Supplementary Information

Cyclohexane selective oxidation over metal-organic frameworks of MIL-101 family: superior catalytic activity and selectivity

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Experimental details

Tert-butyl hydroperoxide (TBHP) was used as 4.7 M solution in decane (Aldrich); the concentration of active oxygen was determined iodometrically prior to use. All other reactants were obtained commercially and used without further purification.

1. Catalyst preparation and characterization

Cr-MIL-101 was synthesized following the procedure of Férey et al.[S1] Typically, a mixture of 1.2 g (3 mmol) of $Cr(NO_3)_3 \cdot 9H_2O$, 500 mg of terephthalic acid (H_2bdc, 3 mmol) and 0.6 mL of 5 M HF (3 mmol) in 15 ml H_2O was heated at 220 °C for 8 h in a teflon-lined stainless steel bomb. The resulting green Cr-MIL-101 solid was passed through a coarse glass filter to remove the unreacted colorless crystals of H_2bdc and then filtered on the dense paper filter. The rude Cr-MIL-101 was purified by double treatment with *N,N*-dimethylformamide (DMF) at 60 °C for 3 h and then by triple treatment with ethanol at 70 °C for 2.5 h. After drying in air at 70–80 °C overnight, pure Cr-MIL-101 (13 wt% Cr) with 3100 m^2 g^{-1} BET surface area and 2.1 cm^3 g^{-1} pore volume was obtained. Activation of Cr-MIL-101 was carried out by drying under vacuum at 150 °C for 5 h and then at 180 °C for 2 h. The activated Cr-MIL-101 catalysts contained 23 wt% Cr.

Fe-MIL-101 was prepared following the protocol described earlier.[S2] In a typical synthesis, a mixture of 0.675 g (2.45 mmol) of $FeCl_3 \cdot 6H_2O$, 206 mg of H_2bdc (1.24 mmol), and 15 mL DMF was heated at 110°C for 20 h in a teflon-lined stainless steel bomb. The resulting brown solid was filtered off and the raw product was purified by a double treatment in ethanol at 60 °C for 3 h. After drying in an oven (70 °C, 30 min), Fe-MIL-101 (13 wt% Fe) with 3200 m^2 g^{-1} BET surface area and

1.4 cm^3 g^{-1} pore volume was obtained. Activated Fe-MIL-101 containing 23 wt% Fe was obtained by drying under vacuum at 120 °C for 7 h.

Textural characteristics of the catalysts were determined from nitrogen adsorption isotherms (Sorbtometr M; before measurements, Fe-MIL-101 and Cr-MIL-101 samples were degassed at 150 and 180 °C, respectively, under vacuum during 6 h). The structure of the MIL-101 materials was confirmed by XRD (Philips APD1700 X-ray diffractometer). The preservation of the MIL-101 structure was also verified by FT-IR spectroscopy (SCIMITAR FTS 2000 spectrometer).

2. Catalytic oxidations of cyclohexane

Catalytic experiments were carried out in thermostated glass vessels under vigorous stirring (500 rpm). Each experiment was reproduced 3-4 times. Typically, the reaction of cyclohexane (CH) oxidation was started by the addition of TBHP (4 mmol) to a mixture containing CH (4.6 mmol) and the MIL-101 catalyst (5 mg, 0.02 mmol Cr or Fe). In the experiments with molecular oxygen, TBHP (0.01 mmol) was added to a mixture that contained MIL-101 (5 mg) and CH (4.6 mmol) and had been preliminary blown with O_2 (1 atm). After the reaction, MIL-101 catalysts were filtered off, washed with acetone, dried at room temperature overnight and then reused.

3. Product analysis

Aliquots of the reaction mixture (5 μL) were withdrawn periodically during the reaction course by a syringe through a septum. Each aliquot was diluted with a solution containing acetonitrile (0.5 mL) and toluene as internal standard for GC.

The oxidation products were identified by GC-MS (HP-5ms 30m×0.25mm and ionic liquid-DiMeImNtf$_2$ 25m×0.22mm capillary columns (the latter allows determination of (di)carboxylic acids without their transformation into esters), GC/MS Agilent 7000B system with triple-quadrupole mass-selective detector Agilent 7000 and GC Agilent 7890B) and quantified by GC (Agilent DB-5MS 30 m×0.25 mm capillary column).

The reaction mixture was thoroughly cooled before taking a sample for GC analysis in order to avoid any loss of substrate by eventual CH evaporation, which may lead to overestimation of CH conversion. Moreover, in a special experiment, with the use of a nonvolatile internal standard, we checked by GC that no change of CH concentration occurred at the reaction temperature during 8 h in the absence of oxidant (TBHP or its mixture with O_2). The calibration curves obtained using the internal standards and authentic samples of CH and of the reaction products were linier in the whole range of concentrations. The internal standard methodology allows avoiding errors in C balance, which may arise due to products not detectable by GC, because the substrate conversion and product yields are determined independently.

For GC analysis of the oxidation products, we used the method described by Shul'pin[S3] and employed successfully by other authors,[S4,S5] which is based on the comparison of chromatograms of the reaction mixture before and after reduction of peroxides present with triphenylphosphine (PPh_3). In the case of CH oxidation with TBHP over Cr-MIL-101, the chromatograms before and after such treatment (10 mg of PPh_3 was added to each aliquot) were identical, indicating that no cyclohexyl hydroperoxide (CHHP) was present among the reaction products. This justified a separate determination of TBHP concentration (and estimation of the oxidant efficiency) after the catalytic reaction by iodometric titration.

On the contrary, for CH oxidation with TBHP over Fe-MIL-101, the ratios of A/K in the chromatograms differed significantly before and after treatment with PPh_3, indicating that CHHP is present among the oxidation products and affects the A/K ratio in the chromatograms.[S3] In this case, the true concentration of cyclohexanol $[A]_{true}$ and that of CHHP were estimated by solving simultaneous equations (1) and (2)

$$[A] = [A]_{true} + n\times[CHHP] \qquad (1)$$

$$[A]_{PPh3} = [A]_{true} + [CHHP] \qquad (2)$$

where [A] and $[A]_{PPh3}$ are the observed concentrations of A determined by integration of the GC peak attributed to A before and after the treatment of the reaction mixture with PPh_3, respectively, and n is a coefficient which reflects the A/K ratio that appears in the chromatogram due to CHHP decomposition in the GC injector. The value of n (0.55) was determined experimentally by injecting a sample of the reaction mixture after 30 min of a blank experiment, when CHHP was the sole oxidation product.[S3]

Accordingly, the true concentration of cyclohexanone ($[K_{true}]$) was quantified by GC through integration of the corresponding peak after the treatment of the reaction mixture with PPh_3 ($[K]_{PPh3} = [K]_{true}$).

Table S1. Solvent-free cyclohexane oxidation over Cr-, Fe- and Co-containing catalysts

Catalyst	Metal content (wt.%)	Oxidant	Conditions	Substrate conversion (%)	TOF [a] (h^{-1})	Product selectivity (mol.%)		Catalyst productivity[b] ($g\ g^{-1}\ h^{-1}$)	Metal leaching (ppm)	Reference
						A	K			
Cr-MIL-101	23 [c]	TBHP	70ºC, 8 h	36	45	8	75	3.4	0.3	this work
Cr-PMO	2.3	TBHP [d]	70ºC, 5 h	12	n.d.	22	70	0.2	9	[S6]
Cr-APO-5	1.5	5 atm O_2	130°C, 5.5 h	10.5	12	5	48	0.2	n.d.	[S7]
Cr-TUD-1	1.0	TBHP	70ºC, 18 h	14	n.d.	1	73	0.1	34	[S8]
Cr-colloids/ silica	1.3	27.5 atm O_2	130°C, 2.5 h	3	190	24	60	4.0	<5 [e]	[S9]
Fe-MIL-101	23 [c]	TBHP + air	70ºC, 8 h	24	54	27	16	1.2	0.5	this work
Fe-TUD-1	1.0	TBHP	70ºC, 16 h	3	n.d.	21	63	0.1	n.d.	[S8]
Fe-ALPO-5	3.5	15 atm air	130ºC, 24 h	7	6	36	16	0.2	n.d.	[S10]
Fe-AlPO-5	3.5	15 atm air + TBHP	130ºC, 24 h	20	26	22	33	0.5	n.d.	[S10]
Co-TUD-1	1.2	TBHP	70ºC, 16 h	10	n.d.	13	79	0.1	no leaching	[S8]
Co-ALPO-5	3.9	15 atm air + TBHP	130ºC, 24 h	12	13	32	56	0.5	n.d.	[S10]
Co/SiO_2	3.4	27.6 atm O_2	130°C, 4 h	4	n.d.	60	30	11	no leaching	[S4]

[a] TOF = (moles of cyclohexane converted)(moles of active metal × time)$^{-1}$; determined from the initial rates of cyclohexane consumption. TOFs for MIL-101 were calculated per coordinatively unsaturated Cr or Fe which is equal to ca. $^{2}/_{3}$ of the total moles of metal.

[b] (Gram of K+A)(gram of catalyst × time)$^{-1}$.

[c] In activated MIL-101.

[d] Acetone was used as solvent.

[e] ppb

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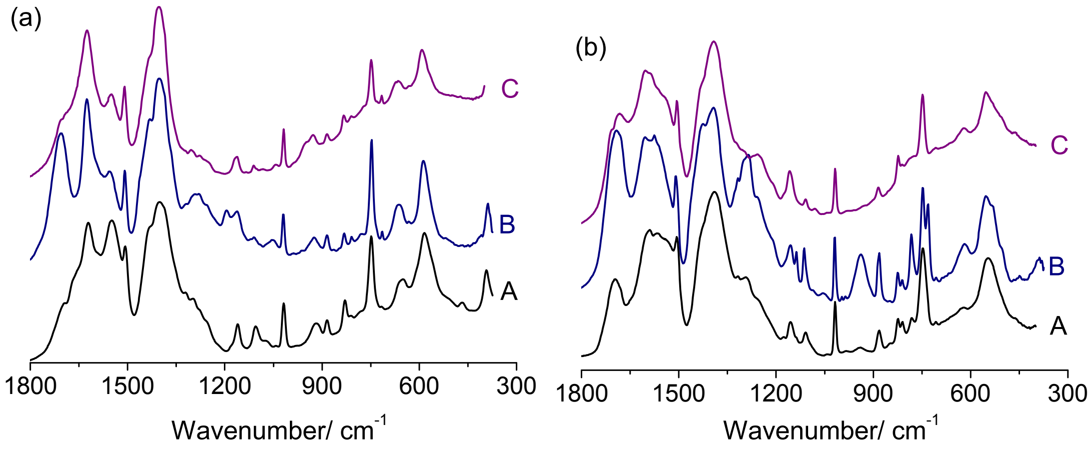
Figures

Figure S1. FT-IR spectra of (a) Cr-MIL-101 and (b) Fe-MIL-101: (A) initial, (B) and (C) after 1 run and 5 runs of CH oxidation with TBHP, respectively. Reaction conditions: CH (4.6 mmol), TBHP (4 mmol), MIL-101 catalyst (5 mg, 0.02 mmol Cr or Fe).

Figure S2. XRD patterns for (a) Cr-MIL-101 and (b) Fe-MIL-101: (A) initial and (B) after CH oxidation with TBHP. Reaction conditions: CH (4.6 mmol), TBHP (4 mmol), Cr-MIL-101 (5 mg, 0.02 mmol Cr) or Fe-MIL-101 (20 mg, 0.08 mmol Fe).

Figure S3. Hot (70 ^{o}C) catalyst filtration test for CH oxidation with TBHP over Cr-MIL-101. Reaction conditions: CH (4.6 mmol), TBHP (4 mmol), Cr-MIL-101 (5 mg, 0.02 mmol Cr).

Figure S4. Reuse of Fe-MIL-101 in CH oxidation with TBHP. Reaction conditions: (a) CH (4.6 mmol), TBHP (4 mmol), Fe-MIL-101 (20 mg, 0.08 mmol Fe), 70 ^{o}C, 8 h (110 TON); (b) CH (2.3 mmol), TBHP (2 mmol), Fe-MIL-101 (2.5 mg, 0.01 mmol Fe), MeCN (0.5 mL), 70 ^{o}C, 8 h (405 TON).



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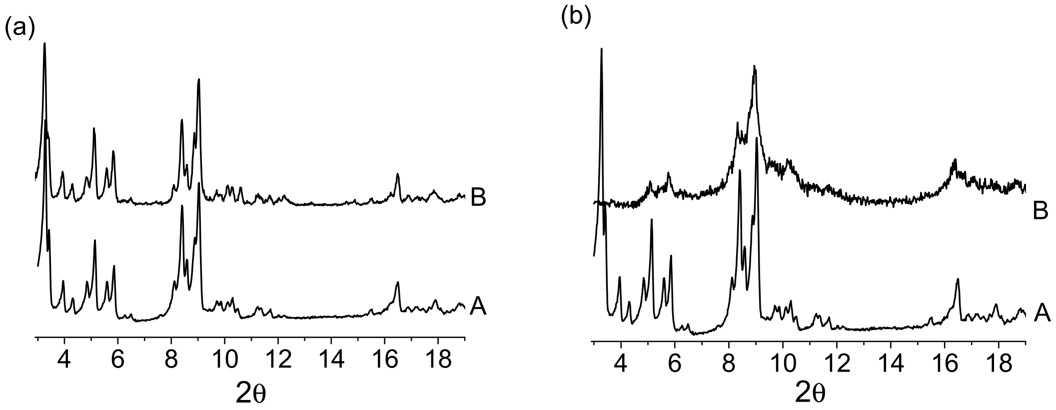

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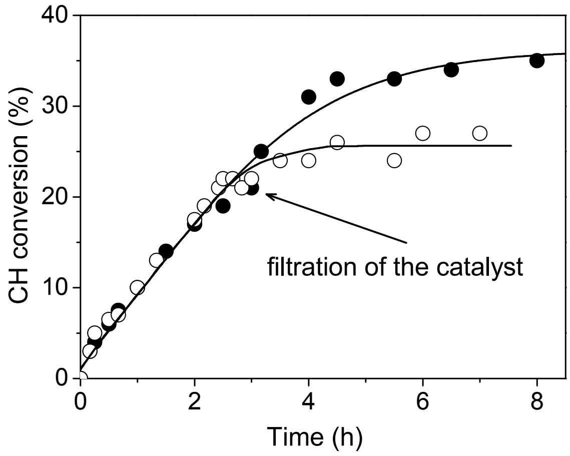

Fig. S3. Hot (70 °C) catalyst filtration test for CH oxidation with TBHP over Cr-MIL-101. Reaction conditions: CH (4.6 mmol), TBHP (4 mmol), Cr-MIL-101 (5 mg, 0.02 mmol Cr).

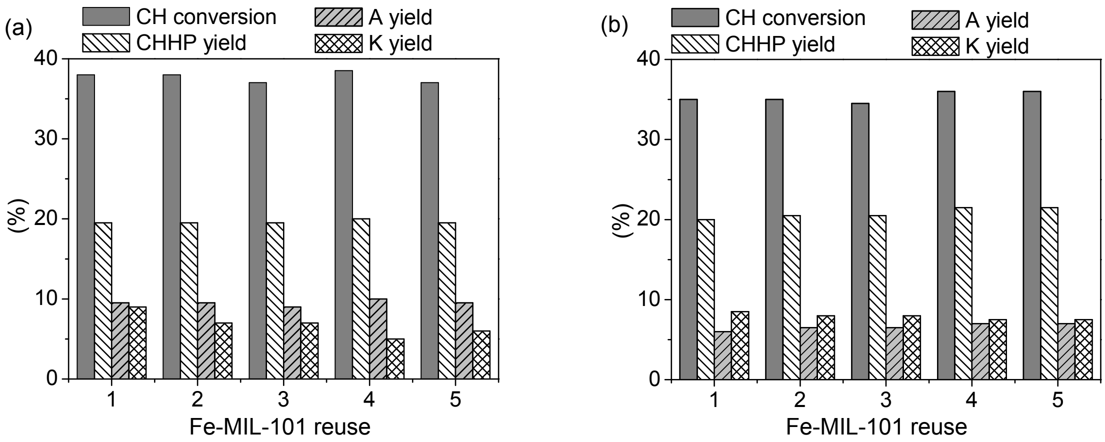

Fig. S4. Reuse of Fe-MIL-101 in CH oxidation with TBHP. Reaction conditions: (a) CH (4.6 mmol), TBHP (4 mmol), Fe-MIL-101 (20 mg, 0.08 mmol Fe), 70 °C, 8 h (110 TON); (b) CH (2.3 mmol), TBHP (2 mmol), Fe-MIL-101 (2.5 mg, 0.01 mmol Fe), MeCN (0.5 mL), 70 °C, 8 h (405 TON).