

Supporting Information

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General Considerations: All reactions were carried out using Schlenk or autoclave under an atmosphere of dry Argon. Water was degassed prior to use by bubbling argon gas directly in the solvent. Other solvents were purchased from Carlo Erba and degassed prior to use by freeze-pump thaw procedure (3 times). NMR spectra were recorded on a 400 MHz and 500 MHz Brücker spectrometer. Proton (^1H) NMR information is given in the following format: multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintuplet; sept, septet; m, multiplet), coupling constant(s) (J) in Hertz (Hz), number of protons. The prefix app is occasionally applied when the true signal multiplicity was unresolved and br indicates the signal in question broadened. Carbon NMR spectra are reported in ppm (δ) relative to CDCl_3 (δ 77.16) unless noted otherwise. HRMS analyses were performed by LCMT analytical services. Neutral activated aluminium oxide was purchased from Alfa Aesar (Brockmann Grade I, 58 Angstroms, -60 Mesh Powder, S.A. 150 m^2/g) and from Merck (Grade I, 90 Angstroms, 70-230 Mesh ASTM). Basic aluminium oxide was purchased from Alfa Aesar (Brockmann Grade I, 58 Angstroms, -60 Mesh Powder, S.A. 150 m^2/g). NMR solvents were filtered through a pad of basic alumina for NMR analysis of iron complexes.

Part 1: Synthesis of MIL-53(Cr) MOF.

MIL-53(Cr) was hydrothermally synthesized and activated in two steps according to the procedures published elsewhere.¹ First, chromium(III) nitrate, terephthalic acid, hydrofluoric acid, and H_2O were mixed in the molar ratio 1:1.5:1:280. Reactants were introduced to a Teflon-lined steel autoclave, and the temperature was set at 493 K for 6 days. A light purple powder was obtained that contained traces of terephthalic acid. The latter was first eliminated by dispersing the powder in an excess of dimethylformamide (DMF) for ca. 10 min with stirring. Next, the free terephthalic acid present in the pores of MIL-53 was evacuated by a solvothermal exchange with DMF (1 g of MIL-53as in 25 mLDMF) by using a Teflon-lined steel autoclave at 423 K overnight. After cooling to room temperature, the solid MIL-53DMF was calcined overnight at 523 K to remove DMF molecules. After cooling in air, the resulting solid adsorbed water at room temperature to give MIL-53LT or $\text{Cr}^{\text{III}}(\text{OH}) \cdot (\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2) \cdot \text{H}_2\text{O}$.

¹ (a) Serre, C.; Bourrelly, S.; Vimont, A.; Ramsahye, N. A.; Maurin, G.; Llewellyn, P. L.; Daturi, M.; Filinchuk, Y.; Leynaud, O.; Barnes, P.; Ferey, G. *Adv. Mater.* **2007**, *19*, 2246-2251. (b) Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louer, D.; Ferey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519-13526.

Part 2: Hydrogenation of carbon dioxide.

General procedure A: In an autoclave, the desired MOF (0.05 mol%), **Fe1** (0.02 mol%), Me₃NO (0.02 mol%) and the corresponding base (5 mmol) were added to a degassed (1:1) H₂O/DMSO mixture (5 mL) under an argon atmosphere. The autoclave was pressurized first with carbon dioxide (20 bar) and then with molecular hydrogen (40 bar) and heated at 100 °C under stirring for 20 hours. The autoclave was cooled down to room temperature and vented. Conversions were determined on the crude mixture (0.4 mL) by ¹H-NMR spectroscopy in D₂O using DMF (15.4 μL) as internal standard. **¹H-NMR (D₂O, 500 MHz)** δ 8.43 (s, HCOOH.TMG), 7.93 (s, 1H, DMF), 2.94 (s, TMG), 2.99 (s, 3H, DMF), 2.83 (s, 3H, DMF) ppm.

Table 1. Hydrogenation of carbon dioxide.

Entry ^[a]	Base	Additive (mol%)	Conv. ^[b] (%)	TON ^[b]
1	DBU	-	29.3	1466
2 ^[c]	DBU	MIL-53(Cr)	38.0	1900
3	DBU	MIL-53(Cr)	43.5	2173
4	TMG	-	34.5	1772
5	TMG	MIL-53(Cr)	60.1	3006
6 ^[d]	TMG	MIL-53(Cr)	traces	-
7	TMG	Cr(CH ₃ CO ₂) ₃	2.0	99
8 ^[e]	TMG	Cr(CH ₃ CO ₂) ₃	-	-
9 ^[e]	TMG	MIL-53(Cr)	-	-
10	TMG	MIL-53(Cr)	-	-
11 ^[f]	TMG	MIL-53(Cr)	1.7	86
12	TMG	MIL-100(Cr)	4.5	224
13	TMG	MIL-101(Cr)	25.3	1265
14	TMG	MIL-53(Cr-Fe)	18.3	913
15	TMG	MIL-53(Fe)	12.0	599
16	TMG	MIL-53(Al)	20.5	1026

^[a] General conditions: base (5 mmol), **Fe1** (0.02 mol%), Me₃NO (0.02 mol%), MOF (0.05 mol%), solvent (5 mL). ^[b] Determined by ¹H-NMR analysis using DMF as an internal standard. ^[c] MIL-53(Cr) (0.02 mol%). ^[d] MIL-53(Cr) (0.5 mol%). ^[e] without complex, without Me₃NO. ^[f] P(CO₂) = 10 bar ; P(H₂) = 20 bar. DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene ; TMG: 1,1,3,3-Tetramethylguanidine.

Part 3: Hydrogenation of sodium hydrogenocarbonate.

General procedure B: In an autoclave, the desired complex (0.01 mol%) and NaHCO₃ (25 mmol) were added to a degassed (1:1) H₂O/DMSO solution (5 mL) under argon atmosphere. The autoclave was pressurized with molecular hydrogen (50 bar) and heated at 100 °C under stirring for 20 hours. The autoclave was cooled down to room temperature and vented. Conversions were determined on the crude mixture (0.4 mL) by ¹H-NMR spectroscopy in D₂O using DMF (15.4 μL) as internal standard. ¹H-NMR (D₂O, 500 MHz) δ 8.41 (s, HCOONa), 7.89 (s, 1H, DMF), 2.97 (s, 3H, DMF), 2.81 (s, 3H, DMF) ppm.

Table 2. Hydrogenation of sodium hydrogenocarbonate.

Entry ^[a]	Additif	Conv. ^[b] (%)	TON ^[b]
1	-	12.5	1246
2 ^[c]	MIL-53(Cr)	13.1	1307
3	MIL-53(Cr)	15.3	1525
4 ^[d]	MIL-53(Cr)	1.0	103
5 ^[e]	Cr(CH ₃ CO ₂) ₃	-	-
6	Cr(CH ₃ CO ₂) ₃	9.9	993
7	MIL-100(Cr)	13.3	1334
8	MIL-101(Cr)	7.8	784
9	MIL-53(Cr-Fe)	1.2	123
10	MIL-53(Fe)	2.3	232
11	MIL-53(Al)	1.4	141

^[a] General conditions: NaHCO₃ (25 mmol), **Fe1** (0.01 mol%), additive (0.05 mol%), solvent (5 mL). ^[b] Determined by ¹H-NMR analysis using DMF as an internal standard. ^[c] MIL-53(Cr) (0.01 mol%). ^[d] MIL-53(Cr) (0.5 mol%). ^[e] without **FeX**, without Me₃NO.

Part 4: Hydrogenation of sodium carbonate.

General procedure J: In an autoclave, the desired complex (0.2 mol%) and Na₂CO₃ (5 mmol) were added to a degassed (1:1) H₂O/DMSO mixture (5 mL) under an argon atmosphere. The autoclave was pressurized with molecular hydrogen (50 bar) and heated at 100°C under stirring for 20 hours. The autoclave was cooled down to room temperature and vented. Conversions were determined on the crude mixture (0.4 mL) by ¹H-NMR spectroscopy in D₂O using DMF (15.4 μL) as internal standard. ¹H-NMR (D₂O, 500 MHz) δ 8.41 (s, HCOONa), 7.89 (s, 1H, DMF), 2.97 (s, 3H, DMF), 2.81 (s, 3H, DMF) ppm.

Table 3. Hydrogenation of sodium carbonate.

Entrée ^[a]	Additif	Conv. ^[b] (%)	TON ^[b]
1	-	3.4	17
2 ^[c]	MIL-53(Cr)	2.7	14
3	MIL-53(Cr)	5.2	26
4 ^[d]	Cr(CH ₃ CO ₂) ₃	-	-
5	Cr(CH ₃ CO ₂) ₃	1.4	7
6	MIL-100(Cr)	4.4	22
7	MIL-101(Cr)	4.4	22
8	MIL-53(Cr-Fe)	4.9	24
9	MIL-53(Fe)	4.6	23
10	MIL-53(Al)	2.7	13

^[a] General conditions: Na₂CO₃ (5 mmol), Fe1 (0.2 mol%), additive (0.5 mol%), solvent (5 mL). ^[b] Determined by ¹H-NMR analysis using DMF as an internal standard. ^[c] MIL-53(Cr) (0.01 mol%). ^[d] MIL-53(Cr) (0.5 mol%).

Part 5: Copies of NMR spectra.

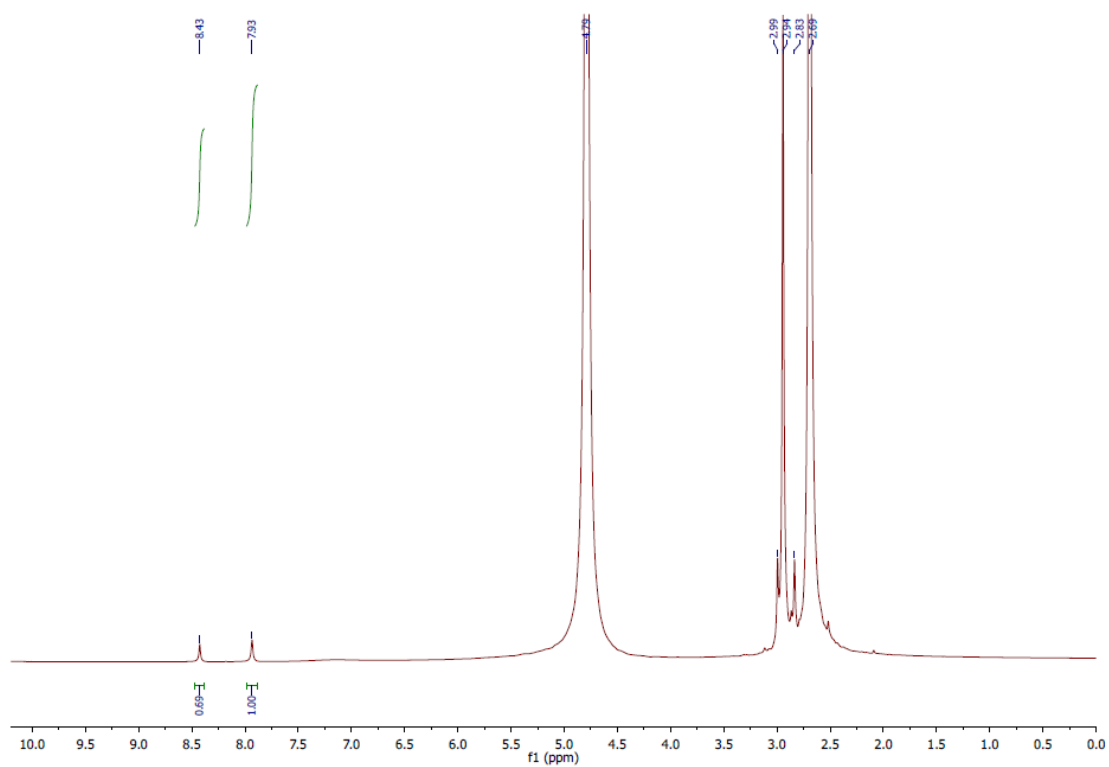


Figure 1. $^1\text{H-NMR}$ spectrum for hydrogenation of carbon dioxide.

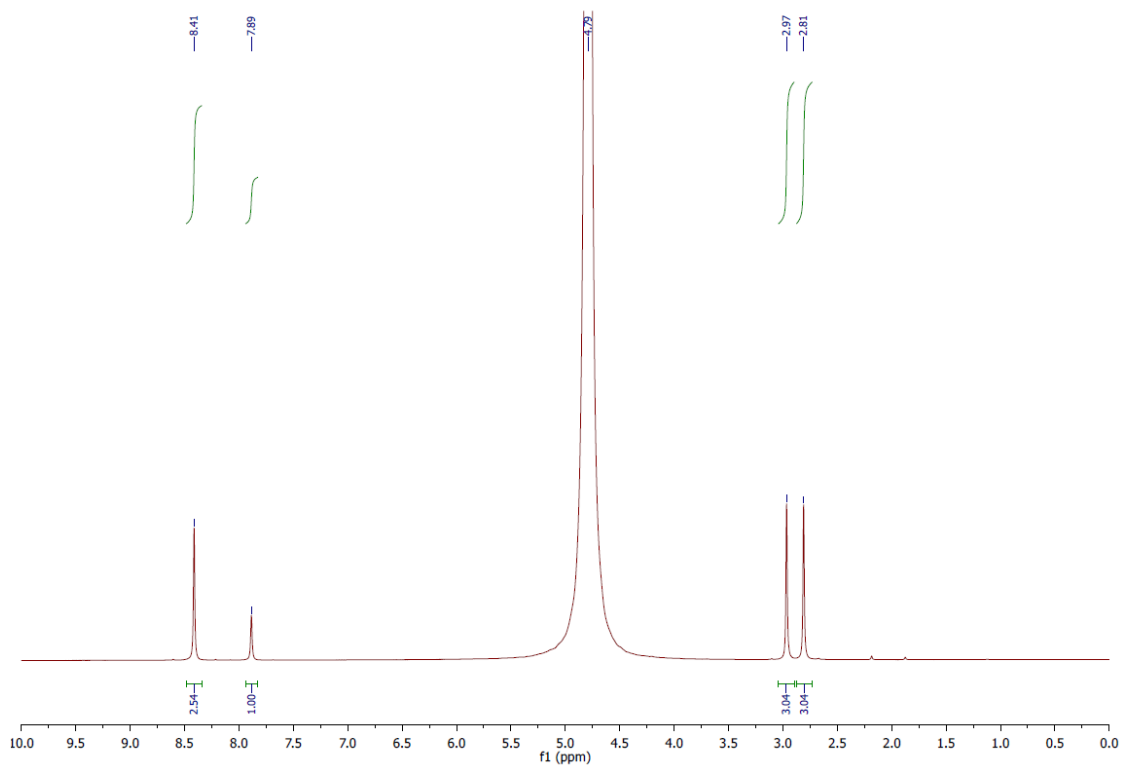


Figure 2. $^1\text{H-NMR}$ spectrum for hydrogenation of NaHCO_3 and Na_2CO_3 .

Part 6: Raman spectra.

Raman spectra were recorded on a Horiba Jobin Yvon Labram 300 confocal microscope. Some liquid was placed on a microscope plate and several spectra were taken at different spots in the liquid. The spectrometer was equipped with a laser at 532 nm and a 1800 lines/mm grating. Laser power on the sample was ca. 0.4 mW, and spectra were typically recorded in 60s (acquisition time in 3 to 10 s with 20 to 6 accumulations).

Results

Figure 3 shows the Raman spectra obtained by analysis of the crude mixture after hydrogenation reaction in the presence of iron complex **Fe1** (standard conditions, see Part 2, spectra a and b) or without iron complex **Fe1** (spectra c-g).

The Raman spectra of the liquid mixture after standard reaction conditions (Figure 3 (a)-(b)) show mainly peaks, which can be attributed to DMSO at 676, 710, 952, 1013, 1350 and 1418 cm^{-1} . Small peaks were also occasionally observed (spectrum (b)) at 866, 1144, 1455 and 1612 cm^{-1} which are due to the presence of MIL-53(Cr). The extremely low amount of MIL-53(Cr) in standard reaction conditions (0.05 mol %) is consistent with the low intensity.

In order to ascertain this attribution and to confirm the stability of the MOF in the reaction mixture, a specific experiment was carried out in which the amount of MIL-53 was increased to 20 mg (standard conditions without the iron complex **Fe1**). The spectra (c)-(g) showed similar features except for the bands at 729, 1039, 1321, 1350 and 1039 cm^{-1} , which might be due to guanidinium formate. The latter was not formed in the absence of iron complex **Fe1**. As indicated above, the peaks at 866, 1144, 1455 and 1612 cm^{-1} were also observed. For both reaction conditions (with or without iron complex), the spectra obtained after subtraction (Figure 3 (h) and (i)) clearly show the presence of the main peaks of MIL-53 spectrum.²

It is noteworthy that, when comparing these peaks intensities to the peaks of the solvent, large variations were observed from one spectrum to the other. This confirms that MIL-53 is still in its original solid form as such variations are observed when heterogeneous samples are analyzed by the Raman microscope. This would not be observed if the MIL-53 solid was degraded, inducing transfer of the ligand in the liquid phase with a constant concentration.

² Hamon, L.; Llewellyn, P. L.; Devic, T.; Ghoufi, A.; Clet, G.; Guillerm, V.; Pirngruber, G. D.; Maurin, G.; Serre, C.; Driver, G.; van Beek, W.; Jolimaître, E.; Vimont, A.; Daturi, M.; Férey, G. *J. Am. Chem. Soc.* **2009**, *131*, 17490-17499.

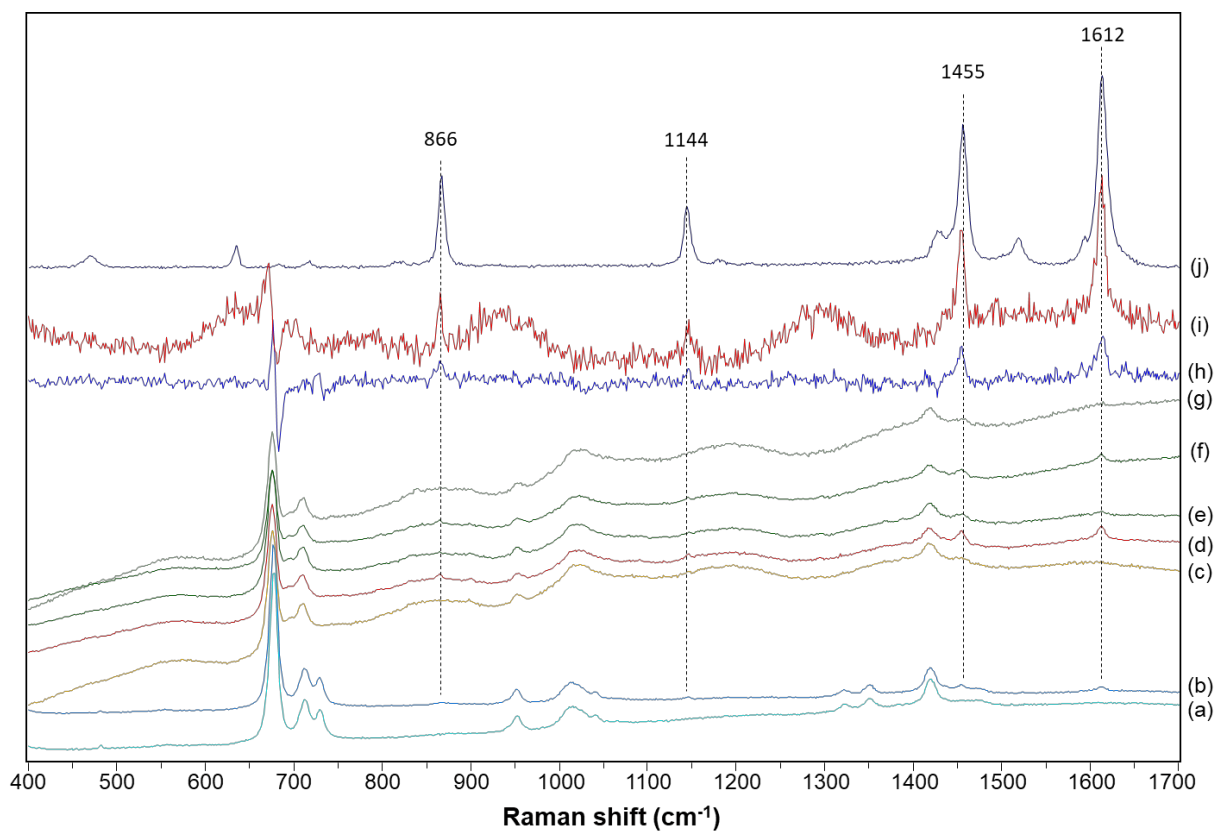


Figure 3. Raman spectra in the liquid phase. (a),(b) : Spectra obtained after hydrogenation reaction in the presence of iron complex **Fe1**; (c)-(g): Spectra obtained after 16 h under hydrogen/CO₂ pressure at 100 °C without iron complex, with a larger amount of MIL-53; (h) difference between spectra (b) and (a); (i) difference between spectra (d) and (c); (j) reference spectrum for pure solid MIL-53(Cr).