Electronic Supplementary Information (ESI†)

for

Cycloaddition of CO_2 with epoxides and esterification reactions using the porous redox catalyst Co-POM@MIL-101(Cr)

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Contents

1. Synthesis of MIL-101(Cr)

MIL-101(Cr) samples were synthesized hydrothermally according to a formerly reported method by Lev Bromberg et al.[1] in the absence of HF. In this method, $Cr(NO_3)_3 \cdot 9H_2O$ (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol), and deionized water (20 mL) were mixed, then the mixture was put in a Teflon lined autoclave reactor and kept in an oven at 218 °C for 18 h without stirring. After the synthesis and cool down to room temperature, the green raw product was separated by centrifugation and washed with water, ethanol, and acetone, and then dried and activated at 100 °C overnight under vacuum.

2. Supporting Figures

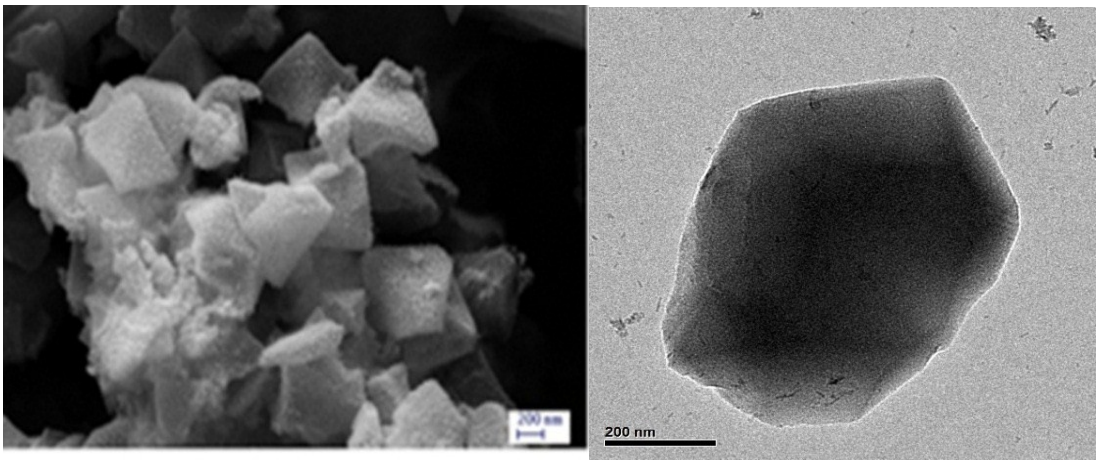
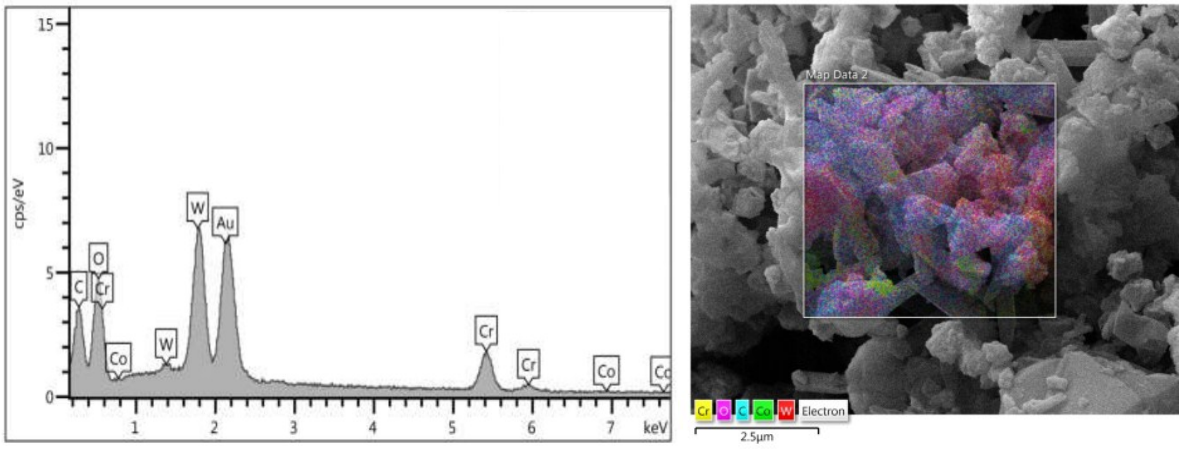


Fig. S1. Left: SEM image and right: TEM image of Co-POM@MIL-101(3).



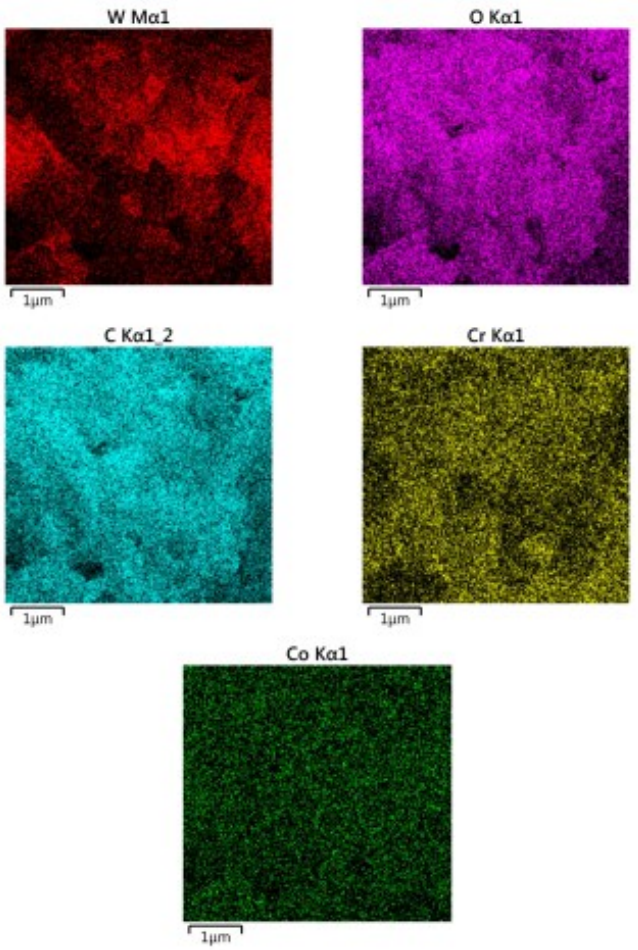


Fig. S2. SEM-EDX mapping of Co-POM@MIL-101(3) (sample holder = Au). The following elemental analysis was obtained: C 33.9(3) wt%, W 27.9(2) wt%, O 25.5(3) wt%, Cr 12.5(1) wt%, Co 0.1(1) wt%.

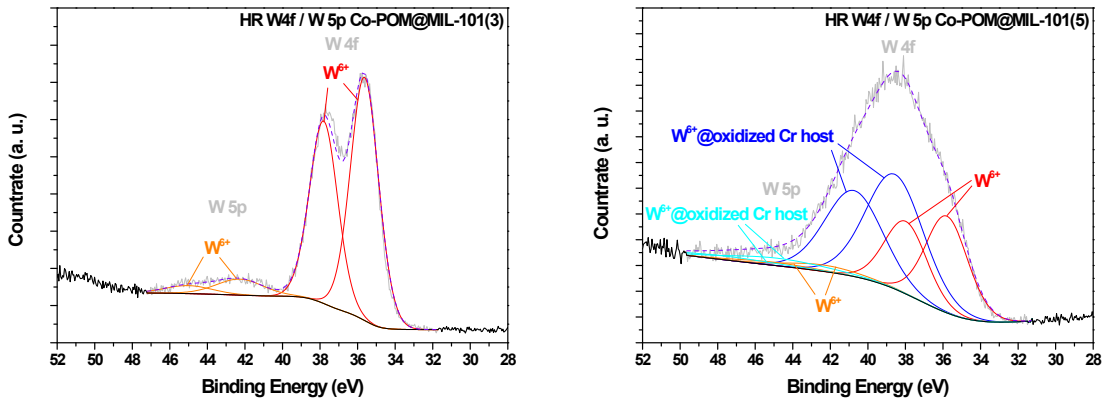


Fig. S3. XPS high-resolution spectra of the W 4f / W 5p region for Co-POM@MIL-101(3) (left) and Co-POM@MIL101(5) (right).

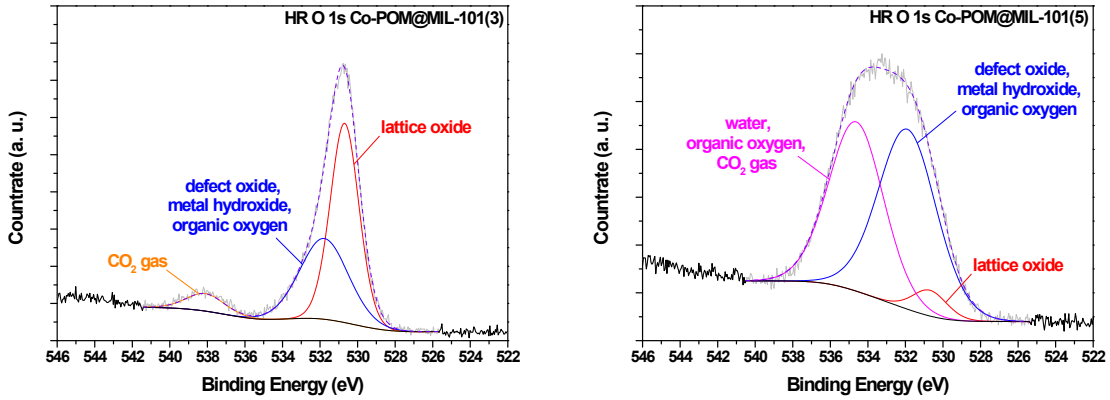


Fig. S4. XPS high-resolution spectra of the O 1s region for Co-POM@MIL-101(3) (left) and Co-POM@MIL-101(5) (right).

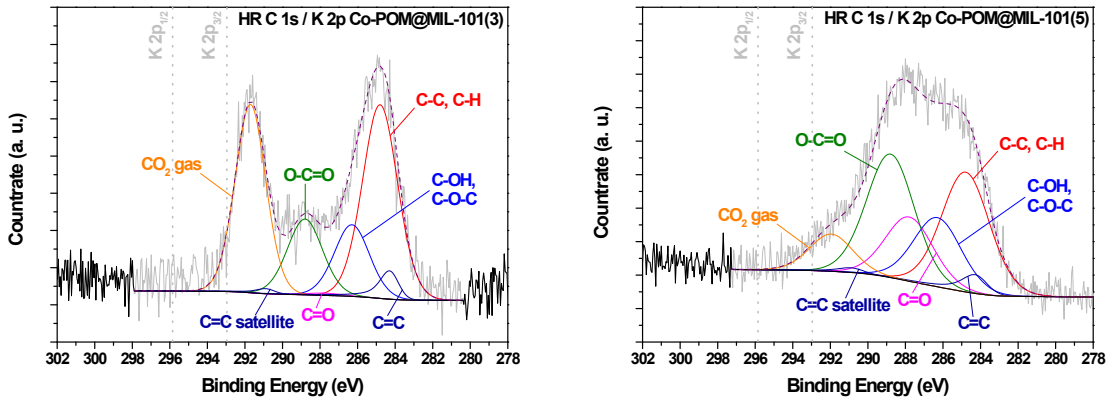


Fig. S5. XPS high-resolution spectra of the C 1s / K 2p region for Co-POM@MIL101(3) (left) and Co-POM@MIL-101(5) (right).

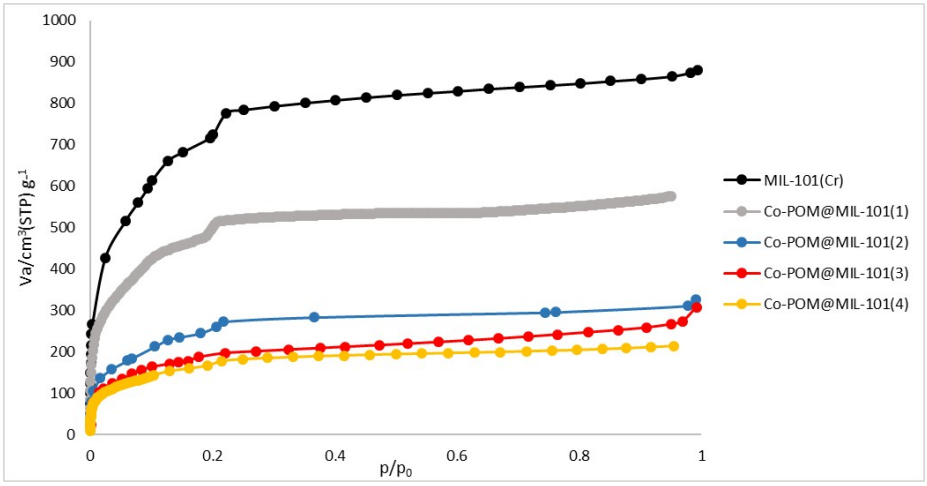


Fig. S6. N_2 adsorption isotherms of Co-POM@MIL-101 containing various amounts of Co-POM (0 g = MIL-101(Cr), 0.4 g = Co-POM@MIL-101(**1**), 0.8 g = -(**2**), 1.0 g = -(**3**), and 2.0 g = -(**4**).

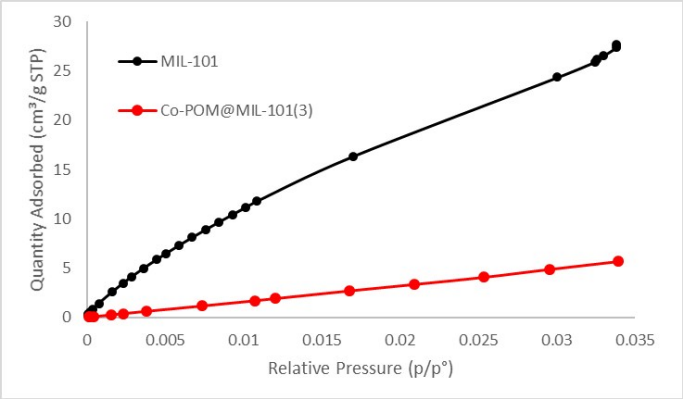


Fig. S7. CO_2 absorption isotherms for MIL-101(Cr) and Co-POM@MIL-101(3)

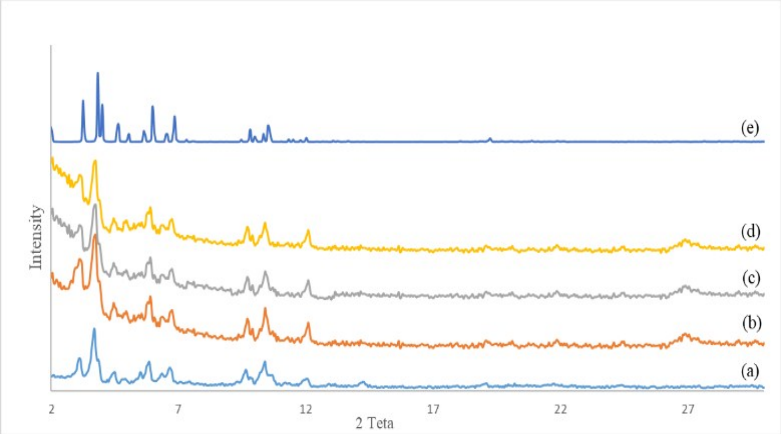


Fig. S8. XRD patterns of (a) MIL-101(Cr), (b) Co-POM@MIL-101(3), (c) reused Co-POM@MIL-101(3) after five runs of cycloaddition of CO_2 with styrene epoxide, and (d) reused Co-POM@MIL-101(3) after seven runs of esterification of acetic acid with benzyl alcohol, (e) simulated pattern of MIL-101(Cr).

3. Supporting Tables

Table S1. Cycloaddition of CO_2 with styrene epoxide catalyzed by Co-POM@ MIL-101(3) - optimization of reaction time.[a]

entry	time (h)	conversion [b] (%)	selectivity [b] (%)	TOF[c] (h^{-1})
1	5	88	88	1320
2	4	88	87	1650
3	3	89	87	2225
4	2	88	88	3300
5	1	42	85	3150

[a] Reaction conditions: 15 mmol styrene epoxide, 200 mg catalyst, 1 mmol TBABr, P_{CO2} = 20 bar, and T = 110 °C.
[b] Yields were determined by GC analysis.
[c] (Mol product/mol Co-POM)h^{-1}

Table S2. Cycloaddition of CO_2 with styrene epoxide catalyzed by Co-POM@MIL-101(3) - optimization of temperature. [a]

entry	*T* (°C)	conversion [b] (%)	selectivity [b] (%)
1	130	79	80
2	110	88	88
3	90	87	88
4	70	55	73

[a] Reaction conditions: 15 mmol styrene epoxide, 200 mg catalyst, 1 mmol TBABr, P_{CO2} = 20 bar, for 2 h.
[b] Yields were determined by GC analysis.

Table S3. Cycloaddition of CO_2 with styrene epoxide catalyzed by Co-POM@MIL-101(3) - optimization of the amount of catalyst) [a]

entry	Co-POM@MIL-101(3) (mg)	conversion [b] (%)	selectivity [b] (%)
1	50	40	83
2	100	52	84
3	150	64	88
4	200	88	88
5	250	88	85

[a] Reaction conditions: 15 mmol styrene epoxide, 1 mmol TBABr, *T* = 90 °C and P_{CO2} = 20 bar for 2 h.
[b] Yields were determined by GC analysis.

Table S4. The effect of initial POM amount in the catalytic activity of the Co-POM@MIL-101 catalysts in the esterification of acetic acid with benzyl alcohol. [a]

sample	Co-POM (g)	yield.[b] (%)	time (min)	TOF[c] (h^{-1})	Co-POM loading (mmol/g) [d]
MIL-101	0	traces	60	-	-
Co-POM@MIL-101(1)	0.4	60	40	8950	0.0050
Co-POM@MIL-101(2)	0.8	78	30	9200	0.0084
Co-POM@MIL-101(3)	1	84	25	10500	0.0100
Co-POM@MIL-101(4)	2	60	25	5800	0.0130

[a] Reaction conditions: 5 mmol acetic acid, 55 mmol alcohol, 100 mg catalyst, *T* = 100 °C).
[b] Yields were determined by GC analysis.
[c] (Mol product/mol Co-POM)h^{-1}.
[d] Determined by ICP.

Table S5. Esterification of acetic acid with alcohol - optimization of the catalyst amount. [a]

entry	Co-POM@MIL-101(3) (g)	time (min)	yield.[b] (%)	TOF[c] (h^{-1})
1	0	60	Negligible	-
2	50	45	40	5300
3	100	25	84	10500
4	150	20	84	8480

[a] Reaction conditions: 5 mmol acetic acid, 55 mmol benzyl alcohol, Co-POM@MIL-101(3), *T* = 100 °C.
[b] GC yield based on acid.
[c] (Mol product/mol Co-POM)h^{-1}.

Table S6. Esterification of acetic acid with alcohol - optimization of the temperature. [a]

entry	*T* (°C)	yield.[b] (%)
1	room temperature	0
2	50	55
3	70	84
4	100	84

[a] Reaction conditions: 5 mmol acetic acid, 55 mmol benzyl alcohol, 100 mg Co-POM@MIL-101(3), 25 min.
[b] GC yield based on epoxide.

References

1. L. Bromberg, Y. Diao, H. Wu, S. A. Speakman and T. A. Hatton, *Chem.Mater.*, 2012, **24**, 1664-1675.