

Synthesis of hetero binuclear macrocyclic Co–V complex bonded to chemically modified alumina support for oxidation of cyclohexane using oxygen

M. Jhansi L. Kishore, G.S. Mishra, Anil Kumar*

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

Received 31 May 2004; accepted 11 November 2004

Available online 15 January 2005

Abstract

A binuclear complex $M_A^{II}M_B^{IV}L^{2+}$ [with $M_A^{II} = Co^{II}$ and $M_B^{IV} = V^{IV}$] has been synthesized with a macrocyclic ligand prepared by condensing 2 equiv. of 2,6-diformyl-4-methylphenol with 2 equiv. of 1,2-phenylenediamine. This has been immobilized on a carbamate-modified alumina support by covalently binding it to the surface. The TGA analysis of the final catalyst showed that it is thermally stable up to 251 °C and it has been shown that it serves as a catalyst for oxidation of cyclohexane forming cyclohexanone and cyclohexanol in the ratio of 14:1 as identified by the GC/MS analysis.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Binuclear macrocyclic ligand; Characterization; Cyclohexane; Oxidation; Mechanism

1. Introduction

The oxidation of cyclohexane [1] is an important reaction in the framework of commercial production of nylon. Past studies have revealed that the main products formed during its oxidation are cyclohexanol, cyclohexanone, adipic acid and several minor products (cyclohexene, cyclohexene-2-one, valeraldehyde and valeric acid) [2,3]. The cyclohexanol and cyclohexanone (formed in almost equimolar amounts) in the reaction mass are separated and are further processed in production of adipic acid and caprolactum, which are ultimately used in the manufacture of nylon 6,6 and nylon 6, respectively [4]. Many efforts have been made to develop new catalysts to oxidize cyclohexane under mild conditions with high selectivity for the target products (cyclohexanol, cyclohexanone or adipic acid) using different oxidizing agents (hydrogen peroxide, *t*-butyl hydroperoxide and molecular oxygen) [5,6].

Normally used catalytic systems for industrial cyclohexane oxidation employ homogeneous cobalt salts (cobalt acetate or naphthanate), molecular oxygen as an oxidant and operate at temperatures above 150 °C. Industrially, in order to suppress the formation of side products, a low conversion per pass (~4.0%) is targeted [7] and the reaction product consists of mainly cyclohexanol and cyclohexanone in almost equal amount and their combined selectivity is about 85%. Many heterogeneous catalysts have been developed for this reaction and generally these catalysts are either oxides or metal cations incorporated on inorganic supports such as silica, alumina, zirconia, active carbon, zeolites [8] or aluminophosphates [9]. The activity of these systems mainly depends on the correct choice of the solvent, which determines the polarity of the medium and the size of the substrate that needs to be adsorbed at the catalytic surface [10]. For example, the solvent effect [11] has been investigated by carrying out oxidation of cyclohexane over CoAPO-5 using different carboxylic acids (formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid and *n*-hexanoic acid) and it was found that the conversion was maximum in case of propionic acid. Sometimes promoters or coreactants like acetaldehyde,

* Corresponding author. Tel.: +91 512 2597195/597811; fax: +91 512 2590104.

E-mail address: anilk@iitk.ac.in (A. Kumar).

cyclohexanone, cyclohexanol and azo-bis isobutyronitrile (AIBN) are also added to reduce the induction period and to increase the cyclohexane conversion with high selectivity for target products (cyclohexanone, cyclohexanol or adipic acid) [12]. Other oxidation catalysts, which have been recently investigated, are the transition metal substituted poly-oxo metals, which in general show high activity in the oxidation of alkanes [13,14].

In our earlier work, we prepared a vanadium Salen [15] complex and bound it chemically to the carbamate-modified silica gel for the oxidation of cyclohexane by molecular oxygen. In presence of this, the oxidation reaction exhibited no induction time and gave an overall conversion (5–20%) with cyclohexanol forming 45 times more than cyclohexanone. We similarly carried out the oxidation reaction using the chemically bound Salen complex of cobalt [16] and we obtained similar result. However, we show in this publication that the binuclear macrocyclic complex $\text{Co}^{\text{II}}\text{V}^{\text{IV}}\text{L}^{2+}$ bound to carbamate-modified alumina, gave an entirely different product distribution forming cyclohexanone 14 times larger than cyclohexanol with negligible side products.

2. Experimental

Binuclear macrocyclic complex $\text{Co}^{\text{II}}/\text{V}^{\text{IV}}$ has been prepared by first synthesizing 2,6-diformyl-4-methylphenol according to Ref. [17] and this complex is bonded to the carbamate-modified alumina support. The detailed synthesis of the catalyst is given below.

2.1. Synthesis of binuclear complex $\text{Co}^{\text{II}}/\text{V}^{\text{IV}}$

The brownish yellow crystals of the 2,6-diformyl-4-methylphenol (mp 131 °C) has been prepared and its ^1H NMR spectrum (2.4 δ -ppm methyl, 7.5 δ -ppm aromatic, 10 δ -ppm aldehyde and 11.2 δ -ppm, phenolic proton) matched with the literature values. In order to prepare, the bimetallic ligand L^{2+} , 2 equiv. of 2,6-diformyl-4-methylphenol is condensed with 2 equiv. of 1,2-phenylene diamine in two stages forming $\text{Co}^{\text{II}}\text{L}'$ and $\text{Co}^{\text{II}}\text{V}^{\text{IV}}\text{L}'$ as described below [18,19]. This gives two identical N_2O_2 sites [20] in the ligand.

2.1.1. $\text{Co}^{\text{II}}\text{L}'$

The 2,6-diformyl-4-methylphenol (1.95 g, 0.012 mol) is dissolved in DMF (50 ml). Then 1,2-phenylenediamine (0.65 g, 0.006 mol) is added along with the same molar quantity of cobalt acetate (1.476 g, 0.006 mol). The solution is stirred until the latter dissolves. After 0.5 h, the crystals of $\text{Co}^{\text{II}}\text{L}'$ precipitate which are washed with diethyl ether and dried. Its FT-IR shows aromatic $-\text{CH}$ at 3010 cm^{-1} , aliphatic $-\text{CH}$ at 2930 cm^{-1} and $-\text{CN}$ at 2358 cm^{-1} .

2.1.2. $\text{Co}^{\text{II}}\text{V}^{\text{IV}}\text{L}$

Vanadyl sulfate (1.164 g, 0.006 mol) is next added to the 20 ml of methanol. The CoL' (2.05 g, 0.045 mol) obtained earlier is added to this and stirred. This is washed with diethyl ether and dried. The FT-IR spectra of the complex shows $\text{C}=\text{N}$ at 1632 cm^{-1} and $\text{C}=\text{O}$ at 1539 cm^{-1} frequencies.

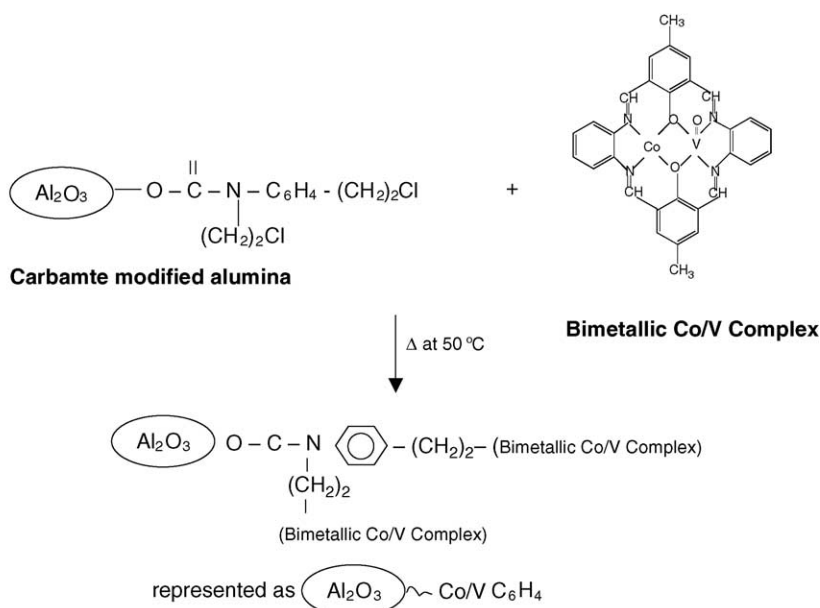
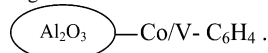


Fig. 1. Reaction scheme of bimetallic vanadium/cobalt complex supported on modified alumina. The final catalyst has been schematically represented as



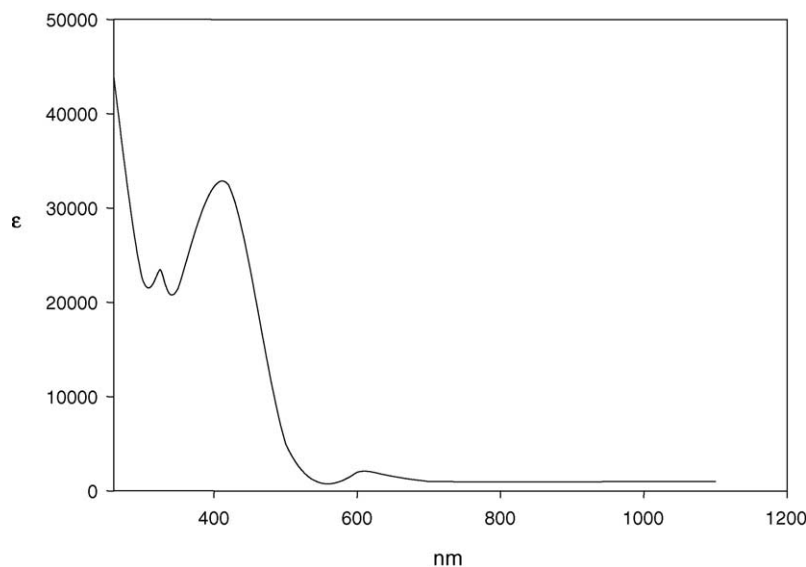


Fig. 2. UV-Vis spectrum of the macrocyclic bimetallic Co/V complex.

2.1.3. $\text{Co}^{\text{II}}\text{V}^{\text{IV}}\text{L}$

At this stage the final capping is done as follows. The $\text{Co}^{\text{II}}\text{V}^{\text{IV}}\text{L}$ (2 g) obtained as above is dissolved in methanol (30 ml) and 1,2-phenylene diamine (0.363 g, 0.0034 mol) is added and stirred. The crystals are formed which are washed with diethylether and dried. The FT-IR spectra of the final complex shows C=N at 1670 cm^{-1} and aromatic -CH at 3025 cm^{-1} frequencies. The bimetallic macrocyclic have been schematically represented as $\text{C}_6\text{H}_4\text{-Co/V-C}_6\text{H}_4$ (Fig. 1) and its C_6H_4 groups could offer possible sites of reaction. To confirm that the complexation had occurred, we carried out CHN analysis, EDX and UV-Vis spectra of the catalyst. The experimental values of the CHN analysis are

determined and the analytical values are given in brackets C: 61.363 (analytical: 62.176), H: 3.5862 (analytical: 3.79), N: 8.229 (analytical: 9.67). The elemental analysis carried out by EDX gave the metal percentages as Co: 17.96%, V: 16.66% and C: 65.38%. The UV-Vis spectrum of the binuclear Co/V macrocyclic complex is shown in Fig. 2. The spectra were observed in the range of 270–1100 nm and shows two major peaks at 316 and 405 nm and a shoulder at 356 nm. All our experiments to grow single crystal failed and we could not carry out the X-ray analysis of the single crystal. To show that the complex has reactive sites (most likely at $-\text{C}_6\text{H}_5$), we reacted it with 1,2-dichloroethane at 70°C for 4 h and the reaction product was analyzed by FT-IR spectroscopy.

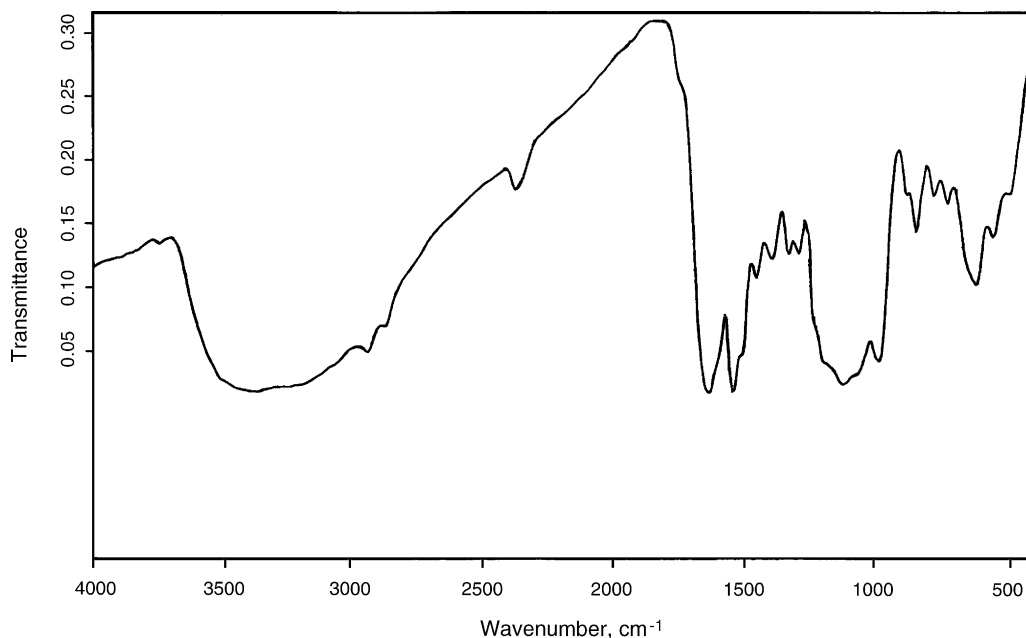
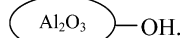


Fig. 3. FT-IR spectrum of the final catalyst.

This showed the chlorine Cl group of $-\text{CH}_2\text{Cl}$ at 3058 cm^{-1} . Similar reaction of chlorosulfonic acid (0.01% in methanol) at 70°C for 4 h showed C–S at 1163 cm^{-1} .

2.2. Preparation of modified alumina support

Phenyl isocyanate has been synthesized according to Ref. [21]. The dried alumina has been shown to have hydroxyl groups on the surface [22] and can be represented as

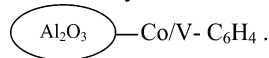


The modified alumina is prepared by reacting oven dried alumina (10 g, 0.133 mol) with this phenyl isocyanate liquid phase (35 ml). The reaction mass was stirred at 40°C for 6 h and the presence of carbamate bonds on the alumina was confirmed by FT-IR (aromatic $-\text{CH}$ at 3027 cm^{-1} , $-\text{NH}$ group at 1595 cm^{-1} , $\text{C}=\text{O}$ at 1690 cm^{-1}). The extent of reaction was estimated by determining the amine group concentration on alumina (determined to be 0.26 meq./g) using the butyl amine method [23]. In the next step, the carbamated modified alumina (3.0 g) is reacted with dichloroethane (50 cm^3) in presence of a Lewis acid catalyst ZnCl_2 (5 mg, 0.037 g mol) at 80°C for 2 h. The modified alumina is washed and dried at 40°C for 5 h (Fig. 1). The FT-IR spectra shows $-\text{N}=\text{C}=\text{O}$ at 2400 cm^{-1} and aromatic $-\text{CH}$ at 3030 cm^{-1} , aliphatic $-\text{CH}$ at 2955 cm^{-1} , $\text{C}=\text{O}$ at 1545 cm^{-1} and C–Cl group at 760 cm^{-1} frequencies.

2.3. Chemical binding of $\text{Co}^{\text{II}}\text{V}^{\text{IV}}\text{L}$ complex to the modified alumina

The binuclear macrocyclic vanadium–cobalt complex (0.5 g) is dissolved in methanol (50 ml) and reacted with the

modified alumina (2.0 g) at 60°C for 4 h. The loaded bimetallic cobalt–vanadium complex catalyst (the FT-IR spectra given, Fig. 3) is washed with methanol and dried at 40°C for 6 h, which gives (light blue-green in colour) the desired catalyst. The final catalyst has been represented by



In order to confirm that the complex is indeed chemically bound to the modified alumina, we have carried out similar reactions of bonding of the complex with low molecular weight compound like *t*-butanol. In the first step, phenyl isocyanate is reacted with *t*-butanol [1] and the product precipitate. The FT-IR of the product shows the $-\text{NH}$ at 3493 cm^{-1} , $-\text{OH}$ at 3500 cm^{-1} , aromatic $-\text{CH}$ at 3030 cm^{-1} , aliphatic $-\text{CH}$ at 2966 cm^{-1} and $\text{C}=\text{O}$ at 2129 cm^{-1} and matches with the literature values for *t*-butyl carbamate [24]. In the next step this is reacted with dichloroethane and its IR shows the presence of C–Cl group at 780 cm^{-1} . The final step consists of reacting the cobalt/vanadium macrocyclic complex with this compound. The FT-IR of the final product shows a considerable reduction of the peak corresponding to the C–Cl group, thus confirming the bond formation between the complex of cobalt/vanadium and the modified *t*-butanol.

2.4. Reaction setup and procedure

A high pressure rocking type batch reactor is used for conducting reactions. The reactor is cylindrical in shape made of stainless steel of 500 cm^3 volume. The reactor has a provision for gas inlet and pressure gauge. An external-heating coil provides heating and the temperature is controlled using an on/off controller with a suitable thermocouple. Oxygenation reactions are carried out in the batch reactor with 100 ml of

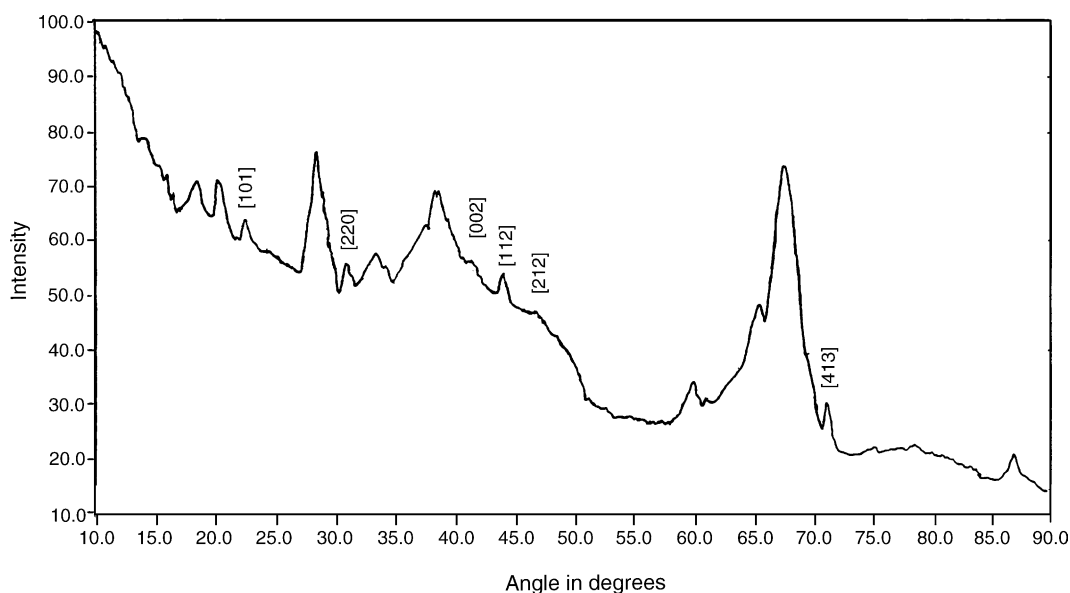


Fig. 4. XRD pattern of the final catalyst. The *hkl* values of [1 0 1] and [4 1 3] are for CoV alloy (JCPDS file no. 05-0705), the *hkl* values of [0 0 2] and [2 1 2] belong to Co alone (in JCPDS file no. 18-0436) and the *hkl* values of [2 2 0] and [1 1 2] belong to V alone (in JCPDS file no. 22-1058).

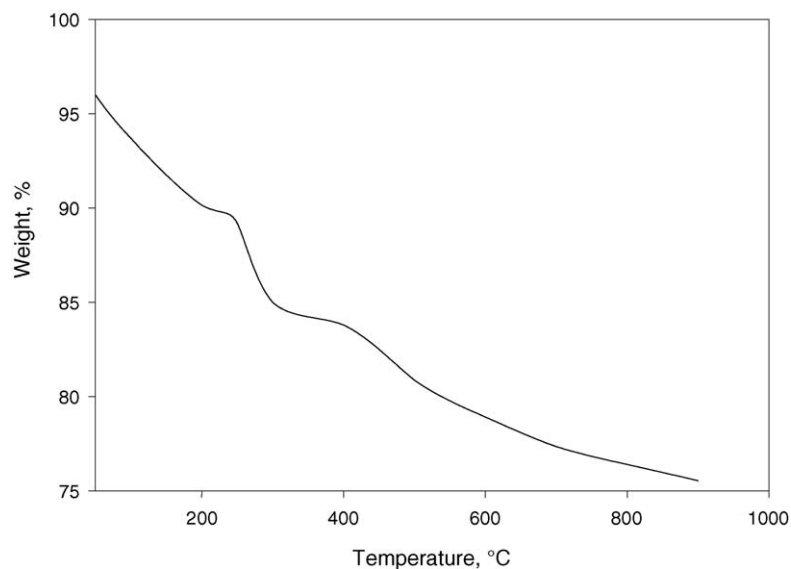


Fig. 5. Thermogravimetric analysis (TGA) of the microcyclic bimetallic Co/V complex catalyst supported on modified alumina, the catalyst is stable up to 251 °C.

cyclohexane and 1.0 g of catalyst in the temperature range 75–220 °C. The cyclohexane to oxygen ratio in the feed was 10. The catalyst was originally light green in colour, which after the oxidation reaction turned into brown in colour and the catalyst was separated by the filter paper. The products were analyzed by the GC/MS analysis.

2.5. Characterization of the catalyst

The metal content of the loaded catalyst is determined by the atomic absorption analysis (AAS). The fresh catalyst has vanadium and cobalt metal in the amount of 0.0543 and 0.0462 wt.%, respectively. After 100 h of oxidation reaction time, both metals reduces to 0.0494 and 0.040 wt.%,

respectively. The above observation shows that there is negligible loss of metal during the oxidation reaction. The X-ray diffraction pattern of the catalyst shows peaks corresponding to cobalt–vanadium alloy (JCPDS file no. 05-0705). The small peaks superimposed with intense diffraction patterns of the Al_2O_3 . The XRD diagram of the catalyst is shown in Fig. 4 in which we have marked various diffraction peaks of cobalt–vanadium alloy. This indicates the presence of both the metals on the surface of the catalyst. In order to assess whether the loaded complex on the alumina is stable at the reaction temperature, thermogravimetric analysis (TGA) of the catalyst was carried out. The thermogram (Fig. 5) shows that the catalyst is stable up to 251 °C.

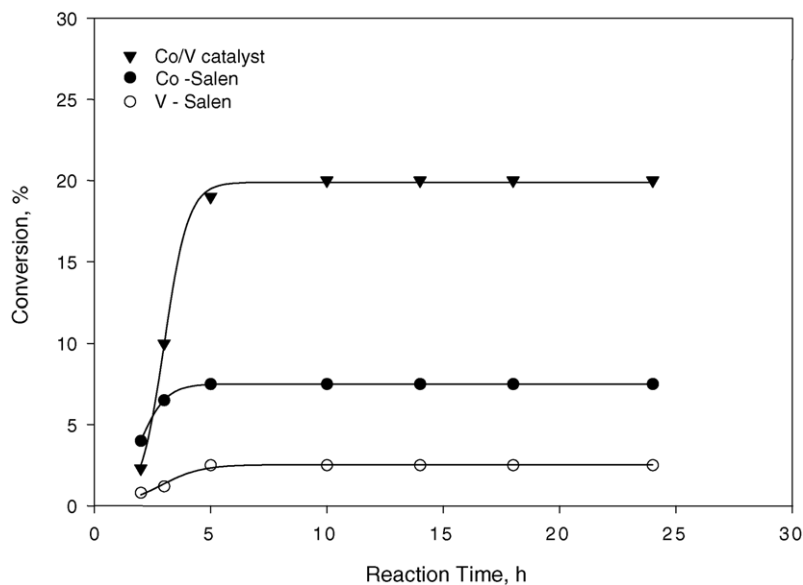


Fig. 6. Comparative percentage conversion graph of Co/V catalyst with Co-Salen and V-Salen catalyst at 150 °C.

3. Results and discussion

The oxidation of cyclohexane in presence of oxygen using the catalyst developed in this work has been conducted in the temperature range of 75–225 °C batch wise. To demonstrate that our catalyst is necessary for the oxidation, the reaction was first carried out without the catalyst for as long as 12 h at 200 °C and we found that there was no product formation. After ensuring this, the catalyst was introduced into the reactor and the strong smell at the end of the oxidation reaction indicated the formation of the product, which is further confirmed by the GC/MS analysis.

As a result of the chemical reaction (at 150 °C, 5.8 atm) the catalyst showed a change in colour from light green to dark brown. The product was subjected to a GC/MS analysis and was shown to consist of cyclohexanone (14.0%) and cyclohexanol (1.0%) for 4 h of reaction time. Adding pure cyclohexanol and cyclohexanone to the reaction product and taking its GC authenticated the individual components. No extra peaks appeared, this way confirming the formation of cyclohexanol and cyclohexanone.

The reaction time was systematically varied from 1.0 to 24 h at 150 °C and the result of the total conversion of cyclohexane has been plotted in Fig. 6. With the increase in the reaction time the total conversion increases and reaches to an asymptotic value of 20% at 150 °C. Therefore the increase in residence time after 4 h has no effect on the final conversion reached. The binuclear macrocyclic catalyst developed in this work is observed to behave differently from the other heterogeneous catalyst. We have reported the catalytic oxidation using Salen complex of cobalt as well as that of vanadium at 150 °C. These results have also been plotted in this figure and for these cases also, the total conversion increases attaining a lower asymptotic value as shown in the figure.

In Fig. 7, we have examined the effect of temperature on the final conversion of cyclohexane reached in 4 h of reaction time for the Co/V bimetallic catalyst. The conversion for the heterobinuclear macrocyclic catalyst increases with the temperature first but beyond 150 °C, it starts falling down. This seems to be the maximum temperature and the fall in conversion may indicate that the catalyst has become inactive at high temperature. We show through the AAS analysis that the metal loss is negligible up to 250 °C and this fall in the conversion suggest the lowering of activity at higher temperatures. To confirm that the loss of activity is not irreversible, we use the same catalyst at 150 °C once again and obtain conversion level of 20.0% in 4 h reaction time. We have also plotted conversion versus temperature for cobalt Salen as well as vanadium Salen catalyst in this figure. This plot shows that generally vanadium Salen catalyst gives lower conversion but for the temperature range studied, the conversion of cyclohexane for both these catalyst continues to rise and at around 200 °C, we obtain the same level of conversion of about 20.0% as obtained for the bimetallic catalyst at 150 °C.

Fig. 8 shows the selectivity of products with increase in temperature. The amount of cyclohexanol formed was very small (~2.0%). As the reaction time increased the amount of cyclohexanol formed remained constant whereas cyclohexanone selectivity increased. Fig. 9 shows the effect of pressure on product distribution. The cyclohexanol selectivity did not change much where as cyclohexanone selectivity varied without following a particular trend. In the macrocyclic Co/V catalyst, the major product is cyclohexanone and the selectivity is found to improve with the increase in temperature even though the overall conversion (as seen in Fig. 7) seems to fall.

In the accepted reaction mechanism [25,26] of functionalization of alkanes using cobalt or vanadium catalysts, they

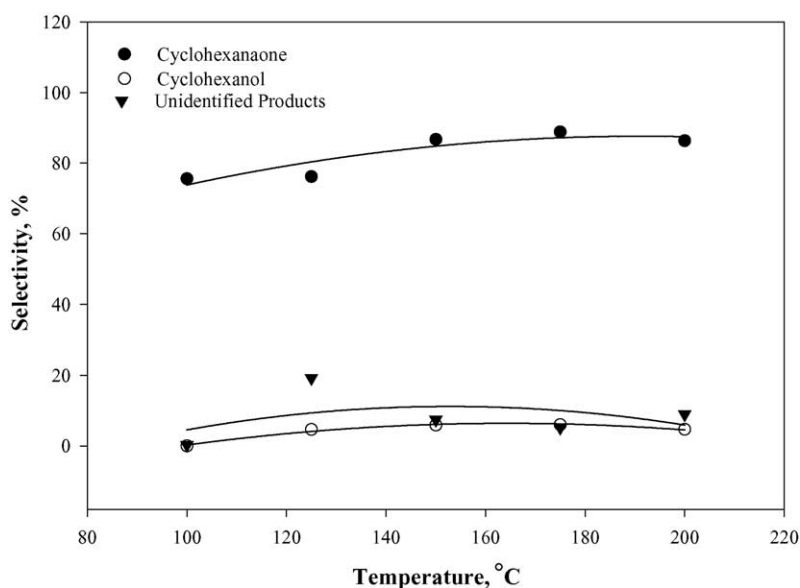


Fig. 7. Effect of temperature on the selectivity of the products formed by the oxidation reaction of cyclohexane in the presence of bimetallic V/Co catalyst at 14.3 atm for 4 h reaction time.

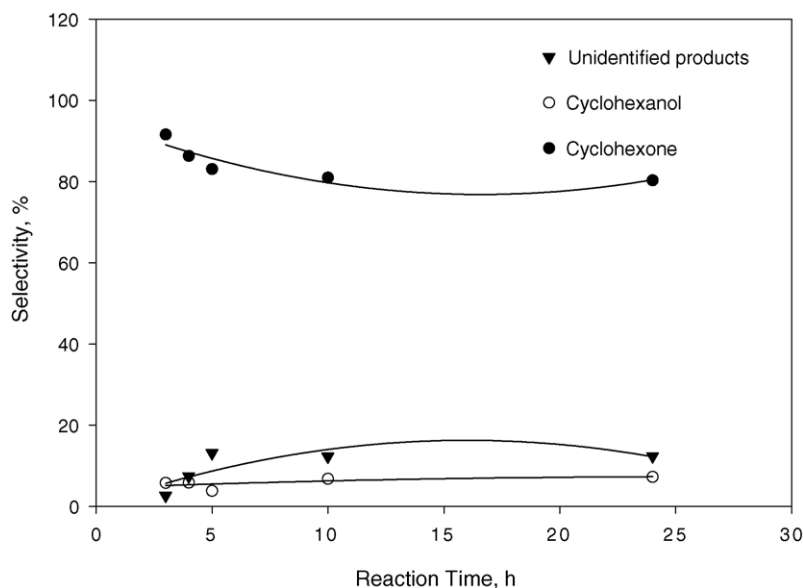


Fig. 8. Effect of time on the selectivity of the product formed by the oxidation of cyclohexane in the presence of Co/V bimetallic catalyst at 150 °C and 5.8 atm.

play a dual role of initiation and termination. The oxidation of cyclohexane with molecular oxygen in presence of the vanadium (or cobalt) catalyst could occur through (i) auto oxidation of free radicals, (ii) the metal ion followed by re-oxidation of the reduced metal, (iii) catalytic oxygen transfer [27]. In order to show that the reaction is not occurring via free radical mechanism, we carried out the oxidation of cyclohexane in presence of free radical initiator, like for example benzoyl peroxide (BPO) and found negligible effect on the initial slow phase or the final conversion reached. In addition to this, we also carried the oxidation reaction in presence of

free radical scavengers like, hydroquinone and once again found no effect upon the final conversion reached.

In our catalyst, we have a heteromolecular macrocyclic bimetallic catalyst, which is bonded to the modified alumina. In this, the potential site of reaction could be metal centre or ligand centre. In the accepted mechanism of air oxidation of cyclohexane, the catalyst site has been proposed to be metal centred and the reaction intermediate cyclohexane hydroperoxide ($C_6H_{11}OO^*$) radicals break to form cyclohexanol and cyclohexanone in equal amount. Since in our reaction, the cyclohexanone is the major product with cyclohexanol in minor

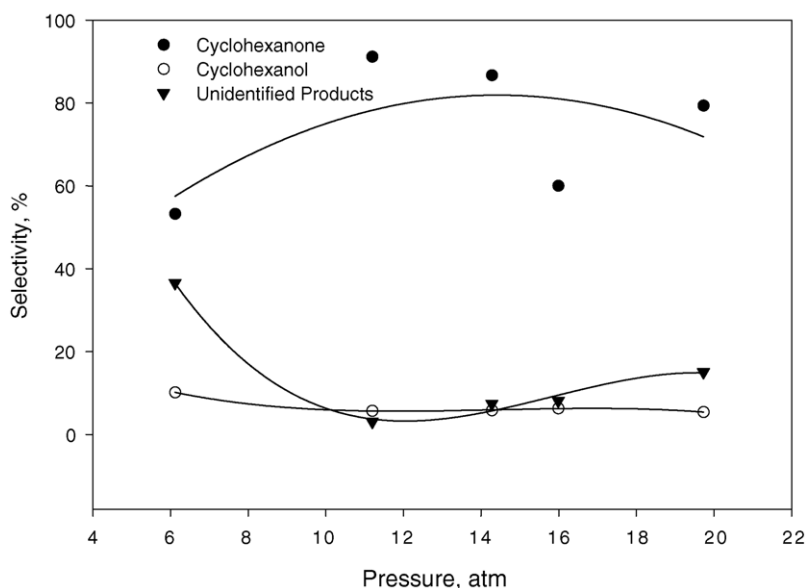
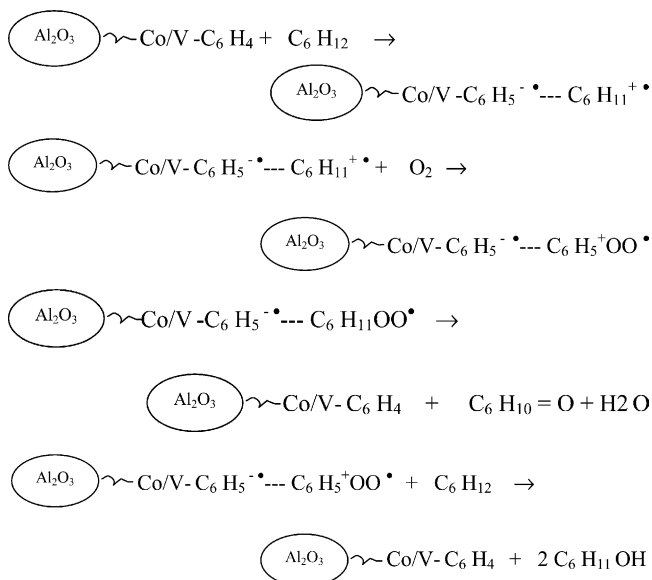


Fig. 9. Effect of pressure on the selectivity of the product form by the bimetallic Co/V catalyst oxidation reaction of cyclohexane at 150 °C temperature for 4 h reaction time.

amount, the mechanism of reaction is expected to be different.

In the given mechanism, the catalyst behaves like a typical Lewis acid in an oxidation reaction [28]. In this, it forms an anion radical through an electron abstractor, which can add an oxygen molecule as shown in reaction (2). The complex, thus formed, can give cyclohexanone (a major product) as shown in reaction (3) or can interact with a cyclohexane molecule in the bulk to form cyclohexanol (a minor product) in reaction (4). In the following, we propose a ligand centred mechanism in which for the air oxidation, the catalyst forms an ion radical intermediate with cyclohexane as follows [29]:



4. Conclusion

In this work, we have prepared a heterogeneous catalyst for the air oxygenation of cyclohexane using molecular oxygen. The formation of binuclear macrocyclic complex has been shown through FT-IR and was chemically bound on the carbamate-modified alumina. The bond formation between the two has been shown to occur by carrying out similar reaction with small homologous compound *t*-butanol. The oxidation reaction shows that cyclohexanone formation is 14 times more than cyclohexanol.

Acknowledgements

One of the authors G.S. Mishra is thankful to Department of Science and Technology, New Delhi for the financial

support under “Young Scientist Scheme” (Project no. SR/FTP/CS-04/2000). We also thank RSIC, CDRI, Lucknow for product analysis by the GC/MS spectroscopy.

References

- [1] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D. Wayne Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J.R. Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B. Ray Stults, Chem. Rev. 101 (2001) 953.
- [2] N. Perkas, Y. Holypin, O. Patalik, A. Gedonken, S. Chandrasekhran, Appl. Catal. A: Gen. 209 (2001) 125.
- [3] W.B. Fisher, J.F. Van Repper, M. Grayson (Eds.), Krik-Othmer Encyclopedia of Chemical Technology, vol. 7, 3rd ed., Wiley, New York, 1979, p. 411.
- [4] K. Weissmermel, H.J. Horpe, Industrial Organic Chemistry, 2nd ed., VCH Press, Weinheim, 1993.
- [5] C.J. Moody, J. O’Connell, Chem. Commun. (2000) 1311.
- [6] C.B. Almquist, P. Biswas, Appl. Catal. A: Gen. 214 (2001) 259.
- [7] A. Sakthivel, P. Selvam, J. Catal. 211 (2002) 134.
- [8] W.A. Carvalho, P.B. Varaldo, M. Wallau, U. Schuchardt, Zeolites 18 (1997) 408.
- [9] U. Schuchardt, D. Cardoso, R. Sercheli, et al., Appl. Catal. A: Gen. 211 (2001) 01.
- [10] S.S. Lin, H.S. Weng, Appl. Catal. A: Gen. 118 (1994) 21.
- [11] S. Kulkarni, M. Alurkar, A. Kumar, Appl. Catal. A: Gen. 142 (1996) 243.
- [12] R. Neumann, A.M. Khenkin, Inorg. Chem. 34 (1995) 5753.
- [13] N. Komiya, S. Noji, S.I. Murahashi, Chem. Commun. (2001) 65.
- [14] R. Raja, G. Shankar, J.M. Thomas, J. Am. Chem. Soc. 121 (1999) 11926.
- [15] G.S. Mishra, A. Kumar, Catal. Lett. 81 (2002) 113.
- [16] G.S. Mishra, A. Kumar Jr, A. Kumar, J. Mol. Catal. A: Chem. 201 (1/2) (2003) 179.
- [17] R.R. Gange, C.L. Spiro, J.J. Smith, C.A. Hamann, A.K. Shiemke, J. Am. Chem. Soc. 103 (1981) 4073.
- [18] M.J.L. Kishore, G.S. Mishra, A. Kumar, J. Mol. Catal. A: Chem. 216 (2004) 157.
- [19] M.J.L. Kishore, G.S. Mishra, A. Kumar, Ind. J. Chem. B, in press.
- [20] L. Lieng-Huang, Adhesive Chemistry, Developments and Trends, Plenum Press, London, 1984.
- [21] G.S. Mishra, A. Kumar, J. Mol. Catal. A: Chem. 192 (2003) 275.
- [22] J. Ryczkowski, Catal. Today 68 (2001) 263.
- [23] S. Siggia, Quantitative Organic Analysis, 3rd ed., Wiley, New York, 1963, p. 558.
- [24] Web site, <http://www.aist.go.jp/RIODB/SDBS/menu-e.html>.
- [25] B.K. Das, J.H. Clark, Chem. Commun. (2000) 605.
- [26] R. Gopinathan, B.K. Patel, Org. Lett. 2 (5) (2000) 577.
- [27] M. Hartmann, S. Ernst, Angew. Chem. Int. Ed. 39 (2000) 888.
- [28] A. Corma, H. Garcia, Chem. Rev. 102 (2002) 3837.
- [29] G. Centi, F. Trifiro, J.R. Ebner, V.M. Franchetti, Chem. Rev. 88 (1988) 55.