

# Effect of vanadium compound on the synthesis of phenol by hydroxylation of benzene with oxygen and hydrogen on platinum catalyst

Takanori Miyake\*, Michiyuki Hamada, Hideyuki Niwa,  
Masaya Nishizuka, Motohiro Oguri

*Yokkaichi Research Laboratory, TOSOH Corporation, 1-8 Kasumi, Yokkaichi-shi, Mie 510-8540, Japan*

Received 1 May 2001; received in revised form 28 July 2001; accepted 9 August 2001

## Abstract

Influence of metal salts on the direct synthesis of phenol by hydroxylation of benzene with oxygen and hydrogen in the liquid phase was investigated for a heterogeneous platinum catalyst supported on silica. Promotive effects were observed with acetylacetonates of vanadium, iron, lanthanum, and yttrium, while with the other elements, the rate of phenol formation was retarded. Among the preferable compounds, vanadium(III) acetylacetonate ( $V(acac)_3$ ) produced the most beneficial effect. The highest rate of phenol formation was obtained at ca. 20 ppm of  $V(acac)_3$ . Among various vanadium compounds studied, the vanadium compounds having  $V=O$  seemed to have the promotive effect. It was estimated that oxygen activated on the vanadium species was transferred to platinum site and as a result, the rate of phenol formation was promoted. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydroxylation; Phenol; Vanadium; Platinum; Benzene

## 1. Introduction

Phenol is now produced by the so-called cumene process and the toluene oxidation process [1]. In the cumene process, the cost of phenol is directly concerned with the effective usage of acetone which is equimolarly produced. On the other hand, in the toluene oxidation process low yield based on toluene is to be improved.

New processes to produce phenol without by-products and with high selectivity have been ex-

plored [2–14]. Kunai et al. [2] showed that phenol was obtained by hydroxylation of benzene with oxygen and hydrogen with almost 100% selectivity on Cu–Pd/SiO<sub>2</sub> catalyst at 60 °C and under atmospheric pressure. Tatsumi et al. [5] reported hydroxylation of benzene with oxygen and hydrogen over palladium-containing titanium silicates. Jintoku et al. [9] reported that phenol was produced from benzene with homogeneous catalyst composed of palladium acetate and phenanthroline in the presence of oxygen and carbon monoxide at 180 °C. These new reactions have a common feature; oxygen was activated with the aid of reducing agent. With the activated oxygen thus formed, direct hydroxylation of benzene to phenol could be attained under mild conditions. In a

\* Corresponding author. Tel.: +81-593-65-9468;

fax: +81-593-636-431.

E-mail address: miyake@tosoh.co.jp (T. Miyake).

previous paper [15], we reported direct hydroxylation of benzene with oxygen and hydrogen on precious metal catalysts supported on silica modified with vanadium oxide.

In this paper, the effect of metal salts added to the reaction mixture on the catalytic performance was investigated intensively.

## 2. Experimental

Experimental procedures were reported in detail in the previous paper [15]. Briefly, catalysts were prepared by the conventional impregnation method. Into a solution containing a tetraamineplatinum dichloride hydrate to give 0.5 wt.% of platinum loading, silica support (Fuji Davison, CARiACT-15, 190 m<sup>2</sup>/g) was added. After drying at 60 °C, the powder obtained was reduced in a tubular glass in 10% H<sub>2</sub> stream (N<sub>2</sub> balance) at 250 °C for 1 h. Dispersion of thus obtained platinum catalyst measured by CO adsorption was 0.02.

### 2.1. Typical hydroxylation reaction

Into the 100 cm<sup>3</sup> glass reactor, a 0.1 g portion of the catalyst, 20 cm<sup>3</sup> of benzene, 25 cm<sup>3</sup> of acetic acid and 10 ppm of an additive were added. After in situ reduction at 60 °C for 30 min, the reaction was started by changing gas composition of air to 40 cm<sup>3</sup>/min and of H<sub>2</sub> to 24 cm<sup>3</sup>/min.

### 2.2. Analysis

Products were analyzed every 1 h with GC by the internal standard method (internal standard; 1-methylnaphthalene). The column used was Silicone W-98 10% Chromosorb W (AW-DMCS). Injection temperature was 205 °C. Column temperature profile was as follows; temperature was maintained at 130 °C for 5 min, then raised by 10 °C/min to 180 °C and held at this temperature for 10 min. Nitrogen of 20 cm<sup>3</sup>/min was used as carrier gas and an FID detector was used. Phenol was predominantly formed and trace amounts of 1,4-benzoquinone and biphenyl were formed as by-products. By the Karl–Fischer method, H<sub>2</sub>O formed was measured after the reaction.

## 3. Results and discussion

### 3.1. Screening of additive

The results of screening of metal salts are shown in Table 1. For acetylacetonates of vanadium, iron, lanthanum, and yttrium, the rate of phenol formation was accelerated while the rate of water formation was decelerated and oxygen conversion was suppressed. As a result, both space-time-yield (STY) of phenol and selectivity based on oxygen were improved. On the other hand, when salts of other metals were added, the rate of phenol formation retarded and phenol selectivity was decreased. Here, it should be stressed that selectivity based on benzene was nearly 100% since the amount of benzoquinone was almost negligible.

Among the metal salts investigated, vanadium acetylacetonate (V(acac)<sub>3</sub>) gave the best result. It is of course too early to conclude that vanadium salt is the best one, because for other metals only one type of salt was tested at a fixed concentration for screening.

Iron and titanium salts were chosen to study the influence of concentration, because iron presented the second superior result and titanium was often used for liquid-phase oxidation catalyst [16].

As was expected, a better result was obtained at lower iron acetylacetonate concentrations (Table 2). The rate of phenol formation was however only one-third of that obtained with V(acac)<sub>3</sub>. On the other hand, when the concentration of titanium acetylacetonate was increased, both the rate of phenol formation and phenol selectivity based on oxygen decreased monotonously.

Consequently, we chose vanadium compounds to investigate further in detail.

### 3.2. Kinds of vanadium compounds

First, 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. It is known that when water and oxygen exist, V(acac)<sub>3</sub> transforms easily to VO(acac)<sub>2</sub> [17]. Therefore, we might say that vanadium compound having vanadyl V=O gave better results.

Table 1  
Screening of metal salts affecting the catalytic performance<sup>a</sup>

Cation	Metal salt	Rate (mmol/h)			O <sub>2</sub> conversion (%)	Selectivity (%) <sup>b</sup>	STY of phenol (g/kg-cat h)
		Phenol	BQ <sup>c</sup>	H <sub>2</sub> O			
V <sup>3+</sup>	V(acac) <sub>3</sub>	0.368	0.0	1.9	5.1	16.1	346
Fe <sup>3+</sup>	Fe(acac) <sub>3</sub>	0.083	0.0	0.5	1.3	14.9	78
La <sup>3+</sup>	La(acac) <sub>3</sub> ·nH <sub>2</sub> O	0.058	0.0	2.7	6.4	2.1	55
Y <sup>3+</sup>	Y(acac) <sub>3</sub> ·nH <sub>2</sub> O	0.051	0.0	2.4	5.6	2.1	48
None		0.029	0.0	4.6	10.6	0.6	27
Cr <sup>3+</sup>	Cr(acac) <sub>3</sub>	0.028	0.0	2.8	6.6	1.0	26
Nb <sup>5+</sup>	NbCl <sub>5</sub>	0.024	0.0	3.4	8.1	0.7	23
Ti <sup>4+</sup>	TiO(acac) <sub>2</sub>	0.016	0.0	5.0	11.7	0.3	15
Zr <sup>4+</sup>	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	0.016	0.0	3.7	8.4	0.4	15
Zr <sup>4+</sup>	Zr(acac) <sub>4</sub>	0.013	0.0	2.8	6.5	0.5	12
Mn <sup>3+</sup>	Mn(acac) <sub>3</sub>	0.009	0.0	3.6	8.4	0.3	9
Sn <sup>2+</sup>	Sn(AcO) <sub>2</sub>	0.007	0.0	3.0	7.1	0.2	6
Mo <sup>6+</sup>	MoO <sub>2</sub> (acac) <sub>2</sub>	0.005	0.0	0.3	0.8	1.4	5
Co <sup>3+</sup>	Co(acac) <sub>3</sub>	0.005	0.0	3.1	7.3	0.2	4
Ni <sup>2+</sup>	Ni(acac) <sub>2</sub> ·H <sub>2</sub> O	0.004	0.0	4.7	10.9	0.1	3
Pb <sup>4+</sup>	Pb(AcO) <sub>4</sub>	0.003	0.0	0.0	0.0	100	3
Bi <sup>3+</sup>	BiOCl	0.002	0.0	0.0	0.0	100	2
Ag <sup>+</sup>	AcOAg	0.000	0.0	0.0	0.0	0.0	0
Cu <sup>2+</sup>	Cu(acac) <sub>2</sub>	0.000	0.0	0.0	0.0	0.0	0

<sup>a</sup> Concentration of metal salt was 10 ppm (only La salt was 100 ppm); catalyst, 0.5 wt.% Pt/SiO<sub>2</sub>, 0.1 g; temperature, 60 °C; pressure, 0.1 MPa; H<sub>2</sub>/O<sub>2</sub> = 3; O<sub>2</sub> = 22 mmol/h; reaction mixture, 40 wt.% benzene/60 wt.% acetic acid (20 cm<sup>3</sup>/25 cm<sup>3</sup>); agitation, 1400 rpm.

<sup>b</sup> Phenol selectivity based on oxygen.

<sup>c</sup> BQ: benzoquinone.

Oxygen conversion was decreased by adding vanadium compounds while the rate of phenol formation increased. Hence, we suppose that the ratio of hydrogen to oxygen on platinum was modified with the existence of vanadium compounds. This will be discussed in later section.

### 3.3. Influence of concentration of vanadium acetylacetonate

As the highest rate of phenol formation was obtained with V(acac)<sub>3</sub>, we studied the effect of concentration of V(acac)<sub>3</sub> and the result is shown in

Table 2  
Influence of concentration of iron acetylacetonate<sup>a</sup>

Cation	Metal salt	Fe (ppm)	Rate (mmol/h)			O <sub>2</sub> conversion (%)	Selectivity (%) <sup>b</sup>	STY of phenol (g/kg-cat h)
			Phenol	BQ <sup>c</sup>	H <sub>2</sub> O			
None	None	0	0.029	0.0	4.6	10.6	0.6	27
Fe <sup>3+</sup>	Fe(acac) <sub>3</sub>	0.5	0.097	0.0	1.2	3.0	7.4	91
		2	0.124	0.0	2.2	5.3	5.4	117
		5	0.131	0.0	0.9	2.4	12.8	123
		10	0.083	0.0	0.5	1.3	14.9	78

<sup>a</sup> Reaction conditions are the same as in Table 1.

<sup>b</sup> Phenol selectivity based on oxygen.

<sup>c</sup> BQ: benzoquinone.

Table 3  
Influence of vanadium compounds added to the reaction medium<sup>a</sup>

Vanadium compound	Concentration of vanadium (ppm)	Rate (mmol/h)			O <sub>2</sub> conversion (%)	Selectivity (%) <sup>b</sup>	STY of phenol (g/kg-cat h)
		Phenol	BQ <sup>c</sup>	H <sub>2</sub> O			
V(acac) <sub>3</sub>	39.0	0.307	0.0	1.1	3.1	21.8	288
VO(acac) <sub>2</sub>	39.3	0.288	0.0	1.2	3.3	19.3	271
VOCl <sub>3</sub>	39.0	0.288	0.0	0.8	2.4	26.2	269
NH <sub>4</sub> VO <sub>3</sub>	37.9	0.218	tr	1.4	3.4	13.9	203
VOC <sub>2</sub> O <sub>4</sub>	40.0	0.144	0.0	– <sup>e</sup>	~0	–	135
VOSO <sub>4</sub>	<38.3 <sup>d</sup>	0.112	0.0	– <sup>e</sup>	~0	–	105
VCl <sub>3</sub>	39.4	0.048	0.0	– <sup>e</sup>	~0	–	45
None	0	0.029	0.0	4.6	10.6	0.6	27

<sup>a</sup> Reaction conditions are the same as in Table 1.

<sup>b</sup> Phenol selectivity based on oxygen.

<sup>c</sup> BQ: benzoquinone.

<sup>d</sup> Not all the salt dissolved.

<sup>e</sup> Too little to measure quantitatively.

Table 4. When the concentration of V(acac)<sub>3</sub> was varied, the rate of phenol formation once increased and passed through a maximum at ca. 20 ppm and thereafter decreased. On the other hand, the rate of water formation decreased monotonously according to the concentration of V(acac)<sub>3</sub> except for the data at 3.4 ppm.

### 3.4. Consideration on the effect of vanadium compound added

In the previous paper [15], some of the authors of this paper studied the same reaction on the platinum supported on silica modified with vanadium oxide and observed the highest rate of phenol formation

at 1.0 wt.% V<sub>2</sub>O<sub>5</sub>. At this loading, the atomic ratio of vanadium to platinum is about 4. When the concentration of V(acac)<sub>3</sub> was 19.2 ppm in Table 4, the atomic ratio of vanadium to platinum was about 6. Comparing these results, the dependence of the activity on vanadium seems very similar to each other. Although there is no direct evidence at this moment, it may be considered that some part of V(acac)<sub>3</sub> was adsorbed on the silica support and affected the reaction. If adsorbed amount is about two-thirds of the V(acac)<sub>3</sub> added into the reaction medium, roughly an equal amount of vanadium (1.0 wt.% V<sub>2</sub>O<sub>5</sub>) was adsorbed to the impregnated vanadium oxide resulting in a similar effect on the catalytic activity.

Table 4  
Effect of concentration of V(acac)<sub>3</sub><sup>a</sup>

Concentration of V(acac) <sub>3</sub> (ppm)	Concentration of V(acac) <sub>3</sub> (mg)	Rate (mmol/h)			O <sub>2</sub> conversion (%)	Selectivity (%) <sup>b</sup>	STY of phenol (g/kg-cat h)
		Phenol	BQ <sup>c</sup>	H <sub>2</sub> O			
0	0	0.029	0.0	4.6	10.6	0.6	27
0.1	0.03	0.060	0.0	4.8	10.7	1.2	56
3.4	1.0	0.361	0.0	1.4	3.9	20.5	338
9.7	3.0	0.368	0.0	1.9	5.1	16.1	346
19.2	5.9	0.412	0.0	1.5	4.2	21.5	385
39.0	9.2	0.307	0.0	1.1	3.1	21.8	288
384	118	0.131	0.0	0.2	0.7	41.1	122

<sup>a</sup> Reaction conditions are the same as in Table 1.

<sup>b</sup> Phenol selectivity based on oxygen.

<sup>c</sup> BQ: benzoquinone.

Before considering the effect of vanadium compound, it is worth discussing the reaction mechanism of this direct hydroxylation reaction.

Kunai et al. [2] referred to the Fenton-type mechanism, namely  $\text{H}_2\text{O}_2$  and hydroxyl radical ( $\bullet\text{OH}$ ) were produced with the aid of cuprous ion. Thus, obtained hydroxyl radical attacked benzene and finally phenol was produced with another hydroxyl radical forming  $\text{H}_2\text{O}$  as a by-product. Although we do not have any direct proof, we would like to consider a similar reaction path on our platinum catalyst system. Namely,  $\text{H}_2\text{O}_2$  was formed on platinum [18–21], and this  $\text{H}_2\text{O}_2$  was homolytically decomposed to hydroxyl radical again on platinum. As we did not observe any dissolved platinum in the reaction medium, the possibility of the Fenton-type mechanism would be little.

As was shown above in Table 1, the platinum catalyst supported on silica had too high oxygen hydrogenation activity and formed a large amount of water. As the ratio of hydrogen to oxygen was 3, predominant adsorption of hydrogen on platinum was estimated. On the other hand, vanadium oxide is a prominent oxidation catalyst [22], and therefore the interaction between vanadium compound and oxygen would be expected. If more oxygen is supplied from the vanadium compound to platinum and the ratio of hydrogen to oxygen on platinum is changed, the loss of  $\text{H}_2\text{O}_2$  by over-hydrogenation on platinum is expected to reduce. Thus,  $\text{H}_2\text{O}_2$  produced would be used effectively. In other words, the rate of phenol formation might have been improved at the expense of water formation, resulting in higher phenol selectivity based on oxygen.

As the concentration of  $\text{V}(\text{acac})_3$  increased more than the appropriate value (*vide supra*), the rate of phenol formation decreased. This may be caused by the unfavorable coverage of platinum site by the increased amount of  $\text{V}(\text{acac})_3$ .

It is frequently reported that some soluble vanadium compound forms a peroxo complex with  $\text{H}_2\text{O}_2$  [23–25]. Therefore, there remains some possibility that the real active species to oxidize benzene is not OH radical but the vanadium peroxo complex. As we did not find out free  $\text{H}_2\text{O}_2$  in the reaction mixture under the conditions adopted, the amount of  $\text{H}_2\text{O}_2$  to form the vanadium peroxo complex was supposed to be small.

## 4. Conclusions

The rate of phenol formation by the direct hydroxylation of benzene with oxygen and hydrogen on the platinum catalyst supported on silica was accelerated when acetylacetonates of vanadium, iron, lanthanum, and yttrium, especially vanadium acetylacetonate  $\text{V}(\text{acac})_3$ , were added to the reaction medium. Degree of acceleration depended on the vanadium compounds added, and  $\text{V}(\text{acac})_3$  improved the rate of phenol formation most significantly. It was speculated that vanadium compounds having vanadyl  $\text{V}=\text{O}$  was effective. The rate of phenol formation depended on the concentration of  $\text{V}(\text{acac})_3$ . It was assumed that oxygen was activated on the vanadium species and transferred to platinum. Thus, the relative amount of oxygen to hydrogen on platinum was affected by a vanadium compound to prevent over-hydrogenation of produced  $\text{H}_2\text{O}_2$ , and as a result, an effective usage of  $\text{H}_2\text{O}_2$  was attained.

## References

- [1] Y.C. Yen, Process Economics Program (Report No. 22), Stanford Research Institute International, Menlo Park, California, 1967.
- [2] A. Kunai, T. Wani, Y. Uehara, F. Iwasaki, Y. Kuroda, S. Ito, K. Sasaki, Bull. Chem. Soc. Jpn. 62 (1989) 2613.
- [3] A. Kunai, T. Kitano, Y. Kuroda, J. Li-Fen, K. Sasaki, Catal. Lett. 4 (1990) 139.
- [4] N. Herron, C.A. Tolman, Symp. Div. Petroleum Chem. Inc., J. Am. Chem. Soc. 32 (1987) 200.
- [5] T. Tatsumi, K. Yuasa, H. Tominaga, Chem. Commun. 1446 (1992).
- [6] T. Tatsumi, Japan Patent Application 5–320, 082, 1993.
- [7] I. Yamanaka, T. Nabeta, S. Takenaka, K. Otsuka, Stud. Scur. Sci. Catal. 130 (2000) 815.
- [8] K. Otsuka, I. Yamanaka, Chem. Lett. (1990) 509.
- [9] T. Jintoku, H. Taniguchi, Y. Fujiwara, Chem. Lett. (1987) 1865.
- [10] T. Jintoku, K. Takaki, Y. Fujiwara, Y. Fuchita, K. Hiraki, Bull. Chem. Soc. Jpn. 63 (1990) 438.
- [11] T. Jintoku, K. Nishimura, K. Takaki, Y. Fujiwara, Chem. Lett. (1990) 1687.
- [12] T. Jintoku, K. Nishimura, K. Takaki, Y. Fujiwara, Chem. Lett. (1991) 193.
- [13] G.I. Panov, G.A. Shereleva, A.S. Kharitonov, V.N. Romannikov, L.A. Vostrikova, Appl. Catal. A 82 (1992) 31.
- [14] A.S. Kharitonov, G.A. Shereleva, G.I. Panov, V.I. Sobolev, Ye.A. Paukshtis, V.N. Romannikov, Appl. Catal. A 98 (1993) 33.

- [15] T. Miyake, M. Hamada, Y. Sasaki, M. Oguri, *Appl. Catal. A: general* 131 (1995) 32.
- [16] K.A. Joergensen, *Chem. Rev.* 89 (1989) 431.
- [17] A.F. Wells (Ed.), *Structural Inorganic Chemistry*, 5th Edition, Oxford Scientific Publications, Oxford, 1984, p. 1195.
- [18] A.I. Dalton Jr., E.J. Greskovich, R.W. Skinner, US Patent 4,389,390, 1983.
- [19] L.W. Gosser, US Patent 4,681,751, 1987.
- [20] L.W. Gosser, J.T. Schwartz, US Patent 4,832,938, 1989.
- [21] Y. Izumi, Japan Patent Application 51-4,097, 1976.
- [22] G.C. Bond, F. Tahir, *Appl. Catal.* 71 (1991) 1.
- [23] M. Bonchio, V. Conte, F.D. Furia, G. Mondera, S. Moro, *J. Org. Chem.* 59 (1994) 6262.
- [24] V. Conte, F.D. Furia, S. Moro, *J. Mol. Catal.* 94 (1994) 323.
- [25] P.M. Reis, J.A.L. Silva, J.J.R. Frausto da Silva, A.J.L. Pombeiro, *Chem. Commun.* (2000) 1845.