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Synthesis, characterization, and catalytic phenol hydroxylation of a novel complex oxide $H_xV_2Zr_2O_9{\cdot}H_2O$

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A novel type of complex oxide $H_xV_2Zr_2O_9{\cdot}H_2O$ with V^{4+} and V^{5+} mixed valence has been hydrothermally synthesized in a V_2O_5–ZrO_2–H_2O system at 240°C for 5 days in presence of NaF. The catalytic data over these complex oxides show that these complex oxides are catalytically very active in phenol hydroxylation by 30% aqueous hydrogen peroxide, and their catalytic activity is dependent on crystal size of the catalysts. The phenol conversion over the catalyst with crystal size of 7 μm is twice that over the catalyst with crystal size of 35 μm. The V^{5+} species are suggested to be the catalytic active sites. Some other factors which influence the catalytic activity were also investigated.

Keywords: complex oxide, vanadium zirconate, phenol hydroxylation, hydrogen peroxide

1. Introduction

The development of ecologically friendly technologies is certainly one of the major present goals of research in chemistry. Phenol hydroxylation to hydroquinone and catechol by H_2O_2 using a TS-1 catalyst is a recent example. Since the 1970's, homogeneous hydroxylation of phenol catalysed by mineral acids [1–3], simple metal ions, and their complexes [4–6] has been extensively investigated. Although some of these catalysts showed potential catalytic activities, the disadvantages of homogeneous reactions are too distinct to prevent their wide use in the catalytic oxidation of hydrocarbons. Pure metal oxides or supported oxides have also been used to catalyse this reaction: 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], but neither the catalytic activity nor the product selectivity of these catalysts is satisfactory. Redox molecular sieves such as TS-1 [13,14] exhibited unique catalytic activity including high activity, minimal non-productive hydrogen peroxide decomposition, and high catalyst stability [15,16], which have led to an extraordinary series of work on the use of transition metal substituted silicalite zeolites as catalysts of phenol hydroxylation. For example, 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 intensively studied. Despite the obvious attractiveness of the titanium silicalite zeolites as catalysts to active hydrogen peroxide, the somewhat complicated synthesis, small pore size, and low reaction rates [25] will perhaps limit their application as a popular tool for oxidation in organic chemistry. Vanadium and zirconium were reported active in some other catalytic oxidation reactions [26], and the compound $H_xV_2Zr_2O_9{\cdot}H_2O$ is a novel complex oxide with two transition metals, showing many advantages compared with TS-1, such as a cheaper preparation and higher stability. The goals of this study are to (1) systematically prepare the novel complex oxide $H_xV_2Zr_2O_9{\cdot}H_2O$, (2) investigate its catalytic properties for phenol hydroxylation.

2. Experimental

The hydrothermal synthesis of $H_xV_2Zr_2O_9{\cdot}H_2O$ was carried out using gels of the following molar compositions: $0.5V_2O_5{:}1.0ZrO_2{:}1.0NaF{:}500H_2O$, where NaF is used as mineralizer. In a typical synthesis, 0.525 g of $NaVO_3{\cdot}2H_2O$ (A.R.), 1.074 g of $ZrOCl_2{\cdot}8H_2O$, and 1.04 g of NaF were mixed in 30 ml of H_2O. After stirring for 2 h, the mixture was transferred into a Teflon-lined stainless steel autoclave, followed by crystallization for 5 days at 240°C. After crystallization, the product was filtered, washed with deionised water, and dried in air at ambient temperature. Furthermore, the samples were characterized by X-ray diffraction (XRD), thermal analysis (DTA and TGA), adsorption, electron spin

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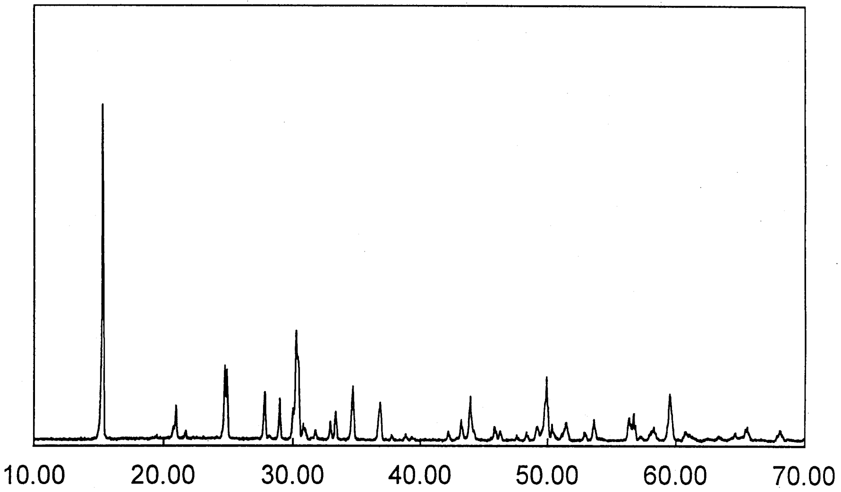

Figure 1. X-ray diffraction pattern of vanadium zirconates ($H_xV_2Zr_2O_9{\cdot}H_2O$).

resonance (ESR), scanning electron micrography (SEM), and X-ray photoelectron spectroscopy (XPS).

Phenol hydroxylation experiments were run in a 50 ml glass reactor and stirred with a magnetic stirrer. In a standard run, 1.6 g of phenol, 1.0 g of catalyst, and 20 ml of solvent were mixed, followed by addition of 2 ml of H_2O_2 (30% aqueous). The reaction temperature was 60–80°C. During reaction for 2–8 h, the products were taken out periodically and analysed by gas chromatography (Shimadzu GC-9A).

3. Results and discussion

3.1. Characterization of the complex oxide

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 (figure 1), a novel phase with a monoclinic system. The ESR spectra of the synthetic products (samples 1, 2, and 3) $H_xV_2Zr_2O_9{\cdot}H_2O$ exhibited an axial symmetry with $g_\perp = 1.99$, $a_\perp = 7.1$ mT, $g_0 = 1.94$, $a_0 = 19.4$ mT, in good agreement with V^{4+} species located in an octahedrally coordinated environment. Element analysis indicated that the molar ratio of the product is 1V : 1Zr : 5O, and it is expected that the V^{4+} species need equivalent amounts of protons to compensate the framework negative charges. Furthermore, XPS investigation showed that the zirconium species are in the chemical state of Zr^{4+}, and the vanadium species are both V^{4+} and V^{5+}. The data characterized by XRD, ESR, TEM, XPS, SEM, and chemical adsorption is presented in table 1.

3.2. Catalytic phenol hydroxylation

To understand the active phase of the catalyst, the catalytic activities in phenol hydroxylation over V_2O_5, ZrO_2, $V_2O_5 + ZrO_2$, and $H_xV_2Zr_2O_9{\cdot}H_2O$ (VZrO) are displayed in table 2. It is interesting to note that the VZrO catalysts (samples 1–3) were more active than the simple oxides (samples 5 and 6) and their mechanical mixture (sample 4). Furthermore, we observe that for the VZrO catalysts the phenol conversion for sample 1 was twice that for sample 2. Considering the higher V^{5+}

Table 1
Characterization of vanadium zirconates ($H_xV_2Zr_2O_9{\cdot}H_2O$) prepared under various conditions

Sample	Preparation conditions	Average particle size [a] (μm)	Surface area [b] $\times 10^5$ (m^2/g)	Chemical state of vanadium [c] V^{4+}/V^{5+}	Chemical state of zirconium	Adsorption of *n*-hexane [d]	Elemental analysis, V/Zr/O
1	–	35	8.7	3/10	Zr^{4+}	no [e]	1/1/5
2	in presence of KI	35	8.7	10/7	Zr^{4+}	no	1/1/5
3	grinding [f] for 30 min	7	44	3/10	Zr^{4+}	no	1/1/5

[a] The particle size was estimated by SEM.

[b] The surface area was estimated by density, also by the BET method (by using an ASAP 2010M instrument, Micro Co. Ltd, USA).

[c] Molar ratio V^{4+}/V^{5+} was roughly estimated by electron spectroscopic chemical analysis (ESCA) for V^{4+}/V^{5+}, respectively.

[d] The diameter of *n*-hexane is 4.3 Å.

[e] No means that the *n*-hexane could not adsorb on the sample, suggesting that there is no micropore (> 4.3 Å) in the sample.

[f] Sample 1 was ground for 30 min at room temperature, giving the average particle size of 7 μm.

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

Sample	Catalyst	Phenol conversion (%)	Reaction rate $\times 10^6$ (mol/(g s))	Product selectivity (%)		
				benzoquinone	catechol	hydroquinone
1	$H_xV_2Zr_2O_9 \cdot H_2O$	13.6	1.11	4.7	60.0	35.3
2	$H_xV_2Zr_2O_9 \cdot H_2O$	8.0	0.66	16.3	43.8	39.9
3	$H_xV_2Zr_2O_9 \cdot H_2O$	28.4	2.34	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	–	0	55	45
9	TS-1 [d]	18.2	–	0	53	47

[a] Reaction conditions: acetonitrile as solvent; reaction temperature = 80°C; reaction time = 6 h; phenol/H_2O_2 ratio = 1; catalyst/phenol (g/g) = 0.05.

[b] Reaction conditions [33]: TS-1 with Ti/(Ti + Si) = 0.091; acetone as a solvent; reaction temperature = 57°C; phenol/H_2O_2 ratio = 3; reaction time = 6 h; catalyst/phenol (g/g) = 0.1.

[c] Reaction conditions [33]: TS-1 with Ti/(Ti + Si) = 0.010; acetone as a solvent; reaction temperature = 57°C; phenol/H_2O_2 ratio = 3; reaction time = 6 h; catalyst/phenol (g/g) = 0.1.

[d] Reaction conditions [33]: TS-1 with Ti/(Ti + Si) = 0.021; acetone as a solvent; reaction temperature = 57°C; phenol/H_2O_2 ratio = 3; reaction time = 6 h; catalyst/phenol (g/g) = 0.1.

amount for sample 1 than for sample 2, it is proposed that V^{5+} may be the active site in the phenol hydroxylation by hydrogen peroxide. 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 twice greater than conversion over the catalyst with a crystal size of 35 μm (sample 1) under the same conditions. The smaller crystal could provide a larger specific surface area, and the catalytic reaction is usually proportional to the exposed catalytic active site (V^{5+}), which increased with specific surface area. Accordingly, if we get smaller crystals by changing the crystallization conditions, higher phenol conversion and better product selectivity than those of sample 3 may be achieved.

The influence of reaction time, temperature, solvent, and phenol/H_2O_2 ratio in phenol hydroxylation by hydrogen peroxide is summarised in table 3. Although prolonging the reaction time will be beneficial for phenol conversion, increased unavoidable deep oxidation from a longer reaction time may reduce the selectivity to the phenol oxidation product. So the optimum reaction time should be kept at 4–6 h. An effective way to improve yields is to use higher reaction temperatures. The fact that the reaction conversion decreased with increasing temperature suggests that the activation energy for hydrogen peroxide decomposition is lower than that for the hydroxylation of phenol.

The solvents used in this reaction are known to have a profound influence on the phenol conversion, hydrogen peroxide decomposition and the ratio of catechol to hydroquinone over titanium silicalites [27,28], vanadium silicalite-2 [23] and vanadium silicate xerogels [29]. Table 3 shows that the catalytic activity in acetonitrile solvent is much higher than in acetone, which suggests that phenol conversion increases with increasing polarity of the solvent.

Additionally, the yields of catechol were especially high when acetonitrile was used as solvent. It is proposed that a polar solvent is preferred for forming a polar product. On the other hand, the products of phenol hydroxy-

Table 3
The influence of reaction time, temperature, solvent, and phenol/H_2O_2 in phenol hydroxylation by hydrogen peroxide over $H_xV_2Zr_2O_9 \cdot H_2O$ catalyst [a] (sample 2)

Reaction time (h)	Reaction temperature (°C)	Ratio of phenol and H_2O_2	Phenol conversion (%)	Product selectivity (%)		
				benzoquinone	catechol	hydroquinone
4	80	1/1	6.4	67.2	33.8	0
6	80	1/1	8.0	16.3	43.8	39.9
8	80	1/1	6.8	15.9	35.0	49.1
10	80	1/1	4.1	14.2	33.2	52.6
6	70	1/1	1.5	100	–	–
6	50	1/1	0.2	100	–	–
6	80	1/2	15.2	10.5	45.7	43.8
6	80	1/4	6.1	100	–	–

[a] Reaction conditions: acetonitrile as a solvent; catalyst/phenol (g/g) = 0.05.

Table 4
The regeneration of the catalyst

Catalytic reaction	Phenol conversion (%)	Product selectivity (%)		
		benzoquinone	catechol	hydroquinone
first run (fresh sample)	13.6	4.7	60.0	35.3
second run (sample used 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

lation over titanium silicalites consist of almost an equimolar mixture of catechol and hydroquinone [8,30–32].

A large excess of 30% hydrogen peroxide reduced yields very significantly. Neumann et al. [29] reported similar results, which were explained by a negative effect from the water added with the hydrogen peroxide. On the other hand, it has been reported [23] that the catalytic conversion was satisfactory even if H_2O was used as solvent for this reaction. We propose that one probable major reason for a lower yield is 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.

4. Conclusion

(1) A novel crystalline complex oxide $H_xV_2Zr_2O_9\cdot H_2O$ with V^{4+} and V^{5+} mixed valence was hydrothermally synthesized.

(2) Like titanium silicalites (TS-1), $H_xV_2Zr_2O_9\cdot H_2O$ catalyst is active for phenol hydroxylation by hydrogen peroxide. A V^{5+} species is proposed to be the active site.

(3) Samples of $H_xV_2Zr_2O_9\cdot H_2O$ with smaller crystal size exhibited much higher catalytic activity for phenol hydroxylation by hydrogen peroxide.

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