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Effects of vanadium supported on ZrO_2 and sulfolane on the synthesis of phenol by hydroxylation of benzene with oxygen and acetic acid on palladium catalyst

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The catalyst system consisting of Pd, transition metal-modified ZrO_2 and acetic acid was found to catalyze the hydroxylation of benzene with molecular oxygen without hydrogen and phenol was formed. Of transition metals employed, only vanadium additive was found to be effective for improving the rate of phenol formation as well as the selectivity, while any other transition metals such as iron, molybdenym, tungsten and yttrium were not promotive. Support effects on vanadium were in the order: $V/ZrO_2 > V/Al_2O_3 > V/SiO_2$. The highest rate of phenol formation was obtained at $0.5wt\%V/ZrO_2$ catalyst. Phenol selectivity was dramatically improved by the addition of sulfolane, while benzene conversion and STY of phenol formation decreased. It is assumed that Pd(II) and Pd(IV) intermediates derived from acetic acid, oxygen and palladium acetate could play an important role in hydroxylation of benzene.

KEY WORDS: hydroxylation; benzene; phenol; Vanadium-modified Palladium; Acetic acid-Sulfolane solvent.

1. Introduction

Phenol is one of the most important intermediates of the chemical industry and mainly produced by the cumene process, which coproduced acetone in 1:1 molar ratio with respect to phenol [1]. Thus, the cost of phenol is directly concerned with the effective usage of acetone. New processes to produce phenol without acetone and with high selectivity have been explored [2, 3]. In these processes, reducing agents such as H2, CO are important for activation of oxygen. The use of oxygen and hydrogen gave phenol on $Cu–Pd/SiO_2$ catalyst [2], over palladium-containing titanium silicates [4], and over Pt/Pd-contg. acid resins [5]. Jintoku *et al.* [3] reported a homogeneous catalyst composed of palladium acetate and phenanthroline in the presence of oxygen and carbon monoxide at 180 °C. Pd(II)-heteropoly acid redox system has been reported in the presence of O2–H2O–AcOH, in which the oxidation of benzene with Pd(II) occurred to form oxidation products and Pd(0), accompanied by reoxidation into Pd(II) by reaction with heteropoly acids [6]. In this case, the role of AcOH is not clear. In a previous paper [7], we reported direct epoxidation of propylene with oxygen and MeOH with Pd(0) and porous oxide, where MeOH is sacrificial reductant. Miyake *et al.* have reported vanadium effect on the reaction with oxygen/hydrogen on platinum catalyst [8]. Furthermore, Balducci *et al.* have reported that sulfolane solvent is effective for improving phenol selectivity on oxidation of benzene with hydrogen peroxide [9]. All these findings stimulated us to try a hydroxylation of benzene with oxygen and AcOH as reductant of oxygen on Pd(0)/oxide catalysts and to investigate the effects of vanadium and sulfolane on the hydroxylation performances.

2. Experimental

Metal-modified oxides as additives were prepared by the impregnation of metal compounds such as $Fe(NO_3)_3$ and NH_4VO_3 with oxides such as ZrO_2, SiO2 and Al2O3, followed by dryness at 373 K for 10 h and finally calcined at 973 K for 3 h. All chemicals were purchased from Soekawa-rikagaku Co. and Wako Pure Chemicals Co and used without further purification.

All reactions were carried out in an 50 ml autoclave, in which 0.125 g of oxide additive and 0.0106 g of $Pd(OAc)_2$ (Pd 0.005 g (0.047 mmol)) were introduced with benzene (30 mmol), acetic acid (120 mmol), and H_2O (30 mmol) and stirred with a magnetic stirrer. The vessel was pressurized with O_2 (3.0 Mpa) and Ar (0.5 Mpa) and the hydroxylation reaction was conducted at 423 K. After reaction, gaseous and liquid phase products were independently subjected to gas chromatographic analyses.

Hydrocarbons and oxygenated compounds were detected by TCD and FID gas chromatographys, the former with Porapack Q (2 m) at 473K, the latter with

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Silicone OV-17 capillary column (ID 0.25 mm, 30 m, 0.25 μm) at 323–523 K. The m-dichlorobenzene was used as an internal standard. Products in the gas phase were analyzed by another TCD equipped with Porapak Q column (3 m) and molecular sieve 5A column (3 m) kept at 383 K. Phenol was predominantly formed and trace amounts of catecol and phenyl acetate and acetophenone were formed as by-products.

3. Results and Discussion

As shown in Table 1, Run 1, MeOH was used as solvent media for hydroxylation of benzene with $Pd(OAc)_2$ and oxygen, but, even at 423 K, no phenol was formed. Then, AcOH was tried, because AcOH has been used for the hydroxylation with oxygen/hydrogen on platinum catalyst [8]. The results of screening of metal salts supported on Al_2O_3 are shown in Table 1, where $Pd(OAc)_2$ was used as catalyst precursor. In the presence of $Pd(OAc)_2$ and AcOH solvent, phenol was formed (Run 2). Some other by-products such as biphenyl, formed by oxidative coupling of benzene [6], and CO_2 were detected with small amounts of catechol, phenyl acetate and acetophenone. Besides these, many undetectable by-products may be produced, because benzene conversion was as high as 75.6%. Addition of Al_2O_3 resulted in the decrease in formation rates of phenol and CO_2 and increase in the rate of biphenyl (Run 3), although benzene conversion of 80.1% was still high. By use of 0.1wt%vanadium/ Al_2O_3, the rate of phenol formation was found to be accelerated while the rate of biphenyl formation was suppressed. As a result, space-time-yield (STY) of phenol as well as the selectivity based on benzene reacted was improved. On the other hand, when Fe, Mo, and Y metals supported on Al_2O_3 were added, the rate of phenol formation retarded, while the rate for W/Al_2O_3 was almost the same as Al_2O_3 alone. For Mo, W, Y on Al_2O_3, the phenol selectivity was improved, while, for Fe/Al_2O_3, it decreased. Thus, vanadium was chosen to study the influence of concentration.

As shown in Table 2, for Al_2O_3 support, the rate of phenol formation increased with increase in vanadium concentration and the highest rate was achieved at 1wt% and decreased thereafter. The phenol selectivity increased monotonously, while benzene conversion decreased. Similar trends were obtained for ZrO_2 support. The highest rate and selectivity of phenol formation were observed at 0.5wt% vanadium concentration, while benzene conversion slightly decreased. For SiO_2 support, the highest rate of phenol formation at 0.25wt% vanadium concentration was below half of that obtained with ZrO_2 support. The highest phenol selectivity was obtained at 0.1wt% vanadium concentration and decreased thereafter, while the lowest benzene conversion at 0.1wt% vanadium was obtained and increased thereafter. Thus, the addition of vanadium was found to be effective for raising the rate and selectivity of phenol formation.

Several kinds of vanadium compounds were studied. As is shown in Table 3, the rate of phenol formation was promoted by every vanadium compound studied. Benzene conversion was decreased by adding vanadium compounds while phenol selectivity as well as the rate of phenol formation increased. Hence, by-product formations could be retarded by adding vanadium compounds. In fact, the rate of biphenyl formation through oxidative coupling of benzene decreased, except for $VO(acac)_2$, as indicated in Table 3. Consequently, we chose catalyst system consisting of $Pd(OAc)_2$ and vanadium/ZrO_2 in order to try to improve phenol selectivity.

Table 1
Hydroxylation of benzene with oxygen and AcOH catalyzed by $Pd(OAc)_2$ and transition metal/Al_2O_3[a]

Run	Metal on Al_2O_3	Rate/ mmol/h[d]			Benzene Conv.%[e]	Phenol Sel.(%)[f]	STY of Phenol/ g/kg-cat.h
		Phenol	Ph–Ph	CO2			
1	−b	0.00	0.00	0.00	0.0	0.0	0.0
2	–	0.127	0.0115	0.619	75.6	8.99	–
3	−c	0.0784	0.0227	0.286	80.1	7.18	54.3
4	V	0.176	0.0118	0.718	59.2	13.9	122
5	Fe	0.0574	0.0221	0.235	66.7	6.89	39.8
6	Mo	0.0705	0.0185	0.212	47.6	11.9	48.9
7	W	0.0783	0.0052	0.433	64.4	9.73	54.3
8	Y	0.0595	0.0167	0.245	52.1	9.14	41.3

[a] Reaction conditions: $Pd(OAc)_2$ (0.0472 mmol; Pd 0.5 g l^{-1}); 0.1wt%M on Al_2O_3, (0.125 g, 12.5 g.l^{-1}); LiOAc (3.0 mmol; 30.6 g.$^{l-1}$) and AcOH/H_2O (120 mmol/30 mmol); gas composition: $O_2/Ar = 6/1$, total pressure 3.5 MPa; temperature 423 K.

[b] MeOH solvent.

[c] Only Al_2O_3 without metal.

[d] Small amounts of catechol, phenyl acetate and acetophenone were detected.

[e] Benzene conversion = (Bi−Bu)/Bi*100, where Bi and Bu denote the amount of benzene initially added and unreacted.

[f] Phenol selectivity = Pp/(Bi−Bu)*100, where Pp denotes the amount of phenol produced.

Table 2
Effect of vanadium concentration supported on various oxides on the benzene hydroxylation catalyzed by Pd species[a]

Oxide support	V/ wt%	Rate/ mmol/h[b]			Benzene Conv.%[c]	Phenol Sel.%[d]	STY of Phenol/ g/kg-cat.h
		Phenol	Ph–Ph	CO_2			
Al_2O_3	0	0.0784	0.0227	0.286	80.1	7.18	54.3
Al_2O_3	0.01	0.0919	0.0105	0.315	49.1	15.0	63.7
Al_2O_3	0.1	0.176	0.0118	0.718	59.2	13.9	122
Al_2O_3	0.5	0.452	0.0164	1.84	53.5	16.9	313
Al_2O_3	1.0	0.523	0.0156	1.79	49.9	20.9	362
Al_2O_3	2.0	0.371	0.0335	1.50	31.8	21.4	257
ZrO_2	0	0.0081	0.0674	0.231	69.9	0.93	5.63
ZrO_2	0.05	0.208	0.0085	0.724	49.8	19.5	144
ZrO_2	0.1	0.233	0.0059	0.989	59.2	15.8	162
ZrO_2	0.5	0.656	0.0171	1.756	50.5	21.6	454
ZrO_2	1.0	0.578	0.155	2.15	52.6	20.1	400
ZrO_2	0	0.0521	0.0223	0.234	74.4	5.14	36.1
SiO_2	0.1	0.265	0.0099	1.36	34.0	26.0	184
SiO_2	0.25	0.271	0.0088	1.12	49.8	18.1	188
SiO_2	0.5	0.234	0.0282	2.10	47.3	9.90	162
SiO_2	1.0	0.107	0.0116	9.21	76.7	9.33	74.3

[a] Reaction conditions, benzene conversion and phenol selectivity: See footnotes of Table 1.

Table 3
Influence of vanadium compounds supported on Al_2O_3 on Pd-catalyzed hydroxylation of benzene with oxygen and AcOH[a]

Vanadium compound on Al_2O_3	Rate/ mmol/h			Benzene Conv.%[c]	Phenol Sel.%[c]	STY of Phenol/ g/kg-cat.h
	Phenol	Ph-Ph	CO_2			
None[b]	0.0784	0.0227	0.286	80.1	7.18	54.3
NH_4VO_3	0.656	0.0171	1.76	50.5	21.6	454
VOC_2O_4	0.676	0.0159	2.30	54.5	20.7	469
$V(acac)_3$	0.569	0.0173	1.83	46.2	24.6	394
$VO(acac)_2$	0.672	0.0329	1.52	42.6	26.3	465
$VOSO_4$	0.599	0.0120	2.47	57.7	17.3	415
VCl_3	0.680	0.0168	2.34	55.7	20.3	472
VOCl−3	0.796	0.0188	2.56	66.4	18.0	551

[a] Vanadium content on ZrO_2 is 0.5wt%. Other conditions are the same as Table 1.
[b] Only Al_2O_3 without metal.
[c] Benzene conversion and phenol selectivity: See footnotes of Table 1.

Sulfolane is a solvent with high dipole moment (4.81 debye) and dielectric constant (43.26), thus having the peculiar property of being able to form complexes with phenolic compounds. In the case of phenol, the formation of the complex was reported [10]. In fact, the use of sulfolane solvent for benzene oxidation with H_2O_2 has been effective for raising phenol selectivity [9]. In our study, influence of organic reductants on the benzene hydroxylation with oxygen in sulfolane solvent was first examined.

As shown in Figure 1, when using AcOH/sulfolane (1.2 g/6.0 g), phenol selectivity of 59.2% was found to be achieved with benzene conversion of 5.2%, while, in case of sulfolane alone, phenol selectivity was only 0.57%. The use of other reductants such as HCO_2H, $EtCO_2H$, EtCHO resulted in a lower phenol selectivity than only AcOH system (See Table 3). Thus, for sulfolane/AcOH system, effect of sulfolane concentration was investigated.

Figure 2 demonstrates the results. The phenol selectivity increased with increase in sulfolane concentration and passed through a maximum at ca. 65% of the concentration and, then, decreased; The highest selectivity was approximately 70% the highest rate was achieved at 1wt% and decreased thereafter. The phenol selectivity increased monotonously, while benzene conversion decreased.

Reverse trends were observed for benzene conversion; The conversion decreased with increase in sulfolane concentration and levelled off above 65% and, then, slightly increased. The STY values decreased monotonously with the increase in sulfolane concentration. Thus, it is found that, for Pd-V/ZrO_2-AcOH-O_2 system, addition of sulfolane was effective for raising phenol selectivity.

In the previous paper [7], the authors studied the epoxidation of propylene with molecular oxygen in the presence of $Pd(OAc)_2$ and MeOH, where $Pd(OAc)_2$ was

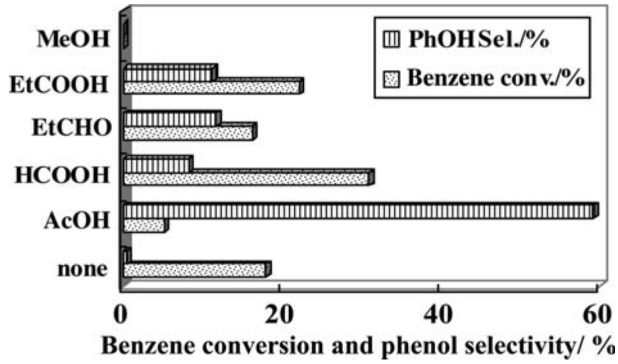

Figure 1. Influence of co-solvent on Pd-catalyzed hydroxylation of benzene with oxygen in the presence of sulfolane. Additive: 0.5wt%V/ZrO2, Solvent: Sulfolane 6g, Co-solvent:1.2g.

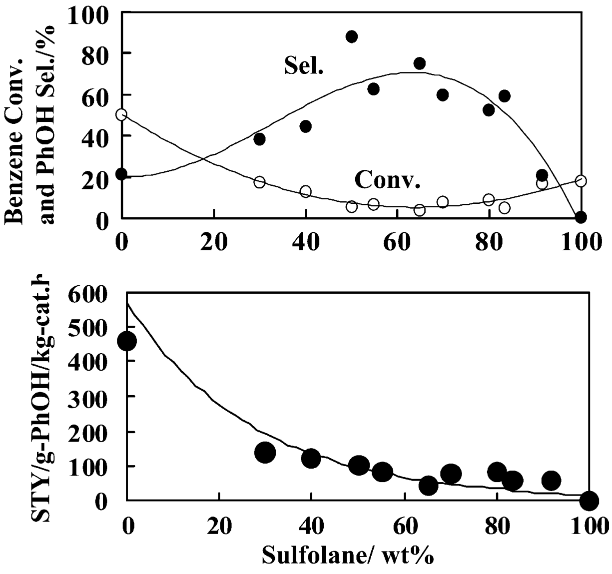

Figure 2. Effect of Sulfolane content. Reaction temp.:423 K, Additive:0.5wt%/ZrO2, Solvent: AcOH/ Sulfolane, Total:7.2g. Other conditions: See Table 1.

reduced with MeOH to form Pd(0) species, which was active for propylene oxidation. However, in this benzene oxidation, no products were formed in MeOH (Table 1, Run 1). Also, no Pd(0) species were detected by X-ray diffraction analyses of the used catalyst. These findings demonstrate that Pd(0) species could not be a predominate for benzene oxidation.

For oxidation of benzene to phenol with O_2 in the presence of catalyst system consisting of $Pd(OAc)_2$, AcOH, H_2O, and vanadium-containing heteropolyacids, Schuchardt *et al.* [11] reported a mechanism containing Pd(II) and Pd(IV), where, biphenyl and phenyl acetate as well as phenol were formed as by-products, being consistent with our results, as shown in Table 1. Therefore, although there is no direct evidence at this moment, it may be considered that both Pd(II) and Pd(IV) species play an important role in our conditions. A postulated scheme is shown in Figure 3. Palladium acetate could electrophilically attack benzene to give phenylpalladium (II) acetate [12], which undergoes further oxidation with AcOH to form phenylpalladium (IV) triacetate, followed by reductive elimination to produce phenylacetate, which finally undergoes hydration to form phenol. Biphenyl is produced by reductive elimination of phenylpalladium (II) acetate. The intermediate palladium (IV) may undergo thermolysis, resulting in the oxidation of an acetate ligand to form $OCOCH_3$ and CH_2COOH radicals [13], which react with molecular oxygen to form formaldehyde, accompanied by reaction with benzene to give polymeric and tary by-products finally. Probably, vanadium may accelerate formation of phenylpalladium triacetate, as previously reported [11, 14]. Sulfolane could stabilize phenol (Angew no bunnken), but reduce the reactivity of palladium acetate with benzene and AcOH; This could be true for all the reaction steps drawn in Figure 3. Thus, the selectivity to phenol was remarkably improved, although benzene conversion and STY decreased, as shown in Figure 2.

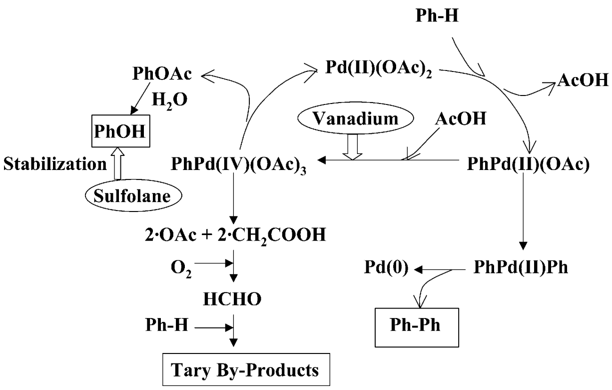

Figure 3. A Postulated scheme of hydroxylation of benzene with oxygen in the presence of Pd(OAc)2 and V/ZrO2 in sulfolane/AcOH solvents.

It is not clear whether or not effective vanadium species are soluble in AcOH/benzene solution. However, it may be considered that some part of vanadium was adsorbed on the support and affected the reaction, because catalyst performances depend on the supports, as shown in Table 2.

4. Conclusions

The catalyst system consisting of Pd, vanadium-modified ZrO_2 and acetic acid was found to catalyze the hydroxylation of benzene with molecular oxygen without hydrogen and phenol was formed. Support effects on vanadium were in the order: $V/ZrO_2 > V/Al_2O_3 > V/SiO_2$. The highest rate of phenol formation was obtained at 0.5wt%V/ZrO_2 catalyst. Phenol selectivity was dramatically improved by the addition of sulfolane, while benzene conversion and STY of phenol formation decreased. Unlike propylene epoxidation with molecular oxygen in the presence of catalyst system consisting of $Pd(OAc)_2$ and MeOH, Pd(II) and Pd(IV), not Pd(0), could play an important role in this benzene oxidation. Vanadium, at least in part, supported on ZrO_2, may accelerate formation of these species.

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