Preparation of heterogeneous vanadium (VO^{2+}) catalyst for selective hydroxylation of cyclohexane by molecular oxygen

G.S. Mishra and A. Kumar *

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

Received 3 October 2001; accepted 11 January 2002

A vanadium(II) Schiff base ligand, [1,4-bis (salicylidene amino)-phenylene] vanadium oxo complex bonded on carbamate-modified silica gel, has been synthesized. The liquid-phase oxidation reaction of cyclohexane with this catalyst was found to give cyclohexanol at moderate condition (reaction temperature 200 °C, pressure 23.8 atm, catalyst concentration 1.0% and 16 h of reaction time) with considerably higher specificity (18 : 1 ratio with cyclohexanone and negligible acid formation). The catalyst has been tested for 200 h of reaction and the leaching of the metal occurs negligibly.

KEY WORDS: vanadium (VO^{2+}) catalyst; selective hydroxylation; cyclohexane hydroxylation.

1. Introduction

Hydrocarbons are cheaply available from the chemical and petrochemical industry and their functionalization through oxidation [1,2] using molecular oxygen poses a present-day challenge in modern catalysis. In earlier works of catalysis, metals and their salts were dissolved in nonvolatile liquids, dispersed on solid phase, and were called supported liquid-phase catalysts (SLPCS) [3]. When employed in liquid-phase oxidation, there is excessive metal leaching and, as a result of this, there has been an effort to anchor transition metals and their complexes on suitable supports [4]. Transition metal carbonyls have been directly connected with organic polymers like polyvinyl pyridine or a suitably modified support with donor groups [5]. There are examples of covalent anchoring, ionic bonding, physical adsorption and chemisorption, and covalent anchoring has been reported to be the most efficient. However, even from these, under the reaction condition of liquid-phase oxidation, metals do get leached [6].

Air oxidation of cyclohexane is industrially carried out using unsupported cobalt catalyst and, in its presence, at least five products (adipic acid, succinic acid, gallic acids, cyclohexyl acetate and cyclohexyl monoadipate) are formed in addition to cyclohexanol and cyclohexanone [7]. In addition to this, there is an induction time, which is reduced in the presence of promoters like acetaldehyde, cyclohexanone, cyclohexanol and azobisisobutyronitrile. Reactions have also been carried out in the presence of cobalt zeolite, CoA-PO-Catalyst [8], which gives acids (like valeric acid and butyric acid) in sufficient quantities [9]. As a variation of this, nano-structured iron and cobalt oxides have been used as catalysts and recently, on using those supported on titania, the products were formed in extremely mild reaction conditions [10] (1 atm, 70 °C) and consisted of a mixture of cyclohexanol and cyclohexanone in the ratio of 1.5 to 1.0. Unsupported vanadium complexes have also been studied as a catalyst for oxidation of cyclohexane. Several complexing agents have been reported and all have been shown to give a mixture of cyclohexanol and cyclohexanone in comparable amount at mild reaction conditions [11].

In this paper, we report a heterogeneous vanadium complex catalyst supported on carbamate-modified silica gel. This hydroxylates cyclohexane using molecular oxygen in moderate reaction conditions giving cyclohexanol in preponderance. After 16 h of the reaction in batch reactors, the catalyst was removed before distillation at 110 °C. This gave 13 ml of the product with distillate having only cyclohexane, as confirmed by GC analysis. The product was subjected to GC-MS analysis and it showed cyclohexanol (78.95%), cyclohexanone (4.53%), succinic acid (6.74%) and unidentified esters (9.78%) and the observed product distribution is entirely different from the literature. The analysis showed the formation of cyclohexanol and cyclohexanone in the ratio of 18 : 1 and with no induction period. There is negligible acid (1.2% succinic acid) formed and the metal leaching in 200 h of reaction time is negligible.

2. Experimental

The catalyst reported in this work has been synthesized by the following four-step procedure. In the

---

* To whom correspondence should be addressed.
E-mail: anilk@iitk.ac.in

1011-372X/02/0700-0113/0 © 2002 Plenum Publishing Corporation

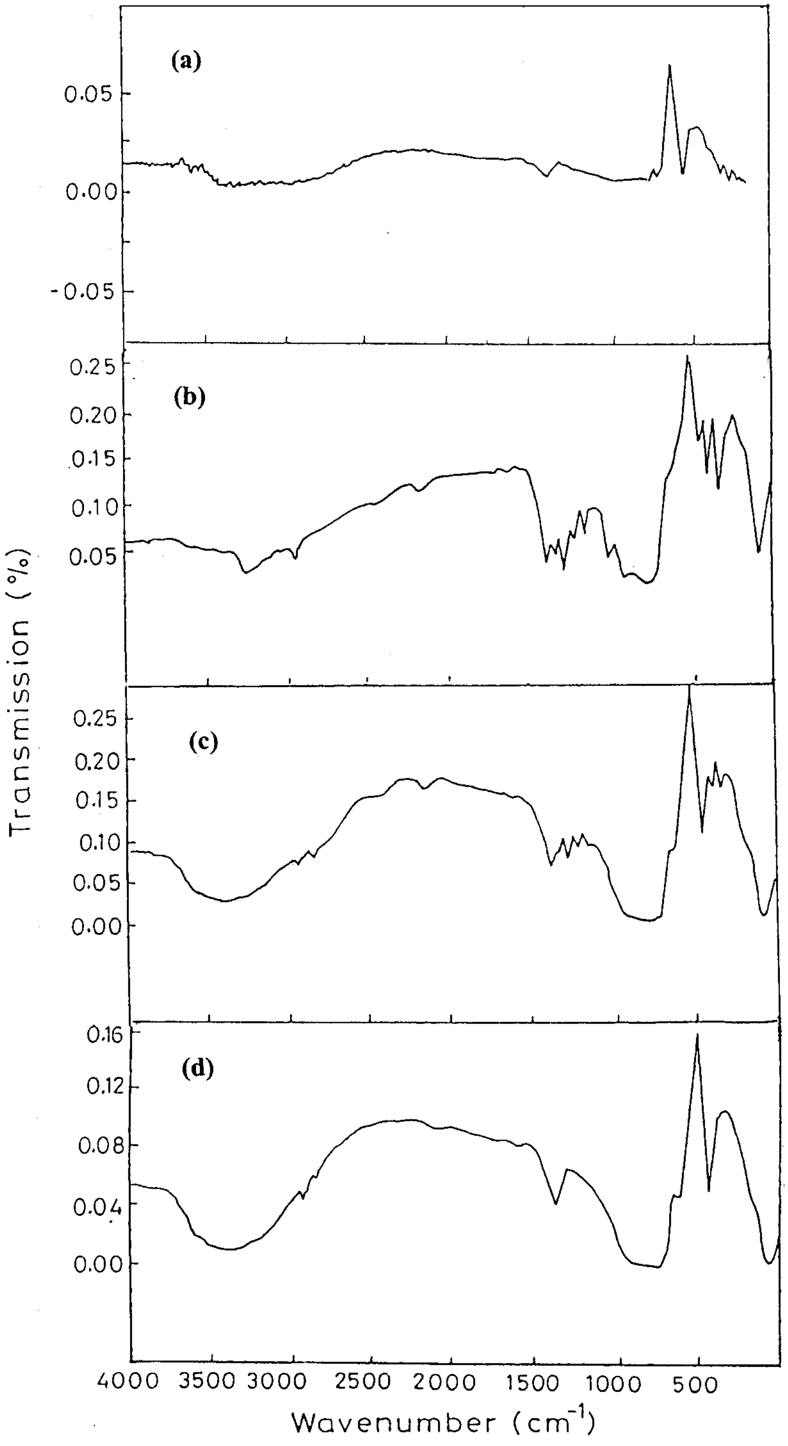

Figure 1. FTIR spectrum of (a) pure silica gel. (b) Silica gel with carbamate bound group (aromatic –CH at 3030 cm^{-1}, –NH group at 1599 cm^{-1}, C=O at 1693 cm^{-1}). (c) Carbamated silica gel with dichloroethane (shows alkyl group $-CH_2$ at 2940 cm^{-1} and chloride group at 740 cm^{-1}). (d) Silica gel supported vanadium metal complex catalyst (aliphatic and aromatic –CH at 2940 and 3030 cm^{-1}, C=O group shifted to 1644 cm^{-1}, at 1509 cm^{-1} with the absence of chloride group).

first step, benzoyl isocyanate was synthesized by the reaction of sodium azide NaN_3 (16.8 g, 0.26 g·mole) with the same number of moles of benzoyl chloride C_6H_5COCl (35 ml, 0.30 g·mole) at 0 °C and its FTIR spectrum matched with the literature. The filtrate was reacted with 5.0 g of silica gel [12], its FTIR spectrum given in figure 1(a) at 40 °C for 6 h. The carbamate group bound on the silica gel was confirmed by FTIR, given in figure 1(b) (aromatic –CH at 3030 cm^{-1}, –NH group at 1599 cm^{-1}, C=O at 1693 cm^{-1}), and the extent of reaction estimated by the butyl amine method [13]. In the second step, the complexing agent was prepared according to ref. [14], in which *o*-phenylene diamine (0.1 g, 0.1 g·mole) is reacted with salicylaldehyde (21.20 ml, 0.2 g·mole) in absolute alcohol solvent for 3 h. After this time, a yellow precipitate of 1,4-bis (salicylidene amino)-phenylene appears having the same IR given in the literature, which is filtered and dried. In the third step, the vanadium complex is prepared by the reaction of the above complex (3.0 g, 9.5 m·mole) with vanadyl sulfate $VOSO_4 \cdot 5H_2O$ (3.0 g, 12.9 m·mole) dissolved in acetonitrile (100 ml) solvent. The reaction mixture was then refluxed (80 °C) for 2 h and, after the reaction, a green-colored precipitate of vanadium complex was formed. The complex was washed with acetonitrile for purification and dried at 80 °C.

In the fourth and final step, the carbamate group of the modified silica gel (2 g) from the first step is reacted with dichloroethane (50 ml) by refluxing (60 °C) in the presence of Lewis acid $ZnCl_2$ catalyst (5.0 mg, 0.037 g·mole) for 2 h at 80 °C. Its FTIR (given in figure 1(c)) shows alkyl group $-CH_2$ at 2940 cm^{-1} and chloride group at 749 cm^{-1}, thus confirming the reaction to have occurred. As a result of this reaction, the support material (modified silica gel) now has $-CH_2CH_2Cl$ groups at the phenyl and the secondary amine groups of the carbamate, and the chloride groups of these react with the vanadium metal complex dissolved in acetonitrile. This is subsequently refluxed (80 °C) for an additional 3 h to give the desired heterogeneous [1,4-bis (salicylidene amino)-phenylene] vanadium oxo complex catalyst. Its FTIR is shown in figure 1(d), which has aliphatic and aromatic –CH at 2940 and 3030 cm^{-1}, the C=O group shifted to 1644 cm^{-1} with the characteristic peaks of metal complexing at 1509 cm^{-1} with the absence of a chloride group.

3. Results and discussion

Experiments have been conducted in a rocking-type, high-pressure reactor. In the presence of the catalyst and the molecular oxygen as the reactant, the cyclohexane is oxidized and the product can be separated by fractional distillation. During the catalyst preparation, in a typical reaction, freshly prepared benzoyl isocynate is reacted with silica gel at room temperature and the carbamate linkages of the modified silica gel have been confirmed by FTIR spectroscopy. Its concentration on the solid was determined to be 1.26 meq/dry gram of silica gel by using the butyl amine procedure given by Siggia [13]. The Schiff base vanadium(II) complexing ligand is prepared using the procedure of the literature and is bound to the modified silica gel in the presence of Lewis acid ($ZnCl_2$). The catalyst thus prepared is used for oxidation of cyclohexane and its vanadium content (0.048 mol% by weight of support) determined by atomic adsorption spectroscopy (AAS).

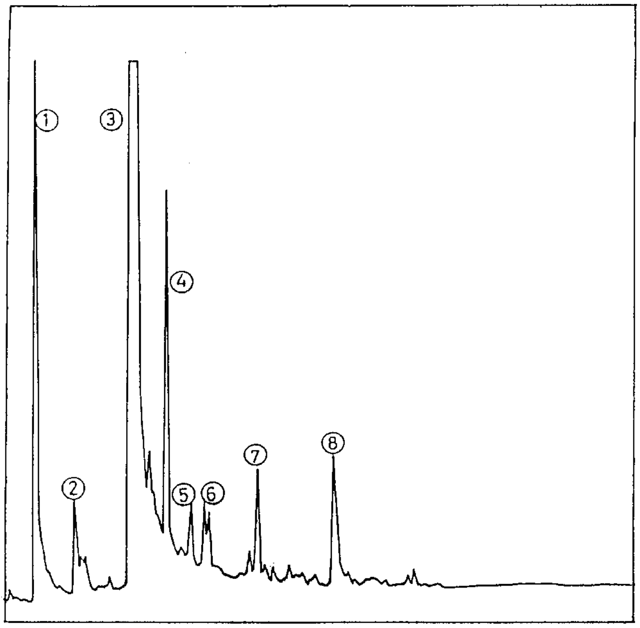

Figure 2. Gas chromatogram of the product distilled between 140 and 180 °C using column Ulbon HR-1, fused silica capillary, Shimadzu QP-2000. Various peaks have been identified to be cyclohexane (peak 1, 5.0%), cyclohenanol (peak 3, 75.0%), cyclohexanone (peak 4, 4.3%), succinic acid (peak 5, 6.4%).

In an exercise to identify the product, 100 ml of cyclohexane was reacted in the presence of the supported catalyst at 2000 °C and 23.8 atm (350 psi) pressure for up to 16 h. The catalyst was recovered completely, conversion in the reaction was small and the direct analysis of the entire reaction mass did not show all products. In view of this, most of the unreacted cyclohexane was distilled at 110 °C while 13 ml of product was collected. This product was subjected to GC-MS (the distillate confirmed through GC analysis to be cyclohexane alone) and its chromatograph is shown in figure 2. The products formed in amounts more than 1.0% have been identified to be peaks numbered as 1 (5.0%), 2 (1.1%), 3 (75%), 4 (4.3%), 5 (6.4%), 6 (1.5%) and 7 (2.7%). Their mass spectra were compared with those given in the literature and have been identified as cyclohexane (peak 1), cyclohexanol (peak 3), cyclohexanone (peak 4) and succinic acid (peak 5). From the mass spectra of peaks 6 and 7, it was inferred that they belonged to cyclohexyl propionate ($C_6H_{11}OOC-CH_2CH_3$) and cyclohexyl malonate ($C_6H_{11}OOCCH_2COOH$) respectively. There were several compounds formed in considerably smaller amounts, which could be regarded as waste, and constitute only about 9.3%.

At 200 °C, 23.8 atm pressure and reaction time of 16 h, the product yield is found to be 13%, which increases as the time of reaction is increased. The final product, cyclohexanol, was separated by distillation and its purity was checked by thin-layer chromatography (TLC) and by the mixed boiling point test. Further confirmation of the product by FTIR spectroscopy (Perkin-Elmer 13290,

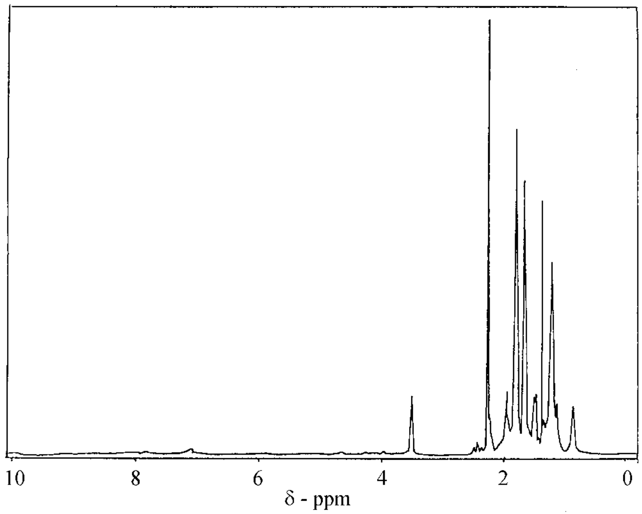

Figure 3. ^{1}H-NMR spectrum of cyclohexanol separated from the product.

3400–3470 cm^{-1} for –OH) and by ^{1}H-NMR spectroscopy (Joel JNK-PMX-60, $CDCl_3$, 0.8–2.2 δ-ppm, m-methine proton, 3.6 δ-ppm-OH group) showed a hydroxyl group and a –CH bond in the compound (figure 3), which matches exactly that available in the literature for cyclohexanol.

The literature indicates that, in the oxidation of cyclohexane, cyclohexanone as well as acids are always formed along with cyclohexanol in comparable amounts and, particularly for cobalt catalysts, there is adipic acid formation [7]. With the supported vanadium catalyst developed in this work, the cyclohexanol is formed at considerably higher amounts compared with cyclohexanone (18 : 1 ratio). The total amount of acid formed is extremely small and the only free acid is succinic acid. We also tried to identify the residue (distillate beyond 180 °C) and found that the residue had peak positions in FTIR similar to cyclohexanol, except that the one at 3500 cm^{-1} for the hydroxyl group was absent. This indicated that the residue is likely to be a set of compounds belonging to the esters of cyclohexanol. Finally, the literature showed that the cobalt catalyst exhibited an induction time, whereas our catalyst showed no such time delays.

From the mechanistic consideration [15,16], oxidation reactions can be divided into three kinds: (1) oxidation *via* free radical mechanism, sometimes auto-oxidation, (2) oxidation through coordination of oxygen to the metal ion and (3) catalyst oxygen transfer. These mechanisms depend upon the reaction conditions (gas or liquid phase, temperature and pressure) and the nature of the metal and the oxidizing agent used. In order to show that the oxygen transfer is occurring through oxo-peroxo interconversion of vanadium and *via* free radical mechanism, we carried out the oxidation of cyclohexane at the same temperature in the presence of azobisisobutyronitryile (AIBN) free radical initiator and found a negligible effect on the final conversion reached. In addition to this, we also carried out the oxidation reaction in the presence of free radical scavengers and hydroquinone, and once again found no effect upon the final conversion reached. The proposed mechanisms for supported vanadium catalyst [17] are shown below in equations (1)–(7).

$$C_6H_{12} + O_2 \longrightarrow C_6H_{11}^{\bullet} + HOO^{\bullet} \tag{1}$$

$$C_6H_{11}^{\bullet} + O_2 \longrightarrow C_6H_{11}OO^{\bullet} \tag{2}$$

$$C_6H_{11}OO^{\bullet} + C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + C_6H_{11}OOH \tag{3}$$

$$C_6H_{11}OOH + VO^{2+} \longrightarrow C_6H_{11}^{\bullet} + OH^- + VO^{3+} \tag{4}$$

$$C_6H_{11}OOH + VO^{3+} \longrightarrow C_6H_{11}OO^{\bullet} + H^+ + VO^{2+} \tag{5}$$

$$C_6H_{11}O^{\bullet} + C_6H_{12} \longrightarrow C_6H_{11}OH + C_6H_{11}^{\bullet} \tag{6}$$

$$2C_6H_{11}OO^{\bullet} \longrightarrow C_6H_{11}OH + C_6H_{10} + O_2 \tag{7}$$

In the above mechanism, the initiation step (equation (1)) is typically very slow, and once the free radicals are formed, these quickly react with dissolved oxygen to form peroxy radicals (equation (2)). In this reaction, the main role of the vanadium metal ions is to catalyze the formation of the intermediate hydroperoxide ($C_6H_{11}OOH$) as in equations (3), (4) and (5). As a result of this, vanadium metal ions generate chain-initiating radicals, which give the formation alcohols as an oxidation product according to equations (6) and (7). However, experimental results for this catalyst (*i.e.* negligible ketone formation) show that equation (6) is the dominating step. The vanadium metal exists in two oxidation states (VO^{2+} and VO^{3+}) with comparable stability and it is the active catalyst for the hydroperoxide decomposition. It was observed that the green color of the freshly loaded silica gel catalyst becomes dark brown after the reaction in the presence of molecular oxygen. We confirmed that all VO^{2+} species (green colored, EPR active) are oxidized to VO^{3+} oxo-peroxo [18–21], because the latter does not give any EPR spectrum (figure 4). This suggests that the hydroxylation of cyclohexane by the oxo and peroxo groups of the loaded catalysts are involved. The catalyst was tested for 200 h of reaction and found that metal content in the fresh catalyst was 0.048 g% vanadium, which after 200 h becomes 0.045 g%.

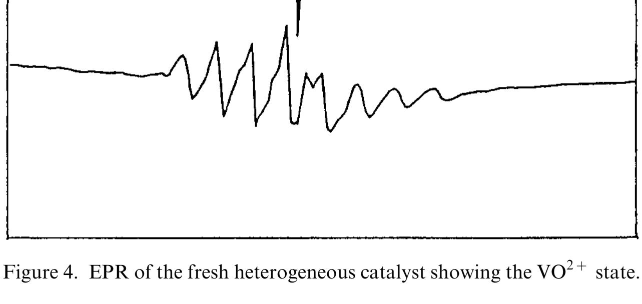

Figure 4. EPR of the fresh heterogeneous catalyst showing the VO^{2+} state.

Acknowledgment

Dr. G.S. Mishra is grateful for the financial support of the Department of Science and Technology (DST), under the Young Scientist Scheme (SR/FTP/CS-04/2000). We also thank RSIC, CDRI, Lucknow, for the GC-MS analysis.

References

[1] Z. Wang, A.E. Marlett and R.J. Motekaitis, Chem. Commun. (1998) 1523.

[2] T. Tagaw, J. Catal. 78 (1993) 201.

[3] L.K. Doraiswamy and R.A. Mashelkar, *Frontiers in Chemical Reaction Engineering* (Wiley Eastern, New Delhi, 1984).

[4] H.G. Lutz, Chem. Commun. (2000) 173.

[5] N. Komiya, S. Noji and S.I. Murahashi, Chem. Commun. (2001) 65.

[6] R. Raja, G. Shankar and J.M. Thomas, J. Am. Chem. Soc. 121 (1999) 11926.

[7] G.N. Kulsreshta, U. Shankar, J.S. Sharma and J. Singh, J. Chem. Tech. Biotechnol. 50 (1991) 57.

[8] S.S. Lin and H.S. Weng, Appl. Catal. A: General 118 (1994) 21.

[9] J.W.N. Steeman, S. Kaarsemaker and P.S. Hoftyzer, Chem. Eng. Sci. 14 (1961) 139.

[10] R. Raja, G. Shankar and J.M. Thomas, Chem. Commun. (1999) 829; Appl. Catal. A: General 209 (2001) 125.

[11] N. Perkas, Y. Koltypin, O. Palchik, A. Gedanken and Chandrasekan, Appl. Catal. A: General 209 (2001) 125.

[12] H. Tbal, J. Morcellet, M. Delporte and M. Mocellet, Eur. Polym. J. 4 (1989) 331.

[13] S. Siggia, *Quantitative Organic Analysis*, third edition (Wiley, New York, 1963) p. 558.

[14] C.A. Root, J.D. Hoeschele, C.R. Cornman, J.W. Kampf and V.L. Pecorano, Inorg. Chem. 32 (1993) 3855.

[15] B.K. Das and J.H. Clark, Chem. Commun. (2000) 605.

[16] R. Gopinath and B.K. Patel, Org. Lett. 2(5) (2000) 557.

[17] M. Hartmann and S. Ernst, Angew. Chem. Int. Ed. 39(5) (2000) 888.

[18] A. Kumar Jr., S.K. Das and A. Kumar, J. Catal. 166 (1997) 108.

[19] S. Kulkarni, M. Alurker and A. Kumar, Appl. Catal. A: General 142 (1996) 243.

[20] G.S. Mishra and A. Kumar, Chem. Con. 1 (2000) REC 41.

[21] S.K. Das, A. Kumar, S. Nandrajog and A. Kumar, Tetrahedron Lett. 36 (1995) 7909.