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Catalytic performance in phenol hydroxylation by hydrogen peroxide over a catalyst of V–Zr–O complex

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Abstract

The hydroxylation of phenol into catechol and hydroquinone with hydrogen peroxide has been carried out over a novel type of complex oxide $H_xV_2Zr_2O_9H_2O$ with V^{4+} and V^{5+} mixed-valence. The catalytic activity depends on crystal size of the catalysts. The phenol conversion over the catalyst with crystal size of 7 μm is double that over catalyst with crystal size of 35 μm. The V^{5+} species are suggested to be the catalytic active sites. The reaction time, reaction temperature, the nature of the solvent, molar ratio of phenol to hydrogen peroxide, and amount of catalysts were found to be major factors for phenol conversion and product selectivity. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic phenol hydroxylation; Hydrogen peroxide; V–Zr–O complex

1. Introduction

Ecologically friendly technologies is one of the most important subjects in chemistry, in particular for partial oxidation of organic compounds. Phenol hydroxylation by hydrogen peroxide is a typical example for ecologically friendly technologies by using catalysts, which is widely applied in industrial chemistry for the preparation of catechol and hydroquinone. Since 1970s, in homogeneous liquid phase, hydroxylation of phenol catalyzed by mineral acid [1–3], simple metal ions, and their complexes [4–6] with H_2O_2 as oxidant, has been extensively investigated. Although some of these catalysts showed potential catalytic activities, the disadvantages of homogeneous reaction are very distinct to prevent their wide use in phenol catalytic oxidation. Pure metal oxide or supported oxides show either the low catalytic activity or undesirable product selectivity [7–12], such as Fe_2O_3 [7], Co_3O_4 [8], Fe_2O_3/Al_2O_3 [9], CuO/SiO_2 [10], MoO_3 [11], V_2O_5 and TiO_2 colloidal particles [12]. Titanium substituted molecular sieves such as TS-1 [13,14] exhibited unique catalytic behavior including fairly high activity and selectivity, and high catalyst stability [15,16], which have led to an extraordinary series of work on the use of transition metal substituted molecular sieves as catalysts of phenol hydroxylation. For examples, TS-2 [17,18], Ti–ZSM-48 [19], Ti-β [20], TAPO-5, TAPO-11 [21], Ti–MCM-41 [22], VS-2 [23], zirconotitanosilicates [24] were widely studied. Despite of the obvious attraction of the titanium silicalite zeolites as catalysts, somewhat complicated synthesis, small pore size and low reac-

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tion rates [25] will perhaps limit their application as a usual tool for oxidation in chemistry. Vanadium was reported to be active in some other catalytic oxidation reactions [26], and the compound of $H_xV_2Zr_2O_9H_2O$ is a novel complex oxide with double transition metal, showing many advantages such as the cheaper preparation and the higher stability than that of TS-1. The goals of this research is to investigate the catalytic properties of the novel complex oxide $H_xV_2Zr_2O_9H_2O$ in phenol hydroxylation.

2. Experimental

The catalysts $H_xV_2Zr_2O_9H_2O$ were hydrothermally prepared according to the report before [27], using gels of the following molar compositions: $0.5V_2O_5$:$1.0ZrO_2$:1.0NaF:$500H_2O$. The products were characterized by X-ray diffraction (XRD, Cu K_α radiation at λ=1.5418 Å, Siemens D5005), adsorption (Cahn-2000), scanning electron micrograph (SEM, Hitachi X-650), and X-ray photoelectron spectroscopy (XPS, ESCALAB-MK II, internal standard with C_{1S} at 284.6 eV).

Catalytic phenol hydroxylation reactions were run in a 50 ml glass reactor and stirred with a magnetic stirrer. In a standard run, 1.67 g of phenol, 0.1 g of catalyst, and 20 ml of solvent were mixed, followed by addition of 2 ml of H_2O_2 (30 wt% aqueous). The range of reaction temperature was 50–80°C. After reaction for 4–8 h, the product was taken out periodically and analyzed by gas chromatography (Shimadzu GC-9A).

3. Results

3.1. Characterization of V–Zr–O complex

Two vanadium zirconates were synthesized. The first was formed in V_2O_5–ZrO_2–NaF–H_2O, and the second sample was crystallized in V_2O_5–ZrO_2–NaF–H_2O in the presence of KI. Both give the same XRD pattern (Fig. 1), and are in accord with their literature spectra.

XPS investigation for sample 1 (Fig. 2) shows that the spectra of $Zr3d_{5/2}$ and $Zr3d_{3/2}$ exhibit peaks at 181.9 and 183.2 eV, respectively, which is in good agreement with those of Zr^{4+}, suggesting that zirconium species are in the chemical state of Zr^{4+}. Furthermore, the spectrum of $V2p_{3/2}$ gives a broad peak at near 516.8 eV, which seems to related to overlapping of V^{4+} and V^{5+}. After computer fitting, it is given two peaks at 514.5 and 517.2 eV, respectively, which are well consistent with those of characteristic V^{4+} and V^{5+} species in literature [28]. These results suggest that the vanadium species in the sample 1 are V^{4+} and V^{5+}, and the molar ratio of V^{4+} and V^{5+} are estimated by peak intensity of $V2p_{3/2}$, as shown in Fig. 2. Similarly, the other samples of V–Zr–O complex were also characterized by XPS.

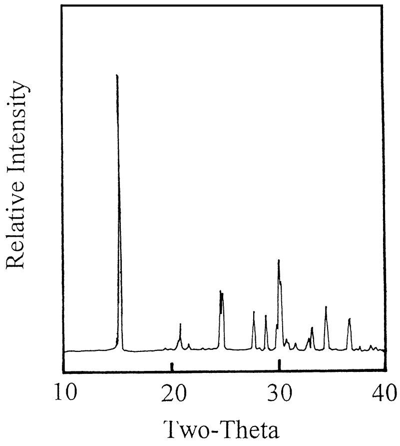

Fig. 1. The XRD pattern of $H_xV_2Zr_2O_9H_2O$ catalyst.

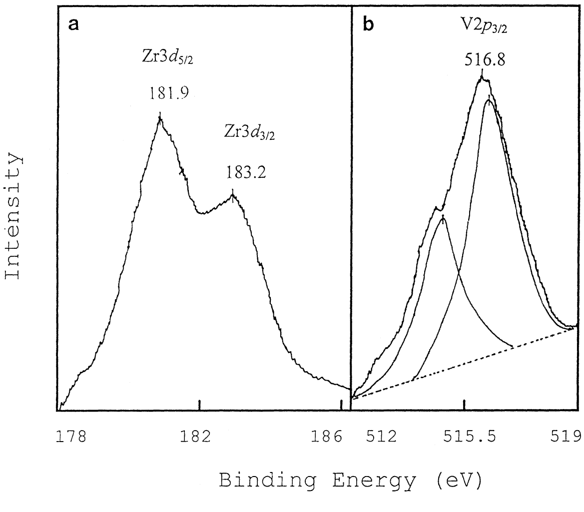

Fig. 2. The XPS spectra of: (a) $Zr3d_{5/2}$ and $Zr3d_{3/2}$ and (b) $V2p_{3/2}$ over $H_xV_2Zr_2O_9H_2O$ catalyst (sample 1).

Table 1
Characterization of vanadium zirconates ($H_xV_2Zr_2O_9H_2O$) prepared from various conditions

Sample	Prepared conditions	Average particle size[a]	Surface area×10^3 (m^2/g)	Chemical state of vanadium[c]	Chemical state of zirconium	Adsorption of water and *n*-hexane[d]	Element analysis
1	–	35	8.7	$V^{4+}/V^{5+}=3/10$	Zr^{4+}	No[e]	V/Zr/O=1/1/5
2	In presence of KI	35	8.7	$V^{4+}/V^{5+}=10/7$	Zr^{4+}	No	V/Zr/O=1/1/5
3	Grinding for 30 min[f]	7	44	$V^{4+}/V^{5+}=3/10$	Zr^{4+}	No[e]	V/Zr/O=1/1/5

[a] The particle size was estimated by scanning electron micrograph (SEM).
[b] The surface area was estimated by density and particle size.
[c] Molar ratio of V^{4+}/V^{5+} was roughly estimated by electron spectroscopic chemical analysis (ESCA) for V^{4+}/V^{5+}, respectively.
[d] The diameter of water and *n*-hexane is 3.0 and 4.3 Å, respectively.
[e] No means that the *n*-hexane could not adsorb on the sample, suggesting that there is no microporous pore in the sample.
[f] Sample 1 was ground for 30 min at room temperature, giving the average particle size of 7 μm.

All data characterized by XRD, ESR, XPS, SEM, and chemical adsorption are summarized in Table 1.

3.2. Catalytic phenol hydroxylation

3.2.1. Catalytic activity

Table 2 presents catalytic activity in phenol hydroxylation by hydrogen peroxide over V_2O_5, ZrO_2, $V_2O_5+ZrO_2$, and $H_xV_2Zr_2O_9H_2O$ (V–Zr–O), and we observed obvious features in the following:

1. ZrO_2 was completely inactive (<0.1%);
2. V_2O_5 exhibited very low phenol conversion (<2.6%), and undesirable product distribution (no formation of catechol);
3. mechanical mixture of V_2O_5, ZrO_2 ($V_2O_5+ZrO_2$) also gave very low conversion (<1.7%);
4. $H_xV_2Zr_2O_9H_2O$ (V–Zr–O) showed high catalytic activity (8.0–28.4%) and high selectivity to catechol and hydroquinone, which is comparable with that of TS-1;
5. when the particle size of the catalyst is changed by grinding to 7 μm (Sample 3), the phenol conversion rises to 28.4%, which is almost two-fold greater than conversion of the catalyst with a crystal size of 35 μm (Sample 1) under the same conditions.

Table 2
Catalytic performance in phenol hydroxylation[a] over various catalysts

Sample	Catalyst	Phenol conversion (%)	Product selectivity (%)		
			Benzenquinone	Catechol	Hydroquinone
1	$H_xV_2Zr_2O_9H_2O$	13.6	4.7	60.0	35.3
2	$H_xV_2Zr_2O_9H_2O$	8.0	16.3	43.8	39.9
3	$H_xV_2Zr_2O_9H_2O$	28.4	0.8	59.9	39.3
4	$V_2O_5+ZrO_2$	1.7	100	–	–
5	V_2O_5	2.6	39.8	–	60.2
6	ZrO_2	0.1	100	–	–
7	TS-1[b]	26.4	2	52	46
8	TS-1[c]	11	0	55	45

[a] Reaction conditions: acetonitrile as solvent; reaction temperature at 80°C; reaction time for 6 h; phenol/H_2O_2 ratio of 1; catalyst/phenol (g/g) value of 0.05.
[b] Reaction conditions [35]: TS-1 with Ti/(Ti+Si)=0.091; acetone as a solvent; reaction temperature at 57°C; reaction time for 6 h; phenol/H_2O_2 ratio of 3; catalyst/phenol (g/g) value of 0.10.
[c] Reaction conditions [35]: TS-1 with Ti/(Ti+Si)=0.010; acetone as a solvent; reaction temperature at 57°C; reaction time for 6 h; phenol/H_2O_2 ratio of 3; catalyst/phenol (g/g) value of 0.10.

Table 3
The influence of the solvent in phenol hydroxylation by hydrogen peroxide over $H_xV_2Zr_2O_9H_2O$ catalyst[a] (Sample 2 in Table 2)

Solvent	Reaction temperature (°C)	Reaction time (h)	Phenol conversion (%)	Product selectivity (%)		
				Benzenquinone	Catechol	Hydroquinone
1,2-Dichloroethane	65	2	–	–	–	–
Acetone	65	2	2.2	100	–	–
Acetonitrile	80	6	8.0	16.3	43.8	39.9

[a] Reaction condition: phenol/H_2O_2 ratio of 1.0; catalyst/phenol (g/g) value of 0.05.

Generally, the catalytic activity and product selectivity in phenol hydroxylation by hydrogen peroxide are strongly influenced by surface area of the catalyst, solvents, reaction time, reaction temperature, molar ration of phenol to hydrogen peroxide, and catalyst amount, which are investigated systematically as follows.

3.2.2. Influence of the solvent

Table 3 presents catalytic data in phenol hydroxylation over V–Zr–O catalyst in solvents of 1,2-dichloroethane, acetone, and acetonitrile. When the 1,2-dichloroethane was chosen as a solvent, the catalytic reaction did not take place; when the acetone was chosen as a solvent, the catalytic reaction gave low conversion (2.2%); when the acetonitrile was chosen a solvent, the catalytic reaction showed much higher conversion (8%). Obviously, acetonitrile is favorable for improving phenol conversion as well as obtaining good product selectivity.

3.2.3. Influence of reaction time

The dependence of catalytic activity on reaction time (Sample 2) in acetonitrile is presented in Table 4. During the first 6 h, along with the hydroxylation, the phenol conversion increased (8.0% at 6 h), then it turned to decline (6.8% at 8 h). In the whole process of the reaction the yields of benzenquinone declined gradually (from 67.2% at 4 h to 14.2% at 10 h), and at the same time, the selectivity for catechol and hydroquinone increased remarkably (from 33.8% at 4 h to 85.8% at 10 h).

3.2.4. Influence of reaction temperature

The influence of reaction temperature on catalytic activity is given in Table 5. The conversion of phenol increased with reaction temperature, that is the higher temperature is benefit for higher conversion of phenol. At relatively low temperature (50°C and 70°C), the product distribution was undesirable, the formation of benzenquinone was significant, but when the temperature was increased up to a satisfactory figure (80°C), catechol and hydroquinone became the primary product, and their total proportion could almost achieve 85%.

3.2.5. Influence of molar ratio of phenol to H_2O_2

Table 6 summarized the catalytic hydroxylation results under various molar ratio of phenol/H_2O_2. In acetonitrile, a one-fold excess of hydrogen peroxide

Table 4
The influence of reaction time in phenol hydroxylation by hydrogen peroxide over $H_xV_2Zr_2O_9H_2O$ catalyst[a] (Sample 2 in Table 2)

Reaction time (h)	Phenol conversion (%)	Product selectivity (%)		
		Benzenquinone	Catechol	Hydroquinone
4	6.4	67.2	33.8	–
6	8.0	16.3	43.8	39.9
8	6.8	15.9	35.0	49.1
10	4.1	14.2	33.2	52.6

[a] Reaction conditions: acetonitrile as a solvent; reaction temperature at 80°C; phenol/H_2O_2 ratio of 1.0; catalyst/phenol (g/g) value of 0.05.

Table 5
The influence of reaction temperature in phenol hydroxylation by hydrogen peroxide over $H_xV_2Zr_2O_9H_2O$ catalyst[a] (Sample 2 in Table 2)

Reaction temperature (°C)	Phenol conversion (%)	Product selectivity (%)		
		Benzenquinone	Catechol	Hydroquinone
80	8.0	16.3	43.8	39.9
70	1.5	100	–	–
50	0.2	100	–	–

[a] Reaction conditions: acetonitrile as a solvent; reaction time for 6 h; phenol/H_2O_2 ratio of 1.0; catalyst/phenol (g/g) value of 0.05.

Table 6
The influence of phenol/H_2O_2 molar ratio in phenol hydroxylation by hydrogen peroxide over $H_xV_2Zr_2O_9H_2O$ catalyst[a] (Sample 2 in Table 2)

Molar ratio of phenol and H_2O_2	Phenol conversion (%)	Product selectivity (%)		
		Benzenquinone	Catechol	Hydroquinone
1/1	8.0	16.3	43.8	39.9
1/2	15.2	10.5	45.7	43.8
1/4	6.1	100	–	–

[a] Reaction conditions: acetonitrile as a solvent; reaction time for 6 h; reaction temperature at 80°C; catalyst/phenol (g/g) value of 0.05.

gives the highest conversion of phenol (15.2%) and the best selectivity towards catechol and hydroquinone (89.5%). Greater excess such as three-fold excess of hydrogen peroxide reduced the conversion about 60%, and the formation of benzenquinone is major. The proportion of the product is sensitive to variations in phenol/H_2O_2 molar ratio.

3.2.6. *Influence of catalyst amount*

The variation of the catalytic activity with the amount of catalyst is listed in Table 7. Both one-fold (0.2 g) and three-fold (0.4 g) excess of catalyst reduced phenol conversion, and restrained the formation of catechol and hydroquinone. Apparently, there is no advantage in addition of additional catalyst as concerns the conversion of phenol. A large excess of catalyst reduced yields significantly and affected the products distribution.

4. Discussion

4.1. *Active phase*

To understand the active phase of the catalyst, the catalytic activity of phenol hydroxylation over V_2O_5, ZrO_2, $V_2O_5+ZrO_2$, and $H_xV_2Zr_2O_9H_2O$ (V–Zr–O) were investigated in detail, and the catalytic data are displayed in Table 2. It is interesting to see that the V–Zr–O catalyst was more active and selective

Table 7
The influence of catalyst amount in phenol hydroxylation by hydrogen peroxide over $H_xV_2Zr_2O_9H_2O$ catalyst[a] (Sample 1 in Table 2)

Catalyst amount (g)	Phenol conversion (%)	Product selectivity (%)		
		Benzenquinone	Catechol	Hydroquinone
0.1	13.6	4.7	60.0	35.3
0.2	11.7	26.7	51.2	22.1
0.4	6.1	34.8	47.2	18.0

[a] Reaction conditions: acetonitrile as a solvent; reaction time for 6 h; reaction temperature at 80°C; phenol/H_2O_2 ratio of 1.0.

than the simple oxides and their mechanical mixture, and its selectivity towards catechol was higher. Some published results had shown that in hydroxylation of phenol on vanadium compounds, in the products hydroquinone and catechol were formed in a 2:1 ratio [29], while others reported the selectivity towards catechol was higher [23], and the latter was similar to ours. Obviously, the relation between active sites and product distribution is not fixed. Furthermore, we observed that for the V–Zr–O catalysts the phenol conversion for Sample 1 was much more than that for Sample 2. Notice that the V^{5+} amount of Sample 1 is higher than that of Sample 2, we can speculate that V^{5+} may be the active site in the phenol hydroxylation by hydrogen peroxide. Under the same condition, the catalyst with crystal size of 7 μm gives rise to 28.4% for phenol conversion which is almost two-fold excess of the catalyst with crystal size of 35 μm. The reason is that the small crystal can provide larger surface area, which is advantaged to the reaction. If we find the optimum synthesis conditions and get smaller crystal, it can be anticipated that the higher phenol conversion and better product selectivity may be achieved.

4.2. *Influence of the solvent*

The solvents used in the catalytic reaction are known to have a profound influence on the phenol conversion, hydrogen peroxide decomposition and the ratio of catechol to hydroquinone over titanium silicates [30,31], vanadium silicalite-2 [23] and vanadium silicate xerogels [29]. The influence of the three solvents on the reaction over V–Zr–O complex oxide is illustrated in Table 3. Phenol conversion increases with the polarity of the solvents. In acetone, after 2 h of reaction, hydrogen peroxide is decomposed completely, but in acetonitrile, this process needs 4 h.

The influence of the solvent on the product distribution is more complex. Benzenquinone is obtained in both two system (acetone and acetonitrile). Interestingly, the yields of catechol is especially high when acetonitrile is used as a solvent. On the other hand, the products of phenol hydroxylation over titanium silicalites consist of almost an equimolar mixture of catechol and hydroquinone [8,32–34]. Tuel et al. [31] have recently reported enhanced yields of catechol in this reaction over TS-1 on changing solvent from methanol to acetone, which is distinguishable to those of V–Zr–O catalysts. Apparently, the product distribution influenced by the solvent is a rather complex phenomenon, which is required more detailed investigation.

4.3. *Influence of reaction time*

Different reaction time had a regular influence on phenol hydroxylation (Table 4). Low residence time led to relatively low phenol conversion as well as undesirable product selectivity. Moreover, the concentration of bezenquinone in the product was rather high. Although prolonging reaction time will be beneficial for the conversion of phenol, increased unavoidable deep oxidation from a longer reaction time may reduce the selectivity to phenol oxidation product. So the reaction time should be keep at 6 h.

4.4. *Influence of reaction temperature*

An effective way to improve yields is to use higher reaction temperature. The fact that the reaction conversion increases with temperature suggests that the activation energy for hydrogen peroxide decomposition is lower than that for the hydroxylation of phenol.

4.5. *Influence of molar ratio of phenol to H_2O_2*

A large excess of hydrogen peroxide (30 wt%) reduced yields very significantly. Ronny Neuman et al. [31] reported the similar results, which were explained by a negative effect from the water added together with hydrogen peroxide. But it maybe the minor reason account for the phenomenon, because in other reports [23], even if H_2O was used as solvent for this reaction, the phenol conversion was fairly satisfactory. We propose that one possible major reason for a lower yield is probably that the large excess of hydrogen peroxide led to deep oxidation of the product, the other is that H_2O_2 catalyses H_2O_2 decomposition and as a result the yield of hydroquinone and catechol was reduced remarkably. Addition of large amount of catalyst to the reaction

Table 8
The regeneration of $H_xV_2Zr_2O_9H_2O$ catalyst[a] in phenol hydroxylation by hydrogen peroxide over (Sample 2 in Table 2)

Catalyst	Phenol conversion (%)	Product selectivity (%)		
		Benzenquinone	Catechol	Hydroquinone
First run (fresh sample)	13.6	4.7	60.0	35.3
Second run (used sample for run 1)	<5	–	–	–
Third run (first regeneration by calcination at 550°C for 2 h)	13.5	5.1	58.3	36.6
Fourth run (second regeneration by calcination at 550°C for 2 h)	13.4	5.3	57.8	36.9
Fifth run (third regeneration by calcination at 550°C for 2 h)	13.4	5.4	57.9	36.7

[a] Reaction conditions: acetonitrile as a solvent; reaction time for 6 h; reaction temperature at 80°C; phenol/H_2O_2 ratio of 1.0; catalyst/phenol (g/g) value of 0.05.

mixture had an negative effect, which is different from TS-1 [35].

4.6. Regeneration of the catalyst

After phenol hydroxylation, the activity of $H_xV_2Zr_2O_9H_2O$ (V–Zr–O) catalysts reduced sharply, but their catalytic activity will be maintained at initial level by regeneration. From the data in Table 8, it was found that phenol conversion was unchanged after regeneration of the catalyst by calcination at 550°C for 2 h. These results indicated that the catalysts had a high stability.

5. Conclusion

In this work, a type of novel crystalline complex oxide $H_xV_2Zr_2O_9H_2O$ (V–Zr–O) with V^{4+} and V^{5+} mixed-valance is hydrothermally prepared, and catalytic data in phenol hydroxylation by H_2O_2 over the complex oxide of $H_xV_2Zr_2O_9H_2O$ show that the V–Zr–O catalysts are very active, and the V^{5+} species is suggested to be the active site.

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