ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 3, pp. 394–397. © Pleiades Publishing, Ltd., 2010.

Oxidation of Benzene to Phenol by Dioxygen over Vanadium Oxide Nano-Plate[1]

Xiaohan Gao[a], Xuechuan Lv[a], and Jie Xu[b]

[a] *School of Chemistry and Material Science, Liaoning Shihua University, China*

[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China*

e-mail: gaoxhan@163.com

e-mail: xujie@dicp.cn

Received January 18, 2009

Abstract—Direct oxidation of benzene to phenol with dioxygen is an attractive and challenging subject. V^{4+} vanadium species play an important role in the reaction. Nano vanadium oxide which consists mainly of the quadrivalence vanadium species was synthesized via hydrothermal method and used to catalyze the reaction without addition of reducing reagent. Investigations about performances of catalysts show that 3.7% conversion of benzene and nearly 100% selectivity of phenol are given over the fresh catalyst VO-N-A. Morphology observations display that the VO-N-A is made of nano-plate. Thermogravimetric curve illuminates that the catalyst is stable under the reaction temperature.

DOI: 10.1134/S0023158410030110

It is known that phenol is an important and versatile intermediate which could be used for the manufacture of petrochemicals, agrochemicals, plastics, and so on [1]. More than 90% phenol of the world is synthesized via the cumene process characterizing with three steps, highly energy-consuming, low phenol yield and producing acetone as by-product. It is a green process to prepare phenol via direct oxidation of benzene in one step from economical and environmental point of view. The researches about the direct oxidation of benzene to phenol with various oxidants, such as hydrogen peroxide [2, 3], nitrous oxide [4, 5], molecular oxygen [6, 7], or a mixture of oxygen and hydrogen [8] have been done. It seems to be more potential for industrial application that the molecular oxygen oxidizes benzene to phenol directly. Vanadium is the effective element for the direct oxidation of benzene to phenol with dioxygen. Many vanadium-containing catalysts show excellent catalytic behavior in the reports [9, 10]. Masumoto et al. [10] reported the synthesis of phenol by the direct oxygenation of benzene using supported vanadium catalyst. The yield of phenol is 0.2% without ascorbic acid as a reducing reagent. If the ascorbic acid was added, the yield was up to 6.5% over the same catalyst [10]. In previous paper, we reported that V/Al_2O_3 was reduced by ascorbic acid before reaction and then used to catalyze the reaction. Yield of phenol is 1.6% without addition of ascorbic acid [11]. The key step is to prepare more V^{4+}-containing catalysts. It is reported that the V^{5+} ions could be reduced to the V^{4+} ions by decomposition of organic amine in the process of hydrothermal synthesis [12, 13]. The ratio of V^{4+} and V^{5+} in product depends on the pH of medium [14–16]. A higher proportion of V^{4+} species may be obtained in the acidic medium. Based on the preceding result, we designed and synthesized nano vanadium oxide.

In this paper, we reported that the direct oxidation of benzene with molecular oxygen to phenol was catalyzed by nano vanadium oxide for the first time. The reactions were performed without reducing agent. Nano vanadium oxide was synthesized by the hydrothermal synthesis method. To get a higher ratio of V^{4+} species, the pH value of medium was adjusted to 1–2 by acetic acid. Activity and recycle performance of catalyst in the reaction were investigated. X-Ray photoelectron spectroscopy (XPS) was used to investigate the vanadium valence of product. Catalyst was characterized by scanning electron microscopy (SEM) and thermogravimetry (TG) to study the character of catalysts.

EXPERIMENTAL

Catalyst Preparation

The procedure of the VO-N-A (N means $-NH_2$ in $C_6H_5NH_2$ and A means the acidic medium) nanoplate preparation is as follows: 20 mmol of ammonium metavanadate and 20 mmol of oxalic acid were mixed with 20 ml of distilled water (solution A). The oxalic acid is in favor of the dissolution of ammonium metavanadate in water. Twenty millimoles of aniline were mixed with 30 ml distilled water (solution B). Solution A was added into solution B slowly through separalory

[1] The article is published in the original.

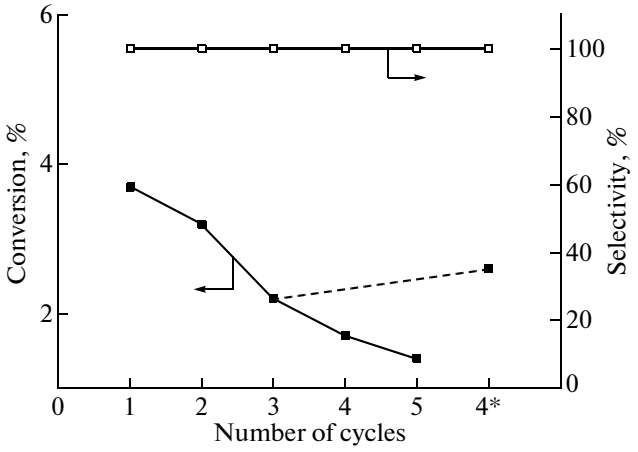

Fig. 1. Catalyst performances and recycling test on the benzene conversions. 4*, the performance of the catalyst after the third run washed in ethanol and used in the fourth run.

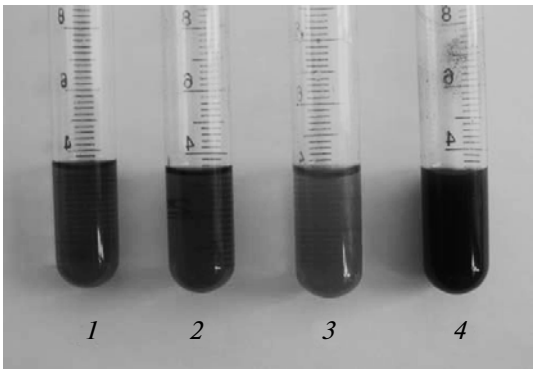

Fig. 2. Phenomenon of liquid with addition of Zn powder: *1*—the reaction liquid, *2*—reaction liquid with addition of Zn powder, *3*—solution of V^{5+}, *4*—the solution of V^{5+} with addition of Zn powder.

funnel. Then, the pH value of medium was adjusted to 1–2 by acetic acid. After stirring for 1 h, the composite was transferred into a Teflon-lined autoclave. The mixture was treated hydrothermally at 413 K for 1 day and then at 453 K for 3 days. The obtained black product was washed with ethanol and distilled water to remove the unreacted amine and its decomposition product. The worked product was dried at 343 K in air atmosphere for 6 h.

Oxidation Reaction and Products Analysis

The liquid-phase oxidation of benzene to phenol with molecular oxygen was performed in a 100 ml Teflon-lined stainless steel reactor with a magnetic stirrer. The standard condition is as follows: 0.10 g of catalyst, 1 ml of benzene (0.011 mol) and 10 ml of acetic acid were loaded into the reactor and heated. After the temperature was raised to 423 K, the oxygen was introduced to 1.00 MPa and the consumed oxygen was supplied at any moment. The reactions were carried out at these conditions for 10 h.

The product was analyzed by gas-liquid chromatography (GC) (Agilent 4890D) with an HP-5 capillary column (15 m × 0.53 mm × 1.5 μm). Qualitative analysis of phenol, catechol, 1,4-benzoquinone, 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.

All the reagents above were analytical reagent.

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.

Scanning electron microscopy image was collected on a JSM-6360LV microscope.

The TG measurement of the sample was carried out by a thermogravimetric analyzer (DT-20B Shimadzu) at the heating rate of 10 K/min in air with flow rate of 30 ml/min.

RESULTS AND DISCUSSION

Performances and Recycle of Catalysts

The performance and recycle test of VO-N-A for the direct oxidation of benzene to phenol show in Fig. 1. The conversion of benzene of 3.7% and nearly 100% selectivity of phenol are given over the fresh catalyst. The used catalyst was separated by filtration and washed with copious amount of water. In the second run, the conversion of benzene dropped to 3.2%. The conversion of benzene decreased as the cycle times increased. In the fifth run, conversion of benzene is 1.4%. The reason may be that the polymers formed in the reaction occupied the active centre; the water-wash can not remove the polymers. The used catalyst after the third run was washed in ethanol to remove the polymers. In the 4*th/run, the conversion of benzene rises to 2.6% which is higher than the activity of catalyst in the third run. After reaction, the liquid is red, which means that few benzoquinone was formed under reaction conditions, whereas quantity of benzoquinone is too small to be detect by GC. It is to be thought that selectivity of phenol is nearly 100%. Another explanation for the color may be the presence of dissolved V^{5+}. The existence of V^{5+} in the solution is VO_2^+, VO_3^- or other ions which could be reduced to V^{4+} with the addition of Zn powder. Simultaneously, the color turns to blue and green. The color of reaction

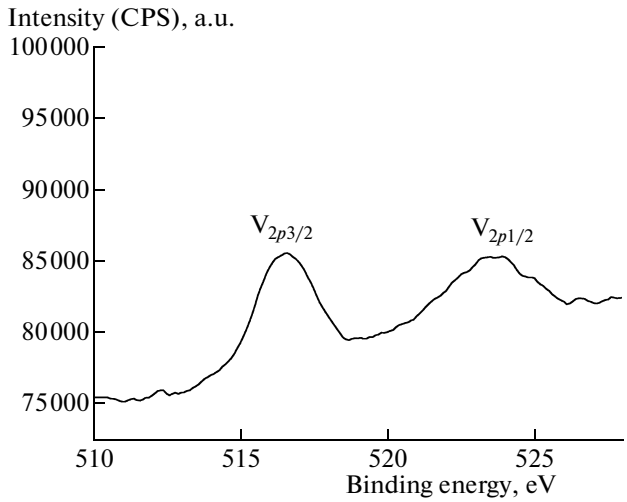

Fig. 3. XPS investigation of VO-N-A.

liquid has no change and remains red as the addition of Zn powder, whereas the solution color V^{5+} turns to green immediately as Zn powder is added (Fig. 2). This observation confirmed that no V^{5+} was dissolved in the reaction liquid.

XPS Analyses of Catalysts

XPS analyses provided additional insight into the composition and vanadium valence state of the surface of the as-obtained examples. It was reported [17–22] that the $V^{3+}_{2p3/2}$ peak was located at about 515.7 eV and $V^{3+}_{2p1/2}$ peak was located at about 523 eV; the $V^{4+}_{2p3/2}$ peak was located at about 516.3 eV and $V^{3+}_{2p1/2}$ peak was located at about 523.4 eV and the $V^{5+}_{2p3/2}$ peak was located at about 517.2 eV and $V^{5+}_{2p3/2}$ peak was located at about 524.3 eV. As can be seen from Fig. 3, the binding energies of $V_{2p3/2}$ and $V_{2p1/2}$ centered at 516.4 and 523.4 eV was well consistent with the above-mentioned results. Therefore, the high resolution XPS region spectrum further confirmed that vanadium oxide consists of V(IV).

Microscopy Investigations of the Samples

Scanning electron microscopy of VO-N-A example demonstrates that it was made almost entirely of nano-plates (Fig. 4). The observation in Figs. 4a and 4b of the sample shows that the thickness of the plates ranges from 50 to 150 nm and the diameter varies from 1.5 μm to a maximum of 2.5 μm. The accidental surface observed from Fig. 4c exposures more active centers, which means that the dioxygen get more chance to contact the catalyst to be activated for oxidation of benzene to phenol.

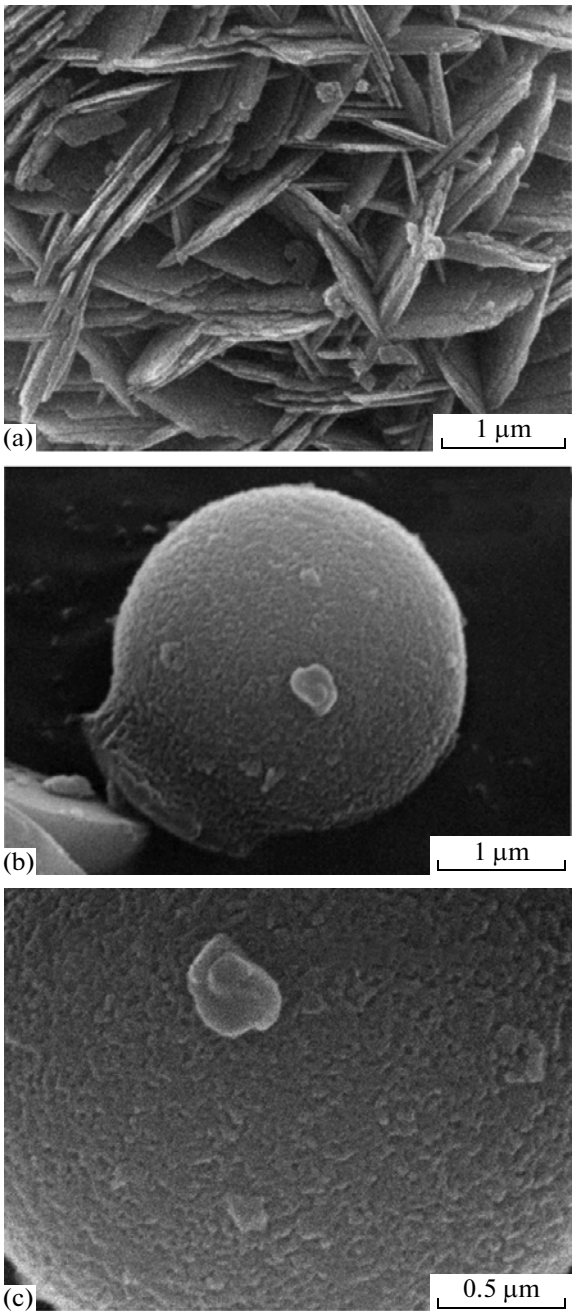

Fig. 4. Scanning electron microscopy of VO-N-A: (a, b) the thickness of the plates ranges from 50 to 150 nm and the diameter varies from 1.5 μm to a maximum of 2.5 μm, (c) the accidental surface exposures more active centers, which means that the dioxygen get more chance to contact the catalyst to be activated for oxidation of benzene to phenol.

TG curve of VO-N-A

Thermal stability is important property for catalyst and the TG curve of VO-N-A illuminated in Fig. 5. A weight loss about 3.5% that occur in the temperature range 293–393 K is associated with the desorption of the adsorbent water. Mass loss (2.5%) from 393 to 498 K can be assigned to the decomposition and loss of

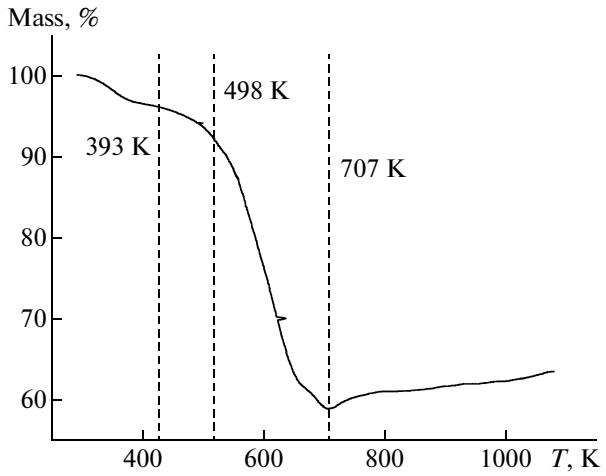

Fig. 5. TG curve of VO-N-A.

water of crystallization. The weight loss (35.0%) between 498 and 707 K is associated with the decomposition of residual organic compound. A weight increase (4.6%) after 707 K corresponds to the oxidation to V^{4+} to V^{5+}. TG curve of VO-N-P-A display that the catalyst is stable under the reaction temperature.

CONCLUSION

The nano vanadium oxide was synthesized and catalysis performance was investigated. Without any reducing reagent, VO-N-A gives 3.7% conversion of benzene in the first run. The results of 4*th run illuminate that the used catalyst could be regenerated. Investigation result of XPS confirms that nano vanadium oxide consists of V^{4+}. Observations of SEM show that the VO-N-A is made of nano-plate. The catalyst is stabile under the reaction temperature from TG curve.

ACKNOWLEDGMENTS

The work was supported by the National Natural Science Foundation of China under the NSFC Grant (nos. 20672111 and 20736010).

REFERENCES

1. Panov, G.V., *CATTECH*, 2000, vol. 4, p. 18.
2. Bianchi, D., Bortolo, R., Tassinari, R., Ricci, M., and Vignola, R., *Angew. Chem., Int. Ed. Engl.*, 2000, vol. 39, p. 4321.
3. Gao, X. and Xu, J., *Appl. Clay Sci.*, 2006, vol. 33, p. 1.
4. Sobolev, V.I., Panov, G.I., Khatitonov, A.S., Romannikov, V.N., Volodin. V.M., and Ione K.G., *J. Catal.*, 1993, vol. 139, p. 435.
5. Kachurovskaya, N.A., Zhidomirov, G.M., Hensen, E.J.M., and van Santen, R.A., *Catal. Lett.*, 2003, vol. 86, p. 25.
6. Ohtani, T., Nishiyama, S., Tsuruya, S., and Masai, M., *J. Catal.*, 1995, vol. 155, p. 158.
7. Gu, Y.Y., Zhao, X.H., Zhang, G.R., Ding, H.M., and Shan, Y.K., *Appl. Catal., A*, 2007, vol. 328, p. 150.
8. Niwa, S., Eswaramoorthy, M., Nair, J., Raj, A., Itoh, N., Shoji, H., Namba, T., and Mizukami, F., *Science*, 2002, vol. 295, p. 105.
9. Murata, K., Yanyong, R., and Inaba, M., *Catal. Lett.*, 2005, vol. 102, p. 143.
10. Masumoto, Y., Hamada, R., Yokota, K., Nishiyama, S., and Tsuruya, S., *J. Mol. Catal. A: Chem.*, 2002, vol. 184, p. 215.
11. Gao, X. and Xu, J., *Catal. Lett.*, 2006, vol. 111, p. 203.
12. Bouhaouss, A. and Aldebert, P., *Mater. Res. Bull.*, 1983, vol. 18, p. 1247.
13. Bouhedja, L., Steunou, N., Maquet, J., and Livage, J., *J. Solid State Chem.*, 2001, vol. 162, p. 315.
14. Takahashi, K., Limmer, S.J., Wang, Y., and Cao, G., *J. Phys. Chem. B*, 2004, vol. 108, p. 9795.
15. Chirayil, T., Zavalij, P.Y., and Whittingham, M.S., *Chem. Mater.*, 1998, vol. 10, p. 2629.
16. Livage, J., *Coordin. Chem. Rev.*, 1998, vol. 178, p. 999.
17. Nefedov, V.I., Salyn, Y.V., Leonhardt, G., and Scheibe, R., *J. Electron. Spectrosc. Relat. Phenom.*, 1977, vol. 10, p. 121.
18. Nefedov, V.I., Firsov, M.N., and Shaplygin, I.S., *J. Electron. Spectrosc. Relat. Phenom.*, 1982, vol. 26, p. 65.
19. Kasperkiewicz, J., Kovacich, J.A., and Lichtman, D., *J. Electron. Spectrosc. Relat. Phenom.*, 1983, vol. 32, p. 12.
20. Mendialdua, J., Casanova, R., and Barbaux, Y., *J. Electron. Spectrosc. Relat. Phenom.*, 1995, vol. 71, p. 249.
21. Leroux, C., Nihoul, G., and Tendeloo, G.V., *Phys. Rev. B: Solid State*, 1998, vol. 57, p. 5111.
22. Demeter, M., Neumann, M., and Reichelt, W., *Surf. Sci.*, 2000, vol. 454, p. 41.