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A Novel Catalyst of Cu–Bi–V–O Complex in Phenol Hydroxylation with Hydrogen Peroxide

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A novel complex oxide of Cu–Bi–V–O was hydrothermally synthesized in a Bi_2O_3–V_2O_5–CuO–H_2O system, and it was found that this compound is catalytically active for phenol hydroxylation by H_2O_2, which is comparable to TS-1. Reaction temperature, solvent, the molar ratio of phenol to H_2O_2, reaction time, catalyst amount, and method of H_2O_2 addition were found to be major factors for phenol conversion and product selectivity. Furthermore, electron spin resonance (ESR) was used to characterize the reaction intermediates, two species assigned to hydroxyl radicals and hydroperoxyl radicals were observed, and the hydroxyl radicals are proposed to play important roles in the formation of products in catalytic phenol hydroxylation by H_2O_2. © 2000 Academic Press

Key Words: **complex oxide of Cu–Bi–V–O; catalytic phenol hydroxylation; hydrogen peroxide; novel catalyst for oxidation reactions.**

INTRODUCTION

Diphenols are important chemical materials; their production from hydroxylation of aromatic compounds is always of great interest to chemists, in particular for phenol direct hydroxylation by H_2O_2 (1). Of the environmentally benign materials, hydrogen peroxide (H_2O_2) is the most attractive for organic laboratory and small-scale procedures because H_2O_2 offers many advantages such as high active oxygen content and the absence of by-products. These reactions, due to absence of by-products, are considered "clean reactions," which are one of the present urgent goals of research in chemistry. Historically, phenol hydroxylation has been widely investigated over various catalysts such as mineral acids (2–4), simple metal ions (5, 6), and metal complexes (7–9). Although some of these catalysts have shown potential catalytic activities, the obvious disadvantages of homogeneous reactions are too distinct to prevent their wide use in phenol catalytic oxidation. A heterogeneous catalytic system has advantages over homogeneous systems since it allows simple separation and recovery of the catalyst from the reaction mixture. Therefore, heterogeneous catalysis over pure metal oxides or supported oxides has been studied extensively, e.g., MoO_3 (10), CuO/SiO_2 (11), Fe_2O_3 (12), Fe_2O_3/Al_2O_3 (13), Co_3O_4 (14), V_2O_5, and TiO_2 colloidal particles (15). However, these oxides show either low catalytic activity or undesirable product selectivity.

Microporous titanosilicalites, due to their high activity in a wide range of oxidation reactions, minimal nonproductive hydrogen peroxide decomposition, and high catalyst stability, have opened an important catalysis area in zeolite research (16–19). The first commercial process utilizing titanium silicalite (TS-1) as a catalyst was the hydroxylation of phenol introduced by Enichem (20, 21). After that, a series of microporous and mesoporous materials containing framework titanium and vanadium species were investigated intensively, such as TS-2 (22, 23), Ti-β (24), Ti-MCM-41 (25), Ti-ZSM-48 (26), TAPO-5, TAPO-11 (27), zirconotitanosilicates (28), and VS-2 (29). Despite the obvious attractiveness of these transition metal substituted molecular sieves, their somewhat complicated synthesis and low reaction rates will limit their application as popular catalysts for catalytic oxidation in organic chemistry. It has been reported that vanadium and copper sites are active in phenol hydroxylation separately, for example, VS-2 (29, 30), V_2O_5–SiO_2 xerogels (31), V–Zr–O complex (32, 33), and $CuAlCO_3$-HTLcs (HTLcs: hydrotalcite-like compounds) (34). However, catalysis on a complex with the two transition metals copper and vanadium has not been reported yet. Here we report the catalytic performance of a novel catalyst (Cu–Bi–V–O) with both vanadium and copper species.

EXPERIMENTAL

Materials

$Bi(NO_2)_3 \cdot 6H_2O$, $NaVO_3 \cdot 2H_2O$, NaOH, $CuCl_2$, H_2O_2, and phenol with A.R. purity were supplied from Beijing

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Chemical Co. Spin trapping reagent of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) with G.R. purity was purchased from Aldrich Chemical Co.

Synthesis of Samples

$Bi(NO_3)_3 \cdot 6H_2O$, $NaVO_3 \cdot 2H_2O$, and $CuCl_2$ were used as the starting materials in the synthesis, and NaOH was employed as a mineralizer. The preparation of $Cu_2Bi_4V_2O_{13} \cdot 3H_2O$ (Cu–Bi–V–O) with starting molar ratio in the reaction was 0.45 Bi_2O_3 : 0.45 V_2O_5 : 0.5 CuO : 5 Na_2O : 550 H_2O (35). A typical synthesis procedure was as follows: (1) 0.426 g $NaVO_3 \cdot 2H_2O$ was first dissolved in 30 ml NaOH (1.0 M) to form a solution, followed by addition of 1.308 g $Bi(NO_3)_3 \cdot 6H_2O$ and 0.255 g $CuCl_2$, forming the reaction mixture; (2) after stirring for 1 h at room temperature, homogeneous gel was formed, which was then sealed in a Teflon-lined stainless steel autoclave; (3) the gel was crystallized at 240°C for 3 days; (4) after crystallization, the product was filtered, washed with deionized water, and dried in air at ambient temperature. Greenish crystalline products were obtained. Furthermore, the sample was characterized by various techniques.

Similarly, the preparation of $Bi_{16}V_4O_{39}$ (Bi–V–O) and Bi_2CuO_4 (Bi–Cu–O) was also synthesized with the hydrothermal method, and their starting molar ratios were at 0.5 Bi_2O_3 : 0.5 V_2O_5 : 7.5 Na_2O : 550 H_2O and 0.5 Bi_2O_3 : 0.5 CuO : 25 Na_2O : 550 H_2O, respectively. The products were both crystallized at 240°C for 3 days.

Characterization Method

X-ray diffraction (XRD) data were collected on Rigaku D/Max IIIA diffractometer with Cu $K\alpha$ radiation, 40 KV, and 30 mA in the range 4–70° at room temperature. Thermal analysis including differential thermal analysis (DTA) and thermogravimetric analysis (TGA) was made with a Perkin–Elmer DTA-1700 and TGA-7PC analyzer with a heating rate of 10°C/min, respectively. X-ray photoelectron spectroscopy (XPS) was measured on an ESCA-LAB MKII spectrometer (VG Co.) with monochromatic light using Al $K\alpha$ radiation, and the base pressure was 10^{-7} Pa. The $C1s$ signal at 284.3 eV was used as the internal standard. The scanning electron micrograph (SEM) investigation was performed with a Hitachi X-650B electron microscope. The sample compositions were determined by inductively coupled plasma (ICP) with a Perkin–Elmer plasma 40 emission spectrometer. The surface area of the catalyst was measured with nitrogen adsorption methods (BET) by using a Micro ASAP 2010 M at 77 K, and the adsorption isotherms, for, e.g., water and hexane, were carried out with the Cahn-2000 microbalance at room temperature (298 K). The sensitivity of the microbalance was ±0.1 μg. Electron spin resonance (ESR) spectra were recorded at room temperature with a Brucker ER 200D-SRC instrument at a frequency of 9.77 GHz, a microwave power of 6.5 mW, a modulation frequency of 100 KHz, a field modulation intensity of 1.25 Gpp, a time constant of 500 ms, a scan range of 100 G, and a mild range of 3480 G.

Catalytic Hydroxylation of Phenol

Phenol hydroxylation experiments were run in a 50-ml glass reactor equipped with a reflux condenser and a magnetic stirrer. In a typical experimental procedure, 80 mg catalyst was mixed with 1.67 g phenol in the glass reactor, followed by addition of 15 ml water as a solvent, which was heated to the reaction temperature. Then, 0.60 ml H_2O_2 (30% aqueous solution) was added into the reaction mixture dropwise using a syringe pump for 40 min. The reaction temperature was in the range 60–90°C. After the reaction, the products including catechol (CAT), hydroquinone (HQ), and benzoquinone (BQ) were taken out periodically and analyzed on gas chromatography (Shimadzu GC-9A) with a flexible quartz capillary column coated with OV-17. The initially programmed temperature was 140°C, and the final temperature was 186°C. The H_2O_2 conversion was determined by two methods: (1) The efficiency conversion of H_2O_2 was calculated as follows: H_2O_2 eff. conv. = 100 · H_2O_2 (mol) consumed in formation of diphenols and benzoquinone/total H_2O_2 (mol) added. (2) The H_2O_2 conversion was determined by decomposition of H_2O_2 experimentally.

ESR Spin-Trapping Measurements

Electron spin resonance (ESR) spectra were recorded at room temperature and DMPO (5,5-dimethyl-1-pyrroline N-oxide) was used as the spin trapping reagent. In a typical run, 24.6 mg sample was mixed with 25 μl DMPO; then 45 μl aqueous H_2O_2 solution was added. Finally, the mixture was fed into the ESR tube, which was inserted into the cavity of an ESR spectrometer. At the same time, the ESR spectra were measured. In order to measure the intensity of radicals quantitatively, a quartz tube of 1 mm diameter was used in all the experiments.

RESULTS AND DISCUSSION

Characterization of Various Catalysts

Figure 1 shows the XRD patterns of the Cu–Bi–V–O sample, which indicates a novel phase with a monoclinic system with cell parameters of $a = 1.497(2)$ nm, $b = 0.3692(1)$ nm, $c = 1.1168(3)$ nm, $\beta = 107.32(2)$, and $V = 0.6153(1)$ nm^3. Similarly, the samples of Bi–Cu–O and Bi–V–O also show new peaks of XRD patterns, indicating that Bi–Cu–O and Bi–V–O are also novel phases.

The molecular formula of the Cu–Bi–V–O sample was investigated by ICP analysis, which showed that the percentages of Bi, V, Cu, and O were at 63.2, 7.7, 9.7, and 19.4%, respectively, indicating that the molar ratio of the product

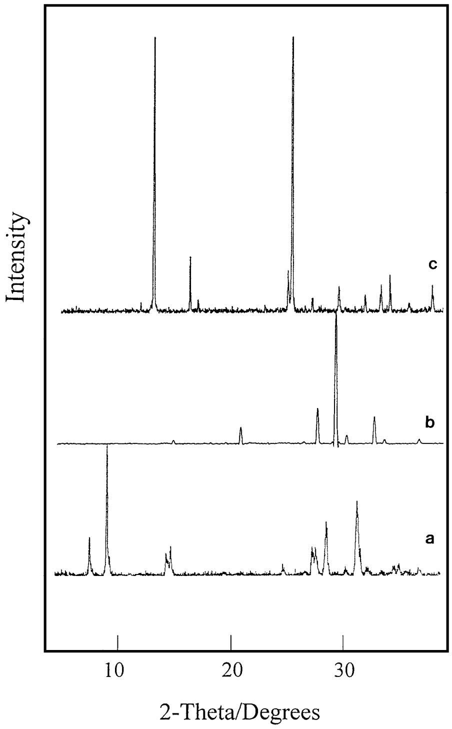

FIG. 1. X-ray powder diffractions for (a) Bi–V–O, (b) Bi–Cu–O, and (c) Cu–Bi–V–O samples.

was at 2Bi : 1V : 1Cu : 8O. Furthermore, the Bi–Cu–O and Bi–V–O samples showed molar ratios at 2Bi : 1Cu : 4O and 16Bi : 6V : 39O, respectively.

Chemical states on the surface of various elements were analyzed by the XPS technique. The spectra of $Bi4f_{7/2}$ and $Bi4f_{5/2}$, $V2P_{3/2}$ and $V2P_{1/2}$, $Cu2P_{3/2}$ and $Cu2P_{1/2}$ over the Cu–Bi–V–O sample exhibit at 158.6 and 163.9 eV, 516.7 and 524.3 eV, 934.0 and 954.0 eV, respectively. These results suggest that the bismuth, vanadium, and copper in the chemical state are at Bi^{3+} (36), V^{5+} (37), and Cu^{2+} (38), respectively. Similarly, XPS spectra show that the chemical states of bismuth, vanadium, and copper in the samples of Bi–Cu–O and Bi–V–O samples are the same as those of Cu–Bi–V–O.

The stability of the samples is investigated by thermal analysis, and DTA and TG curves show that all samples are stable below 500°C.

Isotherms for N_2 at 77 K over the samples of Cu–Bi–V–O, Bi–Cu–O, and Bi–V–O show that there is little adsorption of nitrogen, indicating that they do not have micropores and mesopores. The surface areas of these samples were measured at 1.5–3.6 m^2/g by N_2 adsorption, and little adsorption resulted from the outer surface of these catalysts. Furthermore, the adsorption of H_2O over Cu–Bi–V–O exhibited a low adsorption amount 1.4%, which was due to the small surface area of the sample. In contrast, we could not, observe the adsorption of *n*-hexane on this sample. The samples of Bi–Cu–O and Bi–V–O showed similar adsorption properties. Moreover, the adsorption of ammonia on these samples showed that there was no chemical adsorption, suggesting that these materials are not acidic, which is similar to TS-1.

The characterization data on surface area, crystal size, chemical adsorption, and elemental composition of various catalysts are summarized in Table 1.

Catalytic Phenol Hydroxylation

Catalytic activities over various catalysts. Catalytic activities in phenol hydroxylation over various catalysts such as CuO, V_2O_5, Bi_2O_3, $CuO + V_2O_5$, Bi–Cu–O, Bi–V–O, and Cu–Bi–V–O are presented in Table 2. V_2O_5 is almost inactive, giving a phenol conversion of only 1.4%. Bi_2O_3 and CuO show low conversions, 4.5 and 9.8%, respectively. The catalytic activity over the mechanical mixture of CuO and V_2O_5 gives low conversion, at 6.7%. Furthermore, the samples of Bi–V–O and Bi–Cu–O catalysts also exhibit low conversions (5.5 and 8.7%). It is very interesting to note that the Cu–Bi–V–O catalyst shows relatively high catalytic activity, giving conversion at 23.1% with diphenols selectivity at 97.7%. This activity is comparable with those of TS-1 which is well known as one of the best catalysts for catalytic oxidation by H_2O_2 (39). Since the surface area is small (3.6 m^2/g) and only the sites in the surface can interact with reactants in catalysis, a very high turnover number of Cu–Bi–V–O is achieved. At 80°C, the turnover frequency (446 h^{-1}) of the Cu–Bi–V–O is much higher than that (7.2 h^{-1}) of TS-1 catalyst. Considering the low activities for Bi–V–O and Bi–Cu–O catalysts, the high activity for Cu–Bi–V–O catalyst may be related to its unique structure.

TABLE 1

Characterization of Various Catalysts

Sample	Average particle size (μm)	Surface area (m^2/g)	Adsorption of *n*-Hexane (%)	Adsorption of Water (%)	Elemental analysis Cu/Bi/V/O	Ammonia adsorption
Cu–Bi–V–O	25	3.6	no	1.4	2/4/2/16	no
Bi–V–O	60	1.5	no	0.5	16/6/39	no
Bi–Cu–O	35	2.5	no	0.8	2/1/4	no

TABLE 2

Catalytic Performance in Phenol Hydroxylation over Various Catalysts[a]

Catalyst	Phenol conv. (%)	H_2O_2 eff. conv. (%)	Product selectivity (%)		
			BQ	CAT	HQ
V_2O_5	1.4	4.0	—	100	—
Bi_2O_3	4.5	14.1	4.6	18.3	77.1
CuO	9.8	32.7	11.3	20.7	68.0
Bi–V–O	5.5	19.4	17.3	65.4	17.3
Bi–Cu–O	8.7	30.1	15.2	62.0	22.8
$CuO + V_2O_5$	6.7	25.2	25.1	73.2	1.7
Cu–Bi–V–O	23.1	70.9	2.3	55.0	42.7
TS-1[b]	26.4	75.0	2.0	52.0	46.0

[a] Reaction conditions: water as solvent; reaction temperature 80°C; reaction time 4 h; phenol/H_2O_2 (molar ratio) = 3; catalyst/phenol (weight ratio) = 0.05.

[b] Reaction conditions (39): TS-1 with Ti/(Ti + Si) = 0.091; acetone as solvent; reaction temperature 57°C; reaction time 6 h; phenol/H_2O_2 (molar ratio) = 3; catalyst/phenol (weight ratio) = 0.1.

Because the highest activity is found on the Cu–Bi–V–O sample, catalytic investigation of various influencing factors for phenol hydroxylation is mainly focused on this catalyst.

Effect of the solvent. It has been reported that the solvent has profound influences on the phenol conversion and the ratio of catechol to hydroquinone over titanosilicalites (40, 41), VS-2 (29), and vanadium silicate xerogels (31). Table 3 presents the effect of various solvents in phenol hydroxylation over Cu–Bi–V–O catalyst. We observed that the sample of Cu–Bi–V–O was almost inactive in the organic solvents of acetone, acetonitrile, and 1,2-dichloroethane. Changing the solvent from organic solvents to water resulted in a significant increase of conversion. Obviously, phenol conversion increased with increasing polarity of the solvents (the conversions at 0, 1.1, 1.8, and 12.5% for acetone, acetonitrile, 1,2-dichloroethane, and water, respectively). In methanol and acetone, the Cu–Bi–V–O sample was inactive; however, both are the best solvents over TS-1 (39, 41). In contrast, over Cu–Bi–V–O catalyst the best solvent is water, which is considerably safer, cheaper, and more environmentally benign than organic solvents in industrial use. Wu *et al.* (34, 42, 43) reported that over the catalysts of $CuAlCO_3$-LTLcs and Iron(II)-8-quinolinol/MCM-41 the change in solvents resulted in large differences in conversion, suggesting that the free radicals were important intermediates in the catalysis. The results for solvent influence may suggest that the mechanism over the Cu–Bi–V–O sample might be different from that over titanosilicalites (20, 22).

TABLE 3

Influence of Various Solvents in Phenol Hydroxylation[a]

Solvent	Phenol conv. (%)	Product selectivity (%)		
		BQ	CAT	HQ
Methanol	inactive	—	—	—
Acetone	inactive	—	—	—
Acetonitrile	1.1	—	79.3	20.7
1,2-Dichloroethane	1.8	—	35.2	64.8
Water	12.5	26.8	56.1	17.1

[a] Reaction conditions: temperature at 60°C; other conditions are the same as those in Table 2.

TABLE 4

Influence of Temperature in Phenol Hydroxylation[a]

Temperature (°C)	Phenol conv. (%)	H_2O_2 eff. conv. (%)	Product selectivity (%)		
			BQ	CAT	HQ
60	13.2	42.9	8.4	52.9	38.7
70	18.9	59.4	4.8	55.9	39.3
80	23.1	70.9	2.3	55.0	42.7
90	20.2	61.2	0.8	54.3	44.9

[a] Reaction conditions are the same as those in Table 2.

Effect of reaction temperature. In order to choose the optimum reaction temperature at which phenol conversion and selectivity are most desirable, we performed this reaction in the temperature range 60–90°C, as presented in Table 4. It is observed that phenol conversion increases with temperature from 13.2 to 23.1% from 60–80°C. Meanwhile, H_2O_2 efficiency also increases with temperature from 42.9% at 60°C to 70.9% at 80°C. However, when the temperature is enhanced to 90°C, phenol conversion decreases to 20.2%, and H_2O_2 efficiency reduces to 61.2%. In addition, benzoquinone selectivity decreases with increasing temperature from 8.4% at 60°C to 0.8% at 90°C. To explain the decrease of conversion at higher temperature, it is proposed that benzoquinone was further oxidized to tar, and similar phenomena have been observed in the literature (44). Therefore, the suitable temperature for this catalytic reaction is 80°C.

Effect of reaction time. Table 5 presents the dependence of the reaction conversion and selectivity on reaction time. Obviously, relatively short reaction time results in incomplete conversion of phenol and H_2O_2. Moreover, the selectivity of benzoquinone in the product is very high at the beginning of the reaction. These phenomena are very similar to those on TS-1 (39). When phenol conversion gives a maximum conversion of 23.1% at 4 h, benzoquinone selectivity is only at 2.3%. When reaction time is prolonged beyond 4 h, phenol conversion and H_2O_2 efficiency reduce remarkably, exhibiting 9.8 and 29.5% at 8 h, respectively. This is assigned to the formation of a large amount of tar

TABLE 5

Influence of Reaction Time in Phenol Hydroxylation[a]

Reaction time (h)	Phenol conv. (%)	H_2O_2 eff. conv. (%)	Product selectivity (%)		
			BQ	CAT	HQ
1	12.9	50.2	29.7	54.8	15.5
2	16.7	56.4	12.6	57.9	29.5
3	20.3	65.8	8.1	55.3	37.6
4	23.1	70.9	2.3	55.0	42.7
6	13.2	40.3	1.7	55.1	42.2
8	9.8	29.5	0.5	56.2	41.3

[a] Reaction conditions are the same as those in Table 2.

TABLE 7

Influence of Phenol/H_2O_2 Molar Ratio in Phenol Hydroxylation[a]

Molar ratio of phenol to H_2O_2	Phenol conv. (%)	H_2O_2 eff. conv. (%)	Product selectivity (%)		
			BQ	CAT	HQ
3 : 1	23.1	70.9	2.3	55.0	42.7
2 : 1	29.6	59.2	—	56.3	43.7
1 : 1	38.9	38.9	—	65.2	34.8
1 : 2	40.7	20.4	—	62.9	37.1
1 : 3	51.2	17.1	—	67.6	32.4

[a] Reaction conditions are the same as those in Table 2.

product for a longer reaction time. The product of benzoquinone is generally considered as the oxidation product of hydroquinone, and benzoquinone is further oxidized to tar (45).

Effect of catalyst amount. Table 6 presents the effect of catalyst amount on catalytic activity and selectivity. Catalytic phenol hydroxylation does not occur in the absence of the catalyst. Phenol conversion increases with catalyst amount in the range 0–5% (weight ratio of catalyst to phenol); however, when the ratio is over 5%, the conversion reduces remarkably. For example, phenol conversion is 23.1% at the ratio 5%, and the conversion is only 13.1% at the ratio 10%. Additionally, we observe that H_2O_2 decomposition in the reaction increases with catalyst amount. When the catalyst amount is at 80 mg, 9.2% of total H_2O_2 is decomposed (2.4% of total H_2O_2 is decomposed over TS-1 catalyst under the same reaction conditions), and when the catalyst amount is 320 mg, 14.5% of H_2O_2 is decomposed. Therefore, having the ratio of catalyst to phenol at 5% is suitable for obtaining higher phenol conversion.

Effect of molar ratio of phenol to H_2O_2. Table 7 presents the effect of molar ratio of phenol to H_2O_2. We observe that phenol conversion increases with increasing molar ratio of H_2O_2/phenol, but H_2O_2 efficiency displays the opposite trend. When the molar ratio of H_2O_2/phenol is 1/3, phenol conversion is 23.1% and H_2O_2 efficiency is 70.9%. When the molar ratio is 3/1, phenol conversion is 51.2%, but H_2O_2 efficiency reduces to 17.1%. Keeping industrial processes in mind, we performed the experiments at a molar ratio of 3 : 1 (phenol/H_2O_2).

Effect of addition method for H_2O_2. The method of H_2O_2 addition has a large effect on conversion and product selectivity. The catalytic results of two methods of H_2O_2 addition are shown in Table 8. In the first method, H_2O_2 is completely added into the reaction mixture in one lot at room temperature, and the system is then slowly warmed to the reaction temperature (80°C). In the second method, the phenol-catalyst mixture is first heated to 80°C, and then H_2O_2 is added dropwise at 80°C over a period of 40 min. Obviously, phenol conversion and H_2O_2 efficiency are higher, and benzoquinone selectivity is lower, in the latter case. When H_2O_2 was added at room temperature, 12.4% of the H_2O_2 was decomposed. When H_2O_2 was added at 80°C, 9.2% of the H_2O_2 was decomposed. It is well known that when H_2O_2 is added into the reaction mixture in one lot, the effective concentration of H_2O_2 in the reaction is much higher than that achieved by dropwise addition, leading to formation of a large amount of benzoquinone, which is the product of further oxidation of hydroquinone. Similar phenomena have been reported in the literature (39).

TABLE 6

Influence of Catalyst Amount in Phenol Hydroxylation[a]

Catalyst amount (wt%)	Phenol conv. (%)	H_2O_2 eff. conv. (%)	Product selectivity (%)		
			BQ	CAT	HQ
0	0	0	0	0	0
1	10.5	33.5	6.5	52.8	40.7
2.5	18.7	57.2	1.9	55.3	42.8
5	23.1	70.9	2.3	55.0	42.7
10	13.1	40.6	3.4	50.1	46.5
20	9.9	31.2	4.9	52.9	42.2

[a] Reaction conditions are the same as those in Table 2.

TABLE 8

Influence of the Method of Addition of H_2O_2 in Phenol Hydroxylation[a]

Method of H_2O_2 addition	Phenol conv. (%)	H_2O_2 eff. conv. (%)	Product selectivity (%)		
			BQ	CAT	HQ
H_2O_2 addition in one lot at room temperature	15.2	47.4	3.9	55.9	40.2
H_2O_2 addition dropwise at 80°C	23.1	70.9	2.3	55.0	42.7

[a] Reaction conditions are the same as those in Table 2.

TABLE 9

Regeneration of the Catalyst in Phenol Hydroxylation[a]

Catalytic reaction	Phenol conv. (%)	Product selectivity (%) BQ	CAT	HQ
First run (fresh sample)	23.1	2.3	55.0	42.7
Second run (used sample from run 1)	18.4	2.2	55.8	42.0
Third run (used sample from run 2)	11.3	4.5	50.3	45.2
Fourth run (used sample from run 3)	6.2	3.9	51.8	44.3
Fifth run (regeneration by calcining used sample from run 4 at 500°C for 2h)	22.5	1.4	51.4	47.2
Tenth run (regeneration 5 times)	22.2	1.8	51.1	47.1

[a] Reaction conditions are the same as those in Table 2.

Regeneration of the catalyst. Phenol conversion reduces drastically from 23.1 to 6.2% after four runs over the Cu–Bi–V–O catalyst (see Table 9); it is proposed that the catalyst surface is poisoned by tar formed by deep oxidation of benzoquinone, preventing its further reaction with phenol. TG analysis on spent catalyst in oxygen atmosphere indicates the weight loss in the region 350–500°C is close to 25%, suggesting that the catalyst surface is partially covered with tar. However, when used Cu–Bi–V–O catalyst is calcined at 500°C for 2 h, its catalytic activity is maintained at the initial level, 22.5%, because the deposited tar on the catalyst surface is burned out. Moreover, the XRD and IR spectra show that the structure of the Cu–Bi–V–O catalyst remains unchanged after calcination, suggesting that it has high stability. Therefore, the catalyst can be regenerated easily without any significant loss in activity.

ESR Investigation for Various Samples

The ESR spectra of the DMPO with H_2O_2 on various samples are shown in Fig. 2. On the Bi–V–O sample, the spectrum shows signals at $a_N = 1.41$ mT, $a_H^\beta = 1.13$ mT, and $a_H^\gamma = 0.13$ mT, which are assigned to the adduct of DMPO with hydroperoxyl radical (46). The spectrum on the CuO sample shows signals at $a_N = a_H^\beta = 1.49$ mT, which are typically assigned to the adduct of DMPO with hydroxyl radical (47). The Bi–Cu–O sample also shows the same signals at $a_N = a_H^\beta = 1.49$ mT, but the intensity is slightly weaker. The spectrum on the Cu–Bi–V–O sample exhibits both very strong signals at $a_N = a_H^\beta = 1.49$ mT and weak signals at $a_N = 1.41$ mT, $a_H^\beta = 1.13$ mT, and $a_H^\gamma = 0.13$ mT, which are assigned to hydroxyl radicals and hydroperoxyl radicals, respectively.

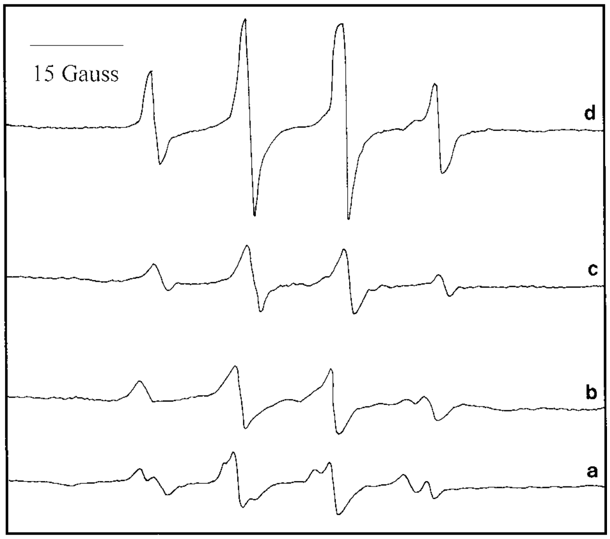

FIG. 2. ESR spectra of DMPO with H_2O_2 on the samples of (a) Bi–V–O, (b) Bi–Cu–O, (c) CuO, and (d) Cu–Bi–V–O.

ESR spin trapping experiments showed that hydroperoxyl radicals were formed in the reaction of Bi–V–O with H_2O_2, and hydroperoxyl radicals might be the intermediates in the phenol hydroxylation on Bi–V–O catalyst. Similar phenomena have been observed on the catalysts VS-1 and VS-2 (29, 30). Because the intensity of the hydroperoxyl radical was relatively low, the catalytic activity of Bi–V–O was also low.

Hydroxyl radicals were observed in the reaction of Bi–Cu–O and CuO with H_2O_2, which resulted from interaction of H_2O_2 with Cu^{2+} species in these catalysts. These hydroxyl radicals are possibly intermediates in the catalysis on CuO and Bi–Cu–O (34, 42, 43). Notably, both hydroxyl radicals and hydroperoxyl radicals were observed in the mixture of Cu–Bi–V–O with H_2O_2, but the intensity of hydroxyl radicals was much stronger than that of hydroperoxyl radicals. Relating to the large difference in catalytic activity on various catalysts, we suggest that the higher activity in the Cu–Bi–V–O catalyst is mainly from a larger amount of hydroxyl radicals, which result from the unique structure of the sample. As shown in Fig. 3, the dependence of the

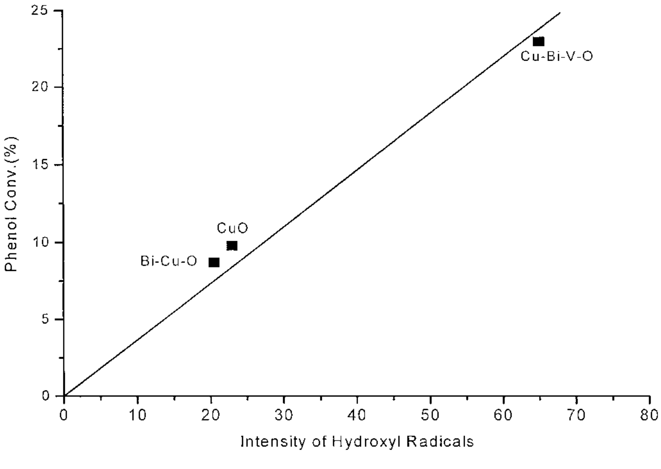

FIG. 3. Catalytic activity as a function of the relative intensity of hydroxyl radicals characterized by ESR.

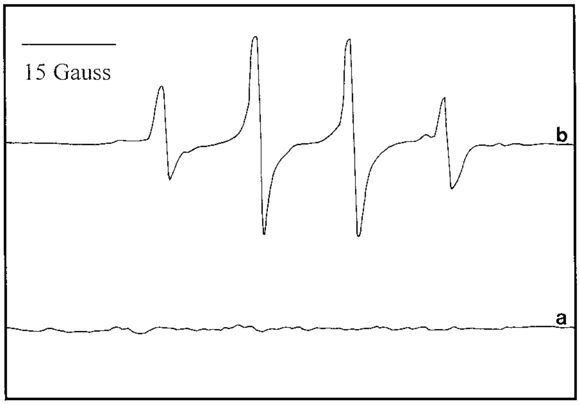

FIG. 4. ESR spectra of (Cu–Bi–V–O)–H_2O_2–DMPO mixture (a) after addition of phenol and (b) without addition of phenol.

intensity of hydroxyl radicals on the catalytic activity over Cu–Bi–V–O, Bi–Cu–O, and CuO is plotted, and a linear relationship between hydroxyl radical intensity with catalytic activity is observed, confirming that the hydroxyl radicals are important intermediates for the phenol hydroxylation by H_2O_2.

Furthermore, when phenol was added into the reaction mixture of the Cu–Bi–V–O catalyst system (catalyst + H_2O_2 + DMPO), the signals assigned to hydroxyl and hydroperoxyl radicals disappeared very quickly (Fig. 4), and the products of diphenols were observed by the characterization of mass spectroscopy technique. These results suggest that these radicals are important intermediates in the catalytic reactions.

Because hydroxyl radicals and hydroperoxyl radicals are electrophile, and tend to allow electrophilic attack at the *ortho* and *para* positions of phenol to form catechol and hydroquinone (48, 49), no resorcinol is detected in this reaction.

As presented in Table 3, it was observed that over Cu–Bi–V–O catalyst phenol hydroxylation in water proceeded better than in the other organic solvents. This phenomenon is possibly explained by these active radicals being more easily formed and dispersed in water than those in the other organic solvents, in good agreement with the literatures (42, 43).

CONCLUSIONS

A novel catalyst of Cu–Bi–V–O complex oxide has been hydrothermally synthesized, and its catalytic data in phenol hydroxylation by hydrogen peroxide show that Cu–Bi–V–O complex oxide is very active, which is comparable with TS-1. Moreover, investigation using the ESR spin-trapping technique on the catalyst has suggested that Cu^{2+} species are major active sites, and hydroxyl radicals are proposed to be major active intermediates in phenol hydroxylation.

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