

SUPPORTING INFORMATION

Tuning the catalytic performance of metal-organic frameworks in fine chemistry by active site engineering

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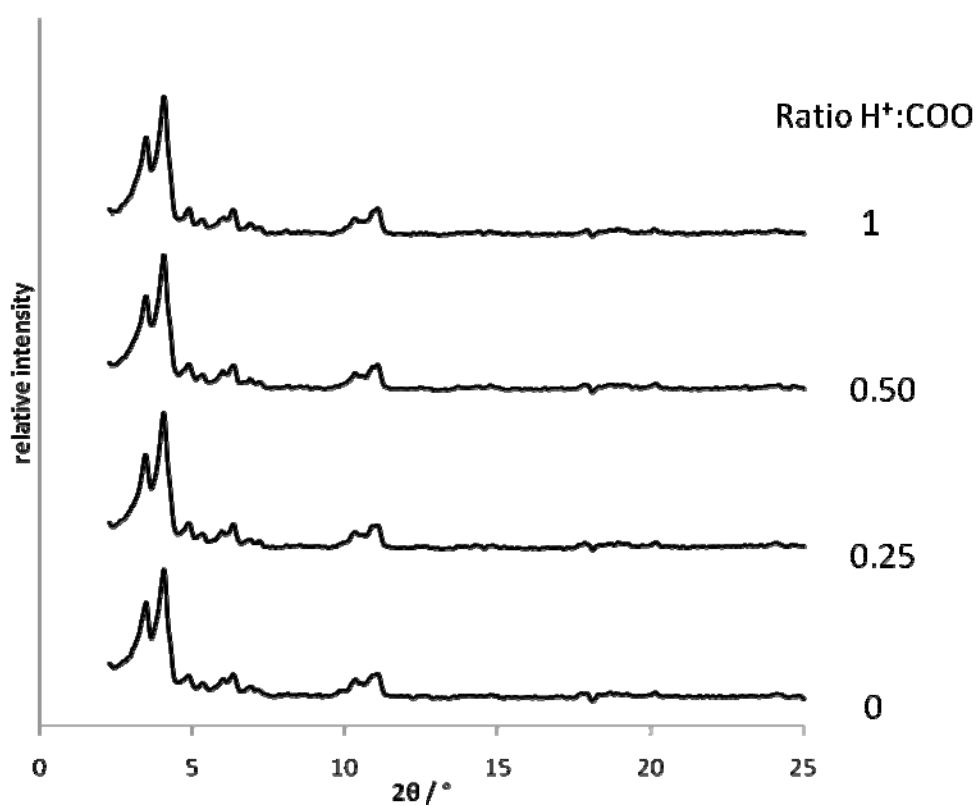


Figure S1. XRD powder patterns of MIL-100(Fe) treated with solutions of CF₃COOH of different concentrations. The ratio of protons in the acid solution to the number of carboxylate moieties present in the lattice is shown at the right.

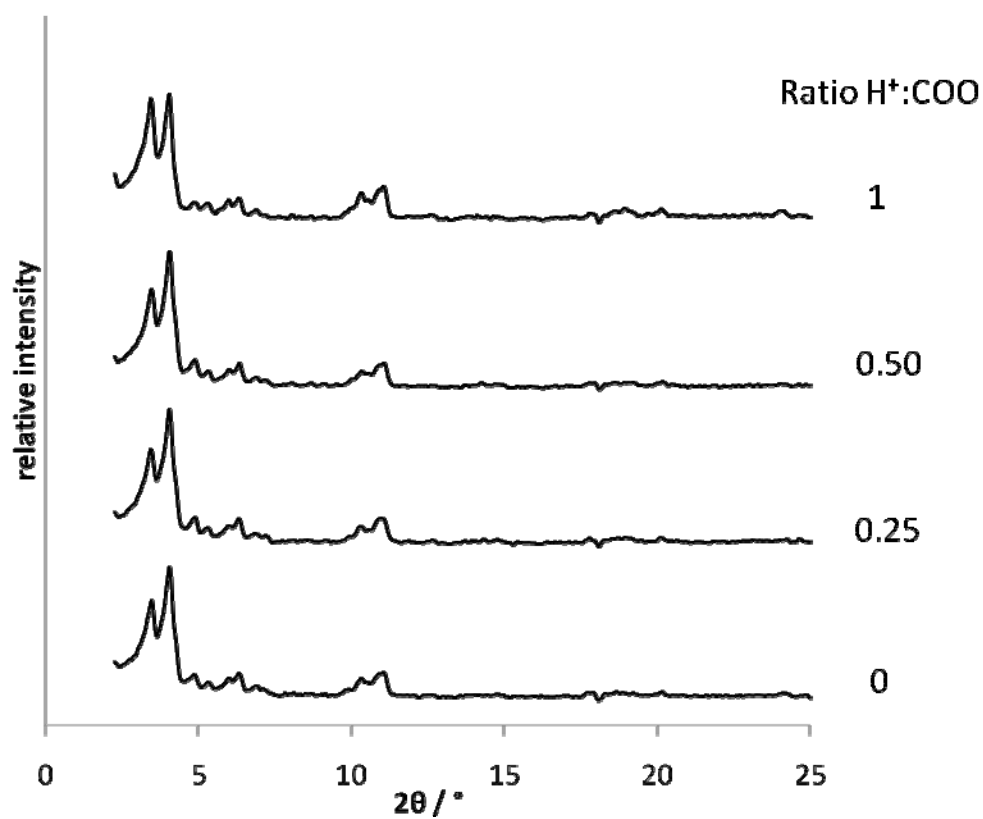


Figure S2. XRD powder patterns of MIL-100(Fe) treated with solutions of HClO₄ of different concentrations. The ratio of protons in the acid solution to the number of carboxylate moieties present in the lattice is shown at the right.

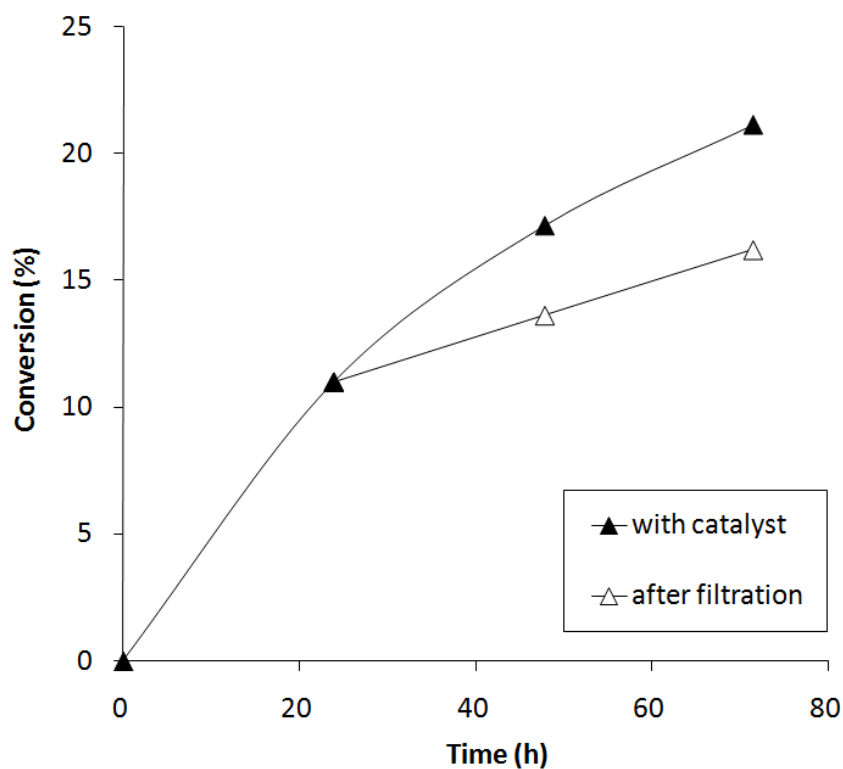


Figure S3. Cyclization of citronellal with MIL-100(Fe) pretreated with a CF_3COOH solution ($\text{H}^+:\text{COO}$ ratio of 0.5): conversion as a function of time. After 24 h, the reaction mixture was split in two parts and the catalyst was withdrawn from one sample. The reaction rate after filtration is equal to the reaction rate of the thermal reaction.

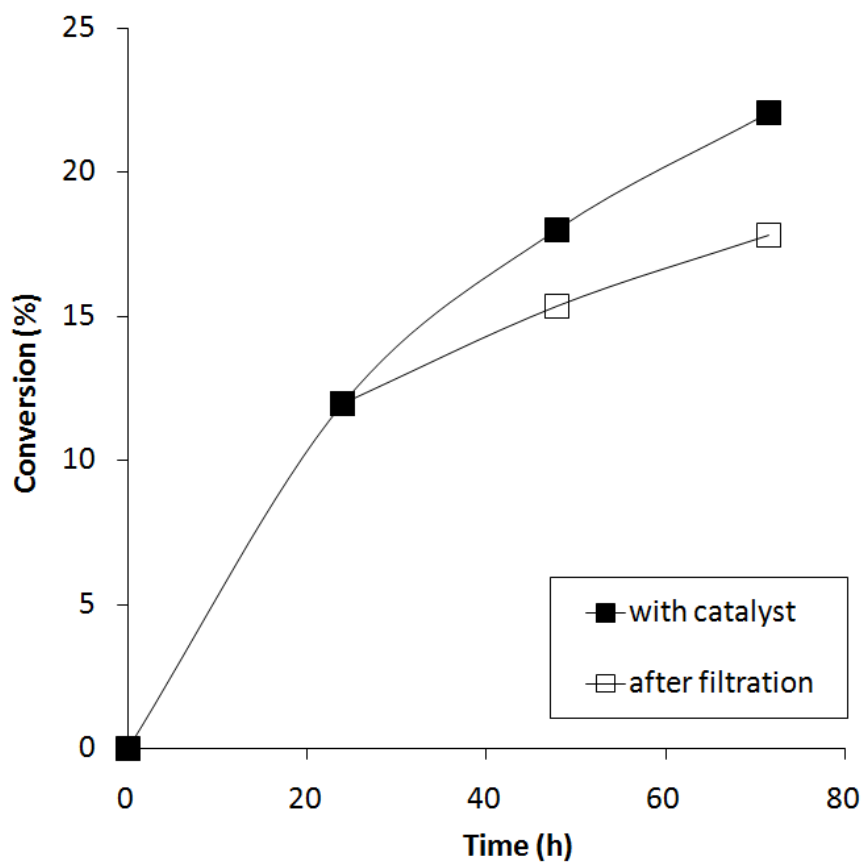


Figure S4. Cyclization of citronellal with MIL-100(Fe) pretreated with a HClO₄ solution (H⁺:COO ratio of 0.5): conversion as a function of time. After 24 h, the reaction mixture was split in two parts and the catalyst was withdrawn from one sample.

Table S1. Conversion (%) after 24 h, of α -pinene oxide using a series MIL-100(Fe) samples that have been immersed in solutions of CF_3COOH or HClO_4 of different concentrations (a ratio of H^+ to lattice carboxylate groups of 0.5 corresponds to an acid concentration of 0.039 M).

H+:COO ratio	MIL-100(Fe)	
	HClO_4	CF_3COOH
0	31	31
0.08	30	26
0.17	30	26
0.25	20	26
0.5	14	13

Table S2. Conversion (%) of citronellal after 24 h using a series of MIL-100(Fe) samples that have been immersed in solutions of CF_3COOH or HClO_4 of different concentrations (a ratio of H^+ to lattice carboxylate groups of 0.5 corresponds to an acid concentration of 0.039 M).

H+:COO ratio	MIL-100(Fe)	
	HClO_4	CF_3COOH
0	14	14
0.08	10	17
0.17	13	16
0.25	15	17
0.5	16	15

Table S3. BET-surface areas (m^2/g) of the different MIL-100(Fe) samples that have been immersed in solutions of CF_3COOH or HClO_4 of different concentrations (a ratio of H^+ to lattice carboxylate groups of 0.5 corresponds to an acid concentration of 0.039 M).

H+:COO ratio	MIL-100(Fe)	
	HClO_4	CF_3COOH
0	1536	1536
0.25	1474	1590
0.5	1427	1450
1	1394	1359