Supporting Information for

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

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**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.
<table>
<thead>
<tr>
<th>sample</th>
<th>(a S_{\text{BET}}) (m²g⁻¹)</th>
<th>(b S_{\text{micro}}) (m²g⁻¹)</th>
<th>(c S_{\text{meso}}) (m²g⁻¹)</th>
<th>(d V_t) (cm³g⁻¹)</th>
<th>(e V_{\text{micro}}) (cm³g⁻¹)</th>
<th>(f V_{\text{meso}}) (cm³g⁻¹)</th>
<th>(g D_{\text{meso}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NENU-9HP-1/30</td>
<td>369.2</td>
<td>311.2</td>
<td>40.0</td>
<td>0.185</td>
<td>0.144</td>
<td>0.038</td>
<td>12.6</td>
</tr>
<tr>
<td>NENU-9HP-1/60</td>
<td>503.5</td>
<td>417.1</td>
<td>57.4</td>
<td>0.330</td>
<td>0.193</td>
<td>0.131</td>
<td>17.9</td>
</tr>
<tr>
<td>NENU-9HP-1/120</td>
<td>624.0</td>
<td>553.4</td>
<td>50.2</td>
<td>0.476</td>
<td>0.254</td>
<td>0.239</td>
<td>30.1</td>
</tr>
<tr>
<td>NENU-9HP-1/240</td>
<td>710.8</td>
<td>594.8</td>
<td>92.8</td>
<td>0.642</td>
<td>0.274</td>
<td>0.416</td>
<td>22.9</td>
</tr>
<tr>
<td>NENU-9HP-1/120-Volatilization</td>
<td>166.6</td>
<td>118.1</td>
<td>44.5</td>
<td>0.145</td>
<td>0.054</td>
<td>0.096</td>
<td>11.1</td>
</tr>
</tbody>
</table>

\(a S_{\text{BET}}\) is the BET-specific surface area. \(b S_{\text{micro}}\) is the t-plot-specific micropore surface area. \(c S_{\text{meso}}\) 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. \(e V_{\text{micro}}\) is the t-Plot micropore volume. \(f V_{\text{meso}}\) is the specific mesopore volume calculated from BJH adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter. \(g D_{\text{meso}}\) 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** $\text{N}_2$ 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 $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, 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 N₂ 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.