Supporting Information for

A gel-like/freeze-drying strategy to construct hierarchically porous polyoxometalate-based metal-organic framework catalysts

Xiao-Hui Li[a], Yi-Wei Liu[a], Shu-Mei Liu[a], Shuang Wang[a], Li Xu[a], Zhong Zhang[a], Fang Luo[a], Ying Lu[a], Shu-Xia Liu[a]*

[a] Key Laboratory of Polyoxometalate Science of the Ministry of Education, College of Chemistry, Northeast Normal University, Changchun, Jilin 130024, China

*e-mail: liusx@nenu.edu.cn

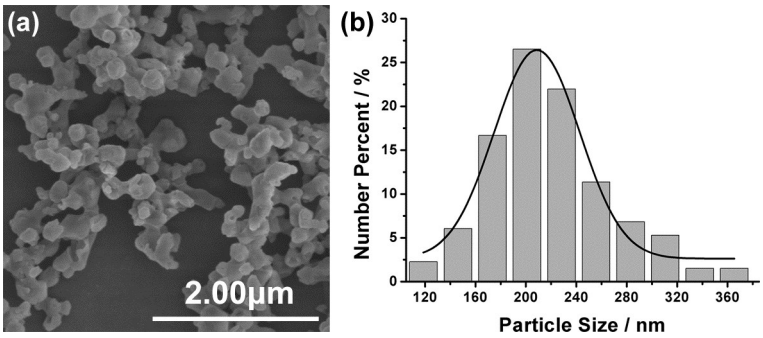

Fig. S1 (a) SEM image and (b) particle analysis of sample synthesized in mix solvent of ethanol and water.

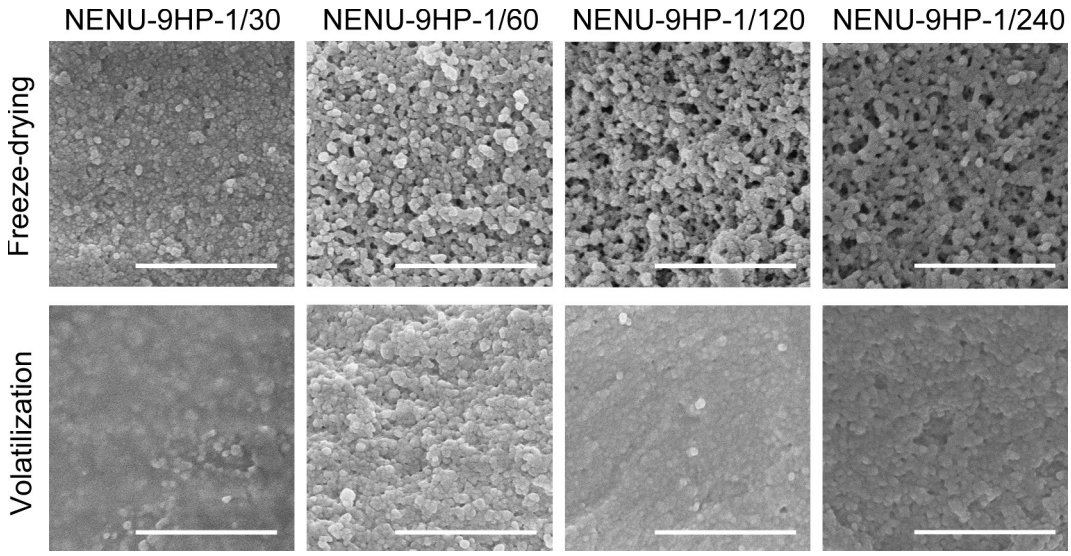

Fig. S2 The comparison of samples prepared by freeze-drying and volatilization. The scale bars are all 1 μm.

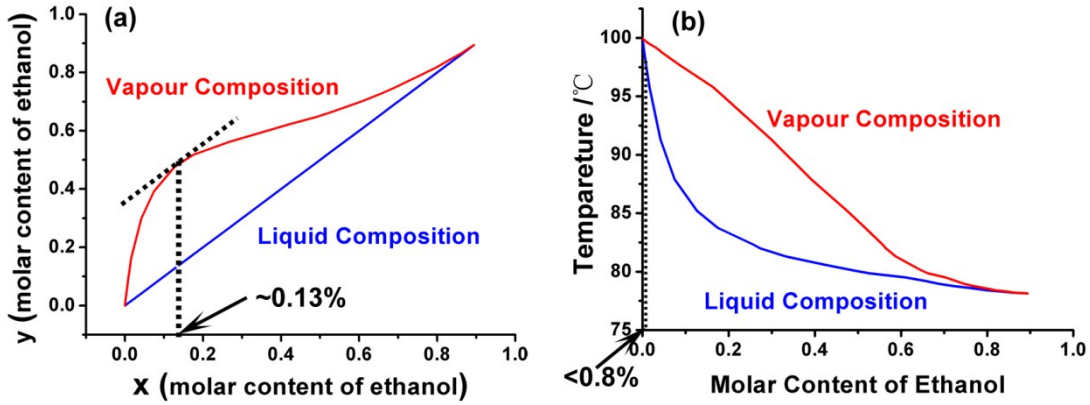

Fig. S3 (a) x-y phase diagram and (b) T-x-y phase diagram of ethanol and water.

Table S1. Porosity properties of NENU-9HP-1/V.

sample	[a] S_{BET} (m^2g^{-1})	[b] S_{micro} (m^2g^{-1})	[c] S_{meso} (m^2g^{-1})	[d] V_t (cm^3g^{-1})	[e] V_{micro} (cm^3g^{-1})	[f] V_{meso} (cm^3g^{-1})	[g] D_{meso} (nm)
NENU-9HP-1/30	369.2	311.2	40.0	0.185	0.144	0.038	12.6
NENU-9HP-1/60	503.5	417.1	57.4	0.330	0.193	0.131	17.9
NENU-9HP-1/120	624.0	553.4	50.2	0.476	0.254	0.239	30.1
NENU-9HP-1/240	710.8	594.8	92.8	0.642	0.274	0.416	22.9
NENU-9HP-1/120-Volatilization	166.6	118.1	44.5	0.145	0.054	0.096	11.1

[a] S_{BET} is the BET-specific surface area. [b] S_{micro} is the t-plot-specific micropore surface area. [c] S_{meso} is the specific mesopore surface area BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter. [d] V_t is the total specific pore volume. [e] V_{micro} is the t-Plot micropore volume. [f] V_{meso} is the specific mesopore volume calculated from BJH adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter. [g] D_{meso} is the mesopore diameter calculated from adsorption isotherm using the BJH method.

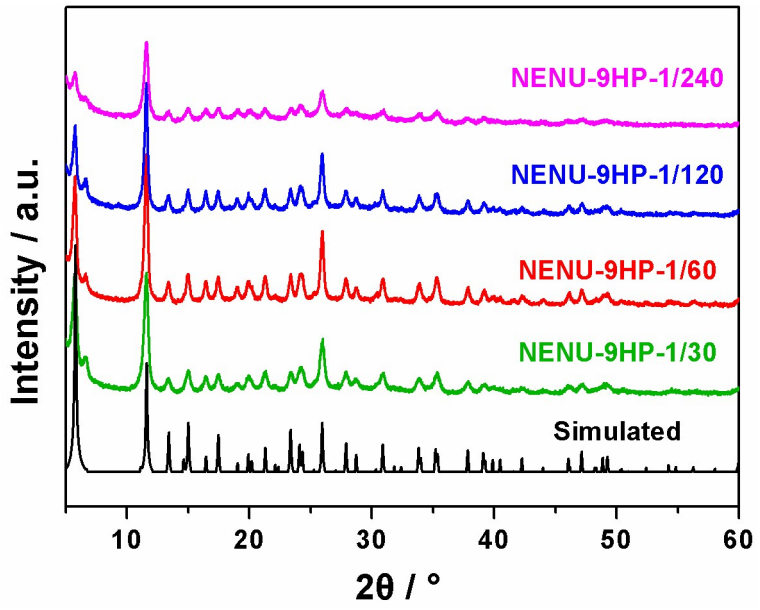

Fig. S4 PXRD patterns of simulated NENU-9 and NENU-9HP-1/V.

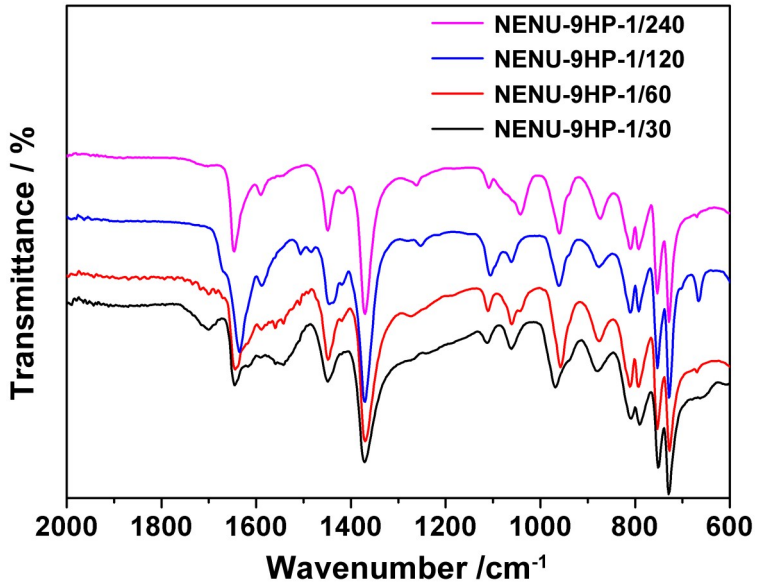

Fig. S5 FTIR spectra of NENU-9HP-1/V.

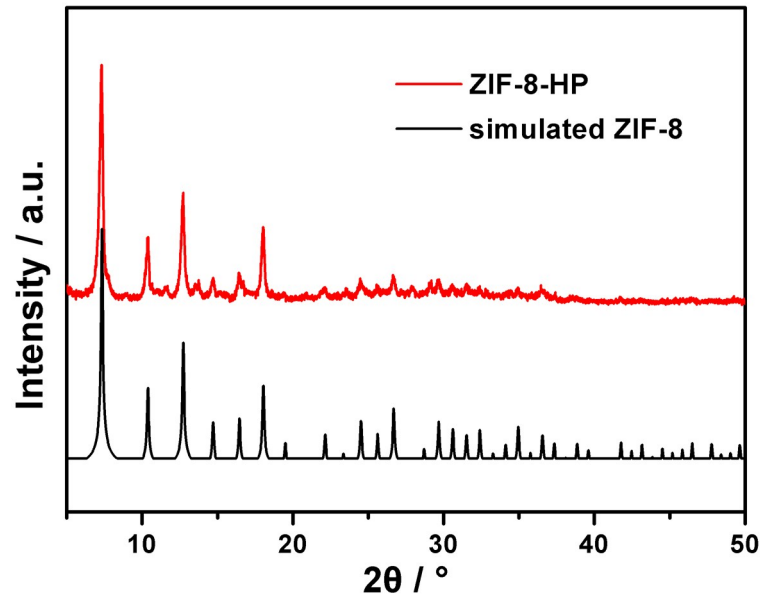

Fig. S6 PXRD patterns of hierarchically porous and simulated ZIF-8.

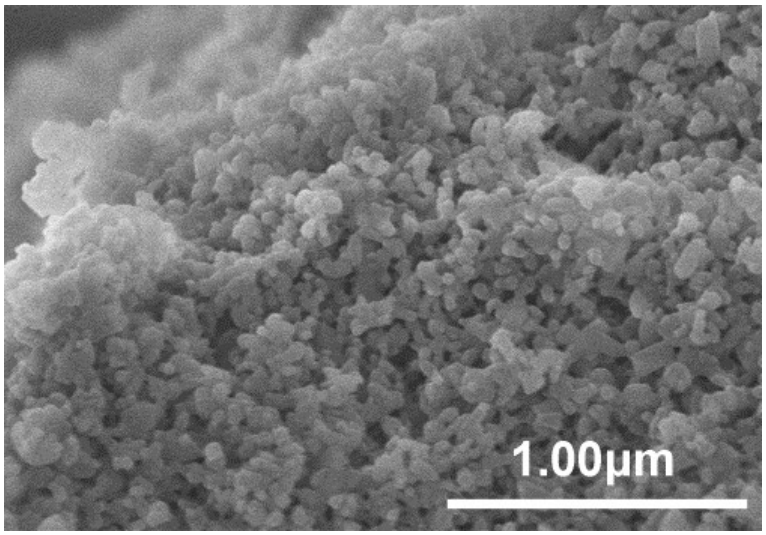

Fig. S7 SEM image of hierarchically porous ZIF-8.

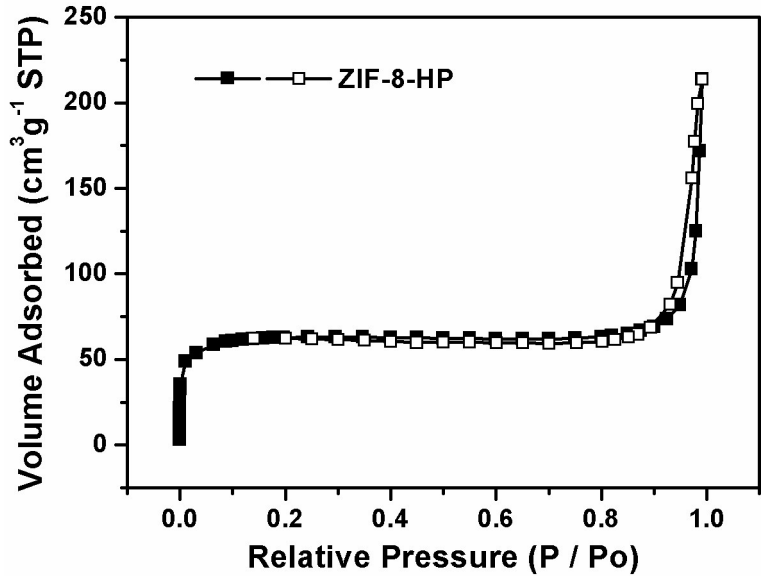

Fig. **S8** N_2 sorption isotherm of hierarchically porous ZIF-8.

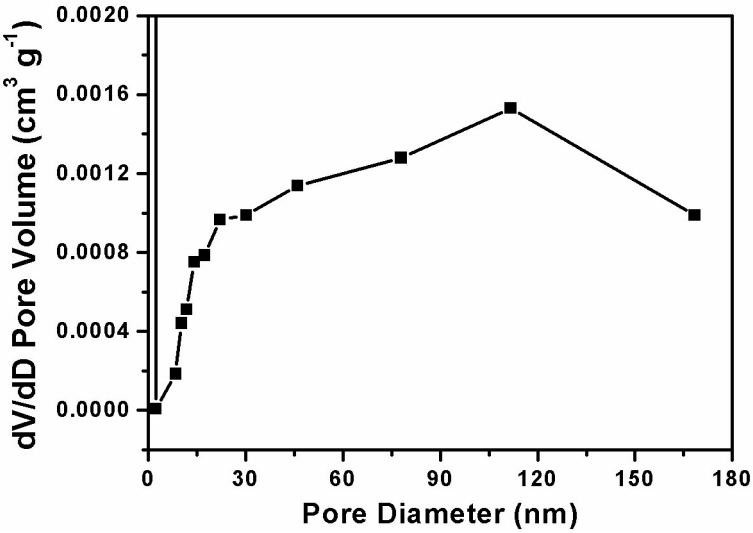

Fig. S9 Mesopore size distribution of hierarchically porous ZIF-8.

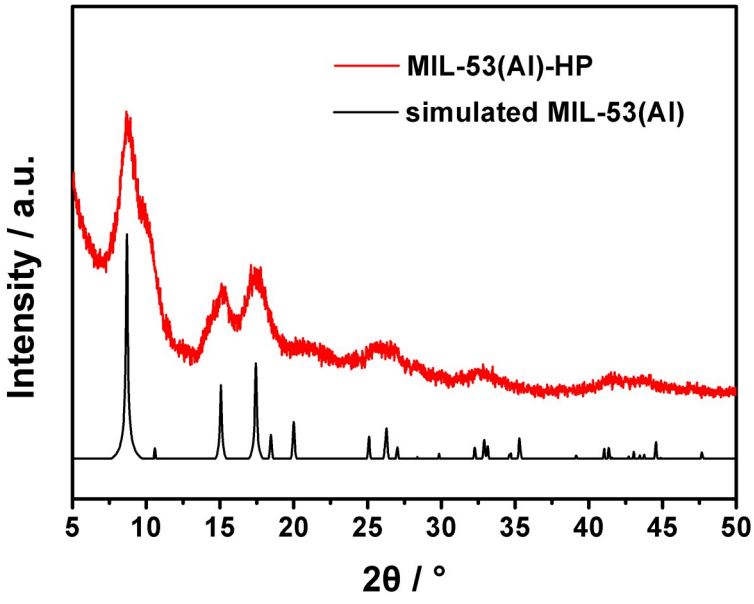

Fig. S10 PXRD patterns of hierarchically porous and simulated MIL-53(Al).

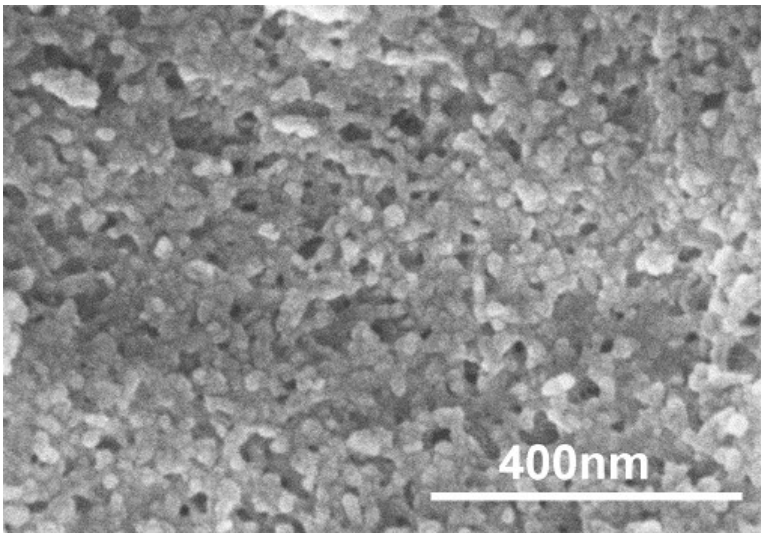

Fig. S11 SEM image of hierarchically porous MIL-53(Al).

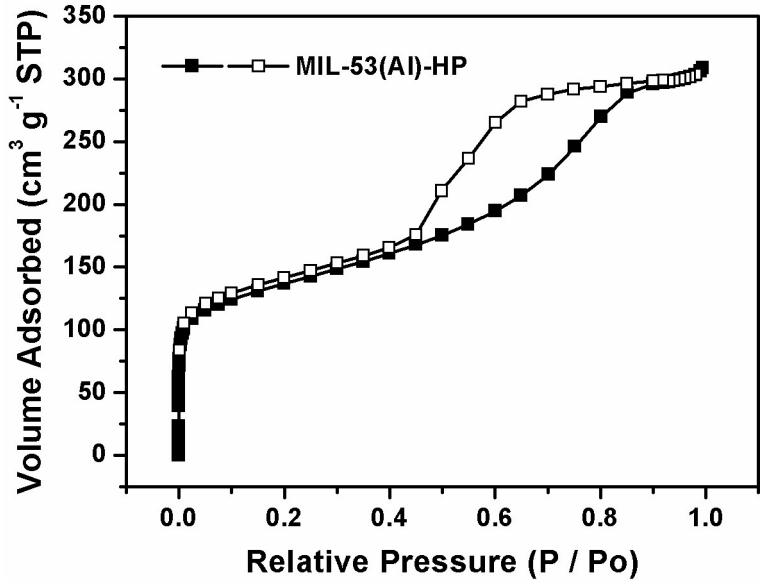

Fig. S12 N_2 sorption isotherm of hierarchically porous MIL-53(Al).

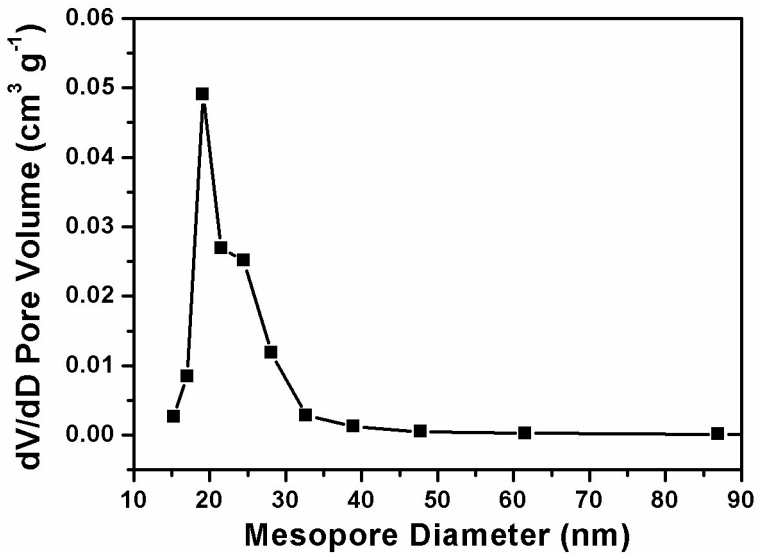

Fig. S13 Mesopore size distribution of hierarchically porous MIL-53(Al).

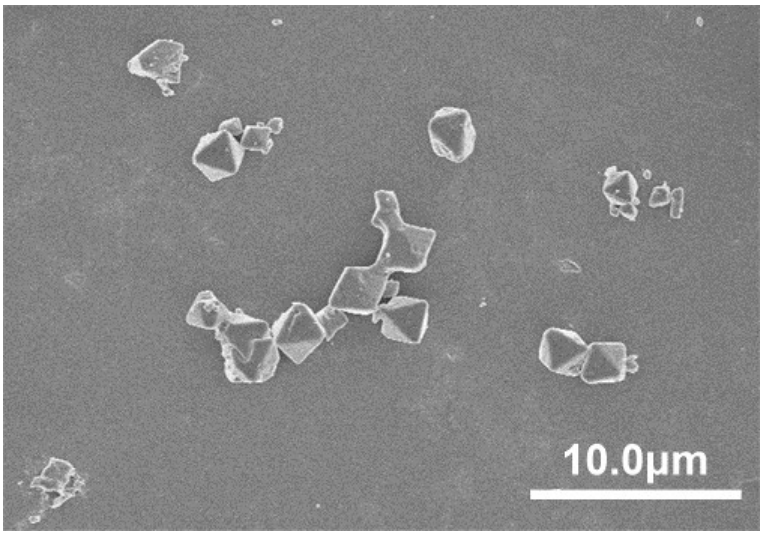

Fig. S14 SEM image of NENU-9N.

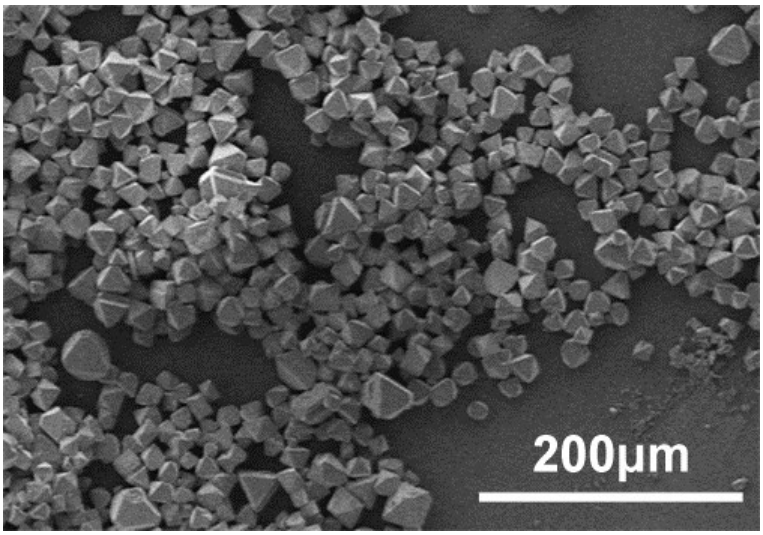

Fig. S15 SEM image of NENU-9HT.

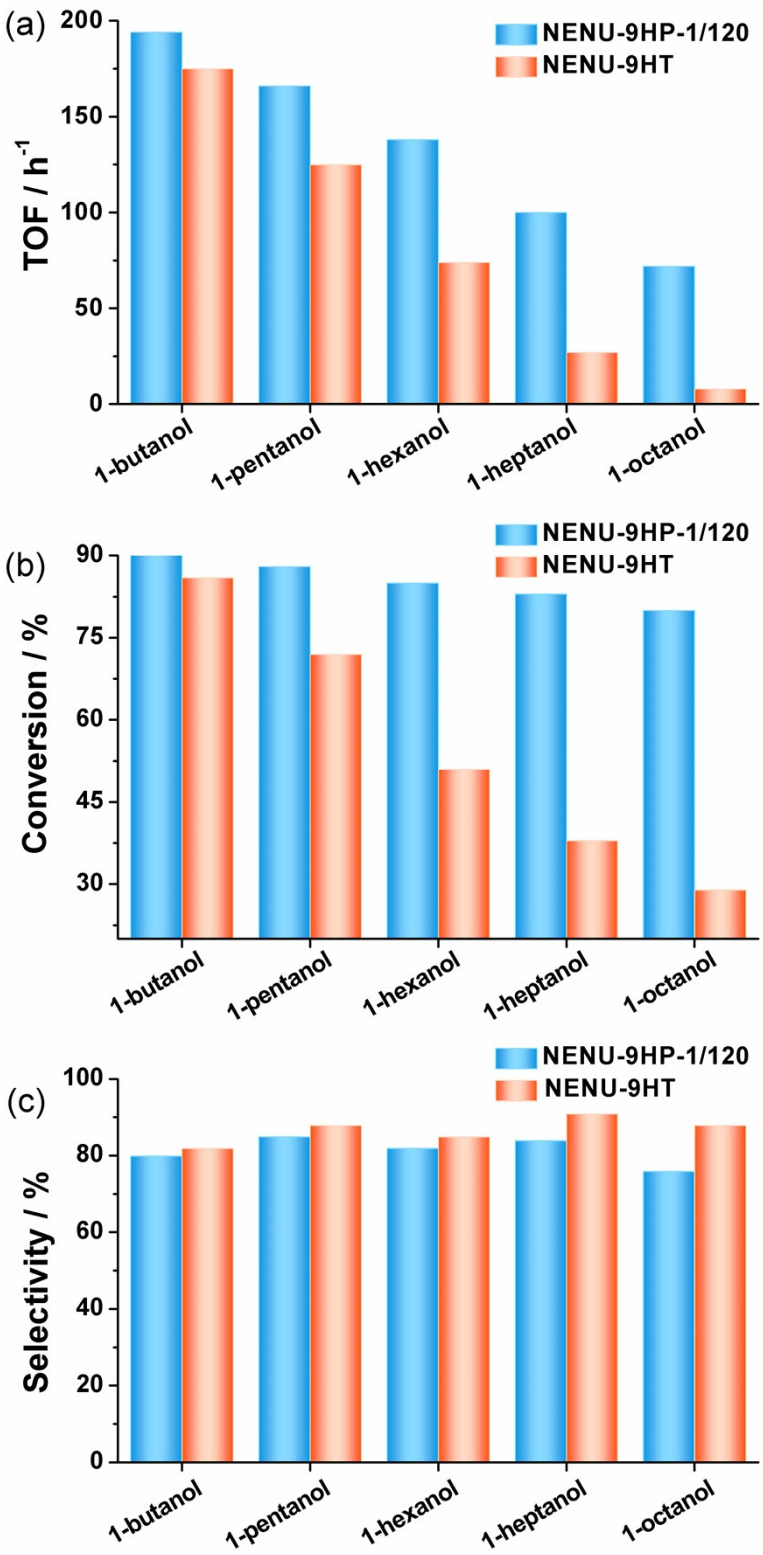

Fig. S16 (a) TOF values evaluated on the basis of the moles of the whole catalyst and reactive moles of substrates in 20 min, (b) conversions after 24 h of different primary fatty alcohols and (c) selectivity towards corresponding aldehydes catalyzed by NENU-9HP-1/120 and NENU-9HT.

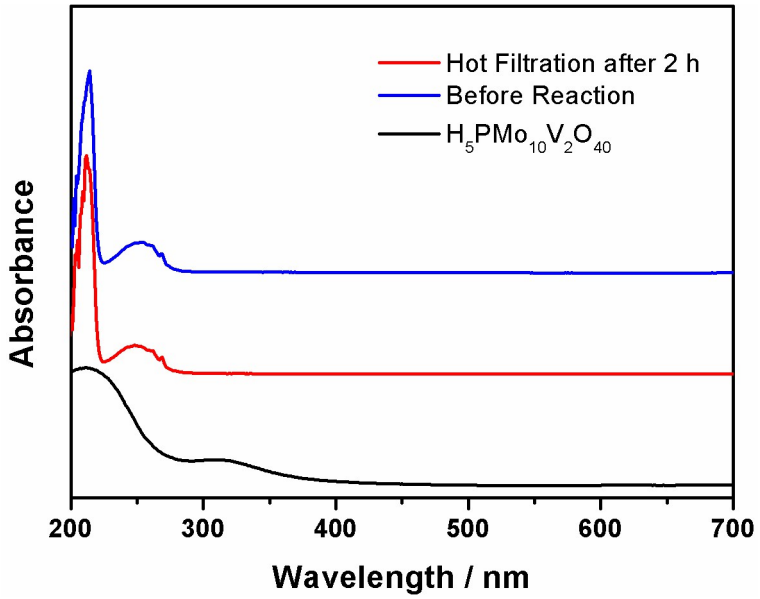

Fig. **S17** UV-Vis spectra of $H_5PV_2Mo_{10}O_{40}$, solution before reaction and filtrate after 2 h of reaction.

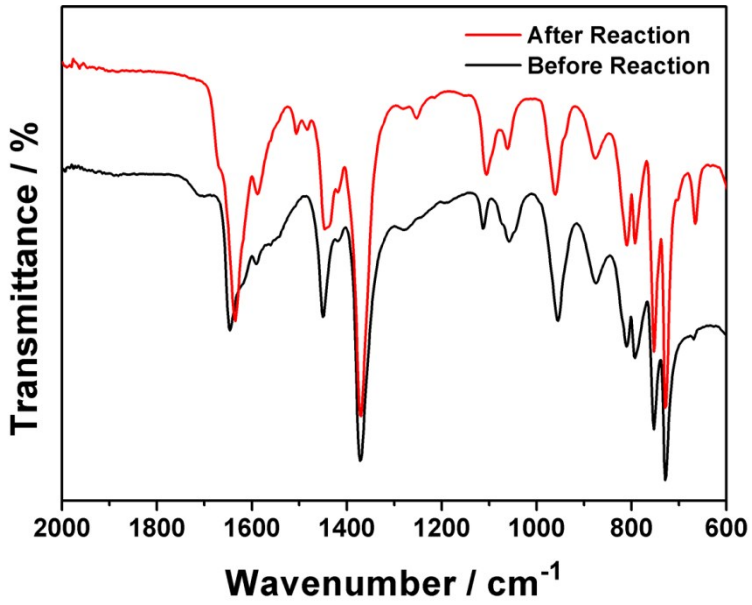

Fig. S18 FTIR spectra of NENU-9HP-1/120 before and after recycling for 5 times.

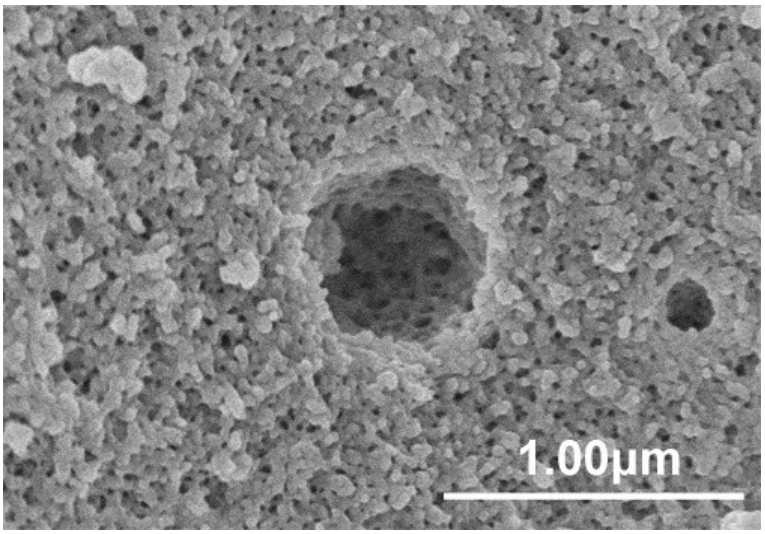

Fig. **S19** SEM image of NENU-9HP-1/120 after recycling for 5 times.

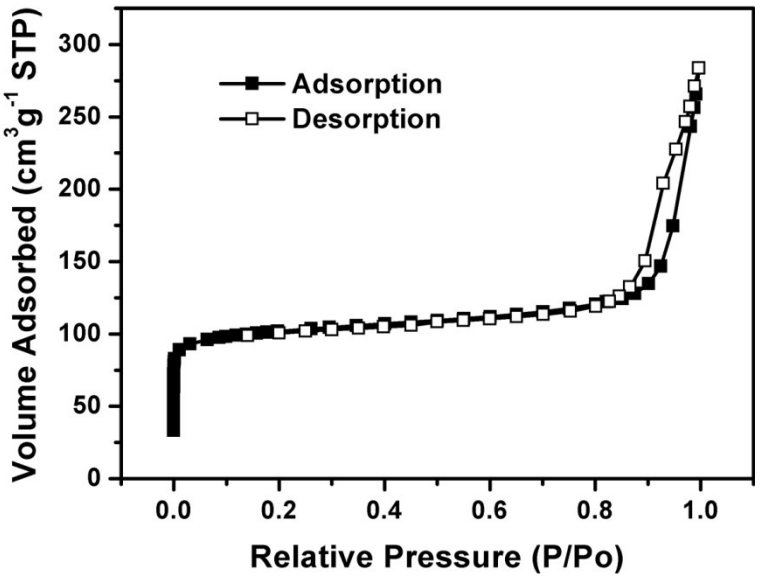

Fig. S20 N_2 sorption isotherm of NENU-9HP-1/120 after recycling for 5 times.

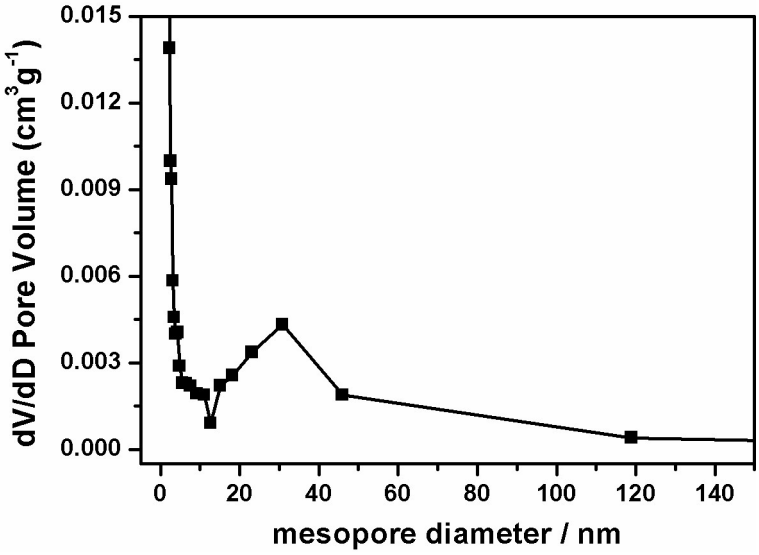

Fig. **S21** Mesopore size distribution of NENU-9HP-1/120 after recycling for 5 times.

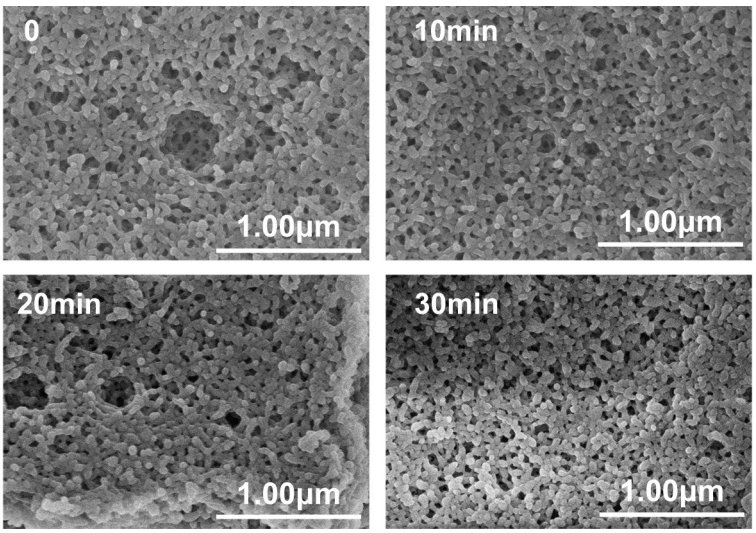

Fig. S22 SEM images of NENU-9HP-1/120 sonicated in ethanol.

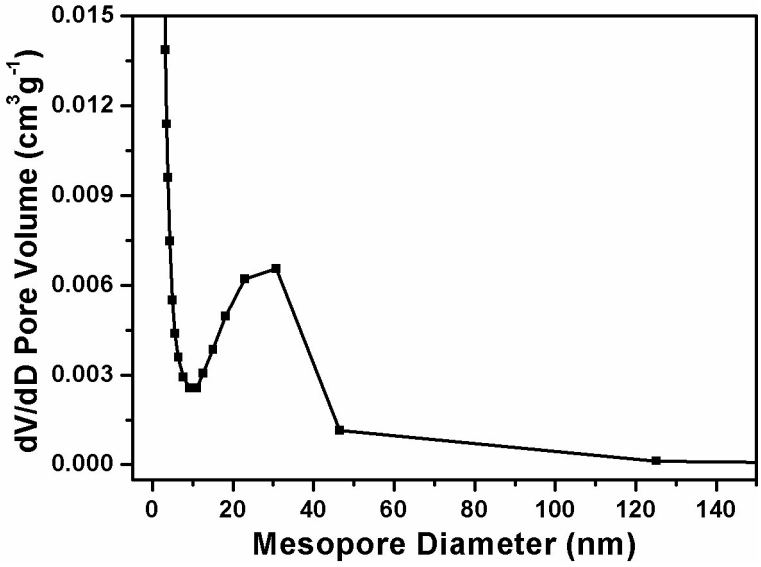

Fig. **S23** Mesopore size distribution of NENU-9HP-1/120 sonicated in ethanol.