neighboring boron atoms are involved in the high-field shift in the NMR spectra. Additional evidence is given by the correlation between the electric dipole moments of the probe molecules and the structural flexibility of the MOF. The higher electric dipole moment of CH_3CN led to a stronger interaction with the Cu(II) sites, which made Cu−F bonds much weaker and resulted in a larger high-field shift of the ^{11}B MAS NMR signal ($\Delta\delta_{11B} = -3.8$ ppm) compared with that observed upon CH_3OH adsorption ($\Delta\delta_{11B} = -2.9$ ppm). After

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† ETH Zürich.
‡ University of Stuttgart.

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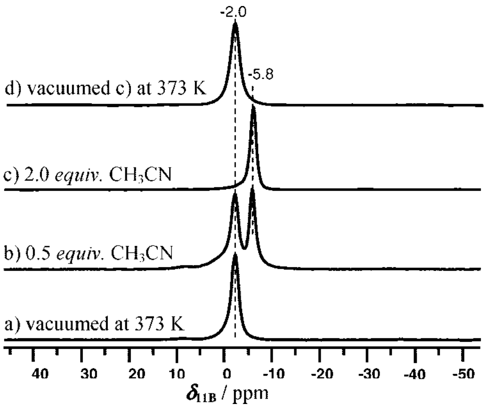

Figure 2. ^{11}B MAS NMR spectra of Cu-MOF vacuumed at 373 K (a), after loading with 0.5 equiv of CH_3CN (b), 2.0 equiv of CH_3CN (c), and evacuation of sample c (d).

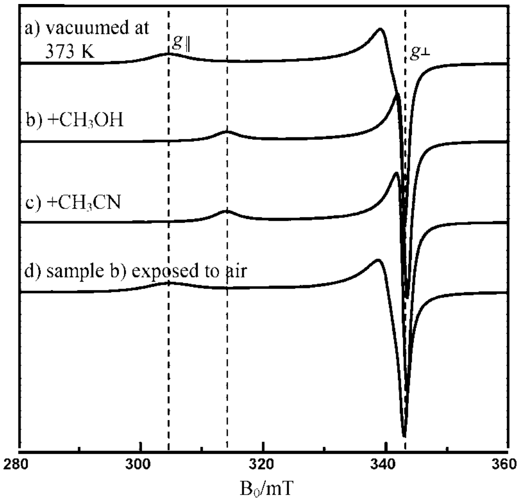

Figure 3. CW EPR spectra of the Cu-MOF vacuumed at 373 K (a), after loading 2.0 equiv of CH_3OH (b), 2.0 equiv CH_3CN (c), and sample b exposed to air (d).

adsorption of CH_3CN the sample was vacuumed at 373 K; the ^{11}B MAS NMR signal in Figure 2d was reversibly shifted back to −2.0 ppm.

To verify binding of the probe molecules and reversible structural changes upon their adsorption, CW X-band EPR spectra of the Cu-MOF loaded with CH_3OH or CH_3CN were recorded. No narrowing of the lines or hyperfine splitting was observed upon cooling from room temperature to 120 K. The spectrum of the Cu-MOF after being vacuumed at 373 K is typical for a six-coordinated Cu(II) complex with an elongated coordination octahedron (Figure 3a). The copper hyperfine interaction is averaged by exchange between neighboring centers.[8] This exchange narrowing does not average the g tensor, as the molecular frames of all copper centers coincide in the crystal structure.[6,7] Axial coordination of BF_4^- is consistent with $g_\parallel = g_z = 2.314$, and a slight splitting of the $g_\perp$ feature is due to the asymmetry of equatorial bpy coordination.

EPR spectra taken after adsorption of CH_3OH or CH_3CN on the Cu-MOF exhibit pronounced shifts of $g_\parallel$ (Figure 3b and 3c), thus indicating coordination changes at all axial sites. These changes in the spectra are accompanied by a color change from violet to lavender blue. Slight sharpening of the $g_\perp$ feature is observed in the high field part of the EPR spectrum. This can be traced back to a closer approach to axial symmetry, i.e., a smaller difference between g_x and g_y (see SI).

Interestingly, when both samples were exposed to air, their EPR spectra (see Figures 3d and S3) were reversibly changed back to the original state. Both the change of $g_\parallel$ and the change in the small orthorhombic splitting in the high field part are reversible. This indicates that the BF_4^- anions again dominantly interacted with Cu(II) at the axial positions. This is consistent with the NMR spectra obtained after vacuum (Figures 1−2) or exposure to air (see Figure S5). Cu-MOF loaded with CH_3OH, which has a lower electric dipole moment, regained the original structure much faster upon exposure to air than that loaded with CH_3CN. Upon air exposure, the Cu-MOF reverted almost completely to the structure of the original material, demonstrating that the humidity of laboratory air was not sufficient for water adsorption in the copper centers. After strong condensation of water a new EPR spectrum with $g_\parallel = 2.259$ is observed (see Figure S4).

In summary, the current work presents direct experimental evidence of MOF structural flexibility during adsorption−desorption, which are important steps in gas storage, separation, and catalysis. Exposure of the Cu-MOF to a few mbar of probe molecules (CH_3OH, CH_3CN) already induced structural changes. The EPR spectra show that these molecules are activated to form complexes at Cu(II) sites, and a change of the Cu-MOF's structure occurs as indicated by a high-field shift of the ^{11}B MAS NMR signal. After desorption, both EPR and ^{11}B MAS NMR results show that the Cu-MOF structure reversibly shifted to the original state. This observation indicates that MOFs can undergo structural changes already under relatively mild conditions. Understanding of these dynamic changes is inevitable for a rational design of MOFs for technical applications.

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Supporting Information Available: Sample preparation, simulation data of CW EPR spectra and ^{11}B MAS NMR spectra upon exposure to air. This materials is available free of charge via the Internet at http://pubs.acs.org.

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