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C_3N_4-$H_5PMo_{10}V_2O_{40}$: a dual-catalysis system for reductant-free aerobic oxidation of benzene to phenol

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Hydroxylation of benzene is a widely studied atom economical and environmental benign reaction for producing phenol, aiming to replace the existing three-step cumene process. Aerobic oxidation of benzene with O_2 is an ideal and dream process, but benzene and O_2 are so inert that current systems either require expensive noble metal catalysts or wasteful sacrificial reducing agents; otherwise, phenol yields are extremely low. Here we report a dual-catalysis non-noble metal system by simultaneously using graphitic carbon nitride (C_3N_4) and Keggin-type polyoxometalate $H_5PMo_{10}V_2O_{40}$ ($PMoV_2$) as catalysts, showing an exceptional activity for reductant-free aerobic oxidation of benzene to phenol. The dual-catalysis mechanism results in an unusual route to create phenol, in which benzene is activated on the melem unit of C_3N_4 and O_2 by the V-O-V structure of $PMoV_2$. This system is simple, highly efficient and thus may lead the one-step production of phenol from benzene to a more practical pathway.

As an important commodity chemical, phenol is industrially produced by the three-step cumene process that suffers from a low one-pass yield *ca.* 5%, high energy cost and large amount of by-products[1,2]. Attempts to overcome these problems prompt the environmental benign one-step processes from benzene to phenol[3–14], in which the direct oxygenation of benzene to phenol by molecular oxygen (O_2) is the most industrially important due to atom economy and economic superiority[5,12]. For decades, various catalysts or catalytic systems have been developed for this aerobic oxidation[2], including low-temperature liquid-phase reactions[5,9–11], membrane process[12] and high-temperature gas-phase catalyses[15–17]. However, promoting its practical application remains great challenge because of the very low efficiency of the currently available catalytic systems[2].

Benzene and O_2 are all inert raw materials in low-temperature liquid-phase reactions. To oxidize benzene to phenol by O_2, sacrificial reducing agents, *i.e.* H_2, CO or ascorbic acid, are usually required to generate active oxygen species[2,9]. Otherwise, noble metal catalysts are needed[18–22], for example, palladium acetate [$Pd(OAc)_2$] with a polyoxometalate (POM) can catalytically convert benzene to phenol in mild liquid-phase aerobic media[18–21]. The utilization of noble metals and/or wasteful reducing agents will largely increase the cost of the catalytic system[2]; therefore, it is very attractive to develop a reductant-free aerobic oxidation of benzene to phenol catalyzed by a non-noble metal catalyst, which is even referred to as a "dream oxidation" in chemical industry[5].

Here we report a non-noble metal dual-catalysis system C_3N_4-$H_5PMo_{10}V_2O_{40}$ for efficient aerobic oxidation of benzene to phenol unaided by any reductant. Graphitic carbon nitride (C_3N_4) is a low price, insoluble and stable solid material[23], and we use it as a heterogeneous catalyst for activating benzene chemically[24]. POMs are transition-metal oxygen anion clusters with structural diversity and have been widely used as acid, redox, and bifunctional catalysts[25,26], among which $H_5PMo_{10}V_2O_{40}$ ($PMoV_2$) is a V-containing POM well recognized as an efficient homogeneous catalyst for organic oxidations with O_2[27]. We thus reason that the well dispersion of C_3N_4 in $PMoV_2$ solution gives rise to a molecular-level contact between them, for which the creation of phenol may be possible from the immediate attack of $PMoV_2$ catalyst to the already activated benzene ring on C_3N_4 surface. Indeed, the present results prove that the combination of C_3N_4 and $PMoV_2$ converts benzene to phenol with a high phenol yield in a low-temperature liquid-phase aerobic system without any reductant. A dual-catalysis mechanism is proposed for understanding the highly efficient process.

Results

The major sample of C_3N_4 employed in this work is designated as C_3N_4(580), with the number in the parenthesis indicating the temperature of 580°C for heating melamine in C_3N_4 preparation. We first measured the single

Table 1 | Aerobic oxidation of benzene over various catalysts. *Reaction conditions: C_3N_4 0.1 g; $PMoV_2$ (PMo, PW, $VOSO_4$, $PMoV_3$, $PMoV_1$ or $CsPMoV_2$) 0.4 g; benzene 4 mL; solvent 25 mL; O_2 2.0 MPa; 130°C; 4.5 h

Entry	Catalyst	Solvent	LiOAc (g)	Phenol Yield (%)
1	C_3N_4(520, 550 or 580)	acetic acid (50 vol.%)	0.6	0
2	$PMoV_2$	acetic acid (50 vol.%)	0.6	0
3	C_3N_4(580)-$PMoV_2$	water (2 mL)	0	2.1
4	C_3N_4(580)-$PMoV_2$	acetic acid (50 vol.%)	0	9.1
5	C_3N_4(580)-$PMoV_2$	acetic acid (50 vol.%)	0.6	13.6
6	melamine-$PMoV_2$	acetic acid (50 vol.%)	0.6	0
7	melem-$PMoV_2$	acetic acid (50 vol.%)	0.6	0
8	C_3N_4(520)-$PMoV_2$	acetic acid (50 vol.%)	0.6	0.3
9	C_3N_4(550)-$PMoV_2$	acetic acid (50 vol.%)	0.6	6.1
10	C_3N_4(580)-PMo	acetic acid (50 vol.%)	0.6	0
11	C_3N_4(580)-PW	acetic acid (50 vol.%)	0.6	0
12	C_3N_4(580)-$VOSO_4$	acetic acid (50 vol.%)	0.6	0
13	C_3N_4(580)-$PMoV_3$	acetic acid (50 vol.%)	0.6	9.5
14	C_3N_4(580)-$PMoV_1$	acetic acid (50 vol.%)	0.6	0
15	C_3N_4(580)-$CsPMoV_2$	acetic acid (50 vol.%)	0.6	0

catalyst by using C_3N_4(580) or $PMoV_2$ alone. Table 1 shows that neither former nor later alone was able to transform benzene in the absence of reductants (entries 1 and 2). On the contrary, a phenol yield of 2.1% was achieved in the dual-catalysis system containing both C_3N_4(580) and $PMoV_2$ even with only a small amount of water solvent (2 mL) (Table 1, entry 3). The phenol yield reached 9.1% by changing the solvent to 50 vol.% aqueous solution of acetic acid (Table 1, entry 4), and arose to the maximum value of 13.6% using LiOAc as an effective additive (Table 1, entry 5)[5,18,20,21]. The above results were obtained at 4.5 h and 130°C optimized from our detailed investigations on various conditions (see Supplementary Fig. S6 online). Many results have been reported on the oxidation of benzene to phenol[5,9–12,15–17], but reductant-free aerobic oxidation of benzene is still scarcely reported so far. Compared to the previous results under the reductant-free condition, the phenol yield of 13.6% over C_3N_4(580)-$PMoV_2$ is more than three times higher than the yield of 3.7% over the nano-plate vanadium oxide catalyst at a longer reaction time (10 h) and a higher temperature (150°C)[28], and even exceeds the yields on noble metal catalysts [*e.g.*, the homogeneous $Pd(OAc)_2$-$PMoV_x$ (X = 1, 2, 3) gives the phenol yield around 10%[18,21], which sharply drops to 3.4% when $Pd(OAc)_2$ is immobilized on porous supports for recovering[21]]. Moreover, the turnover frequency (TOF) of our work 5.9 h^{-1} calculated by the definition mmol phenol/(mmol POM catalyst × h reaction time) is much higher than the POM-catalyzed systems with CO as the sacrificial reducing agent (1.5 h^{-1})[5], or with ascorbic acid as the sacrificial reducing agent (0.86 h^{-1} and 2.0 h^{-1})[10,11], convincing that our reductant-free catalysis is even more active than those reductant-aided systems. Therefore, the present non-noble metal catalytic system C_3N_4(580)-$PMoV_2$ shows a remarkably superior efficacy at the reductant-free condition.

Heating melamine in air at high temperatures has been a common approach for preparing C_3N_4, so the influence of heating temperatures for melamine on this reaction is investigated. The XRD patterns of Fig. 1a shows that heating melamine at 520°C and 550°C led to the formation of graphitic C_3N_4 products of C_3N_4(520) and C_3N_4(550), similar to C_3N_4(580), but the low heating temperature 400°C resulted in melem, an intermediate toward C_3N_4[29,30]. The non-C_3N_4-mediated systems of melamine-$PMoV_2$ and melem-$PMoV_2$ yielded no product (Table 1, entries 6 and 7). Though C_3N_4(520) and C_3N_4(550) were also inactive when used alone (Table 1, entry 1), their combination with $PMoV_2$ gave phenol yields of 0.3% and 6.1%, respectively (Table 1, entries 8 and 9), much lower than 13.6% for C_3N_4(580)-$PMoV_2$. The results prove that the C_3N_4 sample obtained at the optimal temperature of 580°C is more active and in favor of the high phenol yield.

We further explored catalytic systems containing C_3N_4(580) and other POMs. With the V-free POMs, *i.e.* $H_3PMo_{12}O_{40}$ (PMo) or $H_3PW_{12}O_{40}$ (PW), to company C_3N_4(580), no phenol product appeared (Table 1, entries 10 and 11), suggesting that the V species should be indispensable. Nonetheless, C_3N_4(580) with the non-POM vanadium species $VOSO_4$ caused an inactive system either (Table 1, entry 12); as a consequence, it is the V species in POM framework that is synergically active with C_3N_4 for this reaction. Moreover,

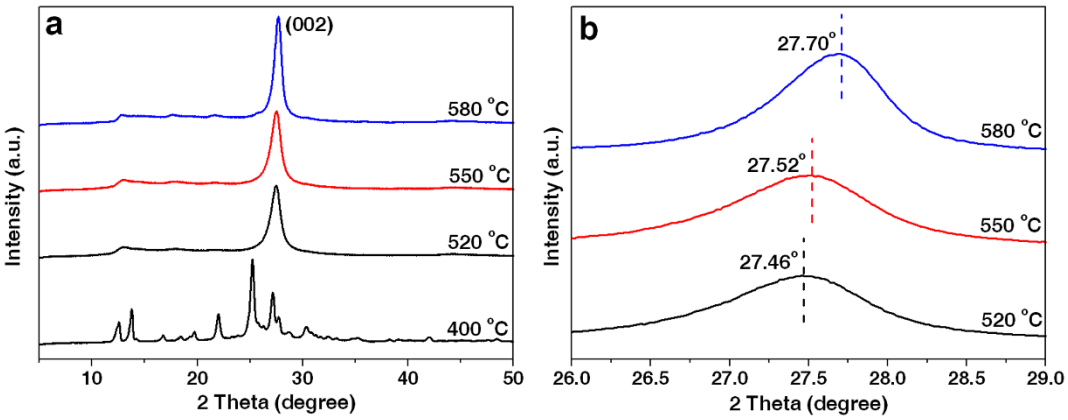

Figure 1 | (a) XRD patterns for the products by heating melamine at 400, 520, 550 and 580°C; (b) Magnification of the peak (002) in the 2θ range 26 ~ 29° for the C_3N_4 products obtained at 520, 550 and 580°C.

when the other two less frequently used V-containing POMs ($PMoV_1$ and $PMoV_3$) were tested, the results show that C_3N_4(580)-$PMoV_3$ exhibited comparable activity to C_3N_4(580)-$PMoV_2$, but C_3N_4(580)-$PMoV_1$ was definitely inactive (Table 1, entries 13 and 14), which means that not all the V species in POM framework can catalyze this reaction with C_3N_4.

Discussion

According to previous studies, the V species in V-POMs are well accepted as the catalytically active sites for versatile organic oxidations[31]. Particularly, for liquid-phase aerobic oxidations, $PMoV_2$ takes a catalytic effect through Mars-van Krevelen-type mechanism, where the lattice oxygen of $PMoV_2$ selectively oxygenates organic substrates *via* a valence variation between V^{5+} and V^{4+}[27,32]. Neumann and co-workers[27,32–35] have systematically studied series of $PMoV_2$-catalyzed homogeneous oxidations, and based on the Mars-van Krevelen mechanism they propose that the isomers of $PMoV_2$ with vanadium atoms in adjacent positions (*i.e.* V-O-V structure) are more likely to form bridge defects, favoring higher activity in oxygen-transfer reactions. Therefore, only $PMoV_2$ and $PMoV_3$ with the highly active V-O-V structure in their frameworks can allow the occurrence of oxygen transfer in hydroxylation of benzene to phenol, while lack of V-O-V is responsible for the inactivity of $PMoV_1$.

Nonetheless, $PMoV_2$ or $PMoV_3$ alone cannot catalyze the reaction because of inertness of the substrate benzene, suggesting that C_3N_4 should play a key role. Recently, Goettmann *et al.*[24,36] conclude an unusual activation of aromatic rings *via* transferring electron density from the melem unit of C_3N_4 to arene based on reaction results plus DFT calculations. Besides, for the high-temperature gas-phase oxidation of benzene with O_2 over copper exchanged HZSM5, a bifunctional catalytic mechanism has been reported: phenol is produced from the simultaneous activation of benzene and O_2 on zeolitic acid and Cu metal sites, respectively[16,17]. From above analyses, a dual-catalysis mechanistic pathway is proposed for understanding the catalytic performance of C_3N_4-$PMoV_2$ in Fig. 2. Benzene is firstly catalytically activated by the melem unit of graphitic C_3N_4, forming a transitional intermediate of electron-enriched benzene ring. Immediately, the original oxidation state of $PMoV_2$ with V^{5+} species, designated as $PMoV_2^{[ox]}$, attacks the intermediate ring to produce phenol, wherein the lattice oxygen of a V-O-V structure in $PMoV_2^{[ox]}$ moves into the benzene ring with the $PMoV_2^{[ox]}$ thus being reduced to the V^{4+}-containing $PMoV_2^{[red]}$. Finally, the catalytic cycle is closed with the resume of $PMoV_2^{[ox]}$ after O_2 re-oxidizes V^{4+} of $PMoV_2^{[red]}$ into V^{5+} species.

In the dual-catalysis mechanism above, the role of C_3N_4 is activating benzene according to the previous finding that the π-conjugated melem unit of C_3N_4 could transfer electron density to aromatic rings[24,36]. It is further revealed that high temperatures for thermal condensation of melamine would enhance the π-conjugation by connecting more tri-s-triazine and extending the polymeric network of C_3N_4[37]. The (002) diffraction peak of C_3N_4 is assigned to the interlayer distance of its graphitic structure[30]. In our case, as shown in the magnification of XRD patterns in Fig. 1b, the gradual shifting of the (002) peak to larger degrees along with the raise of heating temperatures means the shortening of the stacking distance and thus the stronger overlap of π orbital in C_3N_4[29,30], indicating that the activation of benzene would be improved by a higher heating temperature up to 580°C. This accounts for the activity order C_3N_4(520)-$PMoV_2$ < C_3N_4(550)-$PMoV_2$ < C_3N_4(580)-$PMoV_2$. On the other hand, melem-$PMoV_2$ is inactive because melem itself has no graphitic characteristic of C_3N_4[30].

Also according to the mechanism in Fig. 2, the catalyst $PMoV_2$ will remain in its reduced state $PMoV_2^{[red]}$ as the reaction occurs in O_2-deficient environment. Thus we conducted a separate run by introducing a much less amount of O_2 (0.3 MPa) (see Supplementary Information) into the batch reactor. In this case, the recovered $PMoV_2$ was green and exhibited an eight-line signal in ESR spectra (Fig. 3), index of the reduced state $PMoV_2^{[red]}$[5,10], whereas the fresh and recovered $PMoV_2$ from O_2-sufficient condition were orange and ESR silent, denoting the oxidation state $PMoV_2^{[ox]}$. The above phenomena and comparisons strongly evidence our proposal that there exists V^{5+}/V^{4+} switch during the reaction.

Moreover, the activation and oxidation of benzene should occur simultaneously in this mechanism. In order to reflect this point, the well-known heterogeneous Cs salt of $PMoV_2$, $CsPMoV_2$[10], was tried as a partner with C_3N_4(580). Though $CsPMoV_2$ was as active as $PMoV_2$ (see Supplementary Table S1 online)[10] in the presence of the sacrificial reducing agent ascorbic acid, C_3N_4(580)-$CsPMoV_2$ was inactive in our reaction system (Table 1, entry 15). The SEM image for $CsPMoV_2$ (see Supplementary Fig. S5 online) shows a spherical morphology with spheres diameters being 800 ~ 900 nm. This bulk $CsPMoV_2$ may not contact well with another solid surface of C_3N_4(580), hindering the simultaneous attachment of substrate with the dual-catalyst. In other words, the intimate and efficient contacts among C_3N_4, benzene and $PMoV_2$ are essential for implementing the overall catalytic cycle, which further supports our mechanism.

Besides benzene, the simplest alkyl aromatic molecule toluene was also attempted as the substrate to further investigate the catalytic behavior of C_3N_4(580)-$PMoV_2$ for aerobic oxidation of aromatic rings (see Supplementary Table S2 online). C_3N_4(580) alone was

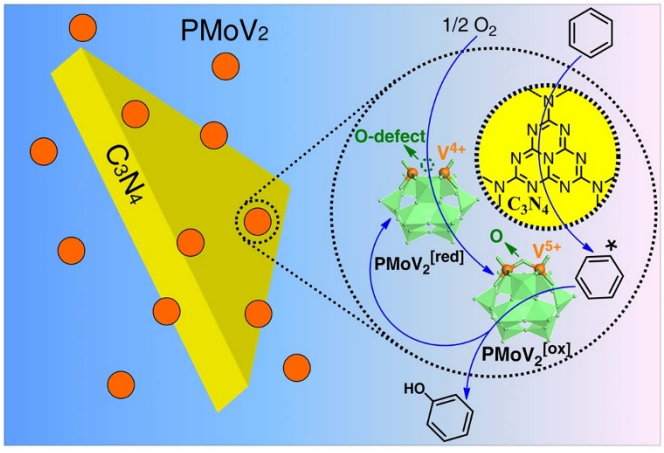

Figure 2 | Proposed mechanistic pathway for C_3N_4-$PMoV_2$-catalyzed aerobic oxidation of benzene to phenol.

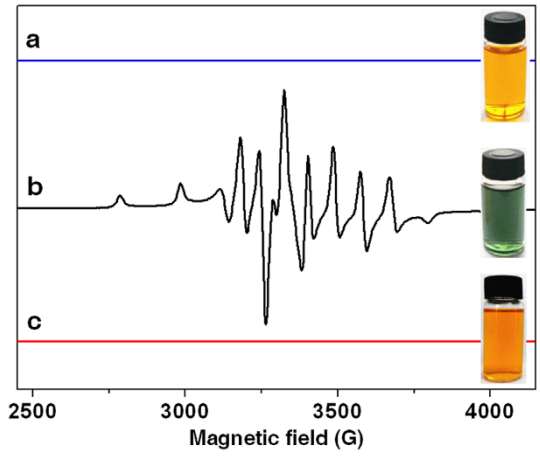

Figure 3 | ESR spectra of (a) fresh $PMoV_2$, (b) recycled $PMoV_2$ from the O_2-insufficient reaction, and (c) recycled $PMoV_2$ from the O_2-sufficient reaction, entry 1 of Table 1.

inert in this system, and yet, bare $PMoV_2$ exclusively produced methyl-oxygenated compounds of benzaldehyde (7.7%) and benzyl alcohol (1.4%) due to the side chain oxidations. For reductant-free oxidations of alkyl aromatics, early studies reveal that oxidations of benzylic C-H bond are preferred rather than the aromatic ring[9,38,39]. On the contrary, the dual-catalysis system C_3N_4(580)-$PMoV_2$ resulted in a desirable yield of cresols (0.4%) due to the ring oxidation. This feature suggests that C_3N_4-$PMoV_2$ should have enhanced the reactivity of the alkylated benzene ring, enabling occurrence of the ring oxygenation through the dual-catalysis mechanism in Fig. 1.

Catalytic reusability was first investigated by recycling C_3N_4(580) alone (Fig. 4). The phenol yield slowly decreased from 13.6% for the fresh catalyst to 12.7% for 1st, 9.8% for 2nd, and still kept at 6.2% for 3rd recycling. The XRD pattern for the last recycled C_3N_4(580) indicates a stable structural stability due to its identical diffraction peak to that of the fresh one (see Supplementary Fig. S1 online). Therefore, the above decrease of phenol yield can be ascribed to the tar deposition according to the gradually darkened color (inserted photos in Fig. 4) and variation of C content (see Supplementary Information) of C_3N_4(580) during the recycling process. In fact, tar is still an inevitable over-oxidation byproduct, because the main product phenol is more reactive than the substrate benzene[4,6,18]. Even so, when C_3N_4(580), $PMoV_2$ and LiOAc were simultaneously recovered (see Methods), the phenol yield was 10.3% and 6.5% for the 1st and 2nd recycling, and still 2.1% for the 3rd recycling (Fig. 4).

All the above results demonstrate that the dual-catalysis non-noble metal system C_3N_4-$PMoV_2$ provides a high phenol yield of 13.6% in reductant-free aerobic oxidation of benzene. A dual-catalysis mechanism involving cooperative activations of benzene on melem unit of C_3N_4 and O_2 by V-O-V structure of $PMoV_2$ is demonstrated for interpreting catalytic results. The present dual-catalysis process appears to be simpler, much more efficient and cost-effective when compared with the currently available catalytic systems, paving a promising step towards practical application of hydroxylation of benzene to phenol by molecular oxygen.

Methods

Materials and general methods. All chemicals were analytical grade and used as received. $H_3PMo_{12}O_{40}$ (PMo) and $H_3PW_{12}O_{40}$ (PW), purchased commercially, were dried before used. XRD patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu Kα radiation source at 40 kV and 20 mA, from 5 to 50° with a scan rate of 0.2° S^{-1}, and before measurements the samples were dried at 100°C for 2 h. Elemental analyses were performed on a CHN elemental analyzer (FlashEA 1112). BET surface areas were calculated from the sorption isotherms measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer; the samples were degassed at 300°C to a vacuum of 10^{-3} Torr before analysis. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4,000–400 cm^{-1} region. ESR spectra were recorded on a Bruker EMX-10/12 spectrometer at X-band. The measurements were done at −110°C in a frozen solution provided by a liquid/gas nitrogen temperature regulation system controlled by a thermocouple located at the bottom of the microwave cavity within a Dewar insert.

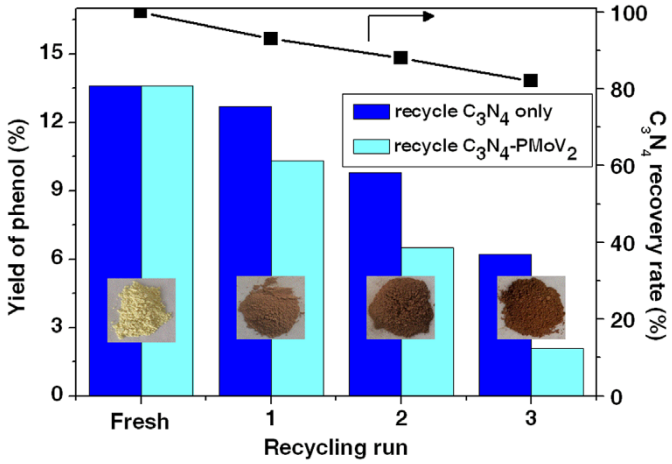

Figure 4 | Phenol yields and C_3N_4 recovery rate during the recycling test; insertion: C_3N_4 photo for each run.

Preparation of catalysts. *Graphitic carbon nitride (C_3N_4).* The procedure for the synthesis of C_3N_4(580) is similar to the previous reports[40,41]. Melamine was transferred into a crucible and heated in a muffle furnace under air at a rate of 15°C/min to reach the temperature of 580°C and kept at 580°C for 4 h, then the resulting yellow sample was cooled to room temperature in the oven. Melem, C_3N_4(520) and C_3N_4(550) were prepared by the similar method at 400°C, 520°C and 550°C, respectively.

$H_5PMo_{10}V_2O_{40}$ ($PMoV_2$). The Keggin-structured double V-containing POM was prepared according to the procedure described in our previous report[42]. The detail of the preparation of $PMoV_2$ procedure is as the following. MoO_3 (16.59 g) and V_2O_5 (2.1 g) were added to deionized water (250 mL). The mixture was heated up to the reflux temperature under vigorously stirring with a water-cooled condenser, then at 120°C the 85 wt% aqueous solution of H_3PO_4 (1.33 g) was added drop-wise to the reaction mixture. When a clear orange-red solution appeared, it was cooled to room temperature. The orange-red powder $PMoV_2$ was obtained by evaporation of the solution to dryness, followed with re-crystallizing for purification.

$Cs_5PMo_{10}V_2O_{40}$ ($CsPMoV_2$) was prepared according to the literature[10], with Cs_2CO_3 instead of $CsNO_3$. FT-IR spectrum for $CsPMoV_2$ is presented in Fig. S4b.

Catalytic tests. The hydroxylation of benzene was carried out in 100 ml stainless steel autoclave equipped with a mechanical stirrer and an automatic temperature controller. In a typical test, 0.1 g C_3N_4, 0.4 g $PMoV_2$, 0.6 g LiOAc, and 4.0 mL benzene were added into 25 mL of the aqueous solution of acetic acid (50 vol%) successively. After the system was charged with 2.0 MPa O_2 at room temperature, the hydroxylation reaction was conducted at 130°C K for 4.5 h with vigorous stirring. After the reaction, 1, 4-dioxane was added into the product mixture as an internal standard for product analysis. The mixture was analyzed by a gas chromatograph (GC) with a FID and a capillary column (SE-54; 30 m × 0.32 mm × 0.25 μm). Yield of phenol was calculated as mmol phenol/mmol initial benzene. Catechol, hydroquinone and benzoquinone were not detected by our GC analysis, so the tar that cannot be detected by the GC technique was the over-oxidation product.

Recycling of the catalyst system. After the reaction, the reaction mixture was centrifuged and the solid C_3N_4(580) was recovered, followed by washing with acetic acid and dried in vacuum, and then reused in the next run. After the solid C_3N_4(580) was separated by centrifuging, water was added into the left liquid phase followed by extraction with isopropyl ether. The combined aqueous extracts were filtered and concentrated by evaporation under reduced pressure. The resulting solid mixture containing used $PMoV_2$ and LiOAc was obtained.

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Author contributions

Z.Y.L. and J.W. conceived and designed the experiments. Z.Y.L. performed all the experiments and analyzed all the data. G.J.C. and W.L.G. performed catalysts characterization. Z.Y.L., Y.Z. and J.W. co-wrote the paper. All the authors discussed the results and commented on the manuscript.

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