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From MOFs to zeolites: zirconium sites for epoxide rearrangement

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Zr₆(OH)₄O₄-met and Zr₁₂(OH)₈O₈-acet cluster preparation

All experiments were carried out in a moisture- and oxygen-free argon atmosphere.

Synthesis of Zr₁₂(OH)₈O₈-acet: Acetic acid (2.62 g, 43.7 mmol) was added dropwise at room temperature to a solution of Zr(OBu)₄ (4.44 mmol, 2.13 g of a 80% solution in 1-butanol) in CH₂Cl₂ (5 mL) whilst stirring in a Schlenk tube. Within 3 h at room temperature colorless crystals were obtained. The crystals were separated and dried in vacuo. To remove the solvate molecules from the crystalline cluster, the solid was dissolved in CH₂Cl₂. The solvent was evaporated and the obtained solid was dried at room temperature and ca. 10⁻² mbar.¹

Synthesis of Zr₆(OH)₄O₄-met: In a tube Schlenk 1 mL of a 70% solution of Zr(OPr)₄ (3.10 mmol) in *n*-propanol was mixed under Ar with 8 mL (11.8 mmol) of methacrylic acid. The closed vessel was stored at room temperature. Colourless crystals were obtained quantitatively from the solution after 1 day.²

References

- 1 M. Puchberger, F. R. Kogler, M. Jupa, S. Gross, H. Fric, G. Kickelbick, U. Schubert, *Eur. J. Inorg. Chem.*, 2006, 3283.
- 2 G. Kickelbick, U. Schubert, *Chem. Ber.*, 1997, **130**, 473.

Table S1 Chemical and textural properties of the materials used as catalysts.

Entry	Catalyst	Metal-content ^a [%]	Surface area ^b [m ² /g]	Pore volume ^c [cm ³ /g]	Mean pore diameter ^c [Å]
1	MCM-41 ^d	--	1070	0.89	28
2	SiO ₂	--	200	0.30	120
3	ZrO-MCM41-1	1.7	741	0.30	26
4	ZrO-MCM41-2	2.5	591	0.16	26
5	ZrO-MCM41-3	2.8	763	0.23	25
6	ZrO-MCM41-6	2.1	555	0.21	28
7	Zr-MCM41-1	1.6	1485	1.01	26
8	Zr-MCM41-2	2.2	987	0.93	32
9	ZrO-SiO ₂	3.5	178	0.48	152
10	MOF UiO-66		726	0.14	
11	MOF UiO-66-NH ₂		390	0.13	

^a Determined by ICP-OES. ^b Determined applying the Brunauer–Emmett–Teller (BET) method to the results of nitrogen adsorption-desorption experiments. ^c Determined by nitrogen adsorption-desorption experiments. ^d MCM-41 support employed for the grafting of the zirconium precursor.

Figure S2 In-situ IR spectroscopy of cyclohexanone adsorbed onto different catalysts (A: Zr-Beta B: Zr-MCM41-2, C: ZrO-MCM41-3, D: MOF-UiO-66, E: MOF-UiO-66- NO_2). Spectra were normalized on the Zr-content for the zeolite and mesoporous materials and on the Zr/3 content for the MOFs since in this case the active sites were supposed to be built from three zirconium atoms. In the figure the corresponding spectra are displayed from the bottom to the top after zeolite desorption at 200 °C, after desorption at 100 °C and after desorption at 50 °C (except for E).

