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Ionic-Liquid-Functionalized Polyoxometalates for Heterogeneously Catalyzing the Aerobic Oxidation of Benzene to Phenol: Raising Efficacy through Specific Design

Zhouyang Long, Yu Zhou, Weilin Ge, Guojian Chen, Jingyan Xie, Qian Wang, and Jun Wang^{*[a]}

By combining nitrile-tethered pyridinium-based ionic liquid dication with the polyoxometalate anion of Keggin $H_5PMo_{10}V_2O_{40}$ (PMoV₂) through precipitation in aqueous solution, an organicinorganic hybrid catalyst 1,1'-(butane-1,4-diyl)-bis(3-cyanopyridine)–PMoV₂ was prepared for heterogeneous hydroxylation of benzene to phenol with O₂ and ascorbic acid as the oxidant and reductant, respectively. The hybrid catalyst not only gave the high phenol yield of 13.0% under the optimized reaction conditions, but also exhibited high potential for reusability. The catalyst and its analogue samples were characterized by elemental analysis, Fourier transform infrared spectroscopy, electron spin resonance spectroscopy, X-ray diffraction, scanning electron microscopy, and nitrogen adsorption–desorption analysis. The structure–activity relationship is discussed according to the characterization and density functional theory calculation results.

Introduction

Owing to their convenient separation and renewability, heterogeneous catalysts are desirable for green chemistry processes.^[1] For liquid-phase selective organic oxidations, however, heterogeneous catalysts are usually confronted with the drawbacks of weak activity and inferior recycling utilization, although many efforts have been made to date.^[2] High-valent transition metals are common active sites in the selective organic oxidations, and their electronic structure is crucial for the catalytic performance,^[3] which results in a dramatic urgency for smart adjustment of the metal electron state to fabricate highly vibrant and stable catalytic centers.

Among various selective organic oxidations, the direct hydroxylation of benzene to phenol, one of the most important raw chemicals, is recognized as a promising alternative to replace the existing three-step cumene process, which causes high energy consumption, low phenol yield, and environmental pollution.^[4] Among various oxidants for this reaction, such as molecular oxygen (O₂), hydrogen peroxide, nitrous oxide, and so on, O₂ is ideal owing to its wide availability, low cost, atomic economy, and the fact that it is environmentally benign.^[5] To date, many efforts have been devoted to the low-

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201402186. temperature liquid-phase hydroxylation of benzene with O₂ in the presence of ascorbic acid, a safe and effective reducing agent.^[4] Nonetheless, the few reported heterogeneous catalysts suffer from low phenol yields, unsatisfactory reusability, or the need for very expensive cocatalysts.^[6-12] Thus, developing efficient reusable heterogeneous catalysts for this reaction system is challenging to achieve.

Polyoxometalates (POMs) are a large family of transitionmetal oxygen anion clusters with compositional and structural diversity, which have been receiving increasing attention in designing multifunctional heterogeneous catalysts for numerous organic transformations.^[13, 14] The well-known V-containing POMs, Keggin-structured molybdovanadophosphoric acids H_{3+} $_{x}PMo_{12-x}V_{x}$ (PMoV_x, x = 1-3), have been proved to be effective catalysts for liquid-phase hydroxylation of benzene with O₂ to phenol.^[9-11, 15] Owing to their solubility in polar solvent, PMoV_x mostly behave as homogeneous catalysts, and heterogeneous PMoV_x-based catalysts for the "benzene and O₂" reaction system are scarce. For example, synthesizing cesium salts of PMoV_x is a conventional approach for heterogenization of PMoV_x, but the heterogeneous CsPMoV_x catalysts gave low phenol yields of 6.5-7.2% with poor reusability.^[9] The utilization of 4,4'-bipyridine for modifying PMoV₁ promoted the reusability, but only gave 7.8% phenol yield over the fresh catalyst.^[10]

Herein, an efficient and reusable heterogeneous $PMoV_2$ based catalyst is prepared for the hydroxylation of benzene with O_2 . The synthesis is achieved by pairing the task-specifically designed nitrile-tethered pyridinium-based ionic liquid (IL) dication with $PMoV_2$ anion (the top line of Scheme 1). Modifying POM with IL cations has demonstrated promising advan-

[[]a] Z. Long,⁺ Dr. Y. Zhou,⁺ W. Ge, G. Chen, J. Xie, Q. Wang, Prof. J. Wang State Key Laboratory of Materials-Oriented Chemical Engineering College of Chemistry and Chemical Engineering Nanjing Tech University Nanjing, Jiangsu 210009 (P. R. China) Fax: (+ 86)25-83172264 E-mail: junwang@njtech.edu.cn
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^{[&}lt;sup>+</sup>] These authors contributed equally to this work.



Scheme 1. Synthesis of the IL dication–PMoV₂ catalysts.

tages in preparing superior IL-POM hybrid catalysts for various organic reactions,^[16,17] but IL-POMs have never been used for the hydroxylation of benzene with O₂. Based on this strategy, heterogeneous catalysts are generated for the hydroxylation of benzene with O₂, and a high phenol yield plus improved reusability are achieved through functionalization of the IL dications to tune the electric state of the V sites. The hybrid catalysts are fully characterized by elemental analysis, Fourier transform infrared (FTIR) spectroscopy, electron spin resonance (ESR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectrometry (EDS), and nitrogen sorption. Furthermore, the structure-activity relationship, especially the modifying effect of IL dications on the PMoV₂ anion, is discussed in depth based on characterizations, density functional theory (DFT) calculations, as well as comparisons with the various analogues shown in Scheme 1.

Results and Discussion

Catalytic assessment

Table 1 compares the phenol yields from the hydroxylation of benzene with O_2 over different hybrid catalysts with similar mole ratios of catalysts to the substrate benzene of 0.2 mol%, for which ascorbic acid is used as the reductant, which is conventional in this catalysis system.^[6-12] All the IL-dication-paired PMoV₂ hybrids acted as heterogeneous catalysts throughout the reaction process. Nitrile-tethered [D-3-CNPy]₂HPMoV₂ showed the highest phenol yield of 7.6% (Table 1, entry 1). Similarly, the other nitrile-tethered analogue [D-4-CNPy]₂HPMoV₂ gave an approximate phenol yield of 7.0% (Table 1, entry 2). In contrast, amino-tethered control sample [D-4-N(Me)₂Py]_{2.5}PMoV₂ exhibited a lower phenol yield of 4.5%

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(Table 1, entry 3), and the nonfunctionalized sample [D-Py]_{2.5}PMoV₂ gave the lowest phenol yield of 2.8% (Table 1, Turnover entry 4). numbers (TONs) calculated based on the phenol yields and the molar amounts of POM anions in catalysts are listed in Table 1, also showing the highest activity for [D-3-CNPy]₂HPMoV₂ among the above four catalysts. These results indicate that the catalytic activities of the IL dication-PMoV₂ hybrid series associate closely with the N-containing functional group tethered in the IL dications. Notably, the homogeneous parent catalyst PMoV₂ presented a phenol yield of 4.2% (Table S1, entry 4, in the Supporting Information), lower

Table 1. Hydroxylation of benzene to phenol over various heterogeneous catalysts with O_2 as the oxidant. $\ensuremath{^{[a]}}$							
Entry	Catalyst	Phenol yield [%] ^[b]	TON ^[c]	N charge			

1	[D-3-CNPy] ₂ HPMoV ₂	7.6	38.9	-0.122		
2	[D-4-CNPy] ₂ HPMoV ₂	7.0	35.8	-0.114		
3	[D-4-N(Me) ₂ Py] _{2.5} PMoV ₂	4.5	24.1	-0.605		
4	[D-Py] _{2.5} PMoV ₂	2.8	14.3	-		
5	[D-3-NH ₂ Py] ₂ HPMoV ₂	9.1	43.6	-0.775		
[a] Reaction conditions: 22.5 mmol (2.0 mL) benzene, 0.10 g catalyst						

(0.2 mol% based on benzene), 0.60 g ascorbic acid, 25 mL aqueous solution of acetic acid (80 vol%), 2.0 MPa O_2 , 100 °C, 10 h. [b] Yield of phenol (%)=mmol phenol/mmol initial benzene. [c] Turnover number=mmol phenol/mmol heteropolyanion in catalyst.

than those over $[D-3-CNPy]_2HPMoV_2$ and $[D-4-CNPy]_2HPMoV_2$. The hot filtration test for the most active catalyst, $[D-3-CNPy]_2HPMoV_2$, showed a phenol yield of 1.8%, similar to that obtained in the presence of ascorbic acid alone (the first data point in Figure S2e), thus demonstrating its heterogeneity for the reaction.

The influences of the reaction conditions were further investigated in detail on the lead catalyst $[D-3-CNPy]_2HPMoV_2$, including reaction temperature, pressure, and reaction time, as well as the amounts of ascorbic acid and catalyst (Figure S2). Accordingly, the optimized conditions are revealed to be 0.2 g catalyst, 0.80 g ascorbic acid, 2.0 mL (22.5 mmol) benzene, 25 mL aqueous solution of acetic acid (50 vol%), 2.0 MPa O₂, 100°C, 10 h, under which $[D-3-CNPy]_2HPMoV_2$ offered the highest phenol yield of 13.0%. Moreover, the catalytic reusability of $[D-3-CNPy]_2HPMoV_2$ under the above optimal conditions is shown in Figure 1. Based on the catalyst weight (0.2 g) used for the fresh run, the recovery ratios for the spent catalysts were weighed to be 76, 64, 55, and 44 wt% for the subsequent

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Figure 1. Catalytic reusability of $[D-3-CNPy]_2HPMoV_2$ for the hydroxylation of benzene with O₂. Reaction conditions: 0.80 g ascorbic acid, 2.0 mL benzene, 25 mL of an aqueous solution containing 50 vol% acetic acid, 2.0 MPa oxygen, 100 °C, 10 h.

three recycling runs. Without adding any fresh catalyst for recycling runs and with the same amount of benzene substrate used for each run, the phenol yields for the four-run test were 13.0, 9.2, 8.1, and 6.8%. EDS tests showed that the Mo/V molar ratio of the fresh catalyst was 5.06, very close to the theoretical value in the Keggin framework, but the Mo/V molar ratio of the last recovered catalyst increased to 7.12, which indicated the leaching of V species in the repeated catalysis processes. Thus the slight leaching of V species can be the primary reason for the slow deactivation in recycling. A similar V-leaching-derived deactivation has been observed on other catalysts for this reaction.^{16,9,12]} Additionally, the catalyst loss during the recovery operation shown in Figure 1 may be another important cause for the slow decrease in phenol yields.

In numerous previous studies on the catalysts for hydroxylation of benzene with O₂ and ascorbic acid, only very few heterogeneous catalysts have been reported so far,^[6-12] and some of them also provided the data for catalytic reusability. The following are the phenol yields obtained therein for one-run tests or multiple-run recycling tests if data are available: V/SiO₂ 3.7%,^[6] Cu/Al₂O₃ 2.5/1.4/0.9%,^[7] LaO_x/HZSM-5 (HZSM-5 = hydrogen form of ZSM-5 zeolite) 4.2/3.3/3.6%,^[8] CsPMoV₂ 7.2/5.1/1.3%,^[9] bipy₂PMoV₁ (bipy=4,4'-bipyridine) 7.8/5.5/4.2/3.7%,^[10] PMo₉V₃@HKUST-1 (HKUST-1 = a stable metal-organic framework compound) 7.37/7.04/6.40/6.35%,^[11] V_xO_y@C 9.4/7.0/2.2%.^[12] Compared with these previous results, the heterogeneous catalyst [D-3-CNPy]₂HPMoV₂ prepared in this work shows a higher activity with a better reusability.

Electronic interaction between organic IL dication and inorganic PMoV_2 anion

Figure 2 A illustrates the FTIR spectra for $[D-3-CNPy]Br_2$, PMoV₂, and fresh and recovered $[D-3-CNPy]_2HPMoV_2$. Four characteristic bands for the Keggin structure were observed at 1061, 961, 867, and 786 cm⁻¹, which are assigned to $P-O_a$ (central oxygen), M-O-M (corner-sharing oxygen; M: metal in POM framework), M-O_c-M (edge-sharing oxygen), and M-O_d (terminal oxygen), respectively.^[18,19] Similar Keggin bands appeared explicitly for $[D-3-CNPy]_2HPMoV_2$, and for the organic moiety



Figure 2. FTIR spectra for IL dication– $PMOV_2$ catalysts. A) a) [D-3-CNPy]Br₂, b) $PMOV_2$, c) [D-3-CNPy]₂HPMOV₂, d) recovered [D-3-CNPy]₂HPMOV₂ from the fourth recycling; B) a) [D-4-N(Me)₂Py]₂₅PMoV₂, b) [D-4-CNPy]₂HPMoV₂, c) [D-Py]₂₅PMoV₂.

the bands at 2252 and 1498 cm⁻¹ are attributed to the stretching vibrations of the nitrile group and the C=N bond in pyridine, respectively.^[18,20] This result suggests that the structures of D-3-CNPy²⁺ dication and $PMoV_2^{5-}$ anion are well retained in the hybrid [D-3-CNPy]₂HPMoV₂. However, compared with the parent PMoV₂, the bands related to M-O_b-M, M-O_c-M, and M-O_d for [D-3-CNPy]₂HPMoV₂ shifted to 946, 866, and 789 cm⁻¹, respectively, and the vibration for central oxygenbonded P-O_a branched into the two bands at 1074 and 1056 cm⁻¹. These changes in IR bands mostly arise from the strong electronic interaction between the two components of PMoV₂⁵⁻ POM anion and D-3-CNPy²⁺ IL cation.^[21] The recovered catalyst $[D-3-CNPy]_2HPMoV_2$ from the third recycling run showed almost the same IR curve as the fresh one, thus indicating its guite good structural durability in this reaction. Therefore, the slow decrease of phenol yields in the catalyst recycling test may also be related to the catalyst loss shown in Figure 1. In addition, FTIR spectra for the other hybrid samples of [D-4-CNPy]₂HPMoV₂, [D-4-N(Me)₂Py]_{2.5}PMoV₂, and [D-Py]_{2.5}PMoV₂ in Figure 2B also suggest the good structural retention of their organic and inorganic parents,^[22] with similar shifting or branching of Keggin bands to those of [D-3-CNPy]₂HPMoV₂.

ESR spectroscopy was performed to obtain more information about the electronic interaction between the organic cation and the inorganic anion. As shown in Figure 3, [D-Py]_{2,5}PMoV₂ was nearly silent in ESR, which indicates that its

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 $\label{eq:Figure 3. ESR signals of IL dication-PMoV_2 catalysts. a) [D-3-CNPy]_2HPMoV_2, b) [D-4-CNPy]_2HPMoV_2, c) [D-4-N(Me)_2Py]_2_5PMoV_2, d) [D-Py]_{2.5}PMoV_2.$

V species is nearly in the original state of the Keggin structure, that is, the highest valent state V⁵⁺. In contrast, sharp signals were observed for all the other three hybrids tethered with N-containing functional groups in dications, with the intensities of eight-line curves following the order: [D-3-CNPy]₂HPMoV₂ > [D-4-CNPy]₂HPMoV₂ > [D-4-N(Me)₂Py]_{2.5}PMoV₂. These eight-line curves evidently suggest the occurrence of the reduction state of V species for these three hybrids.^[23] Therefore, among the samples tested, [D-3-CNPy]₂HPMoV₂ possesses the greatest amount of reduced V species owing to the mostly remarkable electron transfer from the nitrile-tethered IL dication to the PMoV₂ anion.

Electronic effect on catalytic activity

For the PMoV₂-catalyzed hydroxylation of benzene to phenol with O₂ as the oxidant and ascorbic acid as the reducing agent, the catalytic cycle is started by electron transfer from ascorbic acid to V^{5+} species in the PMoV₂ anion, which causes the reduction of V^{5+} to V^{4+} species and the formation of the adduct by combining ascorbic acid and the PMoV₂ anion.^[4,10,24] Immediately, the V⁴⁺-involving ascorbic acid–PMoV₂ intermediate activates O₂ to create active oxygen species, which then attack benzene to give the final hydroxylation product phenol. Accordingly, we suggest that the IL dication used in this work may facilitate and stabilize the ascorbic acid-PMoV₂ adduct by the additional electron transfer from the IL dication to PMoV₂ anion, through which the phenol yield is enhanced. Moreover, the IL-dication-stabilized adduct may avoid the consumption of active oxygen species by the unwanted oxidation with uncombined ascorbic acid.^[25] This proposal is strongly evidenced by the sequence of the phenol yields in the series of IL dication–PMoV₂ hybrid catalysts (Table 1): [D-3-CNPy]₂HPMoV₂ $7.6\% > [D-4-CNPy]_2HPMoV_2$ $7.0\% > [D-4-N(Me)_2Py]_{2.5}PMoV_2$ $4.5\% > [D-Py]_{2.5}PMoV_2$ 2.8%, which corresponds well with the decreasing tendency in intensities of the ESR eight-line curves (Figure 3). Therefore, the highest activity of [D-3-CNPy]₂HPMoV₂ seems to be owing to the strongest electron transfer from its nitrile-tethered IL dication to the PMoV₂ anion.



Figure 4. Charge distribution on the IL dications calculated by DFT. A) D-3- $CNPy^{2+}$, B) D-4- $CNPy^{2+}$, C) D-4- $N(Me)_2Py^{2+}$, D) D- Py^{2+} .

To gain insight into the electronic interaction between the organic cation and the inorganic anion, DFT calculations were performed for exploring the charge distribution of the pyridinium-based IL dications, particularly the functional N atoms tethered on pyridine rings (Figure 4). Functional groups with partially negative N atoms, which result from their lone-pair electrons, lie at the ring edge of the dications. It can be seen in Table 1 that the negative charge value of -0.122 on the N atoms of the functional nitrile groups for [D-3-CNPy]₂HPMoV₂ is more negative than the -0.114 for [D-4-CNPy]₂HPMoV₂ merely because of the slight difference in substitution position of nitrile on the pyridine ring. It has been reported that the N atoms with lone-pair electrons in an organic moiety usually undergo charge transfer with the combined POM anions, thereby reducing the high-valent metal ions in POM anions toward a lower valent state.^[10,26] The vanadium in the cage structure of Keggin PMoV₂ is a better electron sink;^[27] consequently, it is reasonable to assume that the excess electron of the nitrile N atoms tethered on pyridine rings prefers to transfer and locate on vanadium sites, thus resulting in partial reduction of V^{5+} species. Therefore, $[D-3-CNPy]_2HPMoV_2$ with more negative charge on nitrile N atoms possesses more V⁴⁺ species than [D-4-CNPy]2HPMoV2, which is confirmed by the ESR test (Figure 3) and accounts for its higher phenol yield. However, the N atoms of the amino-tethered hybrid [D-4- $N(Me)_{2}Py]_{25}PMoV_{2}$ are much more negative (-0.605) than the above two nitrile-tethered ones, but both the intensity of the ESR eight-line curves and the phenol yield for [D-4-N(Me)₂Py]_{2.5}PMoV₂ are clearly lower than those of the latter two. The phenomenon is not surprising considering the steric shielding effect of the two methyl groups on the nitrogen electron lone pair.[28] One thus imagines that an unshielding amino functional group may exert a positive effect. This was true when we prepared and catalytically tested the control hybrid [D-3-NH₂Py]₂HPMoV₂ (Scheme 1) with bare primary amino functional groups tethered on pyridine rings. Under the conditions in Table 1, [D-3-NH₂Py]₂HPMoV₂ showed a phenol yield of 9.1% with TON of 43.6, higher than that of [D-3-CNPy]₂HPMoV₂. Moreover, under the optimized conditions the highest yield of 14.6% was obtained over [D-3-NH₂Py]₂HPMoV₂. Based on DFT calculations for [D-3-NH₂Py]₂HPMoV₂ (Figure 5 A), the negative charge value of -0.775 of the primary amino N atoms is much more negative than that for [D-3-CNPy]₂HPMoV₂, well consistent with the much sharper peaks in its ESR signals (Figure 5B), which provides rational interpretation for the enhanced phenol yield. However, the recovered

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Figure 5. A) Charge distribution on the D-3-NH $_2Py^{2+}$ dication. B) ESR signals for $[D-3-NH_2Py]_2HPMoV_2$.

 $[D-3-NH_2Py]_2HPMoV_2$ only gave phenol yields of 6.8 and 3.1% for the succeeding two recycling tests, and exhibited less catalytic stability than $[D-3-CNPy]_2HPMoV_2$. Taken together, $[D-3-CNPy]_2HPMoV_2$ is considered to be the best catalyst in this work.

Pore effect on catalytic activity

XRD, SEM, TEM, and nitrogen adsorption-desorption experiments were performed to investigate the crystal and pore structures of the hybrid catalysts. As shown in Figure 6, the XRD patterns for the two highly active hybrid catalysts, [D-3-CNPy]₂HPMoV₂ and [D-3-NH₂Py]₂HPMoV₂, only showed a broad Bragg reflection at the low angle of about 8.6°, which suggests a noncrystalline structure involving a regular ion-pair array.^[29] The SEM images in Figure 7A and B further illustrate that the morphology of these two samples is loosely stacked nanoparticles (50-100 nm) with the Brunauer-Emmett-Teller (BET) surface areas of 41.4 and 46.6 m^2g^{-1} , respectively, which match well the values for previously reported macrocation-modified POM-based hybrids.^[30] The TEM image in Figure 7E further shows the random mesopores among the loosely stacked nanoparticles of [D-3-CNPy]₂HPMoV₂. In the more highly magnified TEM image of Figure 7F, the primary ion-pair unit with a size of about 1 nm was distributed homogeneously throughout the nanoparticles. This observation is in accordance with the *d* spacing of 1.03 nm calculated from the broad Bragg reflection at 8.6° in the XRD pattern of [D-3-CNPy]₂HPMoV₂. All





 $\label{eq:Figure 6. XRD patterns of IL dication-PMoV_2 catalysts. a) [D-3-CNPy]_2HPMoV_2, b) [D-3-NH_2Py]_2HPMoV_2, c) [D-4-CNPy]_2HPMoV_2, d) [D-4-N(Me)_2Py]_{25}PMoV_2.$



Figure 7. A–D) SEM images of IL dication–PMoV₂ catalysts: A) [D-3-CNPy]₂HPMoV₂, B) [D-3-NH₂Py]₂HPMoV₂, C) [D-4-CNPy]₂HPMoV₂, D) [D-4-N(Me)₂Py]₂₅PMoV₂. E, F) TEM images of [D-3-CNPy]₂HPMoV₂.

the above results indicate that the primary ion-pair unit of $[D-3-CNPy]_2HPMoV_2$ assembles to form nanoparticles, which stack together to build random mesopores. A similar phenomenon has been reported for IL–POMs in our previous study.^[31] The less active $[D-4-CNPy]_2HPMoV_2$ and $[D-4-N(Me)_2Py]_{2.5}PMoV_2$ gave sharp diffraction peaks in the XRD patterns (Figure 6) and exhibited bulk morphology (Figure 7 C, D), which corresponded with their low BET surface areas of 9.3 and 9.5 m²g⁻¹, respectively. Generally, nanoparticles with higher surface areas facilitate fast mass transfer and accessibility of active sites to substrates, thus benefiting superior activities.^[31] In this study, it was found that the nanoparticles with higher surface areas are positive for the higher activities of $[D-3-CNPy]_2HPMoV_2$ and $[D-3-NH_2Py]_2HPMoV_2$ than for $[D-4-CNPy]_2HPMoV_2$ and $[D-4-N(Me)_2Py]_{2.5}PMoV_2$. However, it is not the determining factor, because the nonfunctionalized hybrid $[D-Py]_{2.5}PMOV_2$ also consists of noncrystalline nanoparticles (Figure S3) with a considerably high surface area of $37.1 \text{ m}^2 \text{g}^{-1}$, but presents a low phenol yield. The above phenomena indicate that it is the strong electronic effect between functional-group-tethered IL dications and the PMoV₂ anion that primarily affects the catalytic activity, although the stacking pores among the nanoparticles also play a passive role.

Conclusion

Nitrile-tethered hybrid catalyst $[D-3-CNPy]_2HPMoV_2$ (see Scheme 1) heterogeneously catalyzes the aerobic oxidation of benzene to phenol in the presence of ascorbic acid, and exhibits a high phenol yield plus superior reusability. The partially negative nitrile N atoms exert an electronic effect on the PMoV₂ anion, thereby accounting for the high catalytic activity of $[D-3-CNPy]_2HPMoV_2$. The present work provides not only a superior catalyst for hydroxylation of benzene with O_{2^r} but also some clues for designing more versatile heterogeneous vanadium-containing polyoxometalates for selective aerobic oxidation of organic substrates.

Experimental Section

Materials and methods

All chemicals were of analytical grade and used as received. ¹H and ¹³C NMR spectra were measured with a Bruker DPX 500 spectrometer at ambient temperature in D₂O using TMS as internal reference. Elemental analyses (C, H, and N) were performed on a CHN elemental analyzer (Vario EL cube). Nitrogen adsorption-desorption was performed at the temperature of liquid nitrogen using a BEL-SORP-MINI analyzer. The samples were degassed at 150 °C to a vacuum of 10⁻³ Torr before analysis. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS10 FTIR instrument (KBr disks) in the 4000–400 cm⁻¹ region. Electron spin resonance (ESR) spectra were recorded on a Bruker EMX-10/12 spectrometer at the X-band. X-ray diffraction (XRD) measurements were made with a SmartLab diffractometer (Rigaku Corporation) equipped with a 9 kW rotating-anode Cu source at 40 kV and 200 mA, from 5 to 50° with a scan rate of 0.2° s⁻¹. Field-emission scanning electron microscopy (FESEM, Hitachi S-4800, accelerated voltage: 5 kV) with energy-dispersive X-ray spectrometry (EDS, accelerated voltage: 20 kV) was used to examine the morphology and Mo/V molar ratio of the catalyst. TEM images were obtained by using a JEOL JEM-2010 (200 kV) TEM instrument.

Catalyst preparation

 $H_5PMo_{10}V_2O_{40}$ (PMoV₂) was prepared according to previous literature reports.^[17,32] MoO₃ (16.59 g) and V_2O_5 (2.1 g) were added to deionized water (250 mL). The mixture was heated to the reflux temperature under vigorous stirring with a water-cooled condenser, then at 120 °C an 85 wt% aqueous solution of H_3PO_4 (1.33 g) was added dropwise to the reaction mixture. When a clear orange-red solution appeared, it was cooled to room temperature. The orange-red powder PMoV₂ was obtained by evaporation of the solution to dryness, followed by recrystallizing for purification.

1,1'-(Butane-1,4-diyl)-bis(3-cyanopyridine) di(bromide) ([D-3-CNPy]Br₂): The dicationic IL precursor [D-3-CNPy]Br₂ (Scheme 1) was prepared by dissolving 3-cyanopyridine (20 mmol) and 1,4-dibromobutane (10 mmol) in ethanol (20 mL) in a 25 mL Teflon-lined autoclave. The mixture was treated at 90 °C for 48 h. The obtained white solid, which was not dissolved in ethanol, was washed with ethanol several times and dried (yield 43%). ^1H NMR (300 MHz, D_2O , TMS): $\delta = 9.57$ (s, 2H; 2(-CH)), 9.23 (d, 2H; 2(-CH)), 8.99 (d, 2H; 2(-CH)), 8.32 (m, 2H; 2(-CH)), 4.83 (s, 2H; 2(-CH₂)), 2.24 ppm (s, 2H; 2(-CH₂)); ¹³C NMR (75.5 MHz, D₂O, TMS): δ = 151.8, 151.0, 131.9, 116.9, 116.0, 64.4, 29.7 ppm. 1,1'-(Butane-1,4-diyl)-bis(4-cyanopyridine) di(bromide), denoted as [D-4-CNPy]Br₂, was prepared in the same way with 4-cyanopyridine and 1,4-dibromobutane (yield 39%). ¹H NMR (300 MHz, D₂O, TMS): $\delta = 9.20$ (d, 4H; 4(–CH)), 8.51 (d, 4H; 4(--CH)), 4.82 (s, 4H; 2(--CH₂)), 2.22 ppm (s, 4H; 2(-CH₂)); ^{13}C NMR (75.5 MHz, D₂O, TMS): $\delta\!=\!$ 148.7, 134.2, 131.1, 117.0, 64.6, 29.9 ppm.

[D-3-CNPy]₂HPMoV₂: The obtained IL precursor [D-3-CNPy]Br₂ (5.0 mmol) was added to an aqueous solution of $H_5PMo_{10}V_2O_{40}$ (2.0 mmol), and then the mixture was stirred at room temperature for 24 h. The formed yellow precipitate was isolated by filtration and washed with water three times, followed by drying in a vacuum. Elemental analysis calcd (wt%): C 16.98, N 4.95, H 1.46; found: C 17.36, N 5.20, H 1.77. The thermogravimetric profile indicated that [D-3-CNPy]₂HPMoV₂ was stable up to 240 °C (Figure S1). [D-4-CNPy]₂HPMoV₂ was prepared in the same way with [D-4-CNPy]Br₂ and $H_5PMo_{10}V_2O_{40}$. Elemental analysis calcd (wt%): C 16.98, N 4.95, H 1.46; found: C 17.23, N 5.13, H 1.58.

1,1'-(Butane-1,4-diyl)-bis-pyridine di(bromide) denoted as $[D-Py]Br_2$ was synthesized according to the previous literature.^[33] [D-Py]_{2.5}PMoV₂ was synthesized by a procedure similar to that for [D-3-CNPy]₂HPMoV₂. Elemental analysis calcd (wt %): C 18.50, N 3.08, H 1.98; found: C 18.00, N 2.86, H 2.06.

1,1'-Methylenebis(4-dimethylaminopyridinium) dichloride and 1,1'methylenebis(3-aminopyridinium) dichloride were synthesized according to the previous literature,^[22] and were denoted as [D-4-N(Me)₂Py]Cl₂ and [D-3-NH₂Py]Cl₂, respectively. [D-4-N(Me)₂Py]_{2.5}PMoV₂ was synthesized by a procedure similar to that for [D-3-CNPy]₂HPMoV₂. Elemental analysis calcd (wt%): C 18.92, N 5.89, H 2.31; found: C 19.06, N 5.95, H 2.37. [D-3-NH₂Py]₂HPMoV₂ was synthesized in the same way. Elemental analysis calcd (wt%): C 12.35, N 5.24, H 1.36; found: C 12.57, N 5.41, H 1.44.

Catalytic test

The hydroxylation of benzene was performed in a temperaturecontrollable pressured titanium reactor (100 mL) equipped with a mechanical stirrer. In a typical experiment, catalyst (0.1 g, 0.2 mol%), ascorbic acid (0.60 g), and benzene (2 mL) were added successively to an aqueous solution of acetic acid (80 vol%, 25 mL). After the system was charged with O2 (2.0 MPa) at room temperature, the hydroxylation reaction was conducted at 100 °C for 10 h with vigorous stirring. After the reaction, 1,4-dioxane was added to the product mixture as an internal standard for product analysis. The mixture was analyzed by a gas chromatography (GC) with a flame ionization detector and a capillary column (SE-54; SE-54; 30 m \times 0.32 mm \times 0.25 μ m). Under the reaction conditions, phenol was the only product detected by GC, and the commonly seen by-products (catechol, hydroquinone, and benzoquinone) were not found. After the first run of the test, the reaction mixture was centrifuged and the recovered solid catalyst was washed with acetic acid, dried in a vacuum, and then reused in the next run.

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The average values of three parallel reaction tests were given for phenol yields.

A hot filtration test was performed with the following procedure. $[D-3-CNPy]_2HPMoV_2$ (0.2 g, 0.2 mol%), ascorbic acid (0.80 g, 4.5 mmol), benzene (2 mL, 22.5 mmol), and an aqueous solution of acetic acid (50 vol%, 25 mL) were added to a flask successively. After stirring at 100 °C for 2 h, the slurry mixture was immediately subjected to hot filtration to remove the solid catalyst, and the resulting filtrate was sealed in an O₂-pressured reactor for reaction under conditions exactly the same as those in Figure 1 (2.0 MPa oxygen, 100 °C, 10 h) but without adding the solid catalyst [D-3-CNPy]_2HPMoV_2 again.

Theoretical calculations

All calculations were performed with the Gaussian 98 program. The unrestricted B3LYP/6-31g density functional theory (DFT) method was used to optimize organic models.^[34]

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