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Hydroxylation of benzene to phenol under air and carbon monoxide catalyzed by molybdovanadophosphates

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ABSTRACT

Direct conversion of benzene to phenol was achieved by allowing it to react with a mixed gas of air and CO in the presence of HPMoV and a very small amount of 5%Pd/C in aqueous acetic acid at 150 °C for 2 h. The TON of HPMoV for the formation of phenol goes up to over 1300. The active species of the present reaction is thought to be V⁴⁺ generated from HPMoV catalyst by the reduction with CO. The role of the Pd species seems to promote the generation of V⁴⁺ from HPMoV. This method is expected to provide a direct route to phenol from benzene.

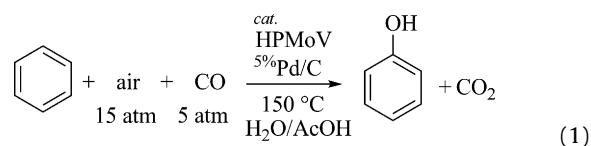
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1. Introduction

Phenols are important raw materials for the synthesis of a wide variety of chemicals like phenol resins, dyes, antioxidants, and pharmaceuticals [1]. In 2005, about 7 megatons of phenol was produced in the world. Although there are several synthetic methods of phenol, most of phenol is now produced by Cumene method found by Hock and Lang in 1944 [2]. The Cumene process consists of three steps involving alkylation of benzene with propylene, aerobic oxidation of the resulting cumene to hydroperoxide followed by decomposition with sulfuric acid to give phenol and acetone. The drawback of this process is as follows: a vast amount of investment is needed to construct plants, and equimolar amount of acetone is formed together with phenol. Therefore, the direct hydroxylation of benzene with O₂ to phenol is regarded as a dream oxidation in chemical industry, and the development of the direct synthesis of phenol from benzene is currently attempted in worldwide. Recently, the direct conversion of benzene to phenol with nitrous oxide [3] has been constructed, but this plant is no longer operated because of difficulty to obtain N₂O with lower cost effectiveness [4]. The synthesis of phenols from benzene is attempted by reacting with H₂O₂ [5] or O₂ [6] under the influence of a reducing agent

like H₂ [7] and CO [8] by transition metals like Cu, Pd, Pt, etc. [9] and heteropolyoxometalates [10]. A one-step conversion of benzene to phenol using O₂ and H₂ by palladium membrane is recently reported by Mizukami and co-workers [7].

In a previous paper, the conversion of benzene to phenol was achieved in 28% yield with air under the influence of CO catalyzed by H_{3+n}PMo_{12-n}V_nO₄₀·nH₂O (HPMoV; HP means heteropoly acid), but the turn-over number (TON) of HPMoV for the production of phenol was not high (ca. 20 mol/mol cat.) [11]. Consequently, our attention has been focused on the improvement of the TON of the HPMoV for the production of phenol. We have now found that the TON of HPMoV for the hydroxylation of benzene with air and CO was considerably improved by adding a very small amount of palladium under ultrasonic irradiation (Eq. (1)).



2. Results and discussion

Benzene (**1**) (300 mmol) was reacted in a mixed solvent of acetic acid (19 mL) and water (1 mL) in 120 mL stainless steel autoclave under air (15 atm) and CO (5 atm) in the presence of H_{3+n}PMo_{12-n}V_nO₄₀ (n = 1–4)·nH₂O (HPMoV) (6.5 μmol) and 5%Pd/C

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Table 1
Hydroxylation of benzene (**1**) with CO/air by HPMoV and ⁵Pd/C under various conditions^a

Entry	HPMoV	Time (h)	TON ^b		STY ^c	
			2	3	2	3
1	H ₃ PMo ₁₂ O ₄₀ ·28H ₂ O	2	–	–	–	–
2	H ₄ PMo ₁₁ VO ₄₀ ·23H ₂ O	2	592	13.0	25.2	0.3
3	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	729	15.2	32.3	0.4
4	H ₆ PMo ₉ V ₃ O ₄₀ ·27H ₂ O	2	678	16.4	31.4	0.4
5	H ₇ PMo ₈ V ₄ O ₄₀ ·25H ₂ O	2	678	17.4	32.8	0.5
6 ^d	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	490	5.5	21.7	0.1
7 ^e	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	767	16.5	34.0	0.4
8 ^f	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	366	15.9	16.2	0.4
9 ^g	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	804	16.5	35.6	0.4
10 ^h	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	746	15.5	33.0	0.4
11 ⁱ	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2 + 2	1324	30.4	29.3	0.4
12 ^j	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	4	934	13.7	20.7	0.2
13 ^k	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	6	757	5.8	11.2	0.05
14 ^l	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	648	8.2	28.7	0.2
15 ^m	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	527	5.7	23.3	0.1
16 ⁿ	H ₅ PMo ₁₀ V ₂ O ₄₀ ·30H ₂ O	2	408	6.8	18.1	0.2

^a See text.

^b TON = 2 (mol)/HPMoV·nH₂O.

^c STY = 2 (g)/g-metal h.

^d The reaction was carried out at 130 °C.

^e **1** (150 mmol), NaOAc (25 μmol), H₂O (0.5 mL), and AcOH (9.5 mL) were used.

^f The reaction was carried out without ⁵Pd/C.

^g ⁵Pd/C (1 mg) was used.

^h Pd(OAc)₂ (0.5 mg) was used in place of ⁵Pd/C.

ⁱ Air (15 atm)/CO (5 atm) was recharged after 2 h.

^j Reaction time was 4 h.

^k Reaction time was 6 h.

^l Air (15 atm), CO (5 atm), and CO₂ (1 atm) were charged.

^m Air (10 atm) and CO (5 atm) were charged.

ⁿ Reaction was carried out without NaOAc.

(0.5 mg) at 150 °C for 2 h. All reactions were carried out under ultrasonic irradiation to avoid the phase separation of benzene and aqueous acetic acid. The results obtained by various HPMoV catalysts are summarized in Table 1.

The reaction gave phenol (**2**) and a small amount of 1,4-benzoquinone (**3**) as major products along with a small amount of undesired side-products which cannot be observed by GC analysis. The catalytic activity of HPMoVs was represented by TON (mol of **2** per mol of HPMoV) and STY, that is, hourly production (g) of **2** per total weight (g) of Mo and V ions), since the HPMoV molecule involve vast amounts of oxygen and crystal water.

It was found that H₃PMo₁₂O₄₀·28H₂O not containing V ion was ineffective for the phenol synthesis from **1** under these conditions (entry 1). A typical reaction using H₅PMo₁₀V₂O₄₀·30H₂O as a catalyst gave **2** and **3** in TON (729) and TON (15.2), respectively (entry

3), and the STY for **2** and **3** was calculated as 32.3 and 0.4, respectively. The STY was increased from 25.2 for H₅PMo₁₁VO₄₀·23H₂O (HPMo₁₁V) to 32.8 for H₇PMo₈V₄O₄₀·25H₂O (HPMo₈V₄) with increasing of V content in HPMoV catalysts (entries 2–5). In a previous paper, we showed that HPMo₈V₄ having an average composition of what the best catalyst for the conversion of **1** to **2** by HPMoV alone, but the STY of **2** was almost the same except for HPMo₁₁V among HPMoV catalysts examined. The reaction at 130 °C under these conditions led to a slight decrease of STY of **2** (entry 6). When the amount of **1** was halved, the STY of **2** was somewhat increased (entry 7). The reaction in the absence of ⁵Pd/C under these conditions resulted in a considerable decrease of STY (entry 8). However, when the amount of ⁵Pd/C was doubled under these conditions, the TON and STY were slightly increased (entry 9). Almost the same results were obtained by the use of Pd(OAc)₂ in place of ⁵Pd/C (entry 10). In a previous paper, we showed that the HPMoV catalyst can be reused without loss of activity after five-time usage [11]. Thus, after carefully purge of the mixed gases from the autoclave under cooling, we tried the hydroxylation of the resulting reaction mixture by recharge of air (15 atm) and CO (5 atm) for an additional 2 h (entry 11). The value of TON of HPMo₁₀V₂ was attained 1324, and the STY (29.3) was almost the same as that for 2 h shown in entry 3. This indicates that the catalytic activity of HPMo₁₀V₂ was not considerably decreased by recharging air and CO. However, when the reaction was continued under air (15 atm) and CO (5 atm) for 4 h without recharge of these gases, the TON was decrease to 934, and the STY of **2** was also decreased to 20.7 (entry 12). When the reaction was prolonged to 6 h, the STY (11.2) of **2** was found to be considerably decreased probably because of the decrease of air and CO concentration in the reaction system (entry 13). As a result, the resulting **2** may be converted to undesired over-reaction products, since the **2** and **3** are more reactive than benzene **1**. To know the influence of CO₂ generated during the reaction course, the reaction was carried out by the use of a mixed gas of air (15 atm), CO (5 atm), and CO₂ (1 atm) under the same reaction conditions (entry 14). It was found that the STY of **2** by HPMo₁₀V₂ was decreased from 32.3 to 28.7. The result suggests that the effect of CO₂ on the hydroxylation of **1** is not high. Therefore, the decrease of STY of **2** is thought to be due to the decrease of air and CO concentration. In fact, the reaction of **1** under air (10 atm) and CO (5 atm) resulted in a considerable decrease of STY (527) of **2** (entry 15). In particular, the formation of **3**, which is thought to be produced by the further oxidation of **2** with air, was depressed to about 1/3. The reaction without NaOAc brought about the decrease of TON (408) and STY (18.1) of **2** (entry 16).

The time-course of the hydroxylation of **1** under air (15 atm)/CO (5 atm) by HPMo₁₀V₂ was compared with that of the hydroxylation of **1** under recharging of air (15 atm)/CO (5 atm) (Fig. 1). The reaction

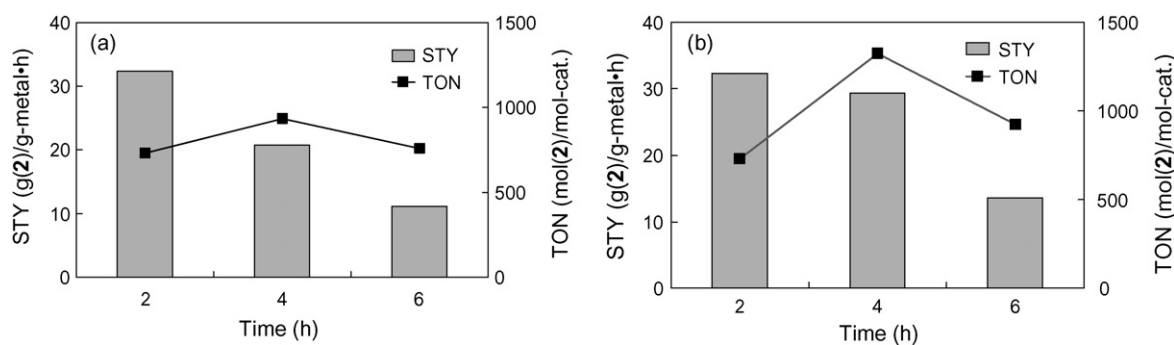


Fig. 1. Time course monitoring for hydroxylation of benzene under the same conditions as entry 3, Table 1 (for (a)), and air (15 atm)/CO (5 atm) was recharged each 2 h under these conditions (for (b)).

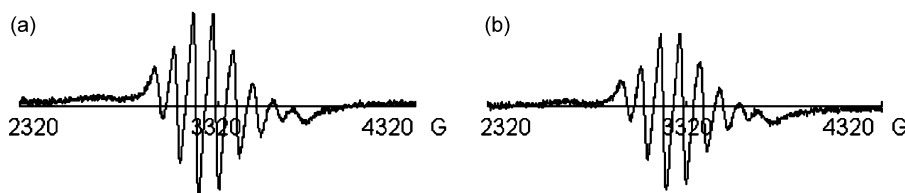


Fig. 2. ESR spectra of $\text{HPMo}_{10}\text{V}_2$ upon treatment with air/CO (15/5 atm) in the presence of ${}^5\text{Pd/C}$ (for (a)) and in the absence of ${}^5\text{Pd/C}$ (for (b)) in aq acetic acid.

was carried out under the same conditions as entry 3 in Table 1 except for recharge of air and CO.

In the reaction without recharging of air and CO, the TON of the catalyst was increased until 4 h but was then decreased (Fig. 1(a)). This indicates that the resulting phenol **2** reacts with air under these conditions to give **3** which is further converted into undesired side-products. Similarly, the STY of **2** by $\text{HPMo}_{10}\text{V}_2$ was decreased with a lapse of time. On the other hand, the TON of $\text{HPMo}_{10}\text{V}_2$ by the recharging system was increased with reaction time and it was reached to 922 after 6 h, while the STY was gradually decreased with extension of the reaction time (Fig. 1(b)).

It is difficult to reveal the role of Pd in the present HPMoV -catalyzed hydroxylation of **1** with air and CO. The Pd catalyst is not thought to promote directly the hydroxylation of **1** to **2**, because the hydroxylation of **1** to **2** was catalyzed by $\text{HPMo}_{10}\text{V}_2$ in the absence of Pd catalyst as shown in entry 8, although the STY of **2** was considerably decreased compared with the reaction in the presence of ${}^5\text{Pd/C}$. In addition, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ not involving V ion in the molecule did not catalyze the present hydroxylation of **1** even in the presence of Pd catalyst. Therefore, it may be reasonable to assume that the palladium catalyst assists the reduction of V^{5+} in the HPMoV to V^{4+} ion with CO. In order to obtain information on the role of Pd species, the generation of V^{4+} from $\text{HPMo}_{10}\text{V}_2$ with CO in the presence or absence of ${}^5\text{Pd/C}$ was followed by ESR measurement (Fig. 2).

It was found that the ESR signal intensity of V^{4+} generated from $\text{HPMo}_{10}\text{V}_2$ (Fig. 2(a)) by treating with CO (5 atm) in aqueous acetic acid at 150°C for 2 h in the presence of ${}^5\text{Pd/C}$ was 1.35 times higher than that in the absence of ${}^5\text{Pd/C}$ (Fig. 2(b)). These results show that the role of Pd species is believed to promote the reduction of V^{5+} to V^{4+} , which is thought to be a real active species for the hydroxylation of **1** to **2**. Thus, the hydroxylation is considered to proceed through the reaction path as shown in Fig. 3. The formed V^{4+} species (**A**) may react with O_2 to generate an activated oxygen

species ($\text{V}^{5+}-\text{O}_2^*$ (**B**)) on which subsequent reaction with **1** may give **2** and generates V^{5+} .

3. Conclusion

Hydroxylation of benzene was successfully achieved by a combined catalytic system of HPMoV and ${}^5\text{Pd/C}$ under the influence of a mixed gas of air and CO in aqueous acetic acid. The TON of HPMoV for the formation of phenol was considerably improved by adding a small amount of ${}^5\text{Pd/C}$ under ultrasonic irradiation and the TOF of phenol was attained 34 g/g-metal h.

4. Experimental

4.1. General

All starting materials were commercially available and used without any purification. GLC analysis was performed with a flame ionization detector using a $0.2\text{ mm} \times 25\text{ m}$ capillary column (BP-5). ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR were measured at 270 and 67.5 MHz, respectively, in CDCl_3 with Me_4Si the internal standard. ${}^{31}\text{P}$ NMR was measured at 109.25 MHz with 85% H_3PO_4 in sealed capillary as the external standard. Heteropoly acids were prepared according to the method reported in literature [12]. The crystal water content of the heteropoly acid was calculated according to DTA/TG. ESR measurements were performed on a JEOL-JES-RE1X (X-band) with 100-kHz field modulation.

4.2. A typical procedure for the hydroxylation of benzene (Table 1, entry 3)

To a 120 mL stainless steel autoclave was placed $\text{H}_5\text{PMo}_{10}\text{V}_2 \cdot 30\text{H}_2\text{O}$ ($\text{HPMo}_{12}\text{V}_2$) (6.5 μmol), ${}^5\text{Pd/C}$ (0.5 mg), NaOAc (50 μmol), **1** (300 mmol), acetic acid (19 mL), and H_2O (1 mL). To the autoclave was charged with 15 atm of air and 5 atm of CO, and the mixture was stirred under ultrasonic irradiation at 150°C for 2 h. After the reaction, the reaction mixture was evaporated under reduced pressure to remove unreacted **1**. Then the residue was extracted with saturated NaHCO_3 (5 mL) and added isopropyl ether (5 mL). The conversions and yields of products were estimated from the peak areas based on the internal standard technique using GC.

4.3. ESR measurements (Fig. 2)

To a 120 mL stainless autoclave equipped with a magnetic stir bar was placed $\text{H}_5\text{PMo}_{10}\text{V}_2 \cdot 30\text{H}_2\text{O}$ (65 μmol), ${}^5\text{Pd/C}$ (5 mg) (sample for Fig. 2(a) only), acetic acid (19 mL), and H_2O (1 mL). To the autoclave was charged with 5 atm of CO, and the mixture was stirred at 150°C for 2 h. Then the resulting solution containing the molybdovanadophosphate ($3.3 \times 10^{-3}\text{ M}$) was charged to the ESR tube. ESR spectra were obtained under the following conditions: sweep width, $3320 \pm 1000\text{ G}$; modulation, 10 G; microwave power, 2 mW. The ESR parameter and intensity was determined by using solid Mn^{2+} ($g = 1.981$) as a standard.

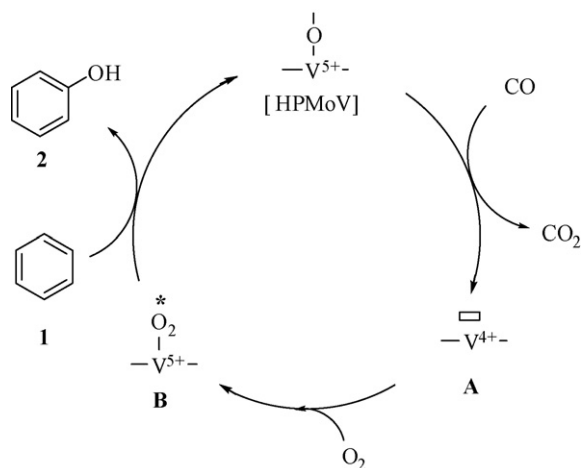


Fig. 3. A plausible reaction path.

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