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A Promising Coupled Process of Pd/γ-Al_2O_3–NH_4VO_3 Catalyzing the Hydroxylation of Benzene with Hydrogen Peroxide Produced In Situ by an Anthraquinone Redox Route

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Abstract A coupled process, of which Pd/γ-Al_2O_3–NH_4VO_3 catalyzed the hydroxylation of benzene with hydrogen peroxide produced in situ by an anthraquinone (AQ) redox route, was carried out via a sealed gaseous inner-circulated device under the atmospheric pressure. By means of such process, 0.57% of benzene conversion, 100% of phenol selectivity and 26.6% of anthraquinone-utilized efficiency were achieved upon the mixed Pd/γ-Al_2O_3–NH_4VO_3 (V/Pd molar ratio for 4) in the presence of benzene/acetic acid (4v/10v). Above all, after the coupled reaction system was recycled three times, the accumulated phenol amount could achieve ca. 0.833 mmol and its average value (ca. 0.278 mmol) was slightly higher than phenol amount obtained in the first run (ca. 0.255 mmol), indicating that such coupled reaction system could be recycled efficiently. In addition, a synergistic mechanism was proposed to explain the favorable effect of V compound on the Pd/γ-Al_2O_3 catalyst.

Keywords Benzene · Phenol · Anthraquinone · In situ · Hydrogen peroxide

1 Introduction

Until now, the dominant process for the production of phenol is the Hock-process [1] that generally involves multi-step syntheses and generates large quantities of by-product acetone. Therefore, the direct synthesis of phenol from benzene is an alternative way to overcome these problems. For example, the direct hydroxylation of benzene by N_2O [2–4] expects to substitute the Hock-process if N_2O can be obtained cheaply as a by-product. On the other hand, the hydroxylation of benzene with hydrogen peroxide (H_2O_2) over various catalysts has been appreciated as a green process [5–7]. However, the oxidant H_2O_2 has some serious drawbacks, such as expensive, inherently corrosive, easily decomposable and especially, in high concentrations, is prone to be lower selectivity etc. Thus, for a long time much attention has been paid to the direct hydroxylation of benzene by O_2 (air) with the assistance of H_2 [8–10], CO [11] or ascorbate [12, 13] and transition-metal catalyst, such as Cu, Pd, or Pt. Nevertheless, there is a potential risk of explosion when H_2 (CO) and O_2 are fed simultaneously and ascorbate as a consumptive reagent might be costly. Therefore, it is highly desirable to develop a safe, cheap and recycle procedure for the hydroxylation of benzene. In principle, the hydroxylation of benzene with H_2O_2 produced in situ via anthraquinone (AQ) redox approach is likely to achieve above goals [14], being due to the following advantages: (i) The potential explosion risk of the O_2–CO, especially O_2–H_2 mixture system can be avoided by use of alternately feeding H_2 and O_2; (ii) Such coupled reaction system may be recycled in comparison with the O_2–ascorbate system. Inspiringly, a similar coupled process has been successfully applied to the epoxidation of olefins [15–17], but only several patents concerned about the coupled process for aromatics oxidations [18, 19]. Herein, we reported the remarkable results obtained from employing Pd/γ-Al_2O_3 and NH_4VO_3 to catalyze the coupled hydroxylation of benzene with H_2O_2 produced in situ via AQ redox route.

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2 Experimental

2.1 Catalyst Preparation

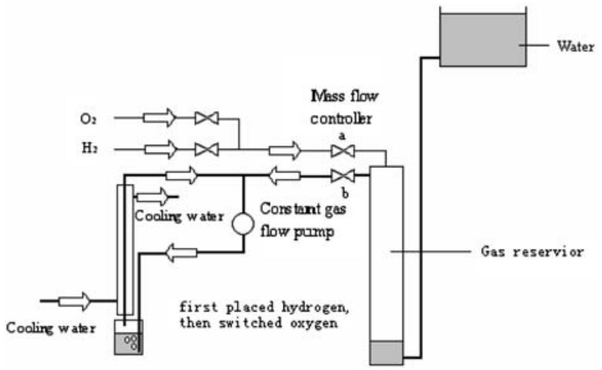
Pd (0.5%)/γ-Al_2O_3 was prepared by the conventional impregnation method. Palladium acetate (ACRŌS+ 47.5%Pd) was dissolved in acetonitrile and then γ-Al_2O_3 (S_g = 167 m^2 g^{-1}, V_g = 1.58 m^3 g^{-1}) was immersed in the solution for 20 h without stirring. After evaporation of acetonitrile with the rotary evaporator at 333 K, the left powder was dried and calcined in air at 773 K for 6 h, then reduced in H_2 atmosphere (30 ml min^{-1}) at 573 K for 2 h.

2.2 Characterization of Catalysts

The diffusion reflection UV–Vis (DRUV-visible) and infrared spectra of fresh and recycled Pd/γ-Al_2O_3 catalysts were recorded on a Hitachi U3310 Diffusion reflection UV–Vis spectrometer and a Nicolet Nexus 510P spectrometer, using KBr pellets, respectively.

2.3 Catalytic Testing

An inner-circulated bubble apparatus was designed to recycle H_2 and O_2, as well as avoid the loss of benzene, as depicted in Scheme 1. A typical run was described as follows: 0.1 g of Pd/γ-Al_2O_3, 0.002 g of NH_4VO_3, 0.2 g of AQ, 4 ml of benzene and 10 ml of anhydrous acetic acid were added to a 50 ml of the two-necked flask equipped with magnetic stirrer, thermometer and a water-cooled condenser. The hydrogenation reaction was performed at 313 K for 2 h under magnetically stirring and cyclically introducing H_2. After the reaction, the stored H_2 was then replaced by O_2. The following oxidation procedure was the same as the above described hydrogenation one except for cyclically introducing O_2 under the atmospheric pressure. Finally, the reaction mixture removed the solid catalyst by centrifuging, was analyzed by use of Agilent1100 HPLC made in USA with ethyl p-hydroxybenzoate as an internal standard (ODS HYPERSIL, 4.6 × 250 mm, eluent methanol/water = 55/45, flow rate = 0.8 ml/min, UV detector λ = 272 nm). The products were identified by use of GC/MS (Warian GC 3900-MS 2100T; injector temperature: 523 K, column temperature from 353 K to 473 K for β = 7K/min).



Scheme 1 Overview of experimental equipment used in this study

3 Results and Discussions

3.1 Characterization

Figure 1 shows the DRUV-visible spectra of fresh and recovered Pd/γ-Al_2O_3 catalysts. The sharp absorption band near 330 nm and the broad background absorption band in the region 400–700 nm could be observed upon the fresh and recovered samples, the two bands correspond to the charge transfer of the absorbed PdO_X and metallic Pd species, respectively, suggesting that part of the Pd is in the +2 oxidation state and the remaining in the zerooxidation state in the samples, the formation of Pd^{2+} species on the fresh sample is likely to a prolonged exposure of Pd^0 species to air. Similar observations were made by Shetti et al. [20] in the DRUV-visible spectra of Pd–TS-1 samples. It is noteworthy that two new bands near 300 and 394 nm, attributable to the V^{5+} and V^{4+} species, respectively [21], can also be observed upon the recovered sample, indicating that the adsorption of VO_3^- ions inside the pores of Pd/γ-Al_2O_3 has occurred during the reaction.

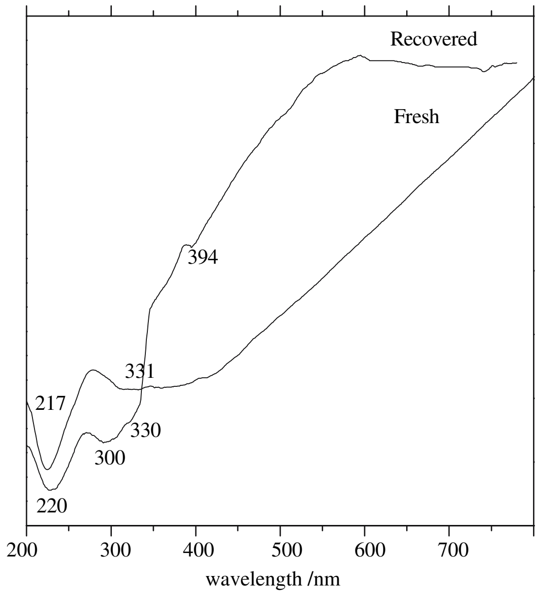


Fig. 1 DRUV-visible spectra of two samples

To further investigate the active V species adsorbed on Pd/γ-Al_2O_3, the above samples were reduced once again at 313 K for 12 h under H_2 and then immediately recorded by FT-IR spectrometer under the atmosphere (see Fig. 2). Compared to the fresh sample, the recovered one shows absorptions at 979 and 902, 625, 663, 567 cm^{-1}, attributable to the characteristic oxo stretching vibration ν(V=O) and the C_{2v} peroxo vibrations, respectively [22, 23], indicating that the newly reduced V species on Pd/γ-Al_2O_3 can activate molecular oxygen to form the V-peroxo intermediates, as reported previously by literature [24].

3.2 Effect of Transition-Metal Compounds

In benzene/anhydrous acetic acid media similar to the AQ working solution, a series of transition-metal compounds as co-catalysts were screened to promote the coupled process catalyzed by Pd/γ-Al_2O_3 and the results are shown in Fig. 3. In each case, the only product phenol was detected by HPLC and further identified by GC/MS. This is likely that H_2O_2 produced in situ has much lower concentration and can avoid the further oxygenation of phenol compared to directly adding H_2O_2 (entries 12–13 in Table 1 give the modest phenol selectivity) [25]. Figure 4 further shows that on addition of co-catalysts to the coupled system could significantly influence the formation of phenol. Among the used co-catalysts, V_2O_5, and especially NH_4VO_3 exhibited a more favorable effect than $FeSO_4$, whereas the other co-catalyst such as $Cu(NO_3)_2$, $Cu(DDS)_2$ and $Fe(DDS)_3$ gave a negative effect on the coupled reaction (Herein, $Cu(DDS)_2$ and $Fe(DDS)_3$, which stands for Cu- and Fe-dodecanesulfinate, respectively, were prepared according to the procedures reported in previous literature [26]).

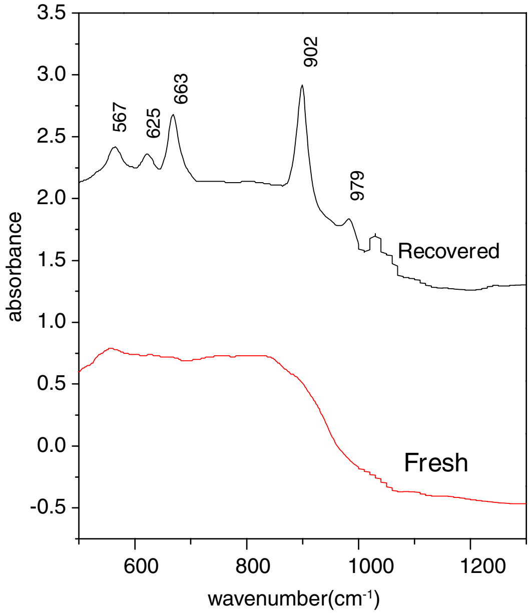


Fig. 2 FT-IR spectra of two samples

3.3 Effects of the Amount of NH_4VO_3 and the Volume Ratio of Benzene to Acetic Acid

The most efficient co-catalyst NH_4VO_3 was then used to study the effects of its amount and the volume ratio of benzene to acetic acid on the formation of phenol and the results are shown in Table 1. When the amount of NH_4VO_3 and the volume ratio of benzene to acetic acid were increased, the formation of phenol once increased and achieved a maximum (ca. 0.255 mmol) at 2 mg of NH_4VO3 and benzene/acetic acid ratio for 4:10, thereafter decreased to some extent (see entries 1–8). The described above results suggest that the homogeneous substrates formed easily in the optimum benzene/acetic acid ratio, may be favorable for improving the formation of phenol. This can be further confirmed from the results of entries 9 and 10, in which adding water to benzene/acetic acid (4/10) or using ethyl-anthraquinone instead of AQ all resulted in an obvious decrease in phenol amount, being due to the appearance of the heterogenized substrates. On the other hand, the co-catalyst NH_4VO_3 should be a nice match for the main-catalyst Pd/γ-Al_2O_3, Interestingly, this match value of V to Pd for 4 just corresponds to the optimum V/Pt atomic ratio on Pt/SiO_2 combined NH_4VO_3 reported previously by literature [8]. Several separated experiments were designed to check the role of Pd/γ-Al_2O_3 on the oxidation stage and the obtained results are listed in Table 1. Entry 11 shows that formation of phenol sharply decreased provided that Pd/γ-Al_2O_3 was removed during the oxidation stage and entries 12–13 further show that the presence of Pd/γ-Al_2O_3 in NH_4VO_3 catalyzing the hydroxylation of benzene with H_2O_2 agent instead of the in situ one, led to the decrease in the formation of phenol

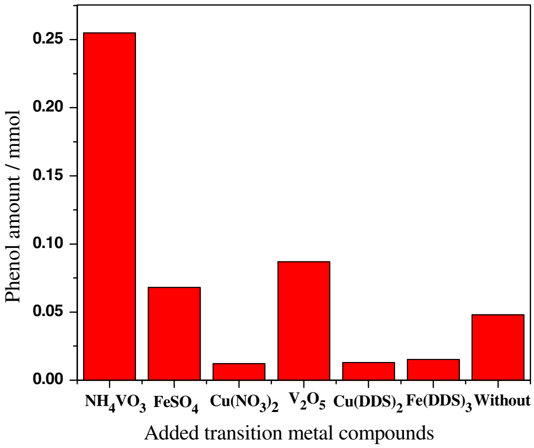


Fig. 3 The effect of transition-metal compounds

Table 1 Effects of NH_4VO_3 amount and reaction media on the coupled reaction[a]

Entry	Benzene/HOAc (ml)	NH_4VO_3 (mg)	Phenol amount (mmol)	Benzene conversion (%)	AQ utilization efficiency (%)[b]
1	4:10	0	0.048	0.11	5.1
2	4:10	1	0.124	0.28	12.9
3	4:10	2	0.255	0.57	26.6
4	4:10	3	0.233	0.52	24.3
5	1:10	2	0.032	0.28	3.3
6	2:10	2	0.083	0.37	8.6
7	6:10	2	0.156	0.23	16.2
8	8:10	2	0.133	0.15	13.8
9[c]	4:10	2	0.157	0.35	16.3
10[d]	4:10	2	0.166	0.37	17.3
11[e]	4:10	2	0.054	0.12	5.6
12[f]	4:10	2	0.51	1.33	–
13[g]	4:10	2	0.76	1.69	–

[a] 0.1 g of Pd (0.5 wt%)/γ-Al_2O_3, reaction temperature for 313 K, the rate of gas for20 ml/min, reaction time for 2 h in the stage of hydrogenation and for 3 h in the stage of oxygenation

[b] AQ (anthraquinone) utilization efficiency based on mmol of phenol/mmol of AQ

[c] Adding 2 ml of H_2O

[d] Ethyl-anthraquinone instead of AQ

[e] The absence of Pd/γ-Al_2O_3 during the oxidation stage

[f] Directly adding hydrogen peroxide 1.2 ml, phenol selectivity 83.7%

[g] Directly adding hydrogen peroxide 1.2 ml without Pd/γ-Al_2O_3, phenol selectivity 75.2%

compared to its absence, suggesting that Pd/γ-Al_2O_3 should participate in the oxidation of hydroanthraquinone (HAQ) to form H_2O_2 rather than the hydroxylation of benzene.

3.4 Effect of the Time of Hydrogenation and Oxygenation

The effects of the hydrogenation and oxidation time on the formation of phenol are shown in Fig. 4. The formation curves of phenol sharply ascends with the reaction time and then levels off at the reaction time >2 h for the hydrogenation stage and 3 h for the oxidation stage, indicating that the optimum hydrogenation and oxidation time are 2 h and 3 h, respectively.

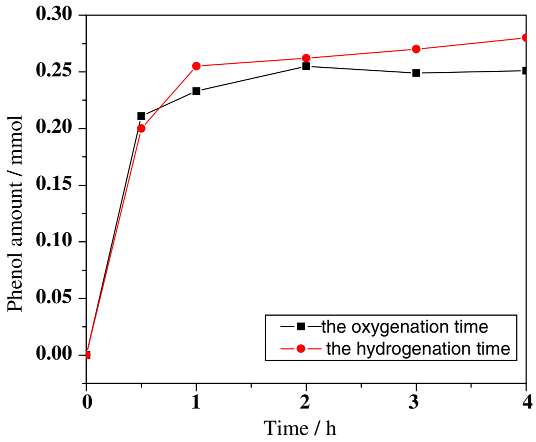


Fig. 4 Effect of the times of hydrogenation and oxygenation reactions

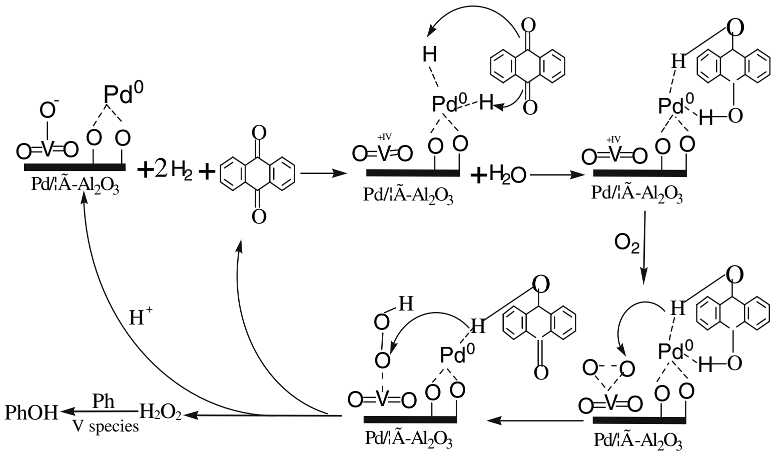
3.5 Recycle Tests

From a practical synthetic viewpoint, it is very important to realize the recycle of AQ and Pd/γ-Al_2O_3. Thus, the above very efficient coupled system (see entry 3 in Table 1) was repeatedly performed for three times and the results obtained are shown in Table 2. It is evident that accumulated benzene conversion and phenol amount after the third run amount to 1.85% and 0.833 mmol, respectively, and both

Table 2 The recycled results of the coupled reaction system[a]

Entry	Repeated times	Phenol amount (mmol)	Benzene conversion (%)	AQ utilization efficiency (%)
1	1st	0.255	0.57	26.6
2	2nd	0.506	1.12	52.7
3	3rd	0.833	1.85	86.7

[a] The recycled procedures were carried out in the same manner as the experimental section, Reactants and catalysts were not treated. The accumulated results after each recycle were listed in this table



Scheme 2 The synergistic mechanism for the hydroxylation of benzene with hydrogen peroxide produced in situ by an anthraquinone redox route

average values (ca. 0.62% and 0.278 mmol) were slightly higher than the results in the first run (ca. 0.57 and 0.255 mmol), forcefully indicating the coupled reaction system could be highly efficiently recycled without any loss.

3.6 Discussions

Based on the described above results, a synergistic catalytic mechanism, similar to one reported by Shetti et al. [20], is proposed for the coupled reaction, as depicted in Scheme 2. Namely, the activated hydrogen molecule on the Pd^0 species easily reacts with AQ to form HAQ and the reduction of the V^{5+} species to the V^{4+} one is simultaneously achieved during the hydrogenation stage. The resulting V^{4+} species then activates oxygen molecule to form the V-peroxo species, just as described in the above IR spectra, and the V-peroxo species successively oxidizes the HAQ adsorbed on the Pd^0 sites back to AQ with concomitant generation of H_2O_2. Finally, the hydroxylation of benzene with the resulting H_2O_2 is achieved on the V catalyst.

4 Conclusion

In summary, we have developed a coupled process of which $Pd\ /\gamma\text{-}Al_2O_3\text{--}NH_4VO_3$ catalyzed the direct hydroxylation of benzene with H_2O_2 produced in situ by an AQ redox route under the atmosphere. Furthermore, this coupled reaction system could be highly efficiently recycled for three times without any loss. It is anticipated that it is a promising route provided that benzene conversion and AQ utilization efficiency in each single run are further improved.

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