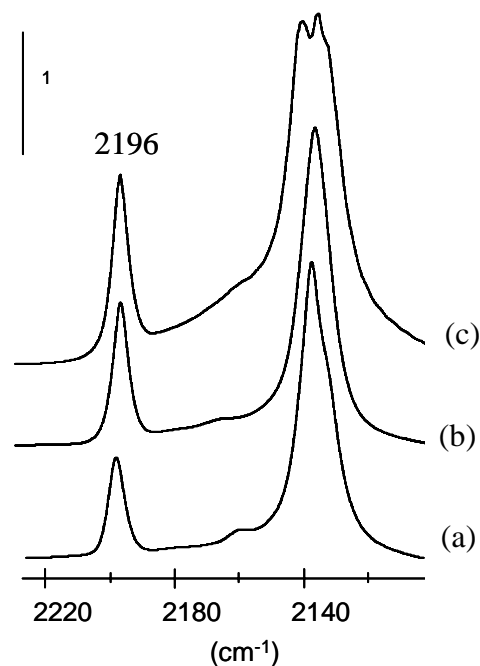


SUPPORTING INFORMATION AVAILABLE

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Figure S1 shows IR spectra recorded at 100 K of MIL-101a, 101b and 101c outgassed at 473 K after introduction of an equilibrium pressure (200 Pa) of CO (spectra a, b and c respectively).



These spectra show only a single sharp $\nu(\text{CO})$ band centered at 2196 cm^{-1} regardless of pre-treatment. The position and the intensity of this $\nu(\text{CO})$ band are close to those assigned to the less acidic Cr^{3+} sites present in the MIL-100. Using an absorption coefficient equal to $2.1\text{ cm}^{-1}\text{ }\mu\text{mol}^{-1}$ [19] it is possible to deduce that the concentration of the Lewis acid sites in the MIL-101a b and c is equal to 500, 700 and $1000\text{ }\mu\text{mol g}^{-1}$ respectively. This concentration is three fold lower than that observed in the MIL-100 showing that accessible Lewis acid sites are stronger and more abundant in MIL-100 than in MIL-101 materials. Since the configuration of the trimers of chromium octahedra is similar in both structures, the lower acidity of the MIL-101 materials could be explained by the presence of extra framework impurities persisting inside the pores even after activation. This is confirmed by the IR spectra here which indicate a C/Cr ratio higher than expected.

Figure S2 shows the IR spectra of MIL-101b (upper curves) and MIL-100 (lower curves) obtained after equilibrium with 2330 Pa CO₂ pressure (a and e) followed by various regeneration treatments :

5 minutes under 1.5 Pa vacuum at 303 K (b and f),

5 minutes under 0.015 Pa vacuum at 303 K (c and g),

Thermal treatment to 473 K under 0.015 Pa (d and h).

