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Supporting information

$H_5PV_2Mo_{10}O_{40}$ Encapsulated into $Cu_3(BTC)_2$ as Efficient Nanocrystalline Heterogeneous Catalysts for Styrene Epoxidation

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1. Experimental procedures

Synthesis of NENU-9N by neat mechanical grinding method[1]

$Cu(NO_3)_2 \cdot 3H_2O$ (0. 24 g, 1 mmol) and $H_5PV_2Mo_{10}O_{40} \cdot 34.5H_2O$ (0. 22 g, 0.092 mmol) were dissolved in deionized water (10 mL) and stirred for 20 min, then the pH of the solution was adjusted to 4 by using 1M NaOH. After evaporating the solvent, the collected solid sample was mixed with H_3BTC (0. 14 g, 0. 67 mmol) and then the mixture was grounded in an agate mortar for 5 minutes. The yielded green solid material was washed several times with deionized water and ethanol respectively. After dried in an oven at 60 ℃ for 24 hours, NENU-9N with a diameter of about 150 nm was obtained.

Synthesis of NENU-9N by liquid-assisted grinding method

$Cu(NO_3)_2 \cdot 3H_2O$ (0. 24 g, 1 mmol) and $H_5PV_2Mo_{10}O_{40} \cdot 34.5H_2O$ (0. 22 g, 0.092 mmol) were dissolved in deionized water (10 mL) and stirred for 20 min, then the pH of the solution was adjusted to 4 by using 1M NaOH. After evaporating the solvent, the collected solid sample was mixed with H_3BTC (0. 14 g, 0. 67 mmol) and ethanol (0.3mL, 0.6 mL and 1.2mL respectively) then the mixture was grounded in an agate mortar for 5 minutes to obtain green solid material. The yielded green solid material was washed several times with deionized water and ethanol respectively. After dried in an oven at 60 ℃ for 24 hours, NENU-9N with a diameter of about 100nm, 70 nm and 80nm were obtained.

Synthesis of NENU-9 by solution method[1]

(a) $Cu(OAc)_2 \cdot H_2O$ (0.2 g, 1 mmol) and $H_5PV_2Mo_{10}O4_0 \cdot 34.5H_2O$ (0. 22 g, 0.092 mmol) were dissolved in deionized water (10 mL) and stirred for 20 min, then the pH of the solution was adjusted to 2.5 by using 1M NaOH to obtain solution A. H_3BTC (0.14 g, 0.67 mmol) was dissolved in ethanol (10 mL), and this solution was added dropwise to solution B with continuous stirring at room temperature. A green precipitate appeared gradually. The yielded green precipitate was washed several times with deionized water and ethanol respectively. After dried in an oven at 60 ℃ for 24 hours, NENU-9 with a diameter of 0.7 μm was obtained.

(b) $Cu(NO_3)_2 \cdot 3H_2O$ (0. 24 g, 1 mmol) and $H_5PV_2Mo_{10}O_{40} \cdot 34.5H_2O$ (0. 22 g, 0.092 mmol) were dissolved in deionized water (10 mL) and stirred for 20 min, then the pH of the solution was adjusted to 2.5 by using 1M NaOH to obtain solution B. H_3BTC (0.14 g, 0.67 mmol) was dissolved in ethanol (10 mL), and this solution was added dropwise to solution A with continuous stirring at room temperature. A green precipitate appeared gradually. The yielded green precipitate was washed several times with deionized water and ethanol respectively. After dried in an oven at 60 ℃ for 24 hours, NENU-9 with a diameter of 1.3 μm was obtained.

Synthesis of NENU-9N by hydrothermal synthesis method[2]

$Cu(NO_3)_2 \cdot 3H_2O$ (0. 24 g, 1 mmol) and $H_5PV_2Mo_{10}O_{40} \cdot 34.5H_2O$ (0. 22 g, 0.092 mmol) were dissolved in deionized water (10 mL) and stirred for 20 min, then H_3BTC (0.21 g, 1 mmol) and $[(CH_3)_4N]OH$ (0.09 g, 1 mmol) were added into the solution. The mixture was stirred for 30 min to obtain a turbid mixture. Then the turbid mixture was transferred into a Teflon-lined autoclave and heated at 180 ℃ for 24 h. Then the mixture was cooled to room temperature at a rate of 10 ℃ per hour, and green crystals were obtained

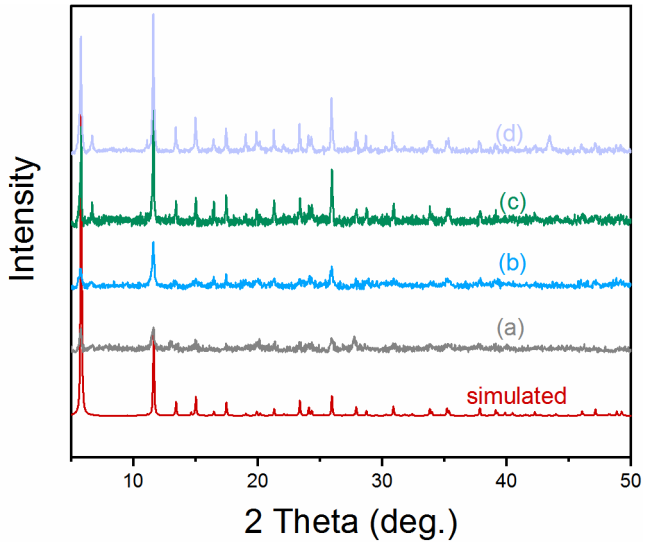


Figure S1 Powder XRD of the simulated NENU-9 and NENU-9N with different ratio of solvent to reactant (a) 0, (b) 0.5μLmg^{-1}, (c) 1μLmg^{-1}, (d) 2μLmg^{-1}.

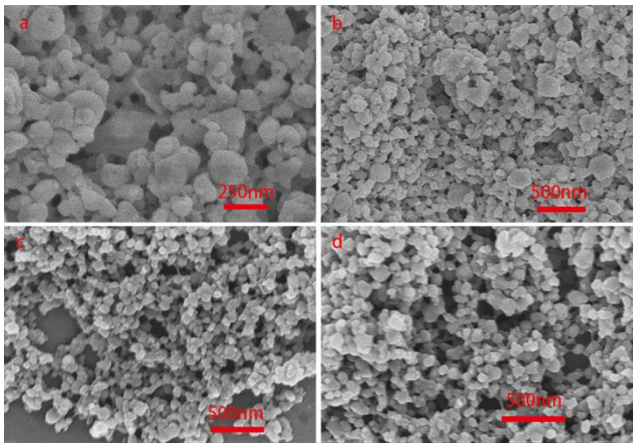


Figure S2 SEM images of NENU-9N with different ratio of solvent to reactant (a) 0, (b) 0.5 μLmg^{-1}, (c) 1 μLmg^{-1}, (d) 2 μLmg^{-1}.

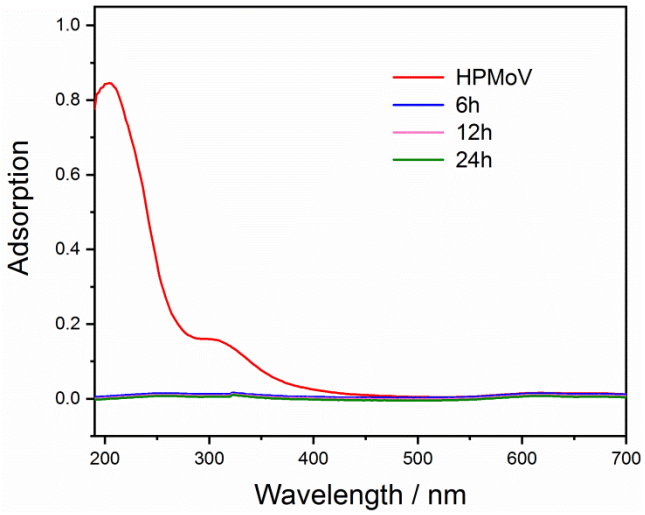


Figure S3 The UV-Vis spectra of HPMoV and the solution in which NENU-9 was soaked for 6h, 12h and 24h.

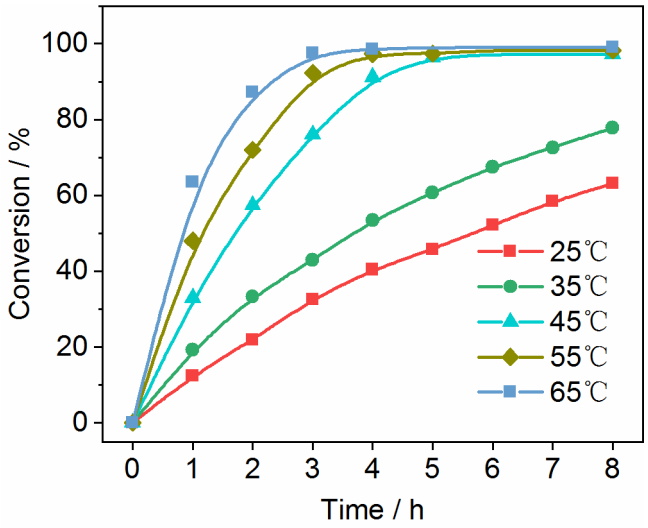


Figure S4 Styrene conversion versus reaction time at different reaction temperatures. Reaction conditions: catalysts (0.005 mmol), styrene (4mmol), isobutyraldehyde (8 mmol), acetonitrile (10 mL).

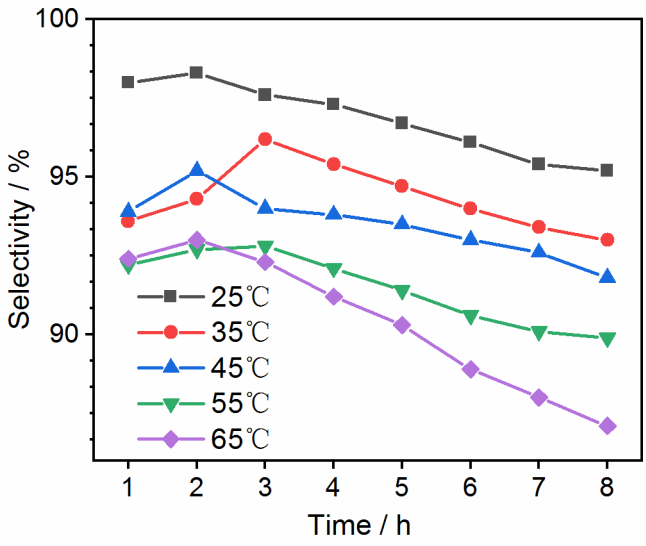


Figure S5 Selectivity of styrene oxide versus reaction time at different reaction temperatures. Reaction conditions: catalysts (0.005 mmol), styrene (4 mmol), isobutyraldehyde (8 mmol), acetonitrile (10mL).

Table S1 The catalytic effects of different catalysts on styrene epoxidation

Entry	catalyst	T/℃	styrene/co-reductant ratio	Time/h	conversion/%	selectivity/%	TOF/h^{-1}	Ref.
1	NENU-9N	45	1:2	5	97.2	93.5	156	This work
2	FeP-CMP	25	1:3	24	55	69	22.9	[3]
3	$[Cu_3(BTC)_2]$	40	1:2	6	58	58	5.7	[4]
4	IRMOF-3	40	1:2	6	52.3	80.7	4.9	[5]
5	[Cu-Imace-H-H] $[BF_4]$	60	1:1	10	76	46	95	[6]
6	Fe3O4/ Fe-MIL-101	25	1:2	4	11	-	1	[7]
7	Co(II)@Cr-MIL-101-P2I	35	1:2	24	80	59	3.28	[8]
8	VO–Salen–SBA	80	1:2.5	8	78.6	71.2	63	[9]

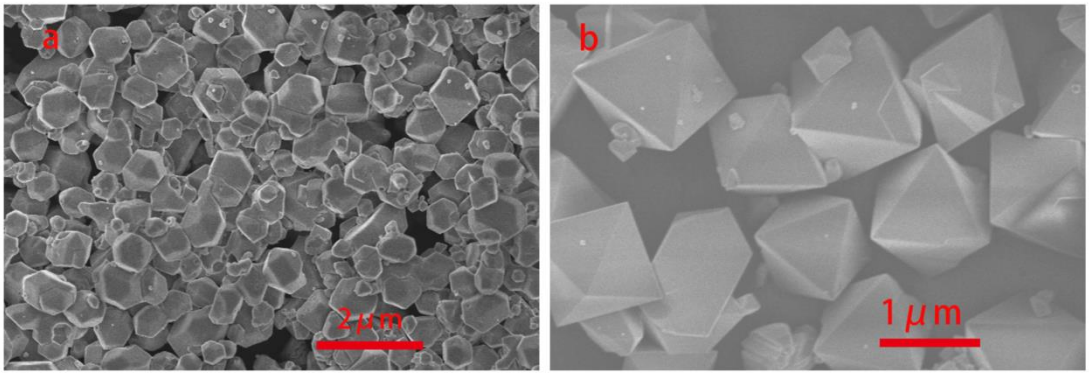


Figure S6 SEM of (a) NENU-9-0.7μm and (b)NENU-9-1.5μm.

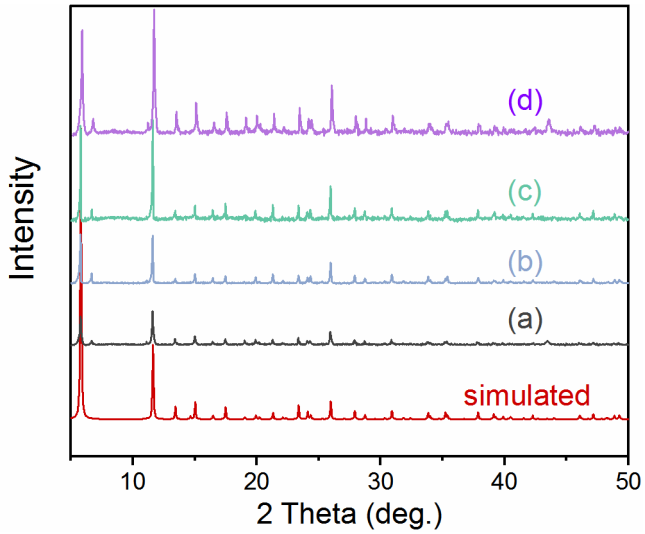


Figure S7 Powder XRD of the simulated NENU-9 and NENU-9 with different particle sizes (a) 70 nm, (b) 0.7 μm, (c) 1.5 μm, (c) 300μm.

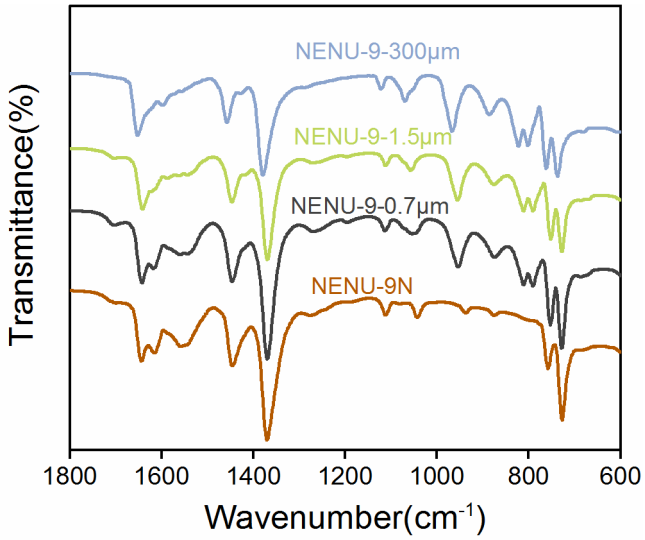


Figure S8 FT-IR spectra of NENU-9ith different particle sizes.

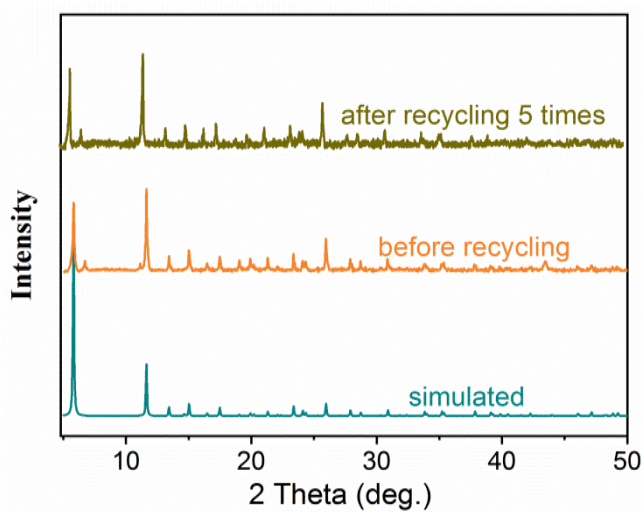


Figure S9 PXRD patterns of simulated NENU-9 and NENU-9N before and after recycling for 5 times.

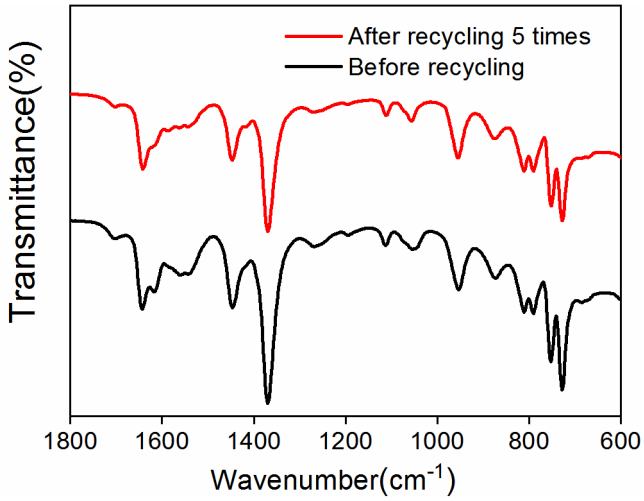
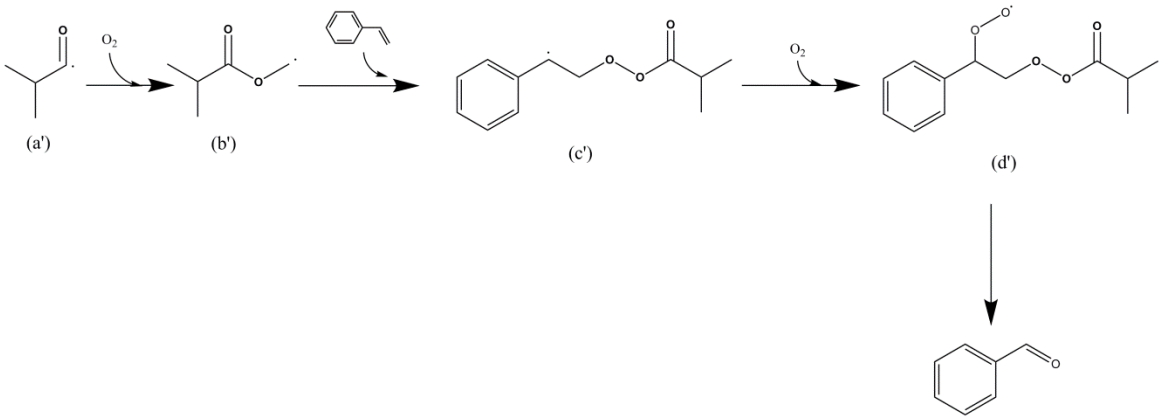


Figure S10 FT-IR spectra of NENU-9 before and after recycling for 5 times.



Scheme S1 The production path of benzaldehyde for the epoxidation of styrene using isobutyraldehyde/O_2 reported by Haber.[10]

Supplemental References

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