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The oxygen activated by the active vanadium species for the selective oxidation of benzene to phenol

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The activation of oxygen is a key step for the selective oxidation of benzene to phenol and the reason is discussed. The active oxygen species is produced from molecular oxygen in a so-called "reductive activation" process. The vanadium oxide supported on alumina was pre-reduced by hydrogen or ascorbic acid to lower valence vanadium species acting as reduction source and the activity is investigated in the reaction. It is found that the V^{4+} valence vanadium (VO^{2+}) is effective for the reaction from the characterization of catalysts by XPS.

KEY WORDS: activation of oxygen; active vanadium species; selective oxidation; benzene; phenol.

1. Introduction

The selective oxidation of hydrocarbon by oxygen is an attractive and challenging subject, especially for the direct hydroxylation of benzene to phenol from economical and environmental point of view, which is an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics [1]. The investigations of direct oxidation of benzene to phenol with various oxidants, such as nitrous oxide [2–4], hydrogen peroxide [5–7], molecular oxygen [8], or a mixture of oxygen and hydrogen [9–11] have been reported. The direct hydroxylation of benzene with molecular oxygen seems to be more potential for industrial application, which proceeds in a green process. Vanadium is a widely used as an active element in several industrial catalysts [12], especially for oxidation reaction. Many efforts have been done to study the direct oxidation of benzene to phenol based on vanadium-contain catalysts [13–14], and the catalysts show good catalytic behavior in the reaction.

Generally, the selective oxidation of hydrocarbon performs from two routes: activate oxygen to generate the active oxygen species of proper reactivity, and activate the starting material to direct the oxidation in the desired way [15]. It is very difficult to activate the substrate for the hydroxylation of benzene to phenol, because the bond energy of the C–H bond of benzene is about 472.2 KJ/mol [16], which is much higher than that of other kinds of C–H bond. The route to activate oxygen is necessary for the reaction. One of ways to generate the activated oxygen species is to reduce molecular oxygen by hydrogen in the process of a so-called "reductive activation" [17]. However, the process is often dangerous for the mixture of hydrogen and oxygen. It is easy for some lower valence metal oxide to be oxidized by dioxygen. Then the metal oxide reduced in advance could act as the role of hydrogen to activate the molecular oxygen to produce the active oxygen species that is a key for the hydroxylation of benzene to phenol.

In this paper, we reported the direct hydroxylation of benzene with molecular oxygen to phenol catalyzed by the vanadium oxide supported on the alumina. The catalyst was reduced by hydrogen or ascorbic acid to get the lower valence vanadium oxide acting as a redox-active source to activate the dioxygen to generate the active oxygen species. The catalysts were characterized by X-ray photoelectron spectroscopy (XPS) to investigate the valence of vanadium species.

2. Experimental

2.1. Catalyst preparation

The supported vanadium catalysts were prepared by the impregnation method. The oxalic acid was added to the solution of ammonium metavanadate before impregnation, the molar ratio of oxalic acid and ammonium metavanadate is 2. The solution was heated to 343 K and remained for 3 h; Al_2O_3 was added and the solution was cooled down. After the evaporation of the water, the supported vanadium was dried at 393 K and calcined at 773 K for 5 h in flowing air. The V-content of catalyst is 3.3% (wt). The V/Al_2O_3 (H)

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means the V/Al_2O_3 catalysts was reduced in flowing hydrogen at 673 K for 5 h, and the V/Al_2O_3 (A) means the V/Al_2O_3 was reduced by ascorbic acid in the aqueous solution at room temperature for 2 h.

2.2. *Oxidation reaction and products analysis*

The liquid-phase oxidation of benzene to phenol with molecular oxygen was performed in a 250 ml stainless steel reactor with a mechanical stirrer. The standard condition is as follows: 1.00 g catalyst, 5 ml (0.056 mol) of benzene, 10 ml of H_2O and 30 ml of acetic acid. After the temperature was raised to 423 K, the oxygen was introduced to 1.00 MPa, and reaction was carried out at these conditions for 2 h. The product was analyzed by GC (Agilent 4890D) with an OV-1 capillary column ($35\ m \times 0.32\ mm \times 0.8\ \mu m$). Qualitative analysis of phenol, 1,4-benzoquinone, catechol, biphenyl and hydroquinone in the products was verified by the retention time of standard samples. The quantitative analysis of the mixture was determined by the calibration curves, toluene as the internal standard.

2.3. *Characterization of catalysts*

The results of XPS were obtained with Amicus (Kratos). Binding energies (BE) were determined using the C_{1S} peak at 284.7 eV as a reference to correct charge effect.

3. Results and discussion

3.1. *The characterization of catalysts*

In order to get lower valence vanadium species which would reduce molecular oxygen to generate active oxygen species, the catalysts of vanadium oxide supported on alumina were reduced by hydrogen and L-ascorbic acid before catalytic the hydroxylation of benzene to phenol, respectively. The vanadium species valence in the catalysts was investigated with XPS and the results are illustrated in Table 1. It shows the vanadium species in catalysts are mix valence comparing with the standard BE of V_{2P} (eV). The BE of V_{2P} in the fresh catalyst is 516.93 eV, which is near the standard BE of V^{5+} (517.2 eV) [18–20]. That means the V^{5+} species is predominanted in the fresh catalyst. When the fresh catalyst is reduced by hydrogen, the BE of V_{2P} is 515.99 eV, that is close to the standard BE of V^{3+} (515.7 eV) [21]. It reveals that the vanadium species prefers existing with V^{3+}, and a little V^{4+} species is present in the sample. The BE of V_{2P} in the catalyst reduced by ascorbic acid appears at 516.13 eV, that approach the standard BE of V^{4+} (516.3 eV) [22]. It shows most vanadium species is quadrivalent. The hydrogen is a strong reductant, it can reduce most pentavalent vanadium species to trivalent vanadium species and a little to quadrivalent vanadium species. Whereas the ascorbic acid is a mild reductant, it reduce most pentavalent vanadium species to quadrivalent vanadium species and a little to trivalent vanadium species

3.2. *Performances of the catalyst*

The activities of the catalysts were investigated in the selective hydroxylation of benzene to phenol and the results were displayed in Table 2. The fresh catalyst gives 0.4% conversion of benzene. The catalyst reduced by hydrogen gives 0.5% conversion, a little more effective than the fresh catalyst. The catalyst reduced by ascorbic acid in advance is more effective than the fresh catalyst and gives 1.6% conversion of benzene. The contrast of the catalysts activities illuminates the quadrivalent vanadium species is responsible for the higher activity on the oxidation benzene to phenol. V^{4+} vanadium species is particularly stable as the vanadyl ion (VO^{2+}) which is an isolated cation [12]. Reduction by ascorbic acid in the solvent is accompanied by breaking the chains of vanadium ions (V^{5+}) into the isolated species (VO^{2+}) resulting that the oxygen has more chance to reach the separate species and to be activated by V^{4+} vanadium species.

3.3. *Influence of the amount of ascorbic acid*

The interesting fact is that the catalyst reduced by ascorbic acid is more active for the oxidation of benzene. The catalytic behavior could be related to the reduction mode. The ascorbic acid was directly added to the reaction system, to realize the reduction continuously of fresh catalyst. The results of benzene hydroxylation are shown in Table 3. The conversions of benzene increased linearly with increase of ascorbic acid amount between 0 and 0.004 mol. Beyond 0.004 mol of the concentration of ascorbic acid, the conversions increased a little. The route of reaction may be as follow: the pentavalent

Table 1
The V_{2p} species in the catalysts characterized by XPS

Catalysts	BE of V_{2P} (eV)	BE of V_{2P} (eV) in standard	Vanadium species in catalysts
V/Al_2O_3	516.93	V^{5+} 517.2	V^{5+} and V^{4+}
V/Al_2O_3 (H)	515.99	V^{3+} 515.7	V^{3+} and V^{4+}
V/Al_2O_3 (A)	516.13	V^{4+} 516.3	V^{4+} and V^{3+}

Table 2
The catalysts performances on the benzene hydroxylation

Catalysts	Conversion (%)	Selectivity (%)
V/Al_2O_3	0.4	>99
V/Al_2O_3 (H)	0.5	>99
V/Al_2O_3 (A)	1.6	>99

Table 3
The influence of amount of the ascorbic acid on the conversion of the benzene

Amount of ascorbic acid (mmol)	Conversion (%)	Selectivity (%)
0	0.4	> 99
0.5	1.1	> 99
1	1.7	> 99
2	2.7	> 99
3	3.6	> 99
4	4.3	> 99
5	4.4	> 99
6	4.5	> 99
8	4.7	> 99
12	4.7	> 99

vanadium species was reduced to form the lower valence (V^{4+}) vanadium species by ascorbic acid, and then the ascorbic acid was oxidized to dehydroascorbic acid; the quadrivalence vanadium species activated the gaseous oxygen to form active oxygen species; the active oxygen species attacked the benzene to form phenol. Below 0.004 mol of the concentration of ascorbic acid, the retardation of phenol formation in the hydroxylation process is ascribed to the failure of the redox cycle vanadium species due to the shortage of ascorbic acid. When the concentration of ascorbic acid is over 0.004 mol, the excessive ascorbic acid is oxidized directly by oxygen to dehydroascorbic acid and could not reduce vanadium oxide.

4. Conclusions

In conclusion, the oxygen can be activated by lower valence vanadium species in the ''reductive activation'' process. The characterization of the samples by XPS and the activity of the catalysts show the V^{4+} vanadium species (VO^{2+}) play an important role in the direct hydroxylation of benzene to phenol. The key step in the hydroxylation of benzene to phenol catalyzed by vanadium oxide is how to reduce pentavalent vanadium species to quadrivalent vanadium species continuously and circularly.

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