An advanced approach for measuring acidity of hydroxyls in confined

space: FTIR study of low-temperature CO and ¹⁵N₂ adsorption on MOF

samples from the MIL-53(AI) series

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SUPPORTING INFORMATION

1. Background spectra in the low-frequency region

The bands in the $1700 - 400 \text{ cm}^{-1}$ region in the spectrum of the M-350 sample (Fig. S1, spectrum a) are due to the organic part of the MOF and some vibrations associated with the OH groups. In particular, the strong bands at 1595 and 1445-1417 cm⁻¹ are attributed to the antisymmetric and symmetric stretching modes, respectively, of carboxylate groups.^{1,2} The sharp band at 1512 cm⁻¹ arises from the C–C ring vibrations. The band at 988 cm⁻¹ is due to the deformation modes of bridging hydroxyl groups. Two weak bands at 1024 and 1019 cm⁻¹ are assigned to the $\delta(CH)$ (v_{18a}) modes of the terephthalate ligands.¹ The position of this mode is indicative of the large pore (1024 cm⁻¹) and narrow pore (1019 cm⁻¹) forms of the MOF structure. The results indicated the co-presence of the two forms in our sample.

When the MIL sample was activated only at 473 K, an additional band, at 1699 cm⁻¹, was detected (Fig. S1, spectrum b). This band is due to the C-O stretching vibrations of the carboxylate groups of residual therephtalic acid.³

The spectrum of the amino-functionalized NM sample (Fig. S1, spectrum c) is also in agreement with the published data for this material³⁻¹¹ and is similar to the spectrum of M-350. In this case, however, additional bands characterizing the amino groups are observed. A band at 1257 cm⁻¹ is associated with the NH₂ deformation modes. Two bands, at 3504 and 3392 cm⁻¹, characterize the symmetric and antisymmetric NH modes of the amino groups.⁵⁻⁷



Figure S1. Background spectra of the M-350 (a), M-200 (b) and NM (c) samples.

2. Computer deconvolution of some hydroxyl bands



Figure S2. Computer deconvolution of the hydroxyl bands of some MOF samples.





Figure S3. Panel A: FTIR spectra of NM sample in the hydroxyl region. Spectrum registered at low temperature and in presence of He (a), evacuation at low temperature (b) and at increasing temperatures up to ambient one (c, d). Panel B: Correlation between the stretching frequency and the FWHM of the band at 3711-3701 cm⁻¹.



4. Adsorbate-induced shift of the deformation OH modes

Figure S4. Difference FTIR spectra registered after adsorption of increasing doses of CO on the samples M-350 (panel A, spectra a-f), M-200 (panel B, spectra g-k) and NM (panel C,

spectra l-q).

5. Spectra of adsorbed CO

Adsorption of CO on the M-350 sample leads to development at low coverage, of an OH-CO band at 2146 cm⁻¹. At high coverage it broadened and shifted to 2145 cm⁻¹ (Fig. S5A). The latter effect is attributed to the formation of geminal complexes.

The results with the M-200 sample show some differences (Fig. S5B). Even at low coverage a band at 2137 cm⁻¹ develops. The relatively high stability of the respective adsorption form indicates that part of the adsorbed CO is bonded simultaneously with its C-and O-ends. Indeed, it is known that coordination of CO through the oxygen atom leads to a decrease of the CO stretching frequency.¹² However, there is no correlation between the intensities of the two carbonyl bands and the intensities of a specific negative hydroxyl band. Therefore, we attribute the appearance of CO which is bonded by the two ends (to an OH group by the C-atom and to the framework by the O-atom) simply to the small size of the pores in the M-200 sample.

Adsorption of CO on the NM sample (Fig. S5C) leads to the appearance of an intense band at 2135 cm⁻¹ and a shoulder at 2127 cm⁻¹ indicating CO bonded via its two ends. Slight interaction with the O-end is also suggested for the band at 2141 cm⁻¹ because of the lower wavenumber as compared to the amino-free sample. This is consistent with the narrow pore structure of the NM material.



Figure S5. FTIR spectra of increasing doses of CO adsorbed on M-350 (A), M-200 (B) and

NM (C) samples.

6. Adsorption of ${}^{15}N_2$ on M-200



Figure S6. Difference spectra of ${}^{15}N_2$ adsorbed on the M-200 sample. The spectra correspond to small changes in the ${}^{15}N_2$ amount and are registered at medium coverages. The coverage increases in the sequence a - e.

7. Calculation of the intrinsic frequency of the hydroxyl groups

Consider a hydroxyl group that is involved in weak H-bonding. This will result in a red shift of v(OH) by x cm⁻¹. Let us suppose that, at first approximation, the existing bond is broken after adsorption of a basic molecule. The real shift of the band maximum will be the measured shift - x. Therefore, to maintain the ratio of 2.8 between the CO- and N₂-induced shifts, Δv_{CO} (OH) and Δv_{NN} (OH), respectively, one could write:

 $\Delta v_{\rm CO}(\rm OH) - x = 2.8 (\Delta v_{\rm NN}(\rm OH) - x)$

From this:

$$x = (\Delta v_{\rm CO}(\rm OH) - 2.8 \, \Delta v_{\rm NN}(\rm OH))/1.8$$

Finally, the intrinsic frequency of the hydroxyl groups can be found by adding the absolute value of x to the measured value.

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