

Short Communication

Aerobic oxidation of benzene to phenol over polyoxometalate-paired Pd^{II}-coordinated hybrid: Reductant-free heterogeneous catalysisZhouyang Long ^a, Yangqing Liu ^a, Pingping Zhao ^b, Qian Wang ^a, Yu Zhou ^a, Jun Wang ^{a,*}^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing, Jiangsu 210009, PR China^b School of Chemical Engineering, Shandong University of Technology, Zibo, Shandong 255049, PR China

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ABSTRACT

Aerobic oxidation of benzene was carried out over the organic–inorganic hybrid catalyst of [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂, a solid catalyst containing the Keggin polyoxometalate PMoV₂ and noble metal Pd(OAc)₂ in its ionic structure. The features of this heterogeneous reaction system were studied by tuning various reaction parameters including solvent selection, function of buffer agent, and effects of reaction time, reaction temperature and catalyst amount. The results show the high phenol yield of 9.8% without aided by any sacrificial reducing reagents. The conjugation of Pd(OAc)₂ and PMoV₂ within the ionic structure of [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ that accounts for its high activity is preliminarily discussed.

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1. Introduction

Energy shortage and environmental pollution are two serious problems in modern society, which are being greatly aggravated by highly energy-consuming and polluting chemical processes. Therefore, energy-efficient and green processes are urgently demanded to realize sustainable chemical production. Phenol is one of the most important raw chemicals, which is currently produced by the three-step cumene process with the disadvantageous of high energy consumption, low phenol yield and serious pollution [1,2]. To replace the cumene process, one-step hydroxylation of benzene to phenol has been extensively investigated for decades [3]. Among the oxidants for this reaction, such as molecular oxygen (O₂), hydrogen peroxide, nitrous oxide, and so on, O₂ is ideal due to its wide availability, low cost and environmental benignity [4].

Up to date, the liquid phase catalytic reactions of aerobic oxidation of benzene with O₂ to phenol are mostly reported in the presence of sacrificial reducing agents (*i.e.* H₂, CO, ascorbic acid), exhibiting relatively high phenol yields [4–7]. It is however very desirable that aerobic oxidation of benzene to phenol could effectively take place in the absence of a sacrificial reducing agent due to more atomic economy, but the early reports are still rare [8–12]. In this context, the combination of Pd(OAc)₂ with V-containing polyoxometalate H₃+_xPMo₁₂–_xV_x (PMoV_x, x = 1–3) is the eminent homogeneous catalyst giving a phenol yield of 9.4% [11]. From the point of view of greener catalysis, a heterogeneous

catalyst is preferred due to the convenience in catalyst isolation [13]. However, very few heterogeneous catalysts for reductant-free aerobic oxidation of benzene to phenol have been reported so far. For example, to achieve a heterogeneous catalyst, Pd(OAc)₂ and PMoV₂ were simultaneously immobilized on the porous support, but leading to a much lowered phenol yield of 0.7% [11]. Further, the nanoparticle catalyst Pd-VO_x synthesized from Pd(OAc)₂ and VO(acac)₂ showed a considerable phenol yield of 5.2% [14], while another advance is obtaining of the high phenol yield of 13.6% over the dual-catalysis system combined by graphitic carbon nitride with PMoV₂, but PMoV₂ is still a homogeneous catalyst in that system [12].

Herein we report a reductant-free heterogeneous system for aerobic oxidation of benzene to phenol catalyzed by a polyoxometalate-paired Pd^{II}-coordinated ionic hybrid. Recently, our group prepared a PMoV₂-based Pd^{II}-coordinated ionic hybrid catalyst [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ specifically for oxidative dehydrogenation of benzene to biphenyl [15]. Based on the known result that the combination of Pd(OAc)₂ with PMoV₂ can effectively catalyze the reductant-free aerobic oxidation of benzene to phenol [11] and the fact that [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ involves both Pd^{II} and PMoV₂ sites within the cation and anion moieties of its ionic structure (Fig. S1), it is rational to expect that the ionic hybrid may be catalytically very active for aerobic oxidation of benzene to phenol. Catalytic tests of this work reveal that [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ exhibits a high yield of phenol for this reaction as a heterogeneous catalyst without adding any sacrificial reducing reagents after optimization of reaction conditions. Catalytic mechanism is preliminarily discussed according to reaction results, catalyst structure, and previous findings.

* Corresponding author. Tel.: +86 25 83172264.

E-mail address: junwang@njtech.edu.cn (J. Wang).

2. Experimental

2.1. Materials and methods

All solvents and reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were performed on a CHN elemental analyzer (Vario EL cube). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS10 FT-IR instrument (KBr disks) in the 4000–400 cm^{-1} region. The amount of leached palladium species in the filtrate after a reaction was measured using a Jarrell-Ash 1100 ICP-AES spectrometer.

2.2. Catalyst preparation

$[(\text{C}_3\text{CNpy})_2\text{Pd}(\text{OAc})_2]_2\text{HPMoV}_2$ has been prepared and characterized by CHN elemental analysis, TG, FT-IR, UV–vis, ESR, SEM and XRD in our previous paper [15]. CHN elemental analysis for the presently synthesized $[(\text{C}_3\text{CNpy})_2\text{Pd}(\text{OAc})_2]_2\text{HPMoV}_2$, found: C 19.11 wt.%, N 4.08 wt.%, H 2.01 wt.%; calcd: C 19.07 wt.%, N 4.04 wt.%, H 2.06 wt.%.

2.3. Catalytic test

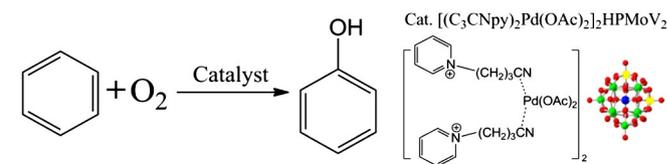
Hydroxylation of benzene was carried out in a customer-designed temperature controllable pressured titanium reactor (25 mL) equipped with a mechanical stirrer. In a typical run, 0.05 g (0.08 mol%) $[(\text{C}_3\text{CNpy})_2\text{Pd}(\text{OAc})_2]_2\text{HPMoV}_2$, 0.2 g LiOAc, 2 mL (22.5 mmol) benzene, and aqueous solution of acetic acid (2 mL acetic acid and 4 mL H_2O) were added into the reactor successively. After the reactor was charged with 2.0 MPa O_2 at room temperature, the reaction was conducted at 110 °C for 4 h with vigorous stirring. After reaction, 1,4-dioxane was added into the product mixture as an internal standard. The mixture was analyzed by gas chromatograph (GC) with a FID and a capillary column (SE-54; SE-54; 30 m \times 0.32 mm \times 0.25 μm). Because only the phenol GC peak was detected as the product when the reaction was performed around the above typical conditions, the GC-measured selectivity for phenol is reasonably estimated to be above 99%. For recovering the solid catalyst, it was filtrated from the reacted mixture, washed with acetic acid and dichloromethane, and dried in vacuum oven at 80 °C for 8 h. The average values of three parallel reaction tests were given for phenol yields.

3. Results and discussion

This work is to reveal the reductant-free heterogeneous catalysis for aerobic oxidation of benzene to phenol over the hybrid catalyst $[(\text{C}_3\text{CNpy})_2\text{Pd}(\text{OAc})_2]_2\text{HPMoV}_2$. However, in our recent paper [15], the same hybrid catalyst has been demonstrated to be highly efficient for oxidative dehydrogenation of benzene with molecular oxygen to biphenyl. Therefore, tuning of reaction conditions should be crucial in this work. Owing to extreme importance of the nature of solvent used in a liquid-phase reaction [16], we started with solvent selection in investigating the effects of reaction parameters, with the results shown in Table 1. It is seen that no phenol was yielded with solvents of aqueous solutions of acetonitrile, ethanol or DMF (dimethylformamide) (entries 1–3), and only low phenol yield of 2.3% was observed with aqueous solution of acetone (entry 4). The highest phenol yield of 5.6% was obtained in aqueous solution of acetic acid (entry 5), indicating that aqueous acetic acid solution is the preferred solvent for this reaction. Then the effect of volume ratio of acetic acid to water on the phenol yield was investigated with the certain volume for the mixed solvent of 6 mL. Entry 6 of Table 1 showed no phenol product with pure water as the solvent. Benzene is immiscible with water; therefore, the solid catalyst well dispersed in water is difficult to contact benzene substrate, which hinders the play of its catalytic role in the reaction. Adding acetic acid into water increases the organic character of the aqueous solvent and thus benefits the solubilization of benzene in the reaction medium,

Table 1

Aerobic oxidation of benzene to phenol catalyzed by $[(\text{C}_3\text{CNpy})_2\text{Pd}(\text{OAc})_2]_2\text{HPMoV}_2$ using different solvents.^a



Entry	Solvent	Volume (mL) ^a	LiOAc (g)	Phenol yield (%) ^b
1	Acetonitrile-H ₂ O	2/4	0.2	0
2	Ethanol-H ₂ O	2/4	0.2	0
3	DMF-H ₂ O	2/4	0.2	0
4	Acetone-H ₂ O	2/4	0.2	2.3
5	Acetic acid-H ₂ O	2/4	0.2	5.6
6	Acetic acid-H ₂ O	0/6	0.2	0
7	Acetic acid-H ₂ O	3/3	0.2	3.1
8	Acetic acid-H ₂ O	4/2	0.2	1.4
9	Acetic acid-H ₂ O	2/4	Without	2.5
10	Acetic acid-H ₂ O	2/4	0.1	4.3
11	Acetic acid-H ₂ O	2/4	0.3	4.0

^a Reaction conditions: benzene 2 mL (22.5 mmol), catalyst 0.05 g (0.08 mol% based on benzene substrate), O_2 2.0 MPa, 110 °C, 4 h.

^b Phenol yield (%) = mmol phenol / mmol initial benzene.

which largely accounts for the much enhanced phenol yield (entry 5). Besides, previous reports [8,10] have suggested that acetic acid participates in the formation of the reactive intermediates $\text{C}_6\text{H}_5\text{PdOAc}$ and $\text{C}_6\text{H}_5\text{Pd}(\text{OAc})_3$, which is crucial for the catalysis (also see this in detail later). However, increasing the acetic acid concentration in the mixed solvent acetic acid-H₂O from 2/4 (entry 5) to 3/3 (entry 7) and further to 4/2 (entry 8) gives phenol yields of 5.6%, 3.1% and 1.4%, respectively. This substantial decrease in phenol yields may associate to excessive oxidation caused by radical processes in the highly concentrated acetic acid aqueous solutions [8].

It is noted that the solvent of aqueous acetic acid used above was buffered with LiOAc. Without LiOAc (entry 9), the phenol yield dropped to 2.5%, with the GC peak of biphenyl clearly detected (though in trace amount) and darkened color of the reacted mixture observed. As the over-oxidation byproducts, catechol, hydroquinone or benzoquinone are well detectable with the present GC analysis, but they were undetectable in this work. Consequently, the observed dark color implies the occurrence of tar as the deep-oxidation byproduct. When the amount of LiOAc increased to 0.1 g and 0.2 g, the phenol yield increased to 4.3% and 5.6% (entries 10 and 5) with complete disappearance of biphenyl, while the dark color of tar could not be visualized any more. The disappearance of biphenyl and enhanced phenol production consist with the previous proposal that the addition of the buffer agent LiOAc favors the hydroxylation at the expense of coupling reaction [10]. In addition, LiOAc buffers the aqueous acetic acid, reduces the overpowering oxygen radicals, and thus enhances the selective hydroxylation process [8,10,17]. However, when excessive amount of LiOAc (0.3 g) was used, the generation of reactive oxygen species may be depressed, and the phenol yield decreased to 4.0% (entry 11).

For an aerobic oxidation process, the oxygen pressure should be one of the most important parameters to influence the reaction result. As shown in Fig. 1 (A), at the relatively low O_2 pressure of 1.0 MPa, only a small amount of phenol (1.2% yield) was obtained with explicit detection of biphenyl (0.4% yield). When the O_2 pressure increased to 2.0 MPa, the phenol yield was pronouncedly enhanced to 5.6% with diminishing of biphenyl to zero. Stoichiometrically, two benzene molecules react with a half O_2 molecule to produce one biphenyl molecule; while the reaction of two benzene molecules with one O_2 molecule leads to the formation of two phenol molecules. The high O_2 pressure

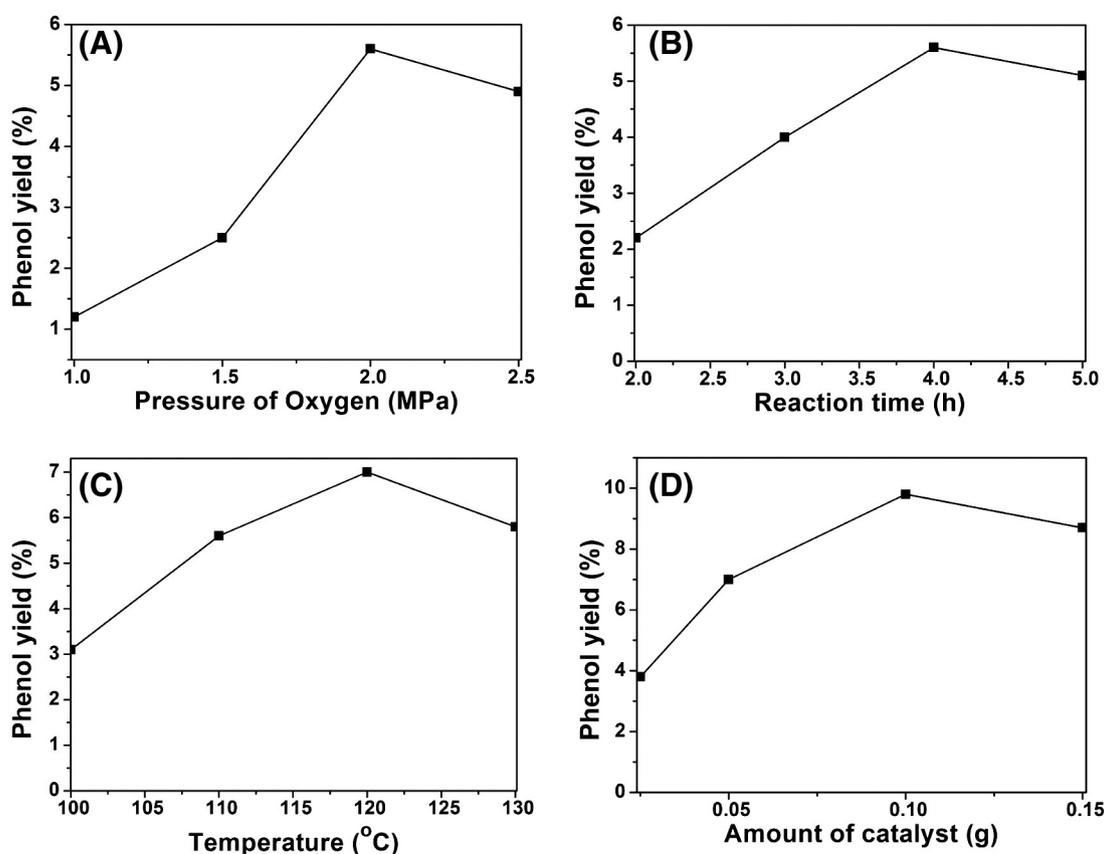


Fig. 1. Effects of reaction conditions on phenol yield in $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ -catalyzed aerobic oxidation of benzene. (A) Oxygen pressure variation with other conditions: 0.05 g catalyst (0.08 mol%), 0.2 g LiOAc, 2 mL HOAc with 4 mL H_2O (solvent), 110 °C, 4 h. (B) Time variation with other conditions: 0.05 g catalyst (0.08 mol%), 2 mL HOAc with 4 mL H_2O (solvent), 0.2 g LiOAc, 2.0 MPa O_2 , 110 °C. (C) Temperature variation with other conditions: 0.05 g catalyst (0.08 mol%), 2 mL HOAc with 4 mL H_2O (solvent), 2.0 MPa O_2 , 0.2 g LiOAc, 4 h. (D) Catalyst amount variation with other conditions: 2 mL HOAc with 4 mL H_2O (solvent), 2.0 MPa O_2 , 0.2 g LiOAc, 120 °C, 4 h; for combined homogeneous catalyst $Pd(OAc)_2 + PMoV_2$: $Pd(OAc)_2$ 0.32 mol%, $PMoV_2$ 0.16 mol%.

means more O_2 molecules dissolved in the liquid phase of the reaction, which therefore favors the formation of phenol rather than biphenyl. However, too much oxygen usually causes the excessive oxidation of the already produced phenol, and correspondingly, the phenol yield decreased to 4.9% at the higher O_2 pressure of 2.5 MPa. Our previous report [15] has shown that at the much lower O_2 pressure of 0.3 MPa, the hybrid catalyst $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ could give a very high biphenyl yield (18.3%) through aerobic oxidative dehydrogenation of benzene, reasonably in agreement with the present observation that low oxygen pressure facilitates the generation of biphenyl. Additionally, that domination of biphenyl product was achieved in the absence of the buffer LiOAc [15], also in accordance with the result in Table 1. The effects of reaction time, reaction temperature and catalyst amount shown in Figs. 1(B)–(D) indicate that 4 h, 120 °C and 0.1 g (0.16 mol%) $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ were suitable reaction parameters. Under more severe conditions (*i.e.*, $t > 4$ h, $T > 120$ °C, catalyst amount > 0.1 g), the phenol yield decreased reversely due to the continuous over-oxidation of phenol into the deep-oxidation byproduct tar, because the product phenol is more reactive than the substrate benzene in this strong oxidation environment [18].

From all the above results, the high phenol yield of 9.8% can be achieved over the hybrid catalyst $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ without being aided by any sacrificial reducing reagents under the optimal conditions: 0.1 g (0.16 mol%) catalyst, 2 mL HOAc with 4 mL H_2O as the solvent, 2.0 MPa O_2 , 0.2 g LiOAc, 120 °C, 4 h. At this moment, TON (turnover number: mmol phenol / mmol Pd) and TOF (turnover frequency: mmol phenol / (mmol Pd \times h reaction time)) for $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ are 30.6 and $7.65 h^{-1}$, respectively. Therefore, both the phenol yield and TON/TOF values given by the

heterogeneous catalyst in this work are much higher than those over the heterogeneous catalysts reported previously (*i.e.*, $Pd(OAc)_2$ and $PMoV_2$ simultaneously immobilized on mesoporous silica with phenol yield 0.7%, TON 3.68 and TOF $0.368 h^{-1}$ [11]; and nanoparticle $Pd-VO_x$ with phenol yield 5.2%, TON 26 and TOF $5.2 h^{-1}$ [14]). The comparison implies that connecting $Pd(OAc)_2$ with $PMoV_2$ into the ionic structure of $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$, rather than immobilizing $Pd(OAc)_2$ and $PMoV_2$ onto a support, must have led to a more remarkable synergistic effect between the two catalytically active moieties. For the homogeneous catalytic system of $Pd(OAc)_2$ with $PMoV_2$, it has been established (Fig. S2) that $Pd(OAc)_2$ first electrophilically attacks the substrate benzene to form the palladium acetate intermediate C_6H_5PdOAc . Then $PMoV_2$ oxidizes C_6H_5PdOAc to phenylpalladium(IV) triacetate and becomes the reduced state $PMoV_2^{red}$ itself. Afterwards the phenylpalladium(IV) triacetate decomposes to produce $Pd(OAc)_2$ and phenyl acetate, with the latter being finally hydrolyzed to phenol. On the other hand, the $PMoV_2^{red}$ is oxidized to its original form $PMoV_2$ to complete the catalytic cycle [8,10]. For the present catalyst $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$, on the one hand, $Pd(OAc)_2$ and $PMoV_2$ are confined in one ionic structure with the shortened distance of the two moieties within molecular level, which may enable $PMoV_2$ to oxidize the intermediate C_6H_5PdOAc from the neighboring Pd(II) site more efficiently. On the other hand, higher oxidation states of coordination compounds might be attainable in the presence of a conjugate polyoxometalate, proposed by Neumann [19]. Accordingly, the Pd(IV) species may be achieved more easily from Pd(II) when it is conjugated by $PMoV_2$, which benefits the valence change between Pd(IV) and Pd(II). It is thus suggested that the above two factors mostly account for the high activity of $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$.

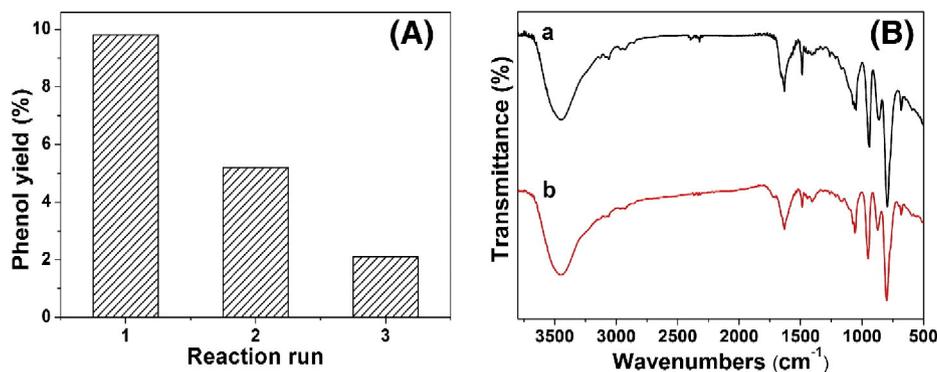


Fig. 2. (A) Catalytic reusability of $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ for aerobic oxidation of benzene to phenol; reaction conditions: 0.1 g catalyst (0.16% mol%), 2 mL HOAc with 4 mL H_2O (solvent), 2.0 MPa O_2 , 0.2 g LiOAc, 120 °C, 4 h. (B) IR spectra of $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$: (a) fresh sample, and (b) recycled sample.

As a heterogeneous catalyst, $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ was recovered by filtration and reused in the next run at the optimal conditions. The recovery rate was weighted to be ca. 93.5%, and the reusability test showed gradual decrease in phenyl yields, from 9.8% for the first run to 5.2% and 2.1% for the following two runs (Fig. 2(A)). The IR spectrum for the recovered catalyst exhibited similar characteristic bands to those of the fresh one (Fig. 2(B)), revealing the good structural durability of the catalyst in this reaction. The elemental analysis found C 22.38 wt.% for the recycled catalyst, higher than that for the fresh catalyst (C 19.11 wt.%). ICP-AES analysis for the catalyst-removed liquid phase of the reacted mixture only detected trace amount of the leached Pd species. These results suggest that the decrease in phenol yields is mainly due to the gradual contamination of the active surface sites by the created tar byproduct. Improving the reusability of the heterogeneous catalyst for this reaction still needs further attempt.

4. Conclusions

In this work, the ionic hybrid $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ is demonstrated to be a highly active heterogeneous catalyst for reductant-free aerobic oxidation of benzene to phenol. Reaction conditions are optimized as follows: 0.1 g (0.16 mol%) catalyst, 2 mL HOAc with 4 mL H_2O as the mixed solvent, 2.0 MPa O_2 , 0.2 g LiOAc, 120 °C, and 4 h, at which it shows the higher phenol yield of 9.8% than previously reported heterogeneous catalysts. Confining of the two active sites of $Pd(OAc)_2$ and $PMoV_2$ within the ionic structure of $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$, as well as the facilitation of $Pd(IV)$ – $Pd(II)$ valence change in catalytic cycle by the conjugated polyoxometalate $PMoV_2$, are suggested to account for the highly catalytic efficacy.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2014.09.031>.

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