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A polyoxometalate-based Pd^{II}-coordinated ionic solid catalyst for heterogeneous aerobic oxidation of benzene to biphenyl

Low-temperature heterogeneous aerobic oxidation of benzene to biphenyl is achieved over an ionic solid catalyst *via* a unique intramolecular electron transfer mechanism. The strategy for synthesizing the ionic catalyst is pairing Keggin Polyoxometalate-anions with nitrile-tethered Pd^{II}-coordinated ionic liquid cations.

As featured in:



See Jun Wang *et al.*,
Chem. Commun., 2012, **48**, 5721.

Cite this: *Chem. Commun.*, 2012, **48**, 5721–5723

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A polyoxometalate-based Pd^{II}-coordinated ionic solid catalyst for heterogeneous aerobic oxidation of benzene to biphenyl†Pingping Zhao,^a Yan Leng,^b Mingjue Zhang,^a Jun Wang,^{*a} Yajing Wu^a and Jun Huang^a

Received 16th March 2012, Accepted 12th April 2012

DOI: 10.1039/c2cc31919e

An ionic solid catalyst by pairing Keggin polyoxometalate-anions with Pd^{II}-coordinated nitrile-tethered ionic liquid cations was synthesized, characterized, and tested for aerobic oxidation of benzene to biphenyl. A unique heterogeneous intramolecular electron transfer mechanism is proposed to understand its high activity.

As an important intermediate for synthesizing polymers and liquid crystals, biphenyl is industrially produced by vapour phase dimerization of benzene.^{1,2} Ullmann³ and Suzuki reactions⁴ also produce biphenyl, but lead to by-products like copper iodide or boric salts. Therefore, a greener low-temperature liquid-phase coupling reaction of benzene affording biphenyl becomes an attractive topic. Actually, Pd-catalyzed liquid-phase aerobic coupling of benzene has been studied extensively; however, the system is a high pressure homogeneous reaction with low yields.⁵

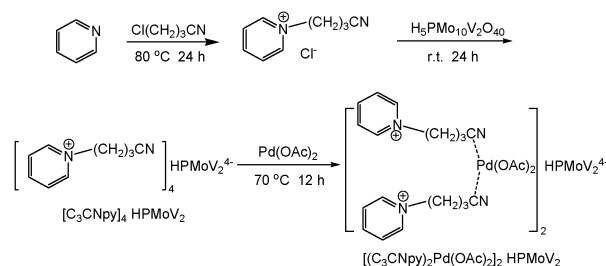
The high valence metal ions in polyoxometalates (POMs) are known to be catalytically active sites for various oxidation reactions.⁶ In Pd-catalyzed acetoxylation, acetalization and Wacker-type oxidation with O₂,⁷ POM was used as a cocatalyst to reoxidize Pd⁰ to Pd^{II}.⁸ Neumann and Etdedgui⁹ coordinated phenanthroline-crown ether with both Pd^{II} and H₅PMo₁₀V₂O₄₀ for accelerating electron transfer from Pd⁰ to Pd^{II} in Wacker oxidation of alkenes. Scheuermann *et al.*¹⁰ combined palladium with a non-POM cocatalyst, which afforded the novel hybrid Pd^{II}-complex of 1,4-quinone-substituted bis-(pyrazol-1-yl)methane. Thus far only the homogeneous Pd–POM–O₂ system has been reported to afford biphenyl from oxidative coupling of benzene,¹¹ wherein the POM and Pd^{II} individually acted as the cocatalyst and major catalyst. To the best of our knowledge, no low-temperature heterogeneous catalysis system has appeared as yet.

On the other hand, functionalized ionic liquids (ILs) have attracted growing interest,¹² and the coordinating group-tethered ILs may immobilize metal catalysts.¹³ Further, POM-anions have been used as counteranions for task-specific IL catalysts.¹⁴

We recently prepared a series of solid-state POM-based IL catalysts for heterogeneous organic transformations.¹⁵ Accordingly, we think it rational to prepare a composite catalyst by pairing POM-anions with Pd^{II}-coordinated IL-cations such that the catalyst contains Pd^{II} and POM sites in an IL-like structure. The resultant ionic solid may be a novel heterogeneous catalyst for aerobic oxidation of benzene to biphenyl.

This communication reports a POM-based Pd^{II}-coordinated ionic catalyst [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ (Scheme 1) prepared by pairing the nitrile-tethered pyridinium IL-cation^{13a} with the Keggin POM-anion HPMo₁₀V₂O₄₀⁴⁻ (HPMoV₂), followed by coordinating palladium acetate Pd(OAc)₂ with the nitriles. Characterization results of CHN elemental analysis, TG, FT-IR, UV-vis, ESR, SEM, XRD, MS, ¹H and ¹³C NMR (ESI†), and the catalytic tests demonstrate that the catalyst leads to a highly efficient heterogeneous system for aerobic oxidation of benzene to biphenyl. An intramolecular electron transfer mechanism is proposed to understand its much higher activity over the earlier-reported homogeneous Pd–POM–O₂ system.

The elemental analysis (found: C 19.02 wt%, N 3.96 wt%, H 2.00 wt%; calculated: C 19.07 wt%, N 4.04 wt%, H 2.06 wt%) and the TG result (Fig. S1, ESI†) (weight loss found: 28.2 wt%; calculated: 30.0 wt%) confirm the chemical composition of [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂. The SEM image (Fig. S2, ESI†) illustrated micron-sized particles, as a solid up to 180 °C. The XRD pattern (Fig. S3, ESI†) showed an amorphous phase for this solid containing large-volume cations and anions, different from the crystal structure of its parent H₅PMoV₂O₄₀.¹⁶ Moreover, the solid is insoluble in commonly used solvents such as water, acetic acid, DMSO, and even in the oxidative media of molecular oxygen or hydrogen peroxide. These features allow trying it as a heterogeneous catalyst for aerobic oxidation of benzene.



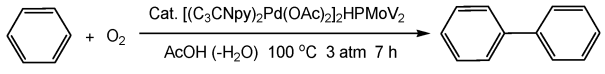
Scheme 1 Synthesis of the POM-based Pd^{II}-coordinated ionic catalyst [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂.

^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China.

E-mail: junwang@njut.edu.cn; Fax: +86-25-83172261; Tel: +86-25-83172264

^b School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

† Electronic supplementary information (ESI) available: Experimental details, optimization of reaction conditions and catalyst characterizations. See DOI: 10.1039/c2cc31919e

Table 1 Catalytic performance of various catalysts for the oxidative coupling reaction of benzene with O₂^a


Entry	Catalyst	Solubility in reaction	Y ^b (%)	Sel ^c (%)
1	[(C ₃ CNpy) ₂ Pd(OAc) ₂] ₂ HPMoV ₂	Insoluble	18.3	88.0
2	Pd ₂ HPMoV ₂	Insoluble	8.2	93.9
3	H ₃ PMoV ₂ O ₄₀ -Pd(OAc) ₂	Soluble	10.4	83.5
4	H ₃ PMoV ₂ O ₄₀ -Pd(OAc) ₂ ^{11b}	Soluble	7.1	88.8
5	[(C ₃ CNpy) ₂ Pd(OAc) ₂] ₂ PMoV ₁	Insoluble	16.1	91.0
6	[(C ₃ CNTMA) ₂ Pd(OAc) ₂] ₂ HPMoV ₂	Insoluble	18.4	81.8
7	[(C ₃ CNmim) ₂ Pd(OAc) ₂] ₂ HPMoV ₂	Insoluble	2.2	93.4
8	[(C ₃ CNpy) ₂ PdCl ₂] ₂ HPMoV ₂	Insoluble	2.8	89.8

^a Reaction conditions: catalyst (0.043 mmol), benzene (30 mmol), HAc (6.6 ml), H₂O (3.4 ml), O₂ (3 atm), 100 °C, 7 h; for entry 3: H₃PMoV₂O₄₀ (0.043 mmol), Pd(OAc)₂ (0.086 mmol). ^b Yields based on benzene. ^c Selectivity to biphenyl; byproducts: *o*-, *m*-, *p*-terphenyls, and phenol.

Catalytic performance of [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ for oxidative coupling of benzene with O₂ is shown in Table 1. The observed liquid–solid biphasic catalysis system exhibited a yield of 18.3% for biphenyl with a selectivity of 88.0% (entry 1; see Fig. S4, ESI† for influence of reaction conditions). In contrast, the inorganic salt Pd₂HPMoV₂, a heterogeneous catalyst prepared by replacing the four protons of H₃PMoV₂O₄₀ with two Pd^{II} ions, gave a remarkably lower yield of 8.2% (entry 2). The conventional homogeneous Pd–POM–O₂ system tested under similar conditions (entry 3) showed a yield of 10.4%. The previous data, 7.1% yield obtained at 90 °C, 1 atm O₂, 15 h in a homogeneous Pd–POM–O₂ system,^{11b} are also included in Table 1 (entry 4). Very clearly, the present heterogeneous system is much more active than the homogeneous Pd–POM–O₂ analogues.

As the single V-containing POM-anion PMo₁₁V₁O₄₀⁴⁻ (PMoV₁) was used instead of the double V-containing PMoV₂ (entry 5), or pyridine was substituted with trimethylamine (TMA) in the IL-cation (entry 6), the control samples [(C₃CNpy)₂Pd(OAc)₂]₂PMoV₁ and [(C₃CNTMA)₂Pd(OAc)₂]₂HPMoV₂ were heterogeneous catalysts and exhibited good yields and selectivities. This observation suggests quite a flexibility for the chemical composition of this kind of ionic solid catalysts. However, when pyridine was replaced with imidazole (mim) in the IL-cation, the resultant [(C₃CNmim)₂Pd(OAc)₂]₂HPMoV₂ gave a very low yield of 2.2% (entry 7). Lastly, the control sample [(C₃CNpy)₂PdCl₂]₂HPMoV₂ obtained by replacing the palladium salt Pd(OAc)₂ with PdCl₂ also presented a much lower yield of 2.8% (entry 8). This result is in agreement with the lower activity of PdCl₂ over Pd(OAc)₂ in the homogeneous oxidative coupling of benzene with H₃PMoV₂O₄₀ as the cocatalyst.^{11b}

Spectral characterization was conducted to obtain insight into the structural features and intermolecular electronic interactions of [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂. As shown in Fig. 1(A), the IR bands for the Keggin structure of neat H₃PMoV₂O₄₀ occurred at 1060, 961, 864 and 788 cm⁻¹ (curve a).¹⁷ The four bands were detected for the two POM–IL hybrids (curves b and c), indicating that the Keggin structure of the POM moiety was well preserved. However, for [C₃CNpy]₄HPMoV₂, the P–O vibration at 1060 cm⁻¹ split

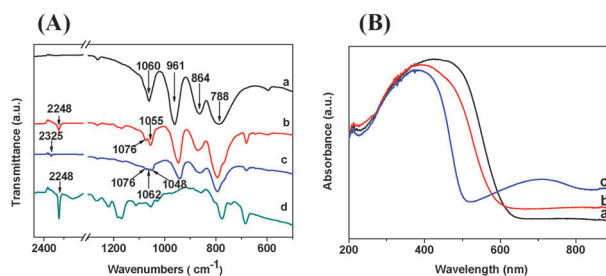


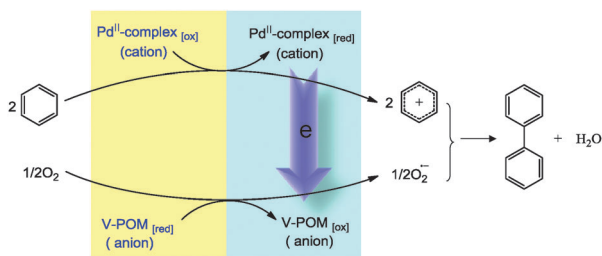
Fig. 1 (A): FT-IR spectra of (a) H₃PMo₁₀V₂O₄₀, (b) [C₃CNpy]₄HPMoV₂, (c) [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ and (d) [C₃CNpy]Cl. (B): UV-vis spectra of (a) H₃PMo₁₀V₂O₄₀, (b) [C₃CNpy]₄HPMoV₂ and (c) [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂.

into two bands at 1055 and 1076 cm⁻¹, implying the distortion of POM's Keggin framework due to the extension of the conjugated π electrons from cations.¹⁸ For [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂, the 1055 cm⁻¹ band further split into 1048 and 1062 cm⁻¹ by the involvement of the larger Pd^{II}-complex cation. In addition, the Pd-free sample [C₃CNpy]₄HPMoV₂ presented a similar nitrile stretching vibration at 2248 cm⁻¹ to that of the IL precursor [C₃CNpy]Cl (curve d), but for the Pd^{II}-complex sample, the band shifted to 2325 cm⁻¹. This is a strong indication for the formation of Pd^{II}-coordinated nitrile structure.¹⁹ These IR results demonstrate well the electron extension from the pyridinium-based Pd^{II}-nitrile complexed organic cations to the inorganic POM-anions. Also, the strong and broad IR band at 3452 cm⁻¹ (Fig. S5, ESI†) for H–O vibrations implies the intermolecular hydrogen bonding networks, which may account for the solid nature of the ionic compound [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂.²⁰

In the UV-vis spectra shown in Fig. 1(B), the broad absorption band at 432 nm for H₃PMo₁₀V₂O₄₀ is assigned to the charge transfer O²⁻ → V⁵⁺ in Keggin POM.²¹ In contrast, for the intermediate [C₃CNpy]₄HPMoV₂, the band shifted to 388 nm due to a stronger charge transfer aided by the neighbouring IL-cations.²⁰ Moreover, for the Pd-bearing [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂, the band was narrower and further shifted to 379 nm, accompanying a large broad one at 500–800 nm for V^V → V^{IV}. The existence of the reduced V^{IV} species is due to the extremely strong electron transfer to POM-anions from the Pd^{II}-complex organic cations.²² Furthermore, the much sharper and stronger ESR signals for [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ (Fig. S6, ESI†) confirm the coexistence of V^V/V^{IV} species.²³

From the above-mentioned spectral results, one can conclude that the redox capability of POM-anions in [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ should have been significantly tuned by the intramolecular charge transfer from the ionically linked Pd^{II}-coordinated organic cations, which is responsible for its high activity for aerobic oxidation of benzene.²⁴

A reaction mechanism over the [(C₃CNpy)₂Pd(OAc)₂]₂HPMoV₂ catalyst is proposed in Scheme 2, wherein the coexistence of V^V/V^{IV} species arising from the intramolecular electron transfer from the reduced state of Pd^{II}-complex cation (Pd^{II}-complex_[red]) to the oxidized state of POM-anion (V-POM_[ox]) has been evidenced earlier. It is because of the intramolecular electron transfer that the transitional active sites of cations and anions are created: the oxidized state of the Pd^{II}-complex cation (Pd^{II}-complex_[ox]) with the



Scheme 2 Proposed intramolecular electron transfer process for $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ -catalyzed heterogeneous aerobic oxidation of benzene to biphenyl.

reduced state of the POM-anion (V-POM_[red]). It is suggested that phenyl cations are produced by the attack of the Pd^{II}-complex_[ox] on the benzene rings,²⁵ while the active oxygen species O₂⁻ are formed from the activation of molecular oxygen by V-POM_[red]. Simultaneously, Pd^{II}-complex_[ox] with V-POM_[red] returns to the original state of the Pd^{II}-complex_[red] with POM_[ox]. In this case, the two reactive intermediates, phenyl cation and O₂⁻, would readily react, giving biphenyl. This heterogeneous intramolecular electron transfer route reflects the rational design of the catalyst involving two active centers Pd^{II} and V-POM within an ionic solid structure. This new route is essentially different from the previous homogeneous intermolecular electron transfer process, catalyzed individually by Pd(OAc)₂ and V-POM (Scheme S1, ESI[†]).²⁶ In addition, the much lower activity of the imidazolium-based catalyst $[(C_3CNmim)_2Pd(OAc)_2]_2HPMoV_2$ than the pyridinium one is mostly because of the hindering of the intramolecular electron transfer by the strong interaction between the highly active C-2 protons of imidazole rings and nitriles.²⁷

After reaction, $[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$ was easily recovered by filtration and vacuum dried with a recovery rate of 96.8%. The reused catalyst showed a similar selectivity (86.4%) to the fresh one, but the yield dropped to 6.8%. The durable structure of the recovered catalyst suggested by the unchanged IR curve (Fig. S7, ESI[†]) seems responsible for the stable selectivity. The very slight leached amount of Pd (1.8 wt%) revealed by the ICP-AES analysis for recovered catalyst cannot account for the largely decreased yield. Moreover, the elemental analysis for the recycled catalyst found C 23.67 wt%, N 3.16 wt%, and H 2.82 wt%. Compared to the fresh catalyst, the recovered one showed a slight increase in H content, but a significant increase in C content, which indicates that the large decrease in yield over the recycled catalyst is possibly due to the coking during the heterogeneous reaction. To increase the catalyst's reusability, further research is still required.

In this study, we design, synthesize, characterize, and catalytically evaluate a new Pd^{II}-coordinated POM-IL hybrid catalyst. The catalyst is synthesized by pairing Keggin POM-anions with Pd^{II}-coordinated nitrile-tethered IL-cations. The novelty of this strategy is the involvement of Pd^{II} and V-POM active sites in an ionic solid, leading to a heterogeneous aerobic coupling of benzene. The catalyst shows much higher activity and easier recoverability than the previous homogeneous Pd-POM-O₂ system. A unique intramolecular electron transfer mechanism is proposed to understand the reaction results. Despite the decrease in yield over the recovered catalyst, we think this result takes a step toward the heterogeneous aerobic oxidative coupling of benzene to biphenyl.

The authors thank greatly the Key Programme of National Natural Science Foundation of China (No. 21136005).

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