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Design of stable mixed-metal MIL-101(Fe/Cr) materials with enhanced catalytic activity for the Prins reaction

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Supplementary Material

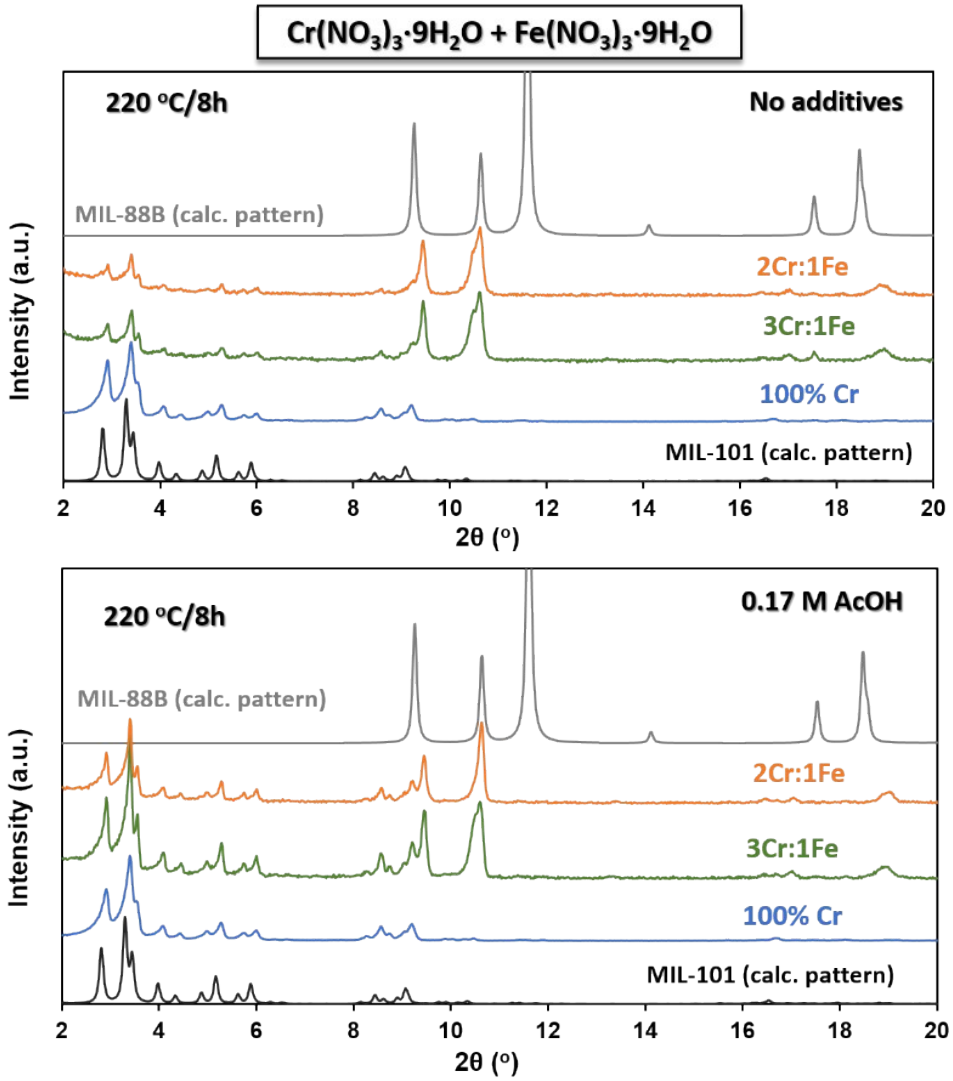

Figure SI-1: Normalized PXRD patterns (λ= 1.54 Å) of the obtained products using different ratios of the metal sources $Cr(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$. Hydrothermal conditions: 220 °C for 8 h; without additives (top) and with 0.17 M AcOH (down).

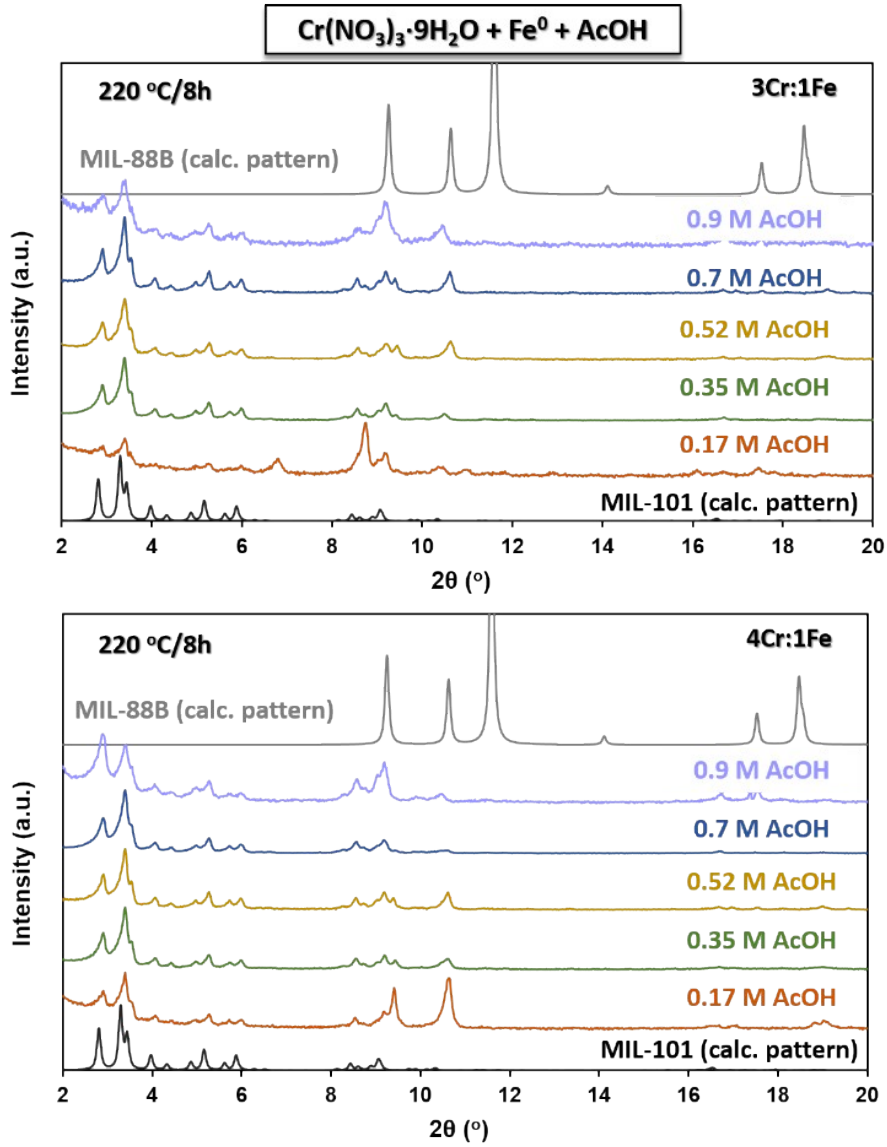

Figure SI-2: Normalized PXRD patterns (λ= 1.54 Å) of the obtained products using as metal sources $Cr(NO_3)_3 \cdot 9H_2O$ and Fe^0 with different concentrations of AcOH (0.17-0.9 M). Hydrothermal conditions: 220 °C for 8 h; metal ratio 3Cr:1Fe (top) and 4:Cr:Fe (down).

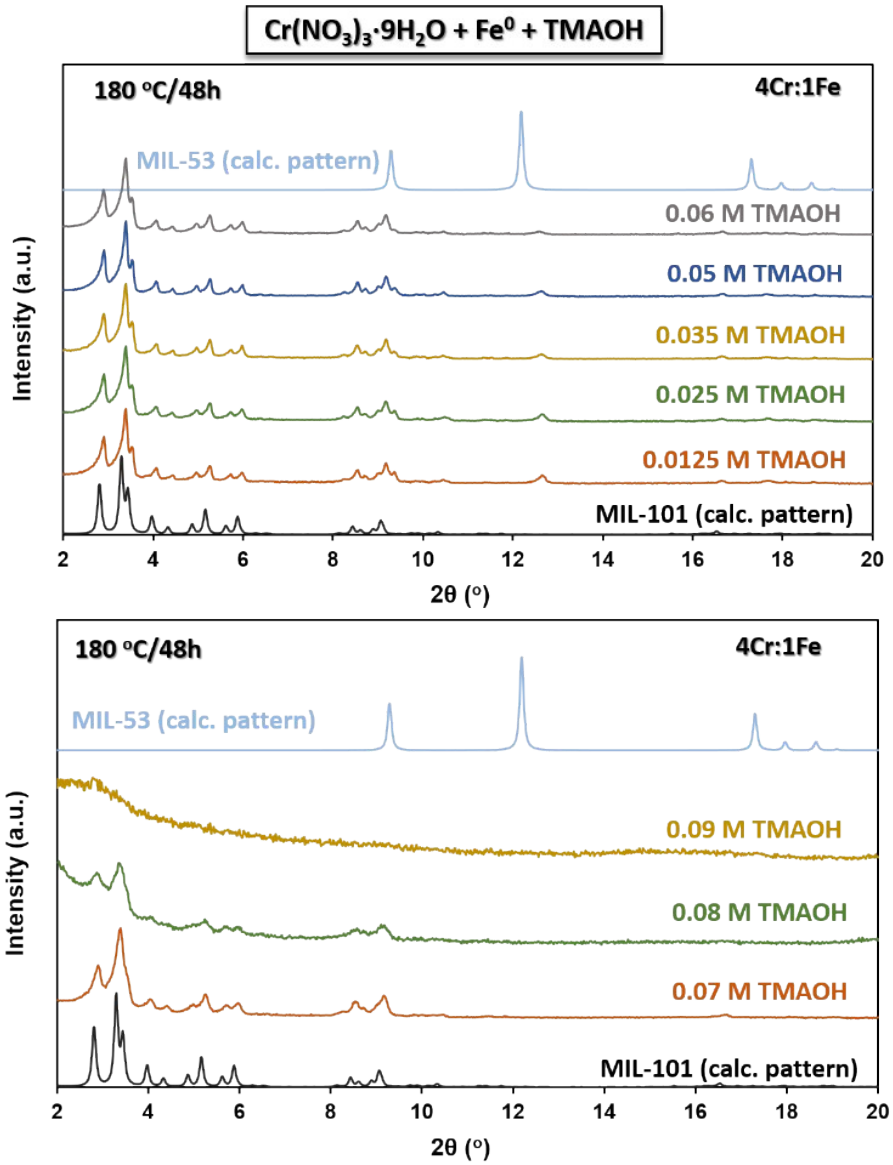

Figure SI-3: Normalized PXRD patterns (λ= 1.54 Å) of the obtained products using as metal sources $Cr(NO_3)_3 \cdot 9H_2O$ and Fe^0, with different concentrations of TMAOH and metal ratio 4Cr:Fe. Hydrothermal conditions: 180 °C for 48 h; [TMAOH] = 0.0125-0.06 M (top) and 0.07-0.09 M (down).

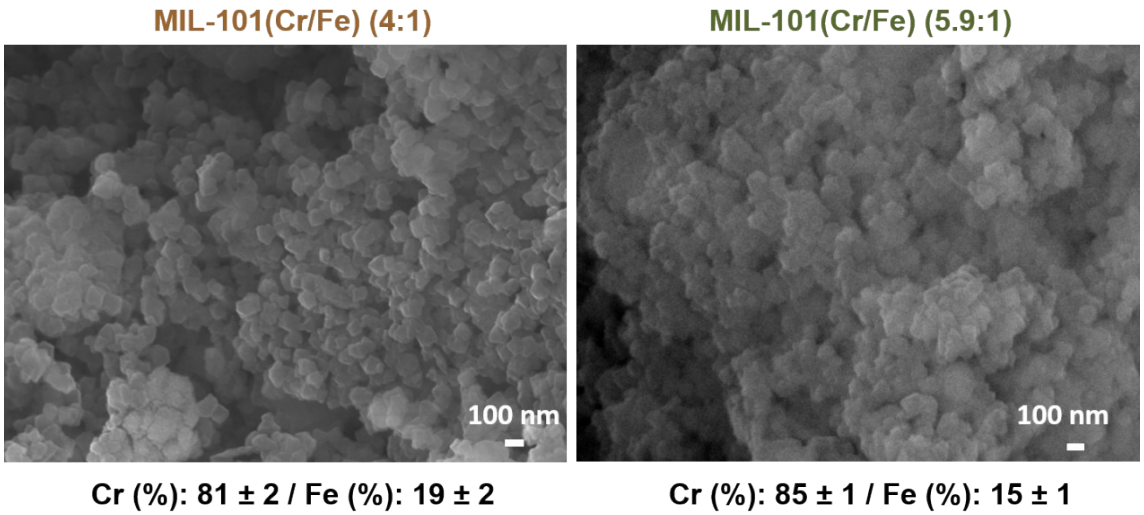

Figure SI-4: SEM-EDX analysis of MIL-101(Cr/Fe) (4:1) and MIL-101(Cr/Fe) (5.9:1).

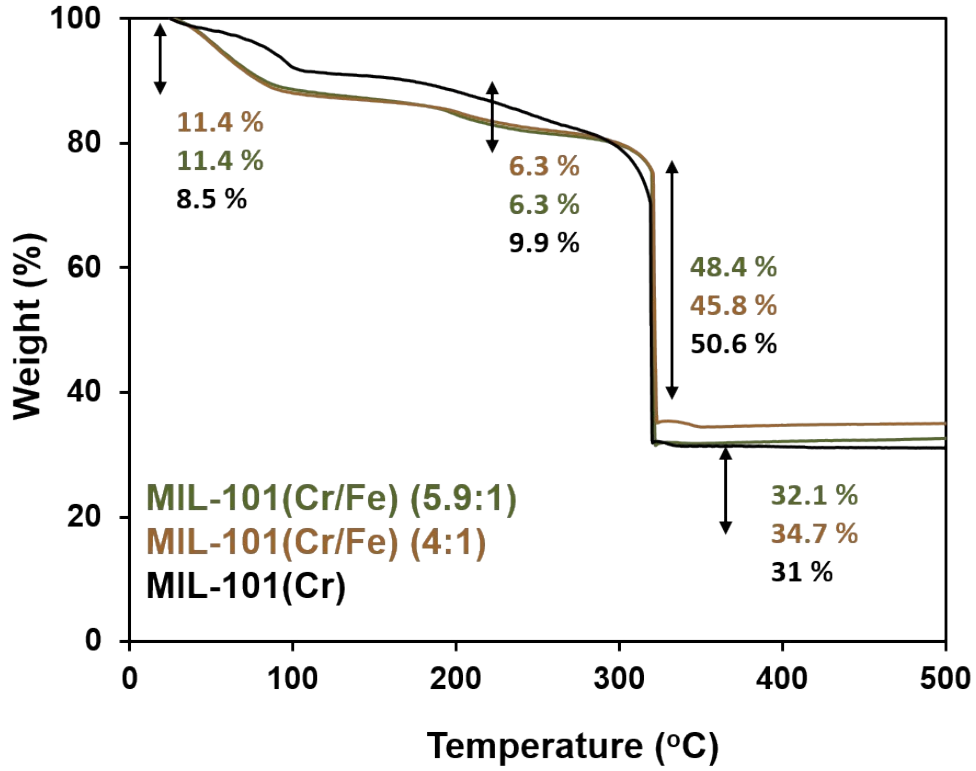

Figure SI-5: TGA curves of MIL-101(Cr/Fe) (4:1), MIL-101(Cr/Fe) (5.9:1) and MIL-101(Cr), under O_2 flow.

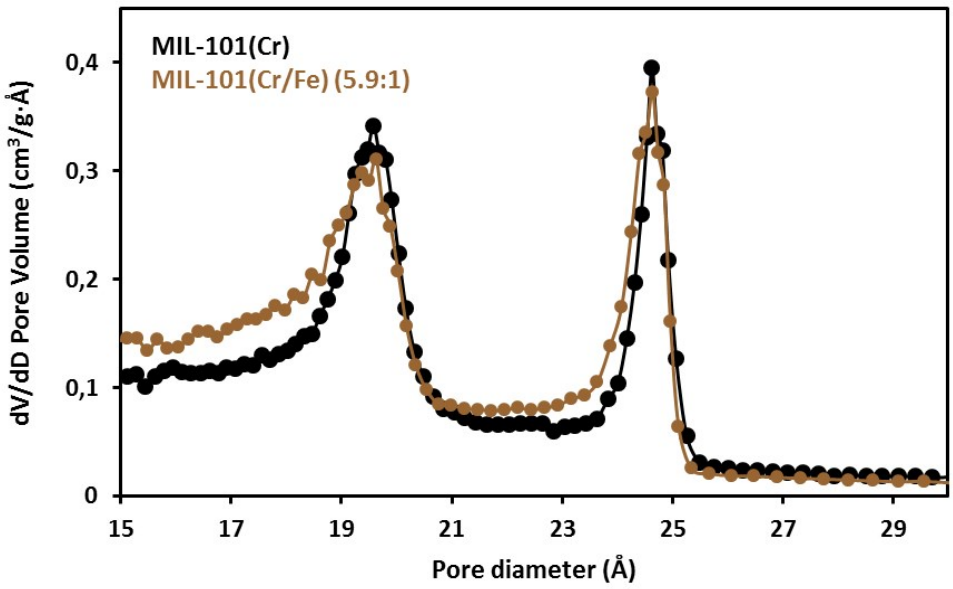

Figure SI-6: BJH pore size distribution of MIL-101(Cr) and MIL-101(Cr/Fe) (5.9:1). Sample activation: 150 °C/16 h, under vacuum.

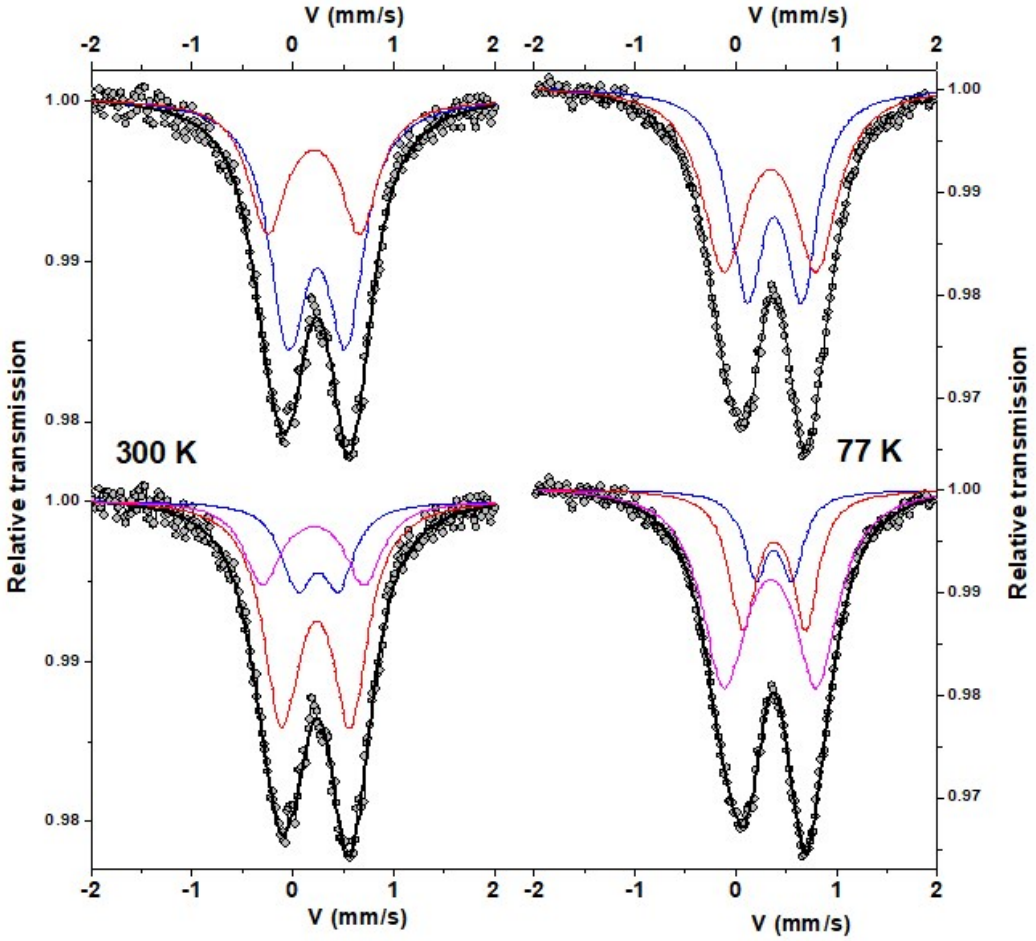

Figure SI-7: Mössbauer transmission spectra of MIL-101(Cr/Fe) (4:1), recorded at 300 K and 77 K with 2 fitting models).

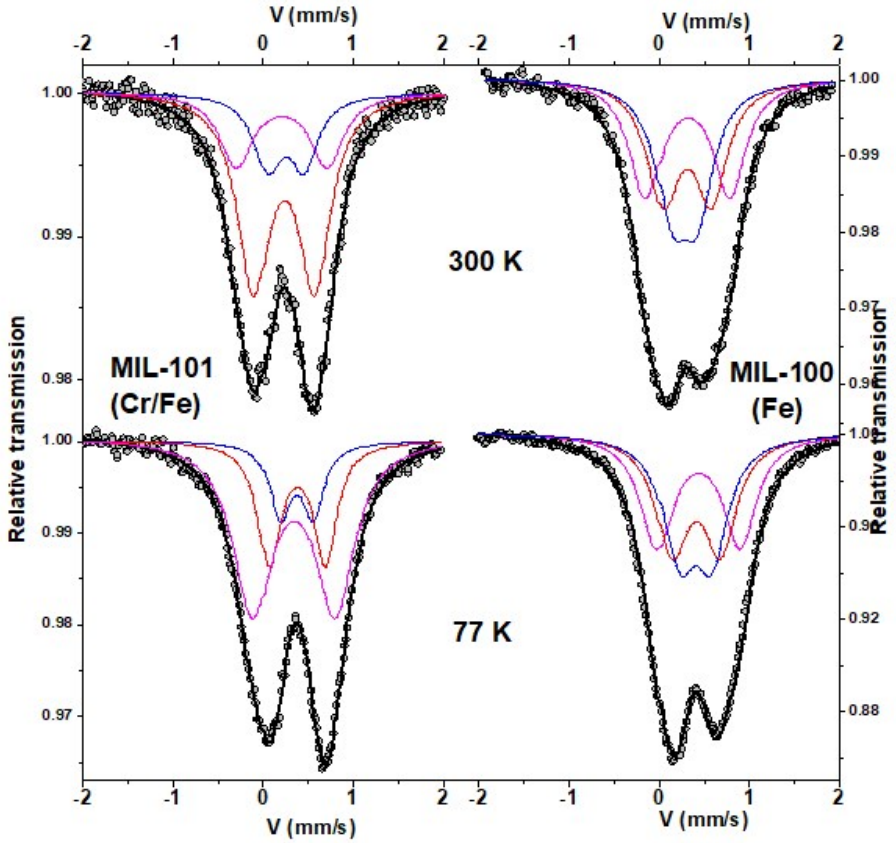

Figure SI-8: Mössbauer transmission spectra of MIL-101(Cr/Fe) (4:1) and MIL-100(Fe), recorded at 300 K and 77 K.

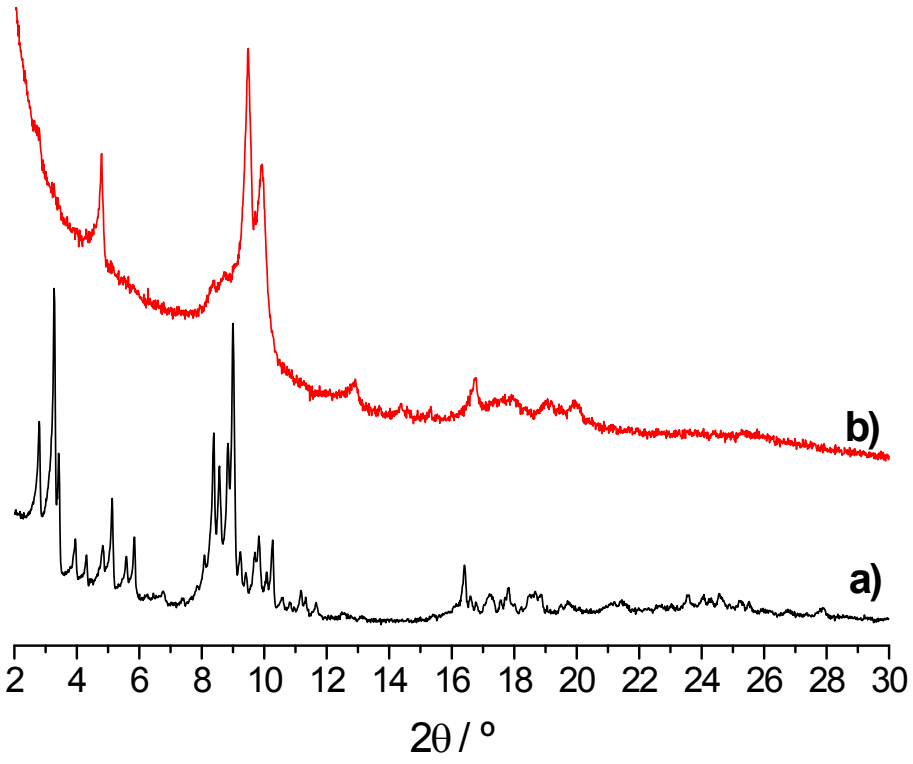

Figure SI-9. PXRD of fresh (a) and used in the Prins reaction (b) MIL-101(Fe). Reaction conditions: Catalyst (0.02 mmol metal), β-pinene (800 µL, 5 mmol), formaldehyde (750 µL, 5 mmol), CH_3CN (1.15 mL), reaction temperature (80 ºC).

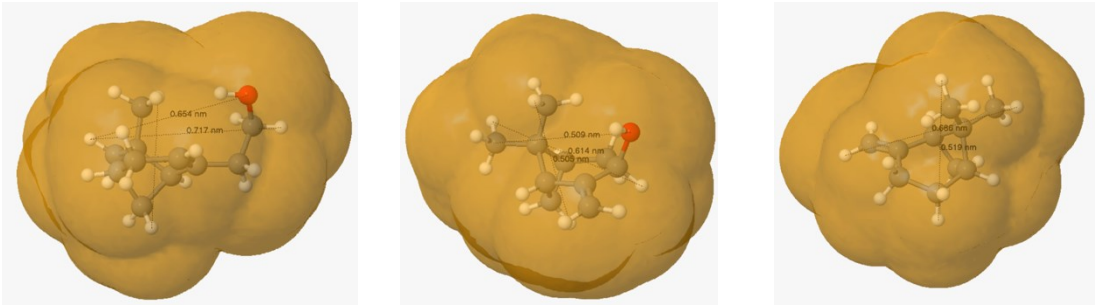

Figure SI-10. Representation of Nopol (left), 10-pinen-3-ol (middle) and β-pinene (right) molecules with selected largest atomic distances. The measured solvent accessible surface is represented in pale orange and calculated as de Van der Waals distances + 1.4 Angstrom. Calculations performed using the molecular calculator software MolCalc.

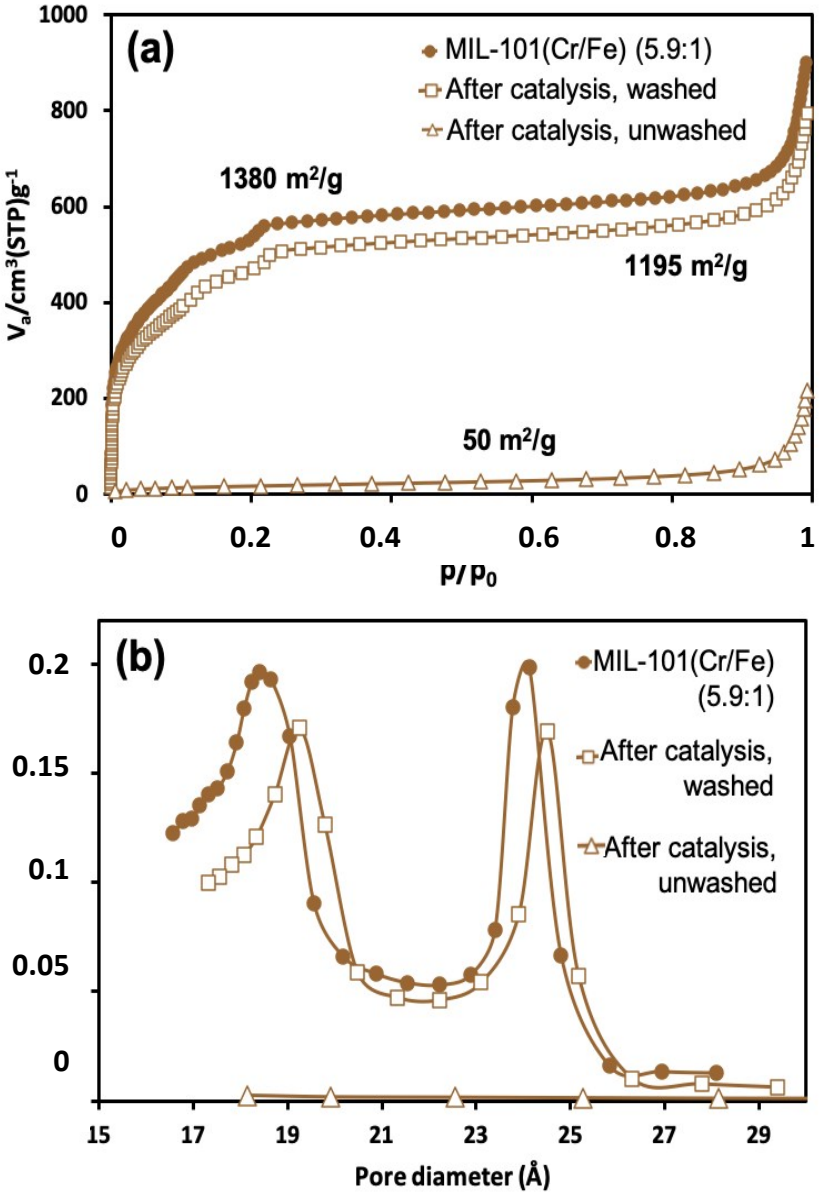

Figure SI-11: (a) Adsorption isotherms and (b) BJH pore size distribution of fresh MIL-101(Cr/Fe) (5.9:1) and after catalysis with (□) or without (Δ) washing. Sample activation: 80 ºC/1 h, under vacuum.

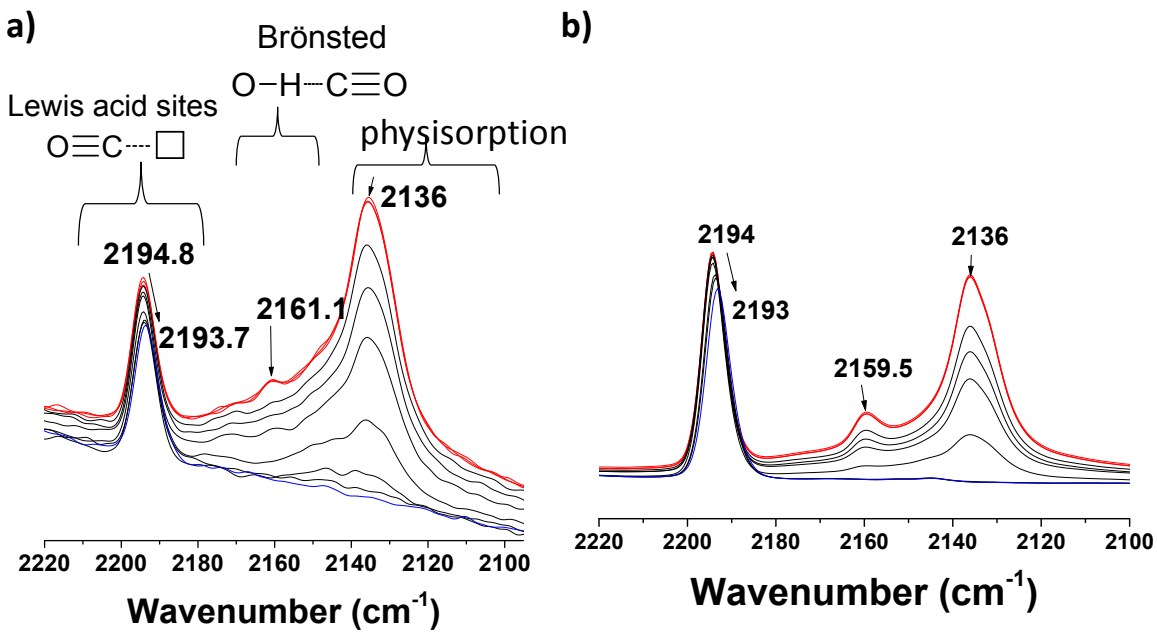

Figure SI-12. FT-IR spectra of CO adsorbed in MIL-101(Cr/Fe) (a) or MIL-101(Cr) (b). Red line spectra show the equilibrated CO adsorbed in the two MOFs; Other color line spectra show the retained CO after outgassing the corresponding MOF for 1 h periods.

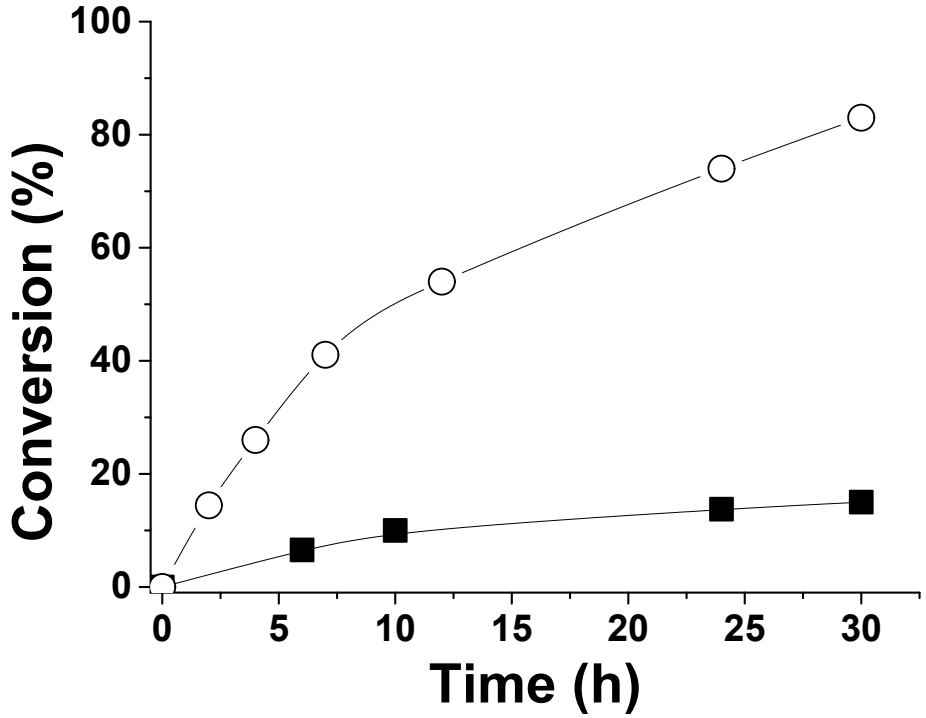

Figure SI-13. Influence of the presence (■) or absence (○) of pyridine as Lewis acid sites quencher in the resulting catalytic activity for the Prins reaction using MIL-101(Cr/Fe) (4:1) as catalyst. Reaction conditions: Catalyst (0.02 mmol of Fe+Cr), β-pinene (800 μL, 5 mmol), formaldehyde (750 μL, 5 mmol), pyridine (1 mmol), acetonitrile (1.26 mL), 80 ºC.

Table S1. Summary of the Nopol and 10-pinen-3-ol yields achieved using several catalysts under study.[a]

Entry	Catalyst	Yield (%)	
		Nopol	10-pinen-3-ol
1	MIL-101(Cr)	25.18	0.31
2	MIL-101(Fe)	25.41	7.59
3	MIL-88(Fe)	32.95	2.05
4	MIL-101(Cr/Fe) (4:1)	63.75	21.25
5	Fe(III) acetate	41.60	10.40
6	MIL-100(Fe)	62.32	13.68
7	MIL-101(Cr/Fe) (5.9:1)	38.92	4.07
8	MIL-101(Cr/Fe) (36:1)	29.08	2.33
9	Cr^{+3} acetate hydroxide	88.50	10.05
10	Cr_2O_3	52.91	35.27
11	Fe_20_3	42.84	35.62

[a] Reaction conditions: Catalyst (0.02 mmol of metal), β-pinene (800 µL, 5 mmol), formaldehyde (750 µL, 5 mmol), acetonitrile (1.26 mL), 80 ^{o}C, reaction time 30 h.