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Imidazole-Functionalized Polyoxometalate Catalysts for the Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran Using Atmospheric O₂

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ABSTRACT: Biomass as a sustainable and abundant carbon source has attracted considerable attention as a potential alternative to petroleum resources. The selective oxidation of 5-hydroxymethylfurfural (HMF), a versatile platform molecule, to value-added 2,5-diformylfuran (DFF) provides an efficient pathway for biomass valorization. Herein, three discrete imidazole-functionalized polyoxometalates (POMs), HPM0₈V^{VI}₄O₄₀(V^VO)₂[(V^{IV}O)(IM)₄]₂·nH₂O·(IM)_m (IM = 1-methylimidazole, n = 4, m = 8 for 1; IM = 1-ethylimidazole, n = 4, m = 9 for 2; IM = 1-propylimidazole, n = 0, m = 4 for 3), have been successfully synthesized by a facile solvothermal method and thoroughly characterized by routine techniques. Compounds 1–3 contain a bi-capped *pseudo*-Keggin

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 ${\rm HPMo_8V_4O_{40}(VO)_2}$ and two imidazole-functionalized ${\rm (VO)(IM)_4}$ groups, which, to our knowledge, represent the first examples of organic-functionalized Mo–V clusters. Compounds 1–3 as heterogeneous catalysts can effectively promote the transformation of HMF to DFF using atmospheric O₂ as oxidant. Under minimally optimized conditions, 95% of HMF was converted by 1 with 95% selectivity for DFF and its catalytic activity was basically maintained after five cycles. Moreover, the important roles of the bi-capped *pseudo*-Keggin cluster and the functionalized V groups in the selective oxidation of HMF have been explored. According to experimental and spectroscopic results, a three-step oxidation mechanism of HMF to DFF has been proposed.

1. INTRODUCTION

With the rapid depletion of fossil fuels and increasing concern about environmental issues, the development of sustainable resources has become imperative. Biomass as a renewable and abundant carbon-containing source provides a promising alternative to fossil-based feedstock.^{1–4} 5-Hydroxymethylfurfural (HMF) is an important biomass-driven platform molecule obtained by the dehydration of glucose or fructose, which can be used as a versatile precursor to produce fine chemicals, plastics, pharmaceuticals, and liquid fuels. Recently, the oxidation of HMF has attracted considerable attention.⁵⁻ As shown in Scheme 1, HMF can be oxidized to 2,5diformylfuran (DFF), 5-formyl-2-furancarboxylic acid (FFCA), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), and 2,5furandicarboxylic acid (FDCA). Among them, DFF is the highest value-added chemical with wide applications in pharmaceuticals,⁸ antifungal agents,⁹ furan-urea resins,¹⁰ functional polymers,¹¹ and so forth. However, the selective oxidation of HMF to DFF is still challenging, due to the existence of an aldehyde group and furan ring.¹

Compared with the methods using stoichiometric oxidants, such as NaOCl and BaMnO₄, the transformation of HMF to DFF using molecular oxygen as the terminal oxidant is more attractive. To achieve the aerobic oxidation of HMF, a series of homogeneous and heterogeneous catalysts based on Ru, Co, Mn, Cu, or V have been developed (Table S1). Among them, those vanadium-containing catalysts have exhibited excellent performance.^{14,15} For example, Ma et al. reported a homogeneous catalytic system, $Cu(NO_3)_2/VOSO_4$, which can convert 99% of HMF with a selectivity of 99% under 0.1 MPa O₂, and then zeolite-supported V₂O₅ was reported to give 84% conversion and 99% selectivity under atmospheric O₂.^{16,17}

Polyoxometalates (POMs) are a family of metal-oxo clusters and their chemical composition and electronic structures can be modulated at the molecular level.^{18,19} POMs have been widely used as catalysts in a series of oxidation reactions due to their reversible proton and electron storage and rich redox properties.^{20–22} The recent studies show that V-containing molybdophosphates with Keggin structure, especially $H_5PMo_{10}V_2O_{40}$, are active for the aerobic oxidation of HMF.²³ However, the strong Brønsted acidity of $H_5PMo_{10}V_2O_{40}$ leads to a low DFF yield. Recent investigations show that the coexistence of a basic center and redox center is

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Scheme 1. Oxidative Transformation of HMF



Scheme 2. Synthesis of Compounds 1-3



beneficial to the selective oxidation of HMF. For example, $H_5PMo_{10}V_2O_{40}$ was immobilized on chitosan nanofibers with an amino group in Wang's group, by which a satisfactory DFF yield (94%) was achieved, but high O₂ pressure (0.8 MPa) was still required in this transformation.²⁴ In this regard, the exploration of POM catalysts to promote the selective oxidation of HMF to DFF using atmospheric O₂ remains challenging and attractive.

In 2013, three imidazole-functionalized polyoxovanadates were first synthesized in our group, which show high catalytic activity for the selective oxidation of alcohols using molecular oxygen as oxidant.²⁵ As part of our ongoing research in developing organic-functionalized POM catalysts, herein we report the synthesis and structures of three imidazolefunctionalized Mo-V clusters, HPMo₈V^{VI}₄O₄₀(V^VO)₂- $[(V^{IV}O)(IM)_4]_2 \cdot nH_2O \cdot (IM)_m$ (IM = 1-methylimidazole, n = 4, m = 8 for 1; IM = 1-ethylimidazole, n = 4, m = 9 for 2; IM = 1-propylimidazole, n = 0, m = 4 for 3), which are composed of a bi-capped pseudo-Keggin { $HPMo_8V_4O_{40}(VO)_2$ } and two imidazole-functionalized $\{(VO)(IM)_4\}$ groups (Scheme 2). Considering that the introduction of imidazole not only activates the vanadium center but also endows the POM clusters with appropriate Lewis basicity, we used compounds 1-3 as heterogeneous catalysts for the selective oxidation of HMF to DFF. Notably, the conversion of HMF reaches 95% with a DFF selectivity of over 95% after 4 h with atmospheric O₂ as oxidant, and its catalytic activity is maintained after five cycles. Moreover, a possible catalytic mechanism was proposed based on control experiments and spectroscopy analysis.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. The chemicals were purchased from commercial source and used without further purification (Table S2). $H_5PMo_{10}V_2O_{40}$ ·34.5 H_2O ,²⁶ (NH₄)₅ $H_6PV_8Mo_4O_{40}$,²⁷ [NH₄]₄ H_- [PMo₈ $V^{IV}_4V^2_2O_{42}$]·24 H_2O ,²⁸ and (V^{IV}O)(mIM)₄SO₄,²⁹ were synthesized according to the literature and identified by Fourier transform infrared (FT-IR) spectra. The FT-IR spectra were recorded as the pressed KBr pellets by Bruker ALPHA spectrometer. The powder Xray diffraction (PXRD) patterns were obtained via a Rigaku MiniFlex 600 diffractometer which worked at 40 kV voltage and 50 mA current with Cu K α X-ray radiation ($\lambda = 0.154056$ nm). Elements C, H, and N were quantified with Eurovecter EA3000 elemental analyzer, and P, Mo, and V were determined by Thermo PerkinElmer inductively coupled plasma atomic emission spectroscopy (ICP-AES). The thermal gravimetric analyses (TGA) were conducted in flowing N2 atmosphere on a Shimadzu DTG-60AH thermal analyzer from room temperature to 800 °C with a heating rate of 10 °C min⁻¹. The X-ray photoelectron spectrum (XPS) analyses were operated on an ESCALAB 250Xi spectrometer, which used an Al K α radiation as the X-ray source (1486.7 eV) with a pass energy of 30 eV and kept the pressure inside at 10⁻⁹ Torr, and the binding energy was calibrated via C 1s (284.8 eV). The selective oxidation of HMF was monitored by gas chromatograph (GC, Shimadzu GC-2014C) with an FID detector equipped with an HP-5 ms capillary column, and the conversion and selectivity were determined by the internal standard method using naphthalene as the internal standard. ¹H nuclear magnetic resonance spectroscopy (¹H NMR) spectra were performed on a Bruker 400 MHz instrument in CDCl₃. The HPLC analyses were performed on Shimadzu LC-20A equipped with UV-vis detector and C₁₈ chromatographic column.

2.2. Synthesis of Catalysts. Synthesis of Compound 1. NH_4VO_3 (0.234 g, 2 mmol), $VO(acac)_2$ (0.265 g, 1 mmol), $H_5PMo_{10}V_2O_{40}$ ·34.5 H_2O (0.45 g, 0.19 mmol), and 1-methylimidazole

(7 mL) were sealed in a 25 mL Teflon-lined stainless steel container, which was heated to 120 °C and the temperature maintained under autogenous pressure for 3 days. After cooling down to room temperature, black block crystals were obtained. Yield: 85% (based on Mo); IR (KBr pellet, v): 3122 (m), 2356 (w), 1658 (m), 1540 (m), 1421 (s), 1283 (w), 1226 (m), 1090 (m), 1046 (s), 930 (s), 893 (s), 767 (m), 661 (m), and 617 (m) cm⁻¹; elemental analysis (%) calcd for compound 1: Mo 23.28, P 0.94, V 12.36, C 23.37, H 3.21, N 13.60; found: Mo 22.94, P 0.98, V 12.89, C 23.37, H 2.96, N 13.61.

Synthesis of Compound 2. Compound 2 was synthesized following a procedure similar to that for compound 1 except that 1-ethylimidazole was used instead of 1-methylimidazole. Yield: 89% (based on Mo); IR (KBr pellet, v): 3117 (m), 2978 (w), 1671 (m), 1514 (m), 1446 (m), 1401 (w), 1354 (m), 1286 (m), 1226 (s), 1094 (s), 961 (s), 933 (s), 775 (m), 665 (m), 624 (m) cm⁻¹; elemental analysis (%) calcd for compound 2: Mo 21.22, P 0.86, V 11.27, C 28.22, H 4.04, N 13.17; found: Mo 20.78, P 0.83, V 11.60, C 28.58, H 3.92, N 13.75.

Synthesis of Compound **3**. Similarly, compound **3** was synthesized by using 1-propyl imidazole (7 mL) as solvent. Yield: 86% (based on Mo); IR (KBr pellet, *v*): 3118 (m), 2965 (w), 2873 (w), 1611 (w), 1521 (m), 1454 (w), 1401 (w), 1285 (w), 1233 (m), 1094 (s), 1050 (w), 928 (s), 760 (m), 658 (m), 618 (w) cm⁻¹; elemental analysis (%) calcd for compound **3**: Mo 23.74, P 0.96, V 12.61, C 26.75, H 3.78, N 10.40; found: Mo 23.88, P 0.95, V 12.88, C 27.32, H 3.49, N 10.26.

Synthesis of $Cs_3PMo_{12}O_{40}$, $H_3PMo_{12}O_{40}$ (0.2 mmol) was dissolved in 20 mL deionized water, and then Cs_2CO_3 (0.3 mmol) was added with stirring and yellow precipitate was formed immediately. After 5 min, the yellow precipitate was collected by centrifugation, washed with deionized water, and then dried at 40 °C for 24 h.

Synthesis of $Cs_5PMo_{10}V_2O_{40}$. $Cs_5PMo_{10}V_2O_{40}$ was prepared by a similar method to that of $Cs_3PMo_{10}O_{40}$ except that $H_5PMo_{10}V_2O_{40}$ was used instead of $H_3PMo_{12}O_{40}$.

2.3. X-ray Crystallography. The crystallographic data for 1–3 were obtained via Bruker APEX 2 DUO CCD single-crystal diffractometer equipped with a sealed Mo tube and a graphite monochromator ($\lambda = 0.71073$ Å). The software used for structure solution and refinement was the SHELEXTL program package (Bruker), and all structures were solved by direct methods and refined by the full-matrix least-squared method.^{30–32} All heavy atoms were refined with anisotropic thermal parameters. The crystallographic data for 1–3 have been archived in the Cambridge Crystallographic Data Center (CCDC), and the corresponding deposition numbers are 2032051 (1), 2032052 (2), and 2032054 (3). The crystallographic details of 1–3 are summarized in Table S3, and the selected bond length and bond angles are given in Table S5. The final molecular formulas of compounds 1–3 were defined by single-crystal X-ray diffraction data combined with elemental analysis and TGA results.

2.4. Selective Oxidation of HMF to DFF. Before the reaction, the sample of catalyst was ground and dried under vacuum at 100 °C for 4 h. In a typical reaction, HMF (15 mg, 0.11 mmol), compound 1 (33 mg, 0.01 mmol) and toluene (1 mL) were added into a Shrek tube equipped with an O_2 balloon, which was heated at 100 °C for 4 h. After the reaction, the catalyst was separated by filtration and the resultant solution was analyzed by GC. For the recycle test, the collected catalyst was washed with ethyl acetate three times, and dried under vacuum at 60 °C for 4 h and then used for the next cycle.

The oxidation of HMF under anaerobic and aerobic conditions was performed as the following procedure. First, HMF (0.11 mmol), compound 1 (0.01 mmol), toluene (1 mL), and naphthalene (48.8 μ mol, internal standard) were added into a Shrek tube and the reactor was cooled to 0 °C by an ice bath. Then, the air in reactor was replaced by N₂ via Schlenk Line and the Shrek tube was heated to 100 °C. After 2 h, O₂ was purged into the Shrek tube by a O₂ balloon and the reaction was performed under otherwise identical conditions for an additional 4 h. The catalytic data in this experiment are from 15 parallel experiments.

3. RESULTS AND DISCUSSION

3.1. Crystal Structures of Compounds 1–3. As shown in Scheme 2, compounds 1–3 were prepared by a facile solvothermal method using $H_5PMo_{10}V_2O_{40}$, NH_4VO_3 , $VO-(acac)_2$, and imidazole as starting materials. During the formation of three clusters, imidazole derivatives play multiple roles: solvents, functionalized ligands, and solvates. Control experiments indicate that changing the length of alkyl chain on imidazole have no effect on the assembly of POM skeleton. Considering the structure similarity of compounds 1–3, only the structure of compound 1 was described here.

Compound 1 crystallizes in the $P\overline{1}$ space group of a triclinic system and consists of one $[HPMo_8V_4O_{40}(VO)_2]^{4-}$ anion, two $[(VO)(1-mIM)_4]^{2+}$ groups, four lattice H₂O, and eight free 1mIM molecules. As shown in Figure 1, the



Figure 1. (a) Ball-and-stick representation of compound 1; (b) polyhedra of $\{Mo_4\}$; (c) polyhedra of $\{PMo_8\}$; (d) structure of *pseudo*-Keggin $\{PMo_8V_4(VO)_2\}$; (e) coordination environment of imidazole-functionalized V center.

[HPMo₈V₄O₄₀(VO)₂]⁴⁻ anion can be described as a *pseudo*-Keggin {PMo₈V₄} cluster capped by two {VO} groups on the square windows of {Mo₄}. The *pseudo*-Keggin {PMo₈V₄O₄₀} cluster can be viewed as a combination of {PMo₈} fragment and four substituted {VO₅} square pyramids. In this cluster, four {MoO₆} octahedra form a {Mo₄} subunit (Figure 1b) by sharing edge and corner O atoms, and two {Mo₄} are connected by a P atom to form {PMo₈} (Figure 1c). Each Mo center exhibits octahedral geometry with Mo–O distances in the range of 1.660(7)–2.514(12) Å. The central P atom is surrounded by eight half-occupied oxygen atoms. The {PMo₈} in our case can be derived from the tetravacant *α*-Keggin cluster by a 90 °C rotation of one {Mo₄} (Figure S1).

Interestingly, there are three types of V centers in compound 1: substituted V in *pseudo*-Keggin {PMo₈V₄} cluster, capped {VO}, and organic-functionalized {(VO)(IM)₄}. Four substituted V atoms lie on the equatorial plane of the *pseudo*-Keggin cluster sandwiched by two {Mo₄} subunits (Figure 1d). Both the substituted and capped V centers are pentacoordinated square pyramids. The substituted V atoms are coordinated by four μ_2 -O (V—O: 1.578(6)–1.924(8) Å) and one terminal O atom (V=O_t: 1.654(6) Å), while the capped V atoms are coordinated by four μ_3 -O atoms (V—O: 1.654(6)–1.914(7) Å) and one μ_2 -O atom (V—O: 1.663(6)–1.914(7) Å). The organic-functionalized V centers are anchored on V caps by sharing corner O atoms with V—O—V bond angles in the range of 178.7(4)–175.8(4)°. Two functionized V are coordinated by four N atoms from 1-mIM

Table 1. Selective Oxidation of HMF into DFF by Different Catalysts^a

	$0 \longrightarrow 0$ OH $+\frac{1}{2}$	O ₂ <u>Cat.</u>		o + H₂O	
	HMF	O_2 balloon, 100°C	DFF		
entry	catalyst	amount of catalyst (mmol)	conversion (%)	selectivity (%)	TON
1	Compound 1	0.01	95	95	9.93
2	Compound 2	0.01	94	95	9.82
3	Compound 3	0.01	92	95	9.61
4	Blank	-	15	39	-
5	Cs ₃ PMo ₁₂ O ₄₀	0.01	76	25	2.09
6	$Cs_5PMo_{10}V_2O_{40}$	0.01	83	32	2.92
7	$H_5PMo_{10}V_2O_{40}$	0.01	93	2	2.05
8	$(NH_4)_5H_6PV_8Mo_4O_{40}$	0.01	78	9	7.72
9	$[NH_4]_4[HPMo_8V^{IV}_4O_{40}(V^VO)_2]$	0.01	96	7	7.39
10	$(V^{IV}O)(mIM)_4SO_4$	0.08	54	92	6.83

^{*a*}Reaction conditions: HMF (0.11 mmol), toluene (1 mL), naphthalene (48.8 μ mol, internal standard), O₂ balloon, 100 °C, 4 h. Turnover number (TON) was calculated by the ratio of the amount of synthesized DFF to the amount of catalyst.

(V—N: 2.104(8)–2.120(9) Å), one μ_2 -O atom (V—O: 2.109(6)–2.110(6) Å), and one terminal O atom (V=O_t: 1.592(6)–1.597(7) Å), resulting in an octahedral environment (Figure 1e). Bond valence sum (BVS) calculations (Table S4) indicate that the oxidation states of capped V atoms are +5 and of the other V atoms are +4, and all the Mo atoms are in the +6 oxidation state. The oxidation states of metal ions were further comfirmed by XPS (Figure S11). The peaks with the binding energies of 235.0 eV (Mo $3d_{3/2}$) and 232.0 eV (Mo $3d_{5/2}$) display the +6 oxidation state of Mo atoms. In the V 2p region, the two peaks at 515.8 and 516.9 eV are attributed to V⁴⁺ and V⁵⁺ oxidation state, respectively, and the peak area ratio of V⁺⁴ to V⁺⁵ is about 2.88, which is basically close to the ratio of V⁺⁴ to V⁺⁵ from BVS calculations.

To date, a handful of *pseudo*-Keggin {PMo₈V₄} clusters have been synthesized including tetra-capped [PMo^V₂Mo^{VI}₆V^{IV}₄-O₄₀(V^{IV}O)₄]^{5-,33} and bi-capped [PMo^V₂Mo^{VI}₆V^{IV}₄O₄₀(V^{IV}O)₂]^{9-,34} [H₅PMo^{VI}₈V^{IV}₄O₄₀(V^{IV}O)₂]^{2-,35} [HPMo^{VI}₈-V^V₄O₄₀(V^{IV}O)₂]^{2-,36} and [HPMo^{VI}₈V^{IV}₄O₄₀(V^{VO})₂]^{4-,28} The structure of [HPMo^{VI}₈V^{IV}₄O₄₀(V^{VO})₂]⁴⁻ in compound 1 is similar to that reported by Xu, but the introduction of imidazole-functionalized [(VO)(1-mIM)₄]²⁺ greatly decreases the negative charge of the cluster. To the best of our knowledge, compounds 1–3 represent the first examples of organic-functionalized Mo–V clusters. Moreover, in the three compounds free imidazole molecules cocrystallize with the imidazole-functionalized cluster (Figures S2–S4).

The phase purity of compounds 1-3 was confirmed by PXRD (Figure S14). The compounds 1-3 have similar FT-IR spectra (Figure S15). The absorption peaks at 1090-1095 cm^{-1} are attributed to the P-O vibration and the M=O_t vibrations (M = Mo or V, t: terminal oxygen atoms) are observed at 928-932 cm⁻¹. The absorption peaks corresponding to M–O–M vibration (M = Mo or V) are at 767-774 cm^{-1} , and the peaks at 661–665 cm^{-1} and 617–624 cm^{-1} are assigned to the vibration of V-N. The absorption peaks in the range of 1540-1226 cm⁻¹ correspond to the vibration of imidazole groups.³⁷ In addition, compounds 1-3 have poor solubility in common solvents, such as water, acetonitrile, methanol, acetone, ethyl acetate, toluene, 1,2,4-trimethylbenzene, 1,2-dichloroethane, and 1,4-dichlorobutan, and can dissolve in N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

3.2. Selective Oxidation of HMF to DFF. Since the Vcontaining molybdophosphates exhibit good catalytic activity in the aerobic oxidation, compounds 1-3 were used to catalyze the selective oxidation of HMF to DFF. In a typical oxidation reaction, catalyst (0.01 mmol), HMF (0.11 mmol), toluene (1 mL), and internal standard (naphthalene 48.8 μ mol) were added in a Shrek tube, and the reaction was performed at 100 °C under atmospheric O2. When compound 1 was used as heterogeneous catalyst, 95% of HMF was converted after 4 h and 95% selectivity for DFF was achieved (Table 1, entry 1) with TON of 9.93. Moreover, no overoxidation product, such as FFCA and FDCA, was detected by high performance liquid chromatography (Figure S21). In comparation, the conversion of HMF was only 15% with the selectivity of 39% in the absence of catalyst (Table 1 entry 4). Similar excellent catalytic performance was obtained by compound 2 (conversion: 94%, selectivity: 95%, TON: 9.82, Table 1 entry 2) and compound 3 (conversion: 92%, selectivity: 95%, TON: 9.61, Table 1 entry 3), indicating that the alkyl chain on imidazole has a negligible effect on the catalytic activity, and so compound 1 was used in the following experiments.

To probe the impact of $[HPMo_8V_4O_{40}(VO)_2]^{4-}$ polyanion and organic-functionalized V centers on the selective oxidation of HMF, a series of control experiments were conducted under the otherwise identical conditions (Table 1 entries 5-10). Keggin-type Cs₃PMo₁₂O₄₀ gave a conversion of 76% (Table 1 entry 5) and the conversion was further improved by $Cs_5PMo_{10}V_2O_{40}$ (Table 1 entry 6), but the selectivity of the two catalysts is not more than 32%. The results above indicate that Mo and V centers in the cluster can promote the conversion of HMF, but they have little influence on the selectivity. In addition, we found that the strong Brønsted acidity of POMs causes the decrease of DFF selectivity. As shown in Table 1 entry 7, despite the high conversion obtained by $H_5PMo_{10}V_2O_{40}$ (93%), it gave a very low selectivity for DFF ($\sim 2\%$). The main reason is that 5-acetoxymethyl-2furcaldehyde as a main byproduct was formed (Figure S26). According to previous investigation,³⁸ levulinic acid was generated in the presence of Brønsted acid, which was transferred to acetic acid under O2 atmosphere, and the reaction of acetic acid with HMF gave rise to 5-acetoxymethyl-2-furaldehyde (Figure S27). Considering there are eight V atoms in compound 1, an eight V-substituted Keggin cluster, $(NH_4)_5H_6PV_8Mo_4O_{40}$, was used, which gave a conversion of 78% and a selectivity of 9%, suggesting that the number of V centers is not a key factor to influence the catalytic activity. To probe the role of organic functionalization in the oxidation of HMF, [NH₄]₄[HPMo₈V^{IV}₄O₄₀(V^VO)₂] (Figure S19) having similar structure to that of compound 1 but without the imidazole-functionalized V and $(V^{IV}O)(mIM)_4SO_4$ (Figure S20) similar to the functionalized $[(VO)(1-mIM)_4]$ group were prepared, respectively. It is found that $[NH_4]_4[HPMo_8 V_{4}^{IV}O_{40}(V^{V}O)_{2}$] can convert 96% of HMF but giving a poor selectivity (7%) (Table 1 entry 9), while (V^{IV}O)(mIM)₄SO₄ yielded a good selectivity (92%) but moderate conversion (54%) (Table 1 entry 10). The control experiments above show that both bi-capped pseudo-Keggin Mo-V cluster and the functionalized V group play a role in the aerobic oxidation of HMF: the $[HPMo_8V_4O_{40}(VO)_2]^{4-}$ facilitates the conversion of substrate, while the imidazole-functionalized V centers are helpful to the improvement of selectivity. Notably, 79% of HMF conversion and 95% of DFF selectivity were achieved by compound 1 when directly using air as oxidant.

To explore the optimal reaction conditions, the influences of reaction temperature, time, and solvent on the selective oxidation of HMF were systematically investigated. As shown in Figure S22, the conversion of HMF dramatically increases with reaction temperature from 18% at room temperature to 95% at 100 °C. Then, the reaction was monitored in the time range of 0-4 h (Figure S23), and the maximum conversion was reached after 4 h at 100 °C. In addition, several solvents with boiling points above 100 °C were used. Interestingly, it is found that the reaction can be significantly influenced by solvents. As shown in Figure 2, compound 1 exhibits excellent



Figure 2. Effect of solvents on the oxidation of HMF to DFF. Reaction conditions: HMF (0.11 mmol), compound 1 (0.01 mmol), solvents (1 mL), naphthalene (48.8 μ mol, internal standard), O₂ balloon, at 100 °C for 4 h.

performance in toluene, chlorobenzene, *o*-dichlorobenzene, and pyridine, but the catalytic activity, especially selectivity, dramatically decrease in paraxylene or 1,2,4-trimethylbenzene. We speculate that the methyl group of paraxylene might be oxidized under the reaction conditions and subsequently react with DFF to form other byproducts.

To verify the heterogeneous nature of compound 1, the leaching test was performed under the turnover conditions. As shown in Figure 3a, catalyst 1 was filtered out when the reaction proceeded for 30 min with the conversion of 28%, and then the conversion increased slightly and the growth trend of

conversion was comparable to that of the blank experiment. Moreover, we evaluated the recyclability and stability of 1 in the oxidation reaction. As shown in Figure 3b, the catalytic performance of 1 is basically maintained after five cycles, and there is no obvious change in IR spectra before and after the reaction (Figure S24a). To compare the catalytic activity of the title compounds with the reported heterogeneous catalysts, the type of oxidant, pressure, temperature, reaction time, conversion of HMF, and selectivity for DFF are summarized in Table S1. Excellent catalytic activity has been achieved by Ag-OMS-2 (conversion: 99%, selectivity: 100%),³⁷ V-Cu-CS (conversion: 99%, selectivity: 98%),39 Ru-PVP/CNT (conversion: 99%, selectivity: 95%),⁴⁰ $H_5PMo_{10}V_2O_{40}/chitosan$ (conversion: 96%, selectivity: 98%),⁴¹ but oxidation of HMF was performed under relatively harsh conditions (O2: 1-0.8 MPa or air: 4-1.5 MPa, temperature: 165-120 °C). In comparison, the transformation of HMF to DFF by compounds 1-3 proceeds smoothly using atmospheric O_2 at 100 °C. Furthermore, the definite crystal structures of our catalysts are helpful to understand the catalytic mechanism relative to the reported composites.

To understand the catalytic role of compound 1 in the oxidation of HMF, a control experiment was performed by using 1 as oxidant to react with HMF under N₂ atmosphere. As shown in Figure 4, in the first 1 h the conversion of HMF increased with reaction time, but after that the conversion of HMF (44%) was nearly unchanged even though the reaction time was prolonged to 2 h. Importantly, when O₂ was purged into the reaction system, HMF was converted showing the maximum conversion (95%) after 6 h. This fact indicates that under anaerobic conditions HMF can be directly oxidized by 1. According to previous investigations, we speculate that a proton coupled electron transfer (PCET) from HMF to POM catalyst might be involved in this process, and as a result, catalyst 1 was gradually reduced, losing its oxidation ability after 1 h. With the addition of O2, the reduced POM catalyst was reoxidized and the oxidizing ability of POM was recovered. To further verify our speculation, the XPS spectrum of the catalyst used under anaerobic conditions was measured. As shown in Figure 5, the peaks of Mo^{6+} with the binding energies of 235.0 and 232.0 eV disappeared, and instead, the peaks of Mo⁵⁺ with the binding energies of 233.0 and 230.0 eV were found. Meanwhile, in the V 2p region, only the peaks of V⁴⁺ with the binding energies of 515.8 and 523.2 eV were detected. This result indicates that not only V but also Mo atoms in compound 1 are involved in the oxidation process.

Based on the experimental results and XPS analysis above, we propose a plausible mechanism for the selective oxidation of HMF (Scheme 3). First, HMF is adsorbed on the surface of catalyst 1. To confirm the interaction between HMF and catalyst 1, we performed the adsorption test, and the amount of adsorbed HMF was determined by GC. As shown in Figure S25, HMF can be rapidly adsorbed by 1 with the maximum adsorbed amount of about 0.52 mg/mg. We speculate that the N atoms on solvated imidazole and O atoms on POM might interact with HMF. Second, 1, denoted as 1-Ox meaning the oxidized state of 1, oxidizes HMF to DFF through PCET, generating the reduced state of 1, denoted as 1-Red. The PCET process can be verified by the experiment of HMF with 1 under anaerobic conditions and the reduced POM was supported by the observation of Mo^{5+} and V^{4+} in XPS measurement. Finally, the reduced state of 1 is reoxidized by molecular oxygen to 1-Ox completing a catalytic cycle with



Figure 3. (a) Leaching test for HMF oxidation by compound 1. (b) Cycle test for HMF oxidation by compound 1. Reaction conditions: HMF (0.11 mmol), compound 1 (0.01 mmol), naphthalene (48.8 μ mol, internal standard), toluene (1 mL), O₂ balloon, at 100 °C for 4 h.



Figure 4. Oxidation of HMF by compound 1 under anaerobic and aerobic conditions. Reaction conditions: HMF (0.11 mmol), 1 (0.01 mmol), toluene (1 mL), naphthalene (48.8 μ mol, internal standard), 0–120 min N₂; 120–360 min O₂, at 100 °C for 6 h.

water as the only byproduct. We speculate that the introduction of imidazole molecules not only adjusted the redox property of Mo–V cluster but also provided basic sites, as the proton acceptor playing a role in the PCET process.





4. CONCLUSIONS

In summary, we have successfully synthesized three new imidazole-functionalized Mo-V clusters by a simple solvo-



Figure 5. XPS analysis of the used catalyst 1 under N₂ atmosphere.

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thermal method. These compounds showed excellent catalytic activity in the selective oxidation of HMF, a biomass-driven platform molecule, to highly value-added DFF by using atmospheric O_2 . The control experiments indicate that both bi-capped <i>pseudo</i> -Keggin cluster and the functionalized V groups contribute to the excellent catalytic performance, and the introduced imidazole plays a key role in the oxidation of HMF. Moreover, a three-step oxidative mechanism has been proposed. This work will provide some insightful guidelines on the catalyst design for the selective oxidation of HMF and deepen understanding of catalytic mechanism and governing factors in this process.	 Beijing 100081, P.R. China; 6888 Peihe Li – Key Laboratory of C Education, Beijing Key Labora Electrophotonic Conversion Ma and Chemical Engineering, Bei Beijing 100081, P.R. China Ni Zhen – Key Laboratory of C Education, Beijing Key Labora Electrophotonic Conversion Ma and Chemical Engineering, Bei Beijing 100081, P.R. China 		
ASSOCIATED CONTENT	Complete contact information is a https://pubs.acs.org/10.1021/acs.		
Supporting Information The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03698. Structural figures, crystal data, selected bond lengths and angles, PXRD patterns, IR spectra, XPS spectra, TGA curves, and catalytic data (PDF)	Author Contributions The manuscript was written th authors. All authors have given ap the manuscript. Dan Liu perform HMF and Baokuan Chen syr functionalized POMs. Jie Li and		
Accession Codes CCDC 2032051–2032052 and 2032054 contain the supple- mentary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12	structures and Peihe Li analyzed Structure refinements were perforn Yingnan Chi and Prof. Changwen Notes The authors declare no competing		
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rough contributions of all proval to the final version of ed the catalytic oxidation of thesized three imidazole-Ni Zhen analyzed crystal part of the catalytic results. med by Zhengguo Lin. Prof. Hu supervised the project.

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