

## Liquid Phase Oxidation of Benzene to Phenol with Molecular Oxygen using Carbon-based Fe-Pd and Cu-Pd Catalyst

Md. Azhar Uddin\*, Manbu Tanihara\*\*, Akinori Muto\*\* and Yusaku Sakata\*\*

(Received November 30, 2005)

### Abstract:

Liquid phase oxidation of benzene to phenol was carried out with O<sub>2</sub> using carbon-based Fe-Pd and Cu-Pd catalysts at 40 °C. The carbon-based Fe-Pd and Cu-Pd catalyst were prepared by modified carbothermal reduction of metal ion exchange method using cation exchange resin as a source of carbon. Fe/carbon, Cu/carbon and Pd/carbon were not effective for the oxidation of benzene to phenol with O<sub>2</sub> when H<sub>2</sub> was used as a catalyst reducing agent, however both Fe/carbon and Cu /carbon catalysts revealed activities when ascorbic acid was used as a reducing agent. Bimetallic catalysts such as Fe-Pd/carbon and Cu-Pd/carbon showed much higher activity for phenol production than the monometallic catalysts even when H<sub>2</sub> was used a reducing agent. Catalytic activity of Fe-Pd catalyst was much (ca. 2.5 times) higher than the Cu-Pd /catalyst. A physical mixture of the single component catalysts such as Fe and Pd or Cu and Pd were not effective in the oxidation of benzene to phenol, suggesting that an intimate contact between Fe or Cu species with Pd species is necessary to formulate an active catalyst.

**Keywords:** *oxidation of benzene, synthesis of phenol, metal-carbon catalyst*

### 1 INTRODUCTION

Recently, large-scale industrial chemical processes, which generally involve several steps affected with the generation of by-products and waste, are subject to continuously increasing environmental concerns. Phenol is an important intermediate for the production of antioxidants, agrochemicals and polymers. More than 90% of the world production of phenol is obtained by the multi-step cumene process, while the direct hydroxylation of benzene has long remained highly desirable. Many attempts to accomplish one-step direct oxidation of benzene by molecular oxygen have not been completely successful.

The one-step synthesis of phenol through the benzene oxidation using gaseous oxygen is one of the most attractive oxidation reactions, though the direct oxygenation of benzene is very difficult due to the stability of benzene ring. Not only from an organic synthetic point of view, but from a practical point of view, the phenol production via the one-step process using gaseous oxygen is of interest, in spite of the established cumene process which includes a three-step scheme and accompanies the production of acetone as a byproduct. The pioneering approach for the liquid-phase direct synthesis of phenol is the liquid-phase benzene oxidation using the ferric sulfate-H<sub>2</sub>O<sub>2</sub> system (Fenton reagent) by Jefcoate et al (1969). The liquid-phase oxidation of benzene catalyzed by supported Cu catalysts supported on silica and zeolites using both gaseous oxygen and ascorbic acid as an oxidant and a reducing reagent, respectively have been reported in the literature (Ohtani *et al.*, 1995; Okamura *et al.*, 1998; Ohtani *et al.*, 2001). A number of catalyst systems consisting of Pt or Pd and

transition metal oxides for affecting an oxidation of benzene with a mixture of O<sub>2</sub> with H<sub>2</sub> in the liquid phase have also been described.

Porous carbon has certain advantages over typical metal oxides as supports for metal /metal compound dispersed catalysts since (1) it is inert under most reaction conditions, (2) the metal precursor can easily be reduced to metal by carbon during catalyst preparation (carbonization) and (3) it provides high dispersion and inhibits sintering of metal/metal compound within its small pore structure. We have developed a novel method of preparation of carbon-based metal/metal compounds catalyst by modified carbothermal reduction (MIER-CTR) method from metal ion-exchanged resin (MIER) paying particular attention to the fact that the metal ions absorbed in an ion-exchange resin are highly dispersed and carbonization of this metal ion-exchange resin will produce nano-particles of metal/metal compounds in the carbon matrix (Lingaiah *et al.*, 2000)

In the present study, we examine the catalytic properties of Fe, Fe-Pd and Cu, Cu-Pd supported carbon catalysts prepared by MIER-CTR method for the liquid phase oxidation of benzene to phenol with molecular oxygen at atmospheric pressure and at 313 K by batch operation.

### 2 EXPERIMENTAL

#### 2.1 Catalyst preparation and characterization

Carbon-based Fe-Pd and Cu-Pd catalysts were prepared by a metal ion-exchanged resin carbothermal reduction method (MIER-CTR). A detail of the MIER-CTR method was given elsewhere (Lingaiah *et al.*, 2000). Briefly, commercially available (Mitsubishi Chemical Co.) chelate type resin having a imino-diachetate (CR-11) group was taken in a glass column and treated with HCl (1 M) to convert it into CR11-H<sup>+</sup> by conventional ion exchange method. Then

\*Graduate School of Environmental Science, Okayama University.

\*\*Graduate School of Natural Science, Okayama University.

this was washed (till pH 7) and dried at room temperature (RT). The known concentration of metal nitrate ( $\text{Fe}(\text{NO}_3)_3$  or  $\text{Cu}(\text{NO}_3)_2$ ) or metal chloride ( $\text{PdCl}_2$ ) aqueous solution (200 ml) was taken in a beaker and the CR-11-H<sup>+</sup> resin was added and kept for 25 h. Then the metal ion-exchanged resin (CR-11-M<sup>n+</sup>; M=  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  or  $\text{Pd}^{2+}$ ) was washed with ion-exchanged water (2 l) and dried at RT for 24 h. The level of metal ion-exchange was varied by varying the concentration of metal salt solution. In a similar way, bimetallic (CR-11-M1<sup>n+</sup>-M2<sup>n+</sup>; M1=Fe or Cu and M2= Pd) ion exchanged resin was prepared by partial ion-exchange method with aqueous solution of  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$  ions. The metal ion exchanged resins were dried at 110 °C for 1h. The carbonization processes for metal ion-exchanged resin was carried out by heat treatment at 800 °C at a constant rate of 5 °C/min in  $\text{N}_2$  (300 ml/min) flow and held for 3 h

X-ray diffraction patterns of the catalysts were recorded on a powder X-ray diffractometer (Rigaku, RINT 2500) using  $\text{Cu K}\alpha$  radiation. The mean

## 2.2 Catalytic oxidation of benzene with $\text{O}_2$

Benzene (reagent grade) was used without further purification. Both acetic acid (reagent grade) and ascorbic acid (reagent grade) were used as received. The liquid-phase oxidation of benzene was carried out in a 100  $\text{cm}^3$  three-necked flat-bottomed flask, in which 10  $\text{cm}^3$  (113 mmol) of benzene in 40  $\text{cm}^3$  of aqueous acetic acid solvent (1N), 5.7mmol of ascorbic acid and 0.5 g of catalyst were mixed using a magnetic stirrer at 303K in a flowing  $\text{O}_2$ (20 ml/min) atmosphere (0.1MPa). Similarly, when  $\text{H}_2$  was used as an reducing agent, 10  $\text{cm}^3$  (22.5 mmol) of benzene in 40  $\text{cm}^3$  of aqueous acetic acid solvent and 0.4 g of catalyst were mixed using a magnetic stirrer at 313K in a  $\text{O}_2$ (67%)/ $\text{H}_2$ (33%) flow at 0.1MPa. The oxidation product was collected periodically and analyzed by a GC with flame ionization detector.

## 3 RESULTS AND DISCUSSION

### 3.1 Physico-chemical properties of Fe/carbon, Cu/carbon, Fe-Pd/carbon and Cu-Pd/carbon catalysts

**Table 1** Physico-chemical properties of the catalysts

No	Exchanged ion	XRD detected species	Specific surface area [ $\text{m}^2/\text{g-cat}$ ] <sup>*</sup>	Metal content [ $\text{g/g-cat}$ ]			Metal particle size [ $\text{nm}$ ] <sup>**</sup>			
				Fe	Cu	Pd	Fe	Cu	$\text{Fe}_3\text{C}$	Pd
1	$\text{Fe}^{3+}$	Fe, $\text{Fe}_3\text{C}$	260	0.291	-	0	19.3	-	26.2	-
2	$\text{Pd}^{2+}$	Pd	90	0	-	0.069	-	-	-	16.0
3	$\text{Fe}^{3+}$ - $\text{Pd}^{2+}$	Pd	350	0.036	-	0.068	-	-	-	13.4
4		Fe, $\text{Fe}_3\text{C}$ , Pd	380	0.111	-	0.054	12.7	-	19.3	11.1
5		Fe, $\text{Fe}_3\text{C}$ , Pd	350	0.149	-	0.048	12.7	-	19.0	10.0
6		Fe, $\text{Fe}_3\text{C}$	360	0.294	-	0.022	13.7	-*	20.8	-
7		Fe, $\text{Fe}_3\text{C}$ , Pd	330	0.123	-	0.015	14.3	-	22.7	11.5
8		Fe, $\text{Fe}_3\text{C}$	300	0.130	-	0.016	12.1	-	-	-
9	$\text{Cu}^{2+}$	Cu	350	-	0.313	0	-	14.8	-	-
10	$\text{Cu}^{2+}$ - $\text{Pd}^{2+}$	Cu	360	-	0.307	0.029	-	12.7	-	-

\* Determined by  $\text{N}_2$  adsorption/desorption method, \*\* determined from XRD spectra using Scherrer equation

crystalline diameters were calculated by Scherrer's equation. The nitrogen adsorption/ desorption isotherms at -196 °C were obtained by using an adsorption unit (BLSORP 28SP, BEL Japan). The BET surface area and total pore volume were obtained from the adsorption isotherms. The Metal content in the catalysts was estimated by using thermogravimetry (TGA 51, Shimadzu) with the 4%  $\text{O}_2$ - $\text{N}_2$  gas (200 ml/min) (temperature program: 0-110 °C (keep 1 h) to 900 °C

The physico-chemical properties of Fe/carbon, Cu/carbon, Fe-Pd/carbon and Cu-Pd/carbon catalysts are presented in Table 1. The surface areas of the catalysts were in range of 260-390  $\text{m}^2/\text{g}$  except for Pd/carbon catalyst. The crystalline phases of the catalysts detected by XRD were metallic Fe and  $\text{Fe}_3\text{C}$  for Fe component, metallic Cu for Cu component and metallic Pd for Pd component. The metal loading of both Fe/carbon and Cu/carbon catalyst was about 30 wt%. For Fe-Pd

**Table 2** Oxidation of benzene to phenol with  $\text{O}_2$  over carbon-based Fe, Cu, Fe-Pd and Cu-Pd catalysts

Sample No	Exchanged ion	XRD detect species	Metal contents [ $\text{g-metal/g-cat}$ ]			Phenol Yield		Rate of phenol production [ $\text{mmol/h}\cdot\text{g-cat}$ ]	
			Fe	Cu	Pd	Reducing agent		Reducing agent	
						Ascorbic acid	$\text{H}_2$	Ascorbic acid	$\text{H}_2$
1	$\text{Fe}^{3+}$	Fe	0.29	-	-	0.2	0	0.074	0
2	$\text{Pd}^{2+}$	Pd	-	-	0.069	-	0	-	0
9	$\text{Cu}^{2+}$	Cu	-	0.31	-	0.11	0	0.041	0
6	$\text{Fe}^{3+}$ - $\text{Pd}^{2+}$	Fe	0.29	-	0.022	0.42	0.65	0.160	0.244
10	$\text{Cu}^{2+}$ - $\text{Pd}^{2+}$	Cu	-	0.30	0.029	0.15	0.03	0.055	0.012

Reaction conditions: benzene: 10 ml (113 mmol), solvent: 1N acetic acid (40 ml); gas flow rate:  $\text{O}_2$  (20 ml/min) or 3% $\text{H}_2$ - $\text{O}_2$  (20 ml/min), reducing agent:  $\text{H}_2$  or ascorbic acid (5.7 mmol); reaction temperature: 313 K; reaction time: 6 h.

(keep 3 h)).

bimetallic catalysts, the Fe loading was varied from 3.6 wt% to a maximum of 30 wt% while the Pd loading was

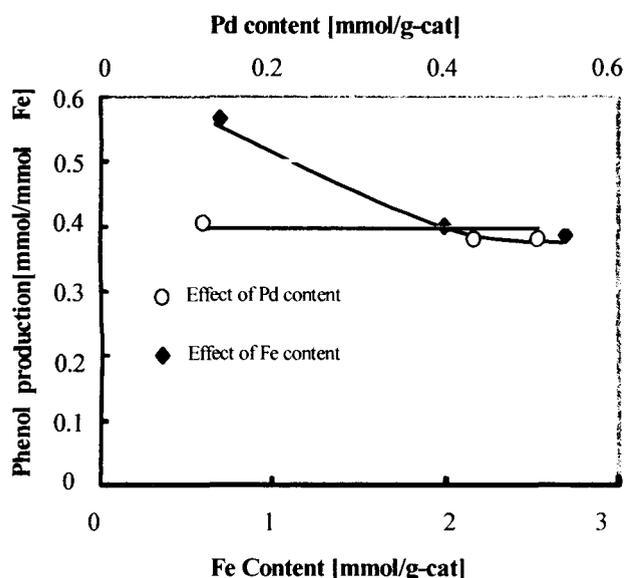
varied from 1.5 wt% to a maximum of 7wt%. Cu and Pd loadings of the Cu-Pd/carbon catalyst were 30 wt% and 3 wt%, respectively. The crystallite sizes determined by Scherrer's equation were 12-20 nm for Fe, 19-26 nm for Fe<sub>3</sub>C, 13-15 nm for Cu and 10-16 nm for Pd.

### 3.2 Catalytic activities of Fe/carbon, Cu/carbon, Fe-Pd/carbon and Cu-Pd/carbon catalysts for oxidation of benzene to phenol

Table 2 shows the catalytic activities of monometallic Fe/carbon and Cu/carbon catalysts and bimetallic Fe-Pd/carbon Cu-Pd/carbon catalysts for the oxidation of benzene to phenol. The yield of phenol after 6 h of reaction time and the rate of phenol production per hour per gm of catalyst are compared for each catalyst in this table. For Fe/carbon catalyst, phenol production observed when ascorbic acid was used as a reducing agent, however phenol was not produced with H<sub>2</sub> as a reducing agent. Similar results were obtained with Cu/carbon catalyst but the rate of phenol production was slower for Cu/carbon than Fe/carbon catalyst. On the other hand a significant enhancement in phenol yield and phenol production rate was observed for bimetallic Fe (29%)-Pd (2.2%)/carbon catalyst. Furthermore, the Fe (29%)-Pd (2.2%)/carbon catalyst was also active for phenol production from benzene oxidation with H<sub>2</sub> as a reducing agent. Cu (30%)-Pd (2.9%)/carbon also revealed a similar trend for phenol production but the activity was lower than the Fe (29%)-Pd (2.2%)/carbon catalyst.

### 3.3 Effect of Fe and Pd contents of Fe-Pd/carbon catalysts on the production of phenol

Figure 1 shows the effect of Fe and Pd contents of the Fe-Pd/carbon catalysts on the phenol production (mmol) per mmol of metal. It is seen that phenol production decreased with the Fe content, while it remained almost constant for the increase of Pd contents. It is also evident that maximum phenol production was obtained for the catalysts containing equimolar amount of Fe and Pd.

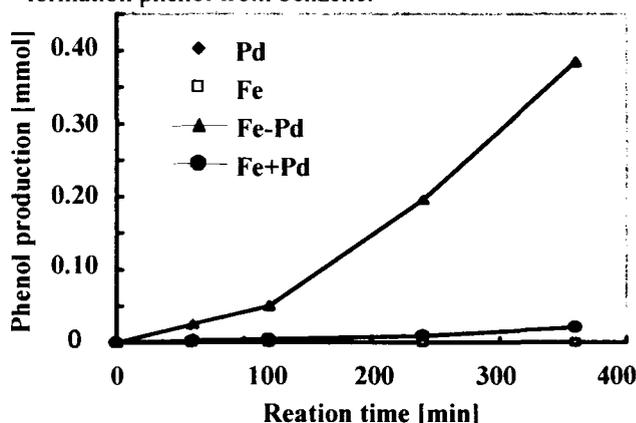


**Fig. 1** Effect of Fe and Pd content of Fe-Pd/carbon catalyst on phenol production

Reaction conditions: benzene: 10 ml (113 mmol), solvent: 1N acetic acid (40 ml); gas flow rate: O<sub>2</sub> (20 ml/min) or 3%H<sub>2</sub>-O<sub>2</sub> (20 ml/min), reducing agent: H<sub>2</sub> or ascorbic acid (5.7 mmol); reaction temperature: 313 K; reaction time: 6 h.

### 3.4 Activity of Physical mixture of Fe/carbon and Pd/carbon catalysts and Fe-Pd/carbon bimetallic catalyst

As we have seen in the previous section that the bimetallic Fe-Pd/carbon catalysts were highly active for phenol production, it is of great interest to investigate whether the existence of both Fe and Pd in the same carbon support is necessary for the enhancement in phenol production. A physical mixture of Fe/carbon and Pd/carbon catalysts were tested for the oxidation of benzene and compared with the activity of Fe-Pd/carbon bimetallic catalyst in which both Fe and Pd exist in the same carbon support. Figure 2 shows the amount of phenol production from benzene oxidation with O<sub>2</sub> in the presence of H<sub>2</sub> at 313 K. The results of this experiment indicate that monometallic Fe/carbon Pd/carbon possess no activity for phenol production. The physical mixture of Fe/carbon and Pd/carbon catalysts produced a very small amount of phenol. On the other hand, for the bimetallic Fe-Pd/carbon catalysts, phenol production increased with reaction time monotonously. The above results suggest that the presence of an intimate contact between Fe and Pd is essential for activation of substrates, in this case O<sub>2</sub>, H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub>, for the formation phenol from benzene.



**Fig. 2** Oxidation of benzene to phenol with O<sub>2</sub> over of Fe/carbon, Cu/carbon, physical mixture of Fe/carbon +Cu/carbon and Fe-Pd/carbon catalyst.

Reaction conditions: benzene: 10 ml (113 mmol), solvent: 1N acetic acid (40 ml); gas flow rate: O<sub>2</sub> (20 ml/min) or 3%H<sub>2</sub>-O<sub>2</sub> (20 ml/min), reducing agent: H<sub>2</sub> or ascorbic acid (5.7 mmol); reaction temperature: 313 K; reaction time: 6 h.

### REFERENCES

- Jefcoate, C.R.E.; Smith, J. R. L.; Norman, R. O. C. (1969): Hydroxylation. IV. Oxidation of some benzenoid compounds by Fenton's reagent and the ultraviolet irradiation of hydrogen peroxide. *J. Chem. Soc.* 8, 1013-18.
- Lingaih, N.; Uddin, M. A.; Muto, A.; Iwamoto, T.; Yusaku Sakata, Y.; Kusano, Y. (2000): *J. Mol. Catal. A:Chem.*, 161, 157-162
- Miyahara, T.; Kanzaki, H.; Hamada, R.; Kuroiwa, S.; Nishiyama, S.; Tsuruya, S. (2001): Liquid-phase oxidation of benzene to phenol by CuO-Al<sub>2</sub>O<sub>3</sub> catalysts prepared by co-precipitation method. *J. Mol. Catal. A: Chem.* 176, 141-150.
- Ohtani, T.; Nishiyama, S.; Tsuruya, S.; Masai, M. (1995): Liquid-phase benzene oxidation to phenol with molecular oxygen catalyzed by Cu-zeolites. *J. Catal.* 155, 158-162.
- Okamura, J.; Nishiyama, S.; Tsuruya, S.; Masai, M. (1998): Formation of Cu-supported mesoporous silicates and aluminosilicates and liquid-phase oxidation of benzene catalyzed by the Cu-mesoporous silicates and aluminosilicates. *J. Mol. Catal. A:Chem.* 135, 133-141.