

Supporting Information

**Enhanced catalysis of vanadium-substituted Keggin-type
polyoxomolybdate supported on M₃O₄/C (M=Fe or Co)
surface enables efficient and recyclable HMF oxidation to
DFF**

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1. Materials

All chemicals and reagents are utilized without any additional purification steps being performed. Sodium metavanadate (NaVO_3), 85% phosphoric acid (85% H_3PO_4), Molybdenum trioxide (MoO_3), concentrated hydrochloric acid (HCl), diethyl ether, ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole, fumaric acid, *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol, methanol, 5-Hydroxymethylfurfural (HMF), 2,5-diformylfuran (DFF), *p*-benzoquinone and isopropyl alcohol were purchased from Aladdin Chemical Co., Ltd.

2. Experimental methods

2.1. Synthesis of $\text{PMo}_{10}\text{V}_2$

The synthesis of $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}] \cdot 32\text{H}_2\text{O}$ ($\text{PMo}_{10}\text{V}_2$) is based on the previously reported literature.¹ The specific synthesis process is as follows: the NaVO_3 (30.0 g), 85% H_3PO_4 (3.4 mL), and MoO_3 (74.0 g) were added to 800 mL of water and refluxed for 8 h. Afterwards, the mixture was acidified using 145 mL of HCl, and the resulting acid was extracted with 200 mL of diethyl ether. Finally, the diethyl ether was removed, and the product was obtained by recrystallization from water.

2.2. Synthesis of MIL-88A(Fe)

The synthesis of MIL-88A(Fe) is based on previously reported literature with slight modifications.² In brief, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.808 g, 0.002 mol) and fumaric acid (0.580 g, 0.005 mol) were added to 100 mL of DMF and stirred at room temperature. The solution was then transferred to a 500 mL round-bottom flask and kept at 75 °C

for 4 h. Subsequently, the suspension was cooled to room temperature. The resulting products were collected by centrifugation and successively washed five times with ultra-pure water and ethanol. MIL-88A(Fe) was obtained after further vacuum drying at 60 °C for 24 h.

2.3. Synthesis of ZIF-67

The synthesis of ZIF-67 is based on previously reported literature.³ In brief, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.328 g, 0.008 mol) was added to 180 mL of methanol, and 2-methylimidazole (2.627 g, 0.032 mol) was added to 140 mL of methanol. Then, the two solutions were quickly mixed and stirred for 2 min. After that, the mixture was allowed to stand at room temperature for 24 h. Finally, the products were collected by centrifugation, washed several times with methanol, and dried at 50 °C.

2.4. HMF Adsorption test

Adsorption ability were characterized to determine the adsorption capacity of catalyst. Typically, 50 mg of HMF and 40 mg of catalyst were added to 4 mL DMSO solution in atmosphere with stirring. Then, the catalyst was separated by centrifuge, and the adsorption amount of HMF was detected by HPLC.

3. Characterization methods

The morphologies of the samples were analyzed using TEM (JEM-2100F, 200 kV) and SEM (FEG-250, 30 kV) equipped with an energy dispersive X-ray spectroscopy. The structures of the samples were identified using PXRD (Philips X'pert MPD) with $\text{Cu K}\alpha$ radiation (50 kV). The XPS spectra were detected by a ESCALAB-MKII spectrometer (VG Co., UK) with Al $\text{K}\alpha$ X-ray radiation as the X-

ray source for excitation. FTIR spectra were obtained using a NEXUS-870 spectrometer with KBr pellets. The products from catalytic reaction were analyzed by high-performance liquid chromatography (HPLC, Shimadzu LC-20A) using a reversed-phase ZOR-BAX Eclipse XDB-C18 column (4.6 × 250 mm) with UV detection (288 nm) and an SPD-20A UV detector. The elemental contents were determined by ICP-OES (Thermo iCAP 6300).

4. HPLC analytical methods

The mobile phase consists of acetonitrile and 0.1 wt% acetic acid with a volume ratio of 50: 950 at a flow rate of 0.5 mL·min⁻¹. The oven temperature is carefully controlled at 30°C to maintain stability. The reaction mixture is diluted to a final volume of 50 mL using pure water. The concentrations of HMF and DFF in the sample are determined using an external standard calibration curve, which is constructed using pure samples. The molar conversion and yield of the target compounds are then calculated based on these measurements.

$$\text{HMF conversion} = \frac{\text{mol of converted HMF}}{\text{mol of initial HMF}} \times 100\% \quad (1)$$

$$\text{DFF yield} = \frac{\text{mol of DFF}}{\text{mol of initial HMF}} \times 100\% \quad (2)$$

$$\text{DFF selectivity} = \frac{\text{DFF yield}}{\text{HMF conversion}} \times 100\% \quad (3)$$

5. Supporting figures

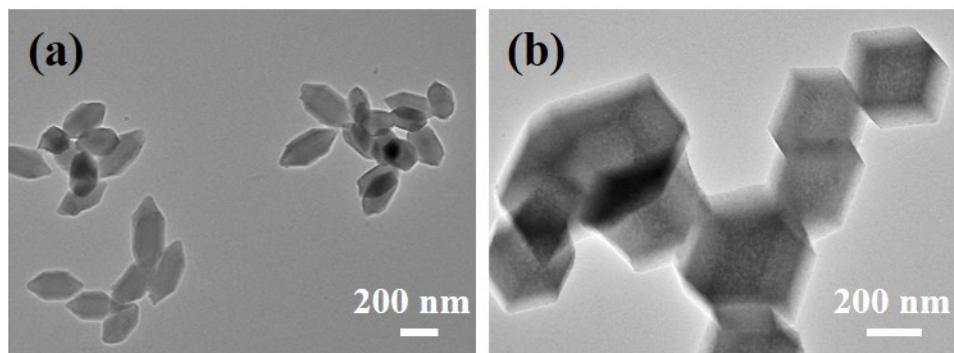


Fig. S1. TEM images of (a) MIL-88A(Fe) and (b) ZIF-67.

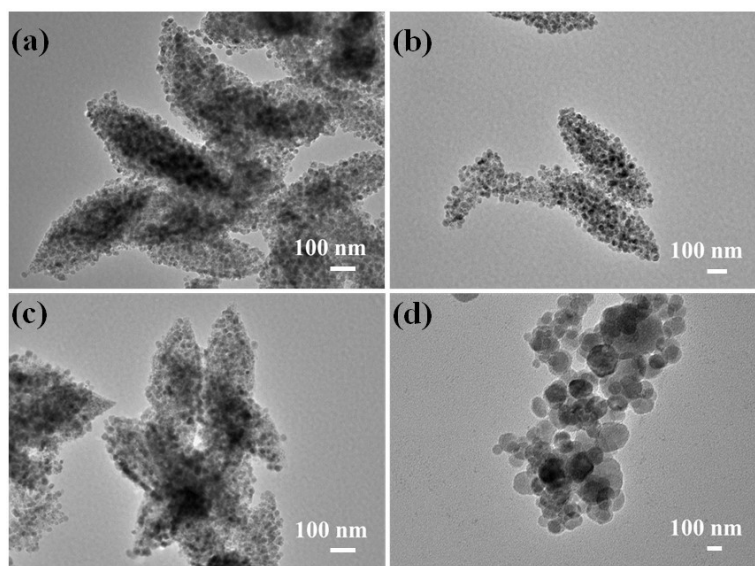


Fig. S2. TEM images of Fe₃O₄/C obtained by the calcination temperature of (a) 350 °C, (b) 450 °C, (c) 550 °C and (d) 650 °C.

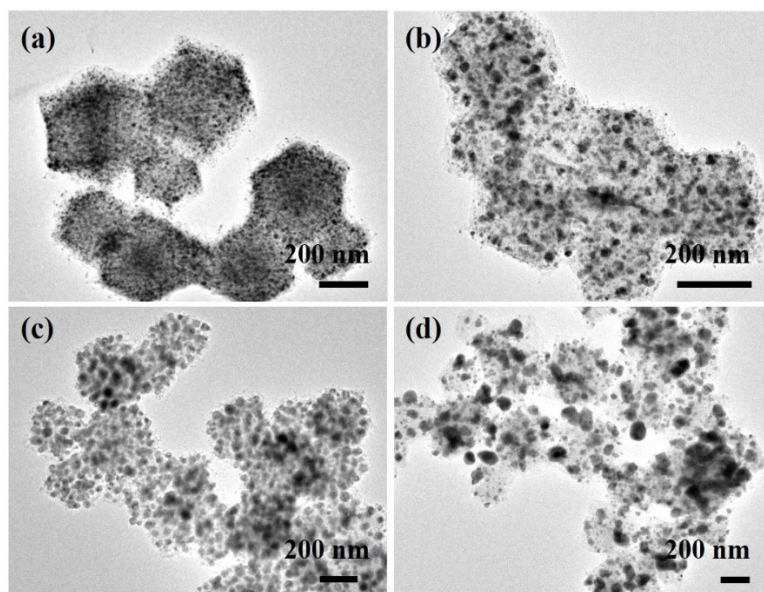


Fig. S3. TEM images of $\text{Co}_3\text{O}_4/\text{C}$ obtained by the calcination temperature of (a) 700 °C, (b) 800 °C, (c) 900 °C and (d) 1000 °C.

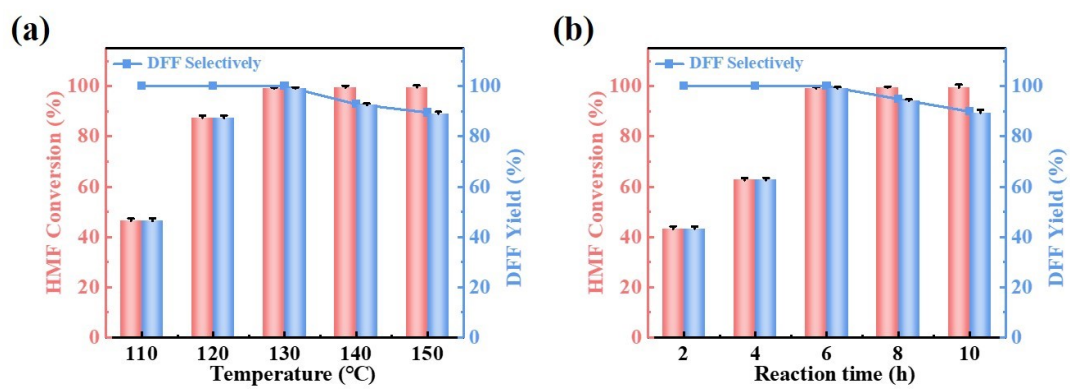


Fig. S4. Optimization of reaction conditions for PMo₁₀V₂@Fe₃O₄/C: (a) temperature and (b) reaction time.

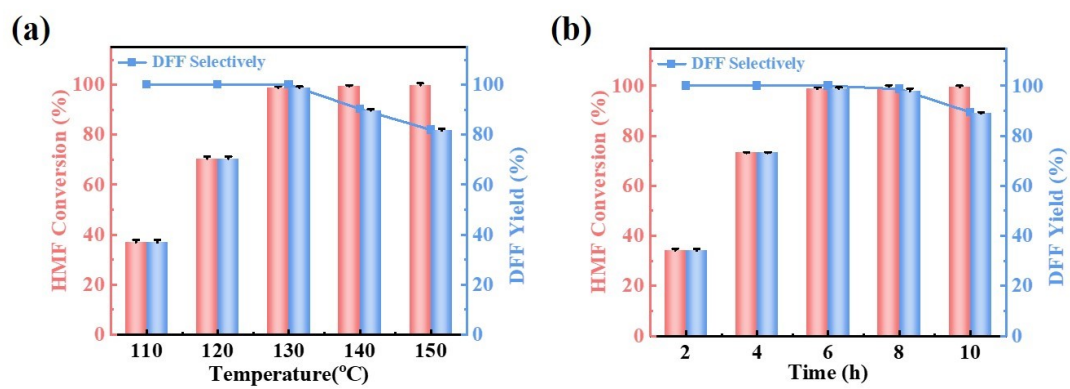


Fig. S5. Optimization of reaction conditions for $\text{PMo}_{10}\text{V}_2@\text{Co}_3\text{O}_4/\text{C}$: (a) temperature and (b) reaction time.

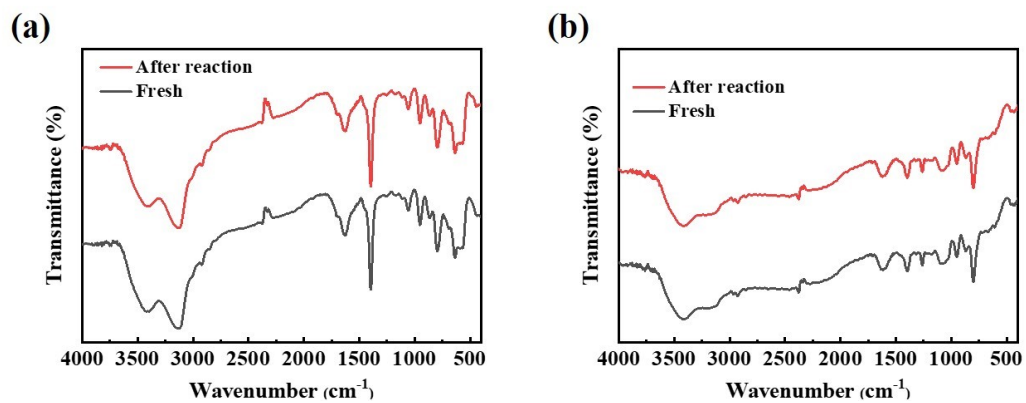


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(b) FTIR spectra of $\text{PMo}_{10}\text{V}_2@\text{Co}_3\text{O}_4/\text{C}$ before and after reaction.

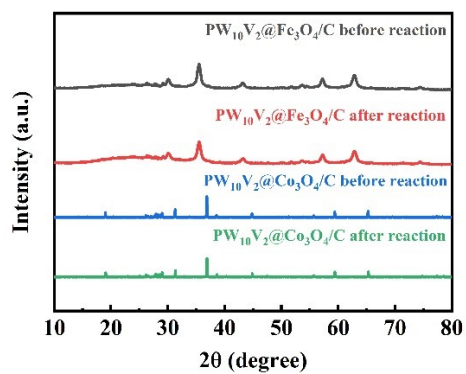


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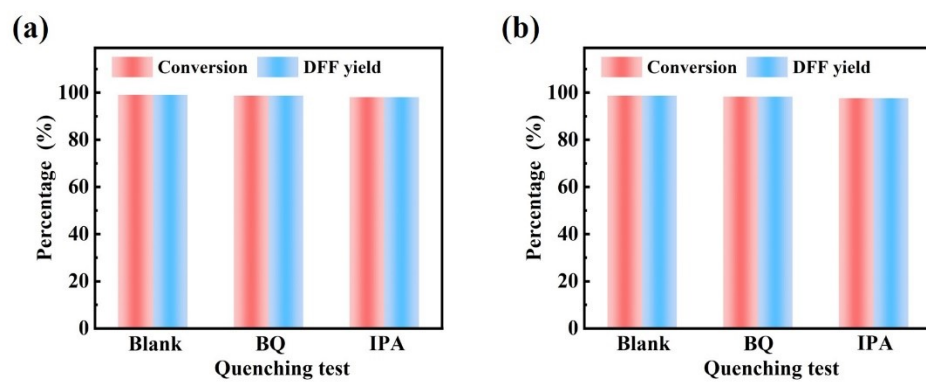


Fig. S8. Quenching tests with (a) $\text{PMo}_{10}\text{V}_2@\text{Fe}_3\text{O}_4/\text{C}$ and (b) $\text{PMo}_{10}\text{V}_2@\text{Co}_3\text{O}_4/\text{C}$ as the catalyst.

Table S1. Fe and Mo concentrations in $\text{PMo}_{10}\text{V}_2\text{@Fe}_3\text{O}_4/\text{C}$ determined by ICP-OES analysis.

| | Fe | Mo |
|-----------------------|---------------------|---------------------|
| Concentration (mg/kg) | 263332.5 (measured) | 157876.9 (measured) |
| Concentration (wt%) | 26.3% | 15.8% |

Table S2. Co and Mo concentrations in $\text{PMo}_{10}\text{V}_2@\text{Co}_3\text{O}_4/\text{C}$ determined by ICP-OES analysis.

| | Co | Mo |
|-----------------------|---------------------|---------------------|
| Concentration (mg/kg) | 197431.8 (measured) | 177715.4 (measured) |
| Concentration (wt%) | 19.7% | 17.8% |

Table S3. Comparison of $\text{PMo}_{10}\text{V}_2@\text{M}_3\text{O}_4/\text{C}$ ($\text{M} = \text{Fe}, \text{Co}$) and other POMs-based catalysts on selective oxidation of HMF to DFF.

| Catalyst | Oxidant | Time (h) | HMF Con. (%) | DFF Yield (%) | Selectivity | Recycle times | Ref. |
|--|------------------------|----------|--------------|---------------|-------------|---------------|-----------|
| $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ | 1.0 MPa O_2 | 8 | 100 | 69 | 69 | - | 4 |
| $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}/\text{SiO}_2$ | 1.0 MPa O_2 | 8 | 92 | 90 | 98 | 10 | 4 |
| $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}/\text{chitosan}$ | 0.8 MPa O_2 | 6 | 96 | 94 | 98 | 10 | 5 |
| $\text{H}_3\text{PMo}_{12}\text{O}_{40}@\text{Cr-MIL-101}$ | 20 mL/min O_2 | 20 | 94 | 91 | 97 | 5 | 6 |
| $\text{CeCu}(\text{OH})_6\text{Mo}_6\text{O}_{18}$ | 20 mL/min O_2 | 8 | 99 | 99 | 100 | - | 7 |
| $\text{Mo}_{72}\text{V}_{30}@\text{Fe}_3\text{O}_4/\text{C}$ | 0.4 MPa O_2 | 4 | 99 | 99 | 100 | 10 | 8 |
| $\text{Cs}_3\text{HPMo}_{11}\text{VO}_{40}$ | 0.1 MPa O_2 | 14 | 100 | 60 | 60 | - | 9 |
| $\text{Cs}_3\text{HPMo}_{10}\text{V}_2\text{O}_{40}$ | 0.8 MPa O_2 | 6 | 99 | 92 | 93 | - | 9 |
| Mo_{132} | Atmosphere | 6 | 99 | 99 | 100 | 5 | 10 |
| $\text{PMo}_{10}\text{V}_2@\text{Co}_3\text{O}_4/\text{C}$ | 1.4 MPa O_2 | 6 | 99 | 99 | 100 | 5 | This work |
| $\text{PMo}_{10}\text{V}_2@\text{Fe}_3\text{O}_4/\text{C}$ | 0.8 MPa O_2 | 6 | 99 | 99 | 100 | 10 | This work |

Table S4. The element percentage in different oxidation states of $\text{PMo}_{10}\text{V}_2@\text{M}_3\text{O}_4/\text{C}$ ($\text{M} = \text{Fe}, \text{Co}$) after the reaction.

| catalyst | element percentage (%) | |
|--|-------------------------|-------------------------|
| $\text{PMo}_{10}\text{V}_2@\text{Fe}_3\text{O}_4/\text{C}$ | Fe^{2+} : 75.8 | Fe^{3+} : 24.2 |
| | V^{4+} : 20.9 | V^{5+} : 79.1 |
| $\text{PMo}_{10}\text{V}_2@\text{Co}_3\text{O}_4/\text{C}$ | Co^{2+} : 55.0 | Co^{2+} : 45.0 |
| | V^{4+} : 14.7 | V^{4+} : 85.3 |

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