Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Heterogeneous epoxidation of menadione with hydrogen peroxide over zeolite imidazolate framework ZIF-8

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Experimental details

Instrumentation

GC analyses were performed using a gas chromatograph Chromos GC-1000 equipped with a flame ionization detector and a quartz capillary column BPX5 (30 m × 0.25 mm). GC–MS analyses were carried out using an Agilent 7000B system with the triple-quadrupole mass-selective detector Agilent 7000 (ZB-Wax, 25 m × 0.25 mm × 0.25 μm). ^{1}H NMR spectra were recorded at 400.130 MHz on a Brüker AVANCE-400 spectrometer. Infrared spectra of 0.5–2.0 wt % samples in KBr pellets were recorded on an Agilent Cary 660 FTIR spectrometer. X-Ray diffraction patterns were collected on the Siemens D500 instrument using CuKα radiation. Scanning electron microscopy (SEM) images were acquired by means of a JEOL JSM-6460 LV instrument or JEOL JSM-6700F (acceleration voltage = 20 kV, current = 10 μA). N_2 adsorption measurements were carried out using a Quantachrome Nova 1200e instrument. Thermogravimetric analysis (TGA) was carried out in airflow (30 mL/min) using a NETZSCH STA 449C instrument. The sample weight was 5 mg in all experiments and the heating rate in TG experiment was 10 °C/min.

Materials

2-Methyl-1,4-naphthoquinone (MNQ, 98%), methyl phenyl sulfide (MPS, 99%), and methyl phenyl sulfoxide (MPSO, 98%) were purchased from Acros. 2-Cyclohexen-1-one (≥95%), tetramethylethylene (TME, 98%), 2-methylimidazole (HMeIM, 99%), zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$ (98%) were purchased from Sigma-Aldrich. Acetonitrile (HPLC–grade, Panreac) was dried and stored over activated 4 Å molecular sieves. The concentration of H_2O_2 (ca. 35 wt % in water) was determined iodometrically prior to use. All the other compounds were the best available reagent grade and used without further purification.

Catalyst synthesis and characterization

Synthesis of ZIF-8 in MeOH. ZIF-8(MeOH) was synthesized following the route first suggested by Cravillon et al.[S1] and then modified by Keser Demir et al.[S2] A solution of 2.3 g (7.74 mmol) $Zn(NO_3)_2{\cdot}6H_2O$ in 75 mL of MeOH was quickly poured into a solution of 5 g (60.98 mmol) 2-methylimidazole in 75 mL of MeOH under stirring at room temperature with pH adjusted by NaOH. After 1 h, the nanoparticles were separated from the mother solution by centrifugation. The resulting white crystals were washed twice by 100 mL of deionized water (18 h in total) and twice by 100 mL of MeOH (24 h in total). The resulting product was dried under a flush of nitrogen at room temperature and activated in a high vacuum at 100 °C for 10 h.

The XRD analysis of the activated material (Figure S1A) revealed a pattern matching with the previously reported data.[S1,S2] N_2 adsorption measurements of the sample activated at 150 °C have shown a BET surface area of $S_{BET} \sim 1350$ m^2/g (the corresponding N_2 adsorption isotherm is provided in Figure S2A). Scanning Electron Microscopy (SEM) showed regularly shaped crystals with the size of ca. 200 nm (Figure S3A-C). The IR spectrum of the sample (Figure S5A) showed a typical fingerprint of the ZIF-8 structure.

Synthesis of ZIF-8 in H_2O. ZIF-8(H_2O) was synthesized according to the protocol reported by He et al.[S3] A portion of 0.594 g (2 mmol) of zinc nitrate hexahydrate was dissolved in 3 mL of water and 0.328 g (4 mmol) of HMeIM was dissolved in 3.76 g (64 mmol NH_3) of ammonia solution. Then, the zinc nitrate solution was added to the HMeIM solution under stirring. A fine white precipitate formed immediately. The resulting suspension was stirred for 10 min at room temperature (25 °C). The product was collected by centrifugation and washed with water three times until the mother liquor had a pH value of 7. After that, the precipitate was dried at 60 °C overnight. Sample activation was carried out by heating under vacuum at 150 °C for 5 h.

The XRD pattern of the activated material (Figure S1B) matched with simulated and previously reported spectra.[S3] The narrow peaks indicate large, well-crystallized particles. The N_2 adsorption measurements of the sample activated at 150 °C revealed a BET surface area of $S_{BET} \sim 1331$ m^2/g (the corresponding N_2 adsorption isotherm is provided in Figure S2B). SEM showed uniform cubic crystals of 0.75-1.25 μm in size with truncated edges exposing {100} and {110} faces (Figure S3D-F). The IR spectrum of the sample (Figure S5B) showed a typical fingerprint of the ZIF-8 structure.

Synthesis of $Zn_5(OH)_8(NO_3)_2$. $Zn_5(OH)_8(NO_3)_2$ was prepared using a slightly modified method reported by N. Nityashree and M. Rajamathi.[S4] A 200 mg portion of ZnO was placed in 3 mL of 0.85 M $Zn(NO_3)_2$ solution. The reaction mixture was stirred for 24 h at 65 °C. The precipitate was filtered off, washed twice with distilled water, and dried in air.

Catalytic oxidations

Catalytic reactions were performed under vigorous stirring (500 rpm) in thermostated glass vessels. Each experiment was reproduced 2–3 times. The reaction products were identified by GC-MS and quantified by GC using biphenyl as an internal standard. The amount of H_2O_2 at the end of the reaction was determined iodometrically.

MNQ oxidation. Reactions of MNQ oxidation were initiated by the addition of H_2O_2 (0.8 mmol) to a solution of MNQ (0.1 mmol) in 1 mL of solvent (typically, CH_3CN) at 70 °C containing 3.3 mg of ZIF-8(MeOH) or ZIF-8(H_2O). Before reuse, the catalyst was separated by filtration, washed with hot methanol and CH_3CN, and then dried in vacuum at 150 °C for 6 h.

Oxidation of α,β-unsaturated carbonyl compounds. Typical reaction conditions for oxidation of α,β-unsaturated *carbonyl compounds* were as follows: substrate 0.1 mmol, H_2O_2 0.8 mmol, ZIF-8(MeOH) 3.3–10 mg, CH_3CN 1 mL, 70 °C.

Oxidation of other organic compounds. Typical reaction conditions for oxidation of TME, MPS and MPSO were as follows: substrate 0.1 mmol, H_2O_2 0.1 mmol, ZIF-8(MeOH) 2 mg, CH_3CN 1 mL, 27 °C. Oxidation of cyclohexanone was performed in the following conditions: substrate 0.1 mmol, H_2O_2 0.4 mmol, ZIF-8(MeOH) 2 mg, CH_3CN 1 mL, 70 °C.

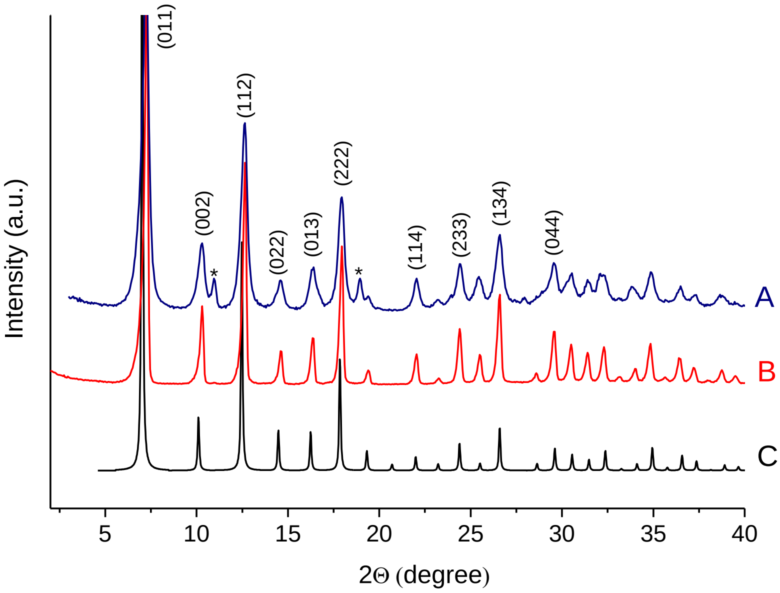
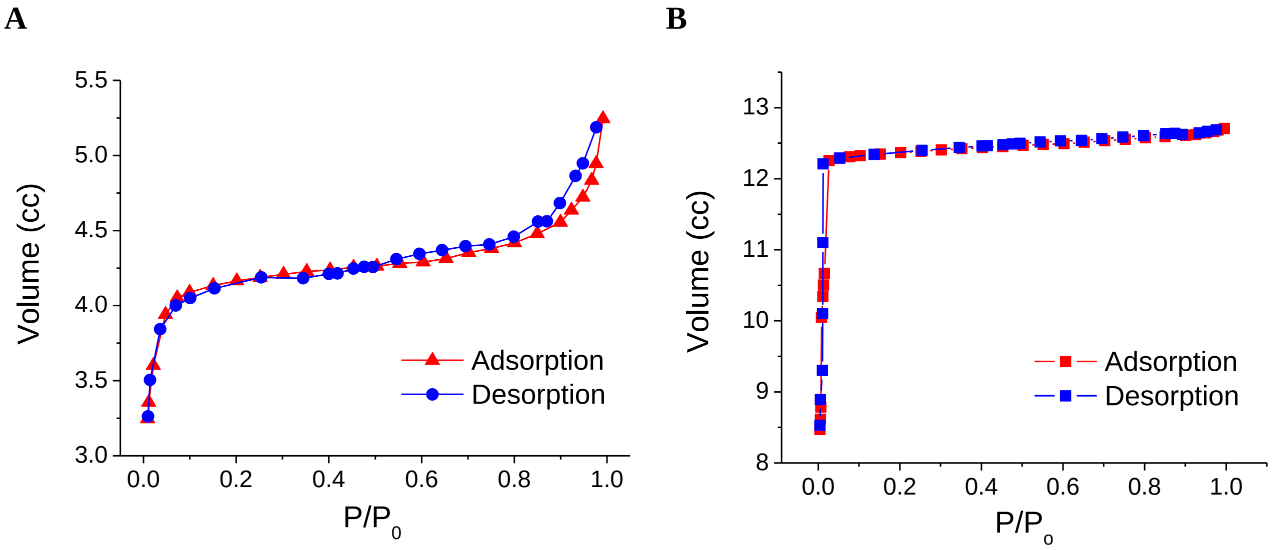


Fig. S1 XRD patterns of synthesized ZIF-8(MeOH) (A) and ZIF-8(H_2O) (B) and simulated ZIF-8 (C).

The two reflections marked with an asterisk in the XRD pattern of ZIF-8(MeOH) (curve A) are associated with $Zn_5(OH)_8(NO_3)_2$, the product of $Zn(NO_3)_2$ hydrolysis,[S5] and are typical of ZIF-8 samples with rather small particles and low crystallinity[S5] and, in particular, typical of ZIF-8 synthesized using MeOH as solvent.[S6] Venna et al. have found that the intensity of these reflections is higher at the initial stage of the synthesis (<30 min), but they do not fully disappear even after 12 h.[S6]



S_{BET} 1210 m^2/g
S_{ext} 72 m^2/g
V_{total} 0.61 cm^3/g
$V_{\mu icro}$ 0.42 cm^3/g

S_{BET} 1788 m^2/g
S_{ext} 24 m^2/g
V_{total} 0.63 cm^3/g
$V_{\mu icro}$ 0.61 cm^3/g

Fig. S2 Nitrogen adsorption isotherms and textural characteristics for ZIF-8(MeOH) (A) and ZIF-8(H_2O) (B).

The adsorption curve for ZIF-8(MeOH) exhibited a hysteresis loop near P/P_0 = 0.9, indicating the presence of interparticle mesoporosity, which is typical of ZIF-8 samples with small particles.[S5] Indeed, the total pore volume for ZIF-8(MeOH) is significantly higher than the volume of micropores (61 vs 42 cm^3/g), pointing to the presence of mesopores. This is not the case of ZIF-8(H_2O) that reveals I type isotherm, typical of completely microporous materials. Indeed, for this sample, the total pore volume and the volume of micropores are nearly the same. The larger external surface of ZIF-8(MeOH) agrees with smaller particle size in this material (see Fig. S3) and is in perfect agreement with the results previously reported by Keser Demir et al.[S2]

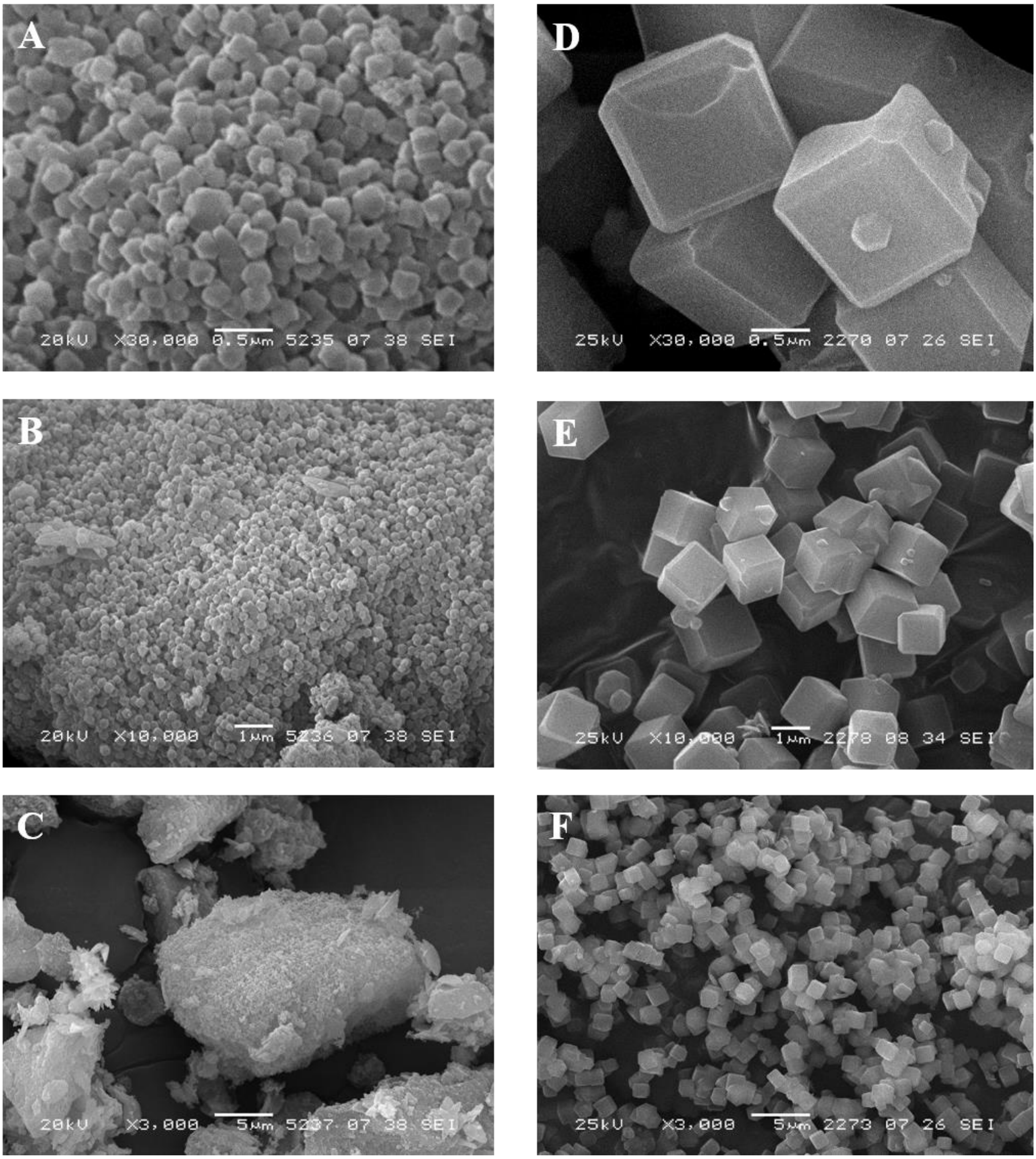


Fig. S3 SEM images of ZIF-8(MeOH) (A, B and C) and ZIF-8(H_2O) (D, E and F).

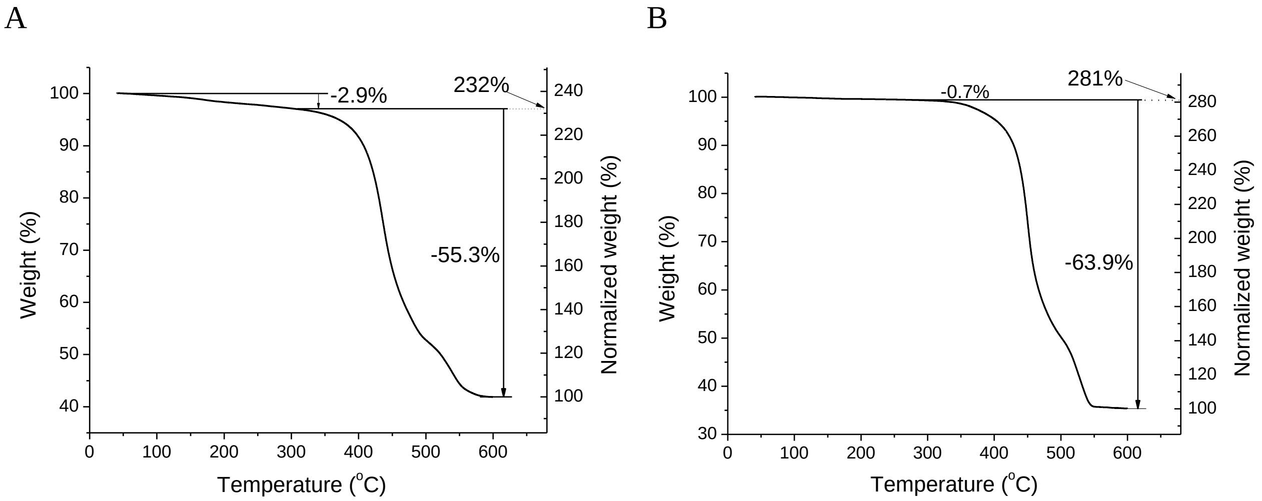


Fig. S4 TGA profiles for ZIF-8(MeOH) (A) and ZIF-8(H_2O) (B).

Complete thermal decomposition of the ZIF-8 structure ($Zn(C_4H_5N_2)_2$; FW 229) yields ZnO (FW 81) as the only solid product. The molecular weight of $Zn(C_4H_5N_2)_2$ is a factor of 2.83 higher than ZnO. Thus, if we normalize the final weight of an aerobic TGA run to 100%, then a plateau should be expected at 283%. In the normalized TGA curve of ZIF-8(MeOH), the plateau reached 232% (Fig. S4A) instead of 283% expected for an ideal ZIF-8, the weight loss corresponding to the loss of *x* MeIM ligands is 132%. Therefore, the number of MeIM ligands in the ZIF-8(MeOH) sample refers to the number of ligands in an ideal ZIF-8 as 132/183 = 0.72. In turn, the plateau in the normalized TGA curve of ZIF-8(H_2O) reached 281% (Fig. S4B). As a result, the number of MeIM ligands in the ZIF-8(H_2O) sample refers to the number of ligands in ideal ZIF-8 as 181/183 = 0.99. Thus, we may conclude that a significant number of defects were present in the ZIF-8(MeOH) sample while the ZIF-8(H_2O) sample had an almost ideal structure.

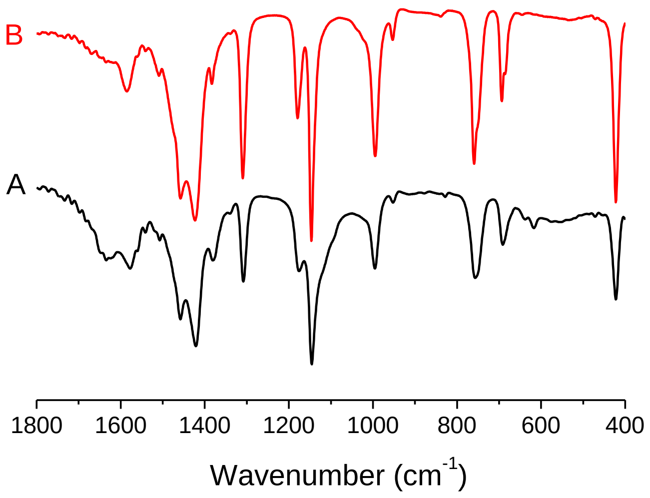


Fig. S5 FTIR spectra of ZIF-8(MeOH) (A) and ZIF-8(H_2O) (B).

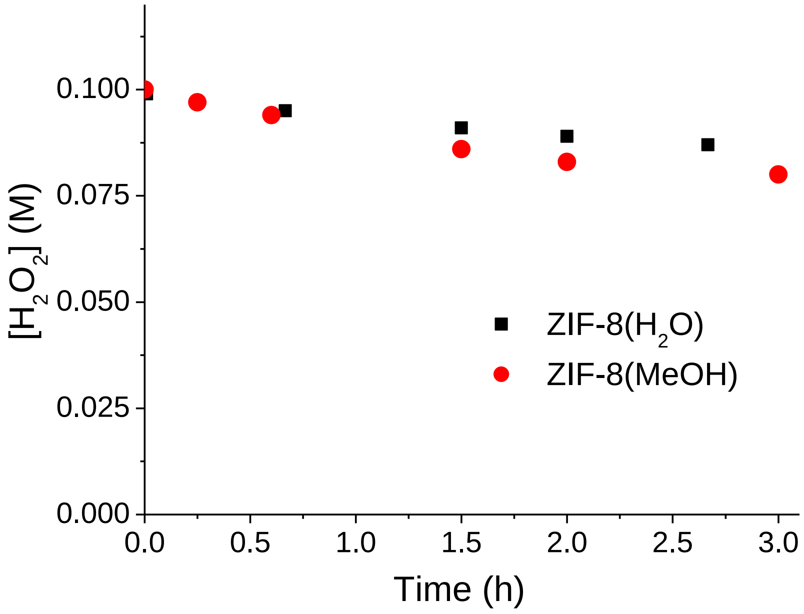


Fig. S6 H_2O_2 degradation in the presence of ZIF-8(H_2O) (■) and ZIF-8(MeOH) (●). Reaction conditions: H_2O_2 0.11 M; ZIF-8 10 mg; CH_3CN 2 ml; 70 °C.

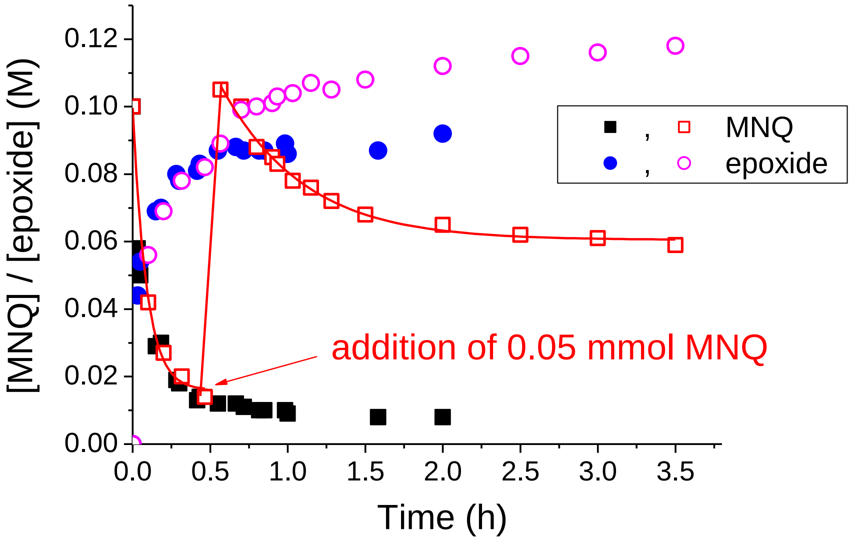


Fig. S7 Catalyst deactivation during the reaction course. Reaction conditions: MNQ 0.05 mmol; H_2O_2 0.8 M; ZIF-8(MeOH) 3.3 mg, CH_3CN 1 mL, 70 °C. An additional portion of MNQ (0.05 mmol) was added after 30 min of the reaction.

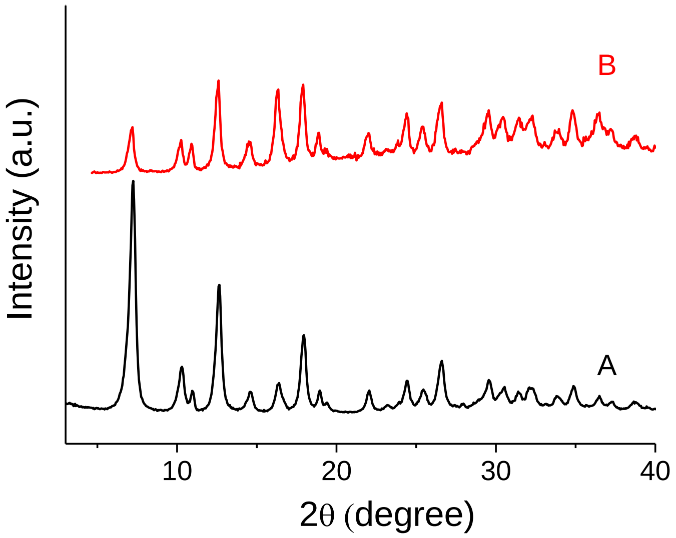


Fig. S8 XRD patterns for ZIF-8(MeOH) before (A) and after (B) MNQ catalytic oxidation.

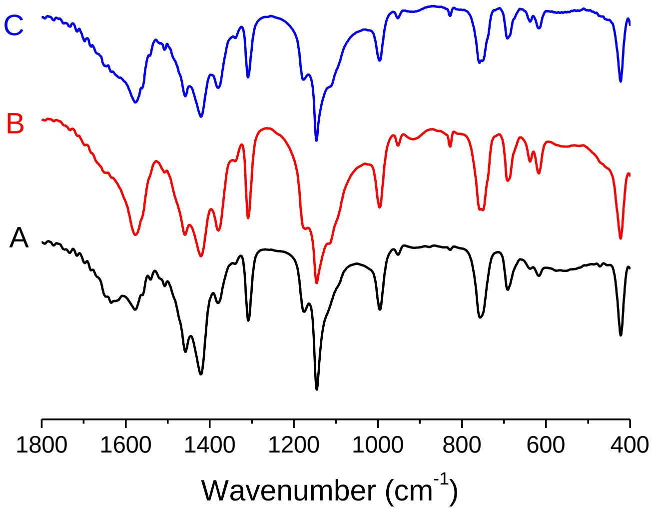


Fig. S9 FTIR spectra of ZIF-8(MeOH): initial (A), after 40 min (B) and after 2 h (C) of the catalytic reaction of MNQ oxidation.

Table S1 MNQ oxidation with H_2O_2 in the presence of HMeIM and zinc nitrate additives[a]

Additive	Additive (mmol)	Time (h)	MNQ conversion (%)	Epoxide yield (selectivity [b]) (%)
-	-	4	6	3
HMeIM	0.0004	2	15	10 (67)
$Zn(NO_3)_2$	0.0004	1	6	2
$Zn(NO_3)_2$/HMeIM	0.0004/0.0008	1	6	3
HMeIM	0.1	0.5	83	54 (65)
$Zn(NO_3)_2$	0.1	2	16	6 (38)
$Zn_5(OH)_8(NO_3)_2$	0.1	3	10	5 (50)
$Zn(NO_3)_2$/HMeIM	0.1 / 0.2	2	15	6 (40)

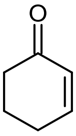
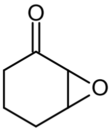
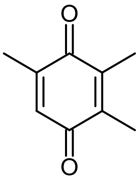
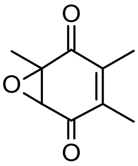
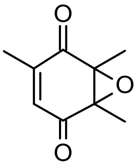
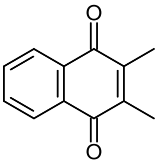
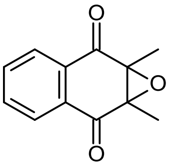
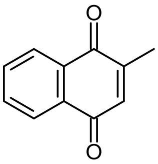
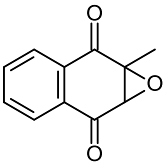
[a] Reaction conditions: MNQ 0.1 mmol; H_2O_2 0.8 mmol; CH_3CN 1 mL; 70 °C. [b] Based on substrate consumed.

Table S2 MNQ oxidation with H_2O_2 over ZIF-8 in different solvents[a]

Solvent	Time (h)	MNQ conversion (%)	Epoxide yield (selectivity[b]) (%)
MeCN	1.5	81	78 (97)
EtOAc	2	35	35 (100)
DMC	2	33	31 (94)

[a] Reaction conditions: MNQ 0.1 mmol; H_2O_2 0.8 mmol; ZIF-8(MeOH) 3.3 mg; CH_3CN 1 mL; 70 °C. [b] Yield based on MNQ converted.

Table S3 Oxidation of α,β-unsaturated carbonyl compounds with H_2O_2 over ZIF-8[a]

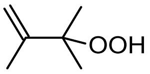
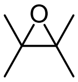
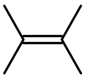
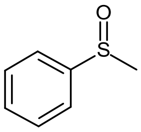
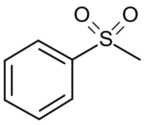
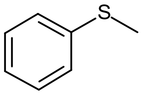
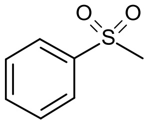
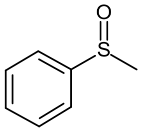
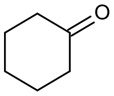
Substrate	ZIF-8(MeOH) (mg)	Time (h)	Conversion (%)	Product yield (selectivity[b]) (%)	
					
	3	5	20	10 (50)[c]	
	10	1.5	20	13 (65)[c]	
					
	3	5	20	4 (20)	12 (60)
	10	1.5	32	4 (13)	25 (78)
					
	3	4	20	18 (90)	
	7	2	35	32 (91)	
					
	3	1.5	81	78 (96)	
	10	0.5	88	82 (93)	

[a] Reaction conditions: substrate 0.1 mmol; H_2O_2 0.8 mmol; ZIF-8(MeOH); CH_3CN 1 mL; 70 °C.

[b] Yield based on substrate converted.

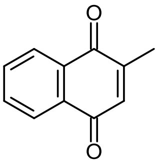
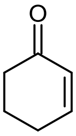
[c] Other products: 4-acetylbutyric acid, 3-hydroxycyclohexanone, 4-hydroxy-2-cyclohexen-1-one.

Table S4 Oxidation of various organic substrates with H_2O_2 over ZIF-8[a]

Substrate	ZIF-8(MeOH) (mg)	Time (h)	Conversion (%)	Product yield (selectivity[b]) (%)	
Electron-rich substrates					
					
	-[c]	24	5	1 (20)	0 (-)
	2	24	9	1 (11)	1 (11)
					
	-[c]	24	9	8 (89)	1 (11)
	2	24	10	7 (70)	3 (30)
Electron-deficient substrates					
					
	-[c]	24	5	5 (100)	
	2	24	18	15 (100)	
 d	-[c]	5	5	-	-
	2	5	4	-	-

[a] Reaction conditions: substrate 0.1 mmol; H_2O_2 0.1 mmol; CH_3CN 1 mL; 27 °C. [b] Based on converted substrate. [c] Blank experiment (no catalyst added). [d] H_2O_2 0.4 mmol; 70 °C.

Table S5 Comparison of catalytic performance of ZIF-8 and UiO-66(67)[a]

Substrate	Catalyst	Time (h)	Conversion (%)	Epoxide yield (selectivity[b]) (%)
	ZIF-8	1.5	81	78 (96)
	UiO-66	4	10	8 (80)
	UiO-67	4	8	7 (88)
	ZIF-8	5	20	10 (50)[c]
	UiO-66	1	20	12 (60)[c]
	UiO-67	1	20	11 (55)[c]

[a] Reaction conditions: substrate 0.1 mmol; H_2O_2 0.8 mmol; catalyst 3 mg ZIF-8(MeOH) or 5 mg of UiO-66(67); CH_3CN 1 mL; 70 °C. [b] Yield based on substrate converted. [c] Other products: 4-acetylbutyric acid, 3-hydroxycyclohexanone, and 4-hydroxy-2-cyclohexen-1-one; data taken from ref. S7.

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