Dioxovanadium(V) complexes of dibasic tridentate ligands encapsulated in zeolite-Y for the liquid phase catalytic hydroxylation of phenol using H_2O_2 as oxidant

Mannar R. Maurya[a,*], Himani Saklani[a], Amit Kumar[a], and Shri Chand[b]

[a] *Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India*
[b] *Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247 667, India*

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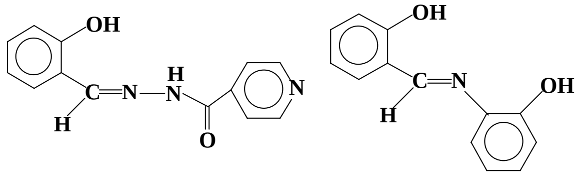
Liquid phase hydroxylation of phenol with H_2O_2 to a mixture of catechol and hydroquinone in acetonitrile has been reported using dioxovanadium(V) Schiff base complexes encapsulated in zeolite-Y as catalysts. The Schiff bases used are derived from salicylaldehyde and isonicotinic acid hydrazide (H_2sal-inh) or *o*-aminophenol (H_2sal-oap). A best-suited reaction condition has been optimized for both the catalysts by considering concentration of the oxidant, amount of catalyst and temperature. Under the optimized reaction conditions, catalytic ability of both the catalysts is comparable and has shown the highest conversion of about 27% after 6 h of reaction time. Both the catalysts are more selective towards catechol formation where $NH_4[VO_2$(sal-inh)] gives 84.6% selectively while $NH_4[VO_2$(sal-oap)] gives 77% selectivity.

KEY WORDS: selective hydroxylation of phenol; dioxovanadium(V) complexes; schiff bases; encapsulation; zeolite-Y.

1. Introduction

Vanadium(V) complexes with O_4N coordination have been regarded as bioinorganic catalysts as prosthetic group present in enzyme vanadate-dependent haloperoxidases have similar coordination environment [1,2]. Several oxo- and dioxovanadium(V) complexes present functional models of haloperoxidases where these complexes catalyze oxyhalogenation of aromatic substrates using H_2O_2 as oxidant in presence of halides [1–4]. Vanadium complexes that model part of the enzymes have also been shown to be active homogeneous catalysts for oxidation reactions [5–7]. Zeolite encapsulated complexes have been suggested as model compounds for enzyme mimicking where zeolite replaces the protein mantle of the enzymes. Recently oxovanadium(IV) complexes have been encapsulated in the cavity of zeolite-Y and studied for the oxidation reactions. For example, oxovanadium(IV) complex [VO(pic)$_2$] (Hpic = picolinic acid) encapsulated in zeolite-Y has been studied for catalytic oxidation of cyclohexene, *iso*-propanol and benzene [8]. [VO(salen)]—Y (H_2salen = *N*,*N*′-bis(salicylidene)ethane-1,2-diamine) and related catalysts have been used for the epoxidation of cyclohexane and oxidation of phenol [9–11]. Encapsulation of metal complexes, acting as homogeneous catalysts, in the cavity of zeolite provides the advantages of heterogeneous catalysts, share many advantageous features of homogeneous catalysts and inimizes the disadvantages of both. [VO(salphen)] (H_2salphen = *N*,*N*′-bis(salicylidene)phenyl-1,2-diamine) immobilized on carba-mate modified silica gel and on AlMCM-41 have also been synthesized [12,13]. The former catalyst has been studied for the oxidation of cyclohexanol while the latter one has been used for the oxidation of *trans*-stilbene and styrene.

In the present investigation, we have prepared and characterized dioxovanadium(V) complexes of ligands I and II (scheme 1) encapsulated in zeolite-Y and tested their catalytic activity for the liquid phase hydroxylation of phenol. Suitable reaction conditions have been optimized to give maximum hydroxylation. Liquid phase hydroxylation of phenol to catechol and hydroquinone using simple oxidants like O_2 and H_2O_2 is a reaction of industrial importance [14,15]. Different types of catalysts have been tested to enhance the hydroxylation of phenol [16–19]. Catalysts based on zeolite encapsulated metal complexes (ZEMC) have played an important role in this regard [20–29].



I: H_2sal-inh **II**: H_2sal-oap

Scheme 1.

2. Experimental

2.1. Materials

NH_4VO_3, salicylaldehyde (sal), isonicotinic acid hydrazide (inh), *o*-aminophenol (oap) and phenol were

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[*] To whom correspondence should be addressed.
E-mail: rkmanfcy@iitr.ernet.in

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purchased from Loba Chemie, India. H_2sal-inh [30] and H_2sal-oap [31] (cf. scheme 1) were prepared according to the literature procedures. All other chemicals and solvents used were also of AR grade. Zeolite Na—Y (Si/Al ~ 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India.

2.2. Physical methods and analysis

IR spectra were recorded as KBr pellet on a Perkin-Elmer model 1600 FT-IR spectrometer. Electronic spectra were recorded in Nujol on Shimadzu 1601 UV–visible spectrophotometer by layering mull of sample to inside of one of the cuvette, while keeping another one layered with Nujol as reference. Thermogravimetric analyses of the pure as well as encapsulated complexes were carried out using TG Stanton Redcroft STA 780. X-ray diffractograms of solid catalysts were recorded using Philips PW 1140/90 X-ray powder diffractometer with CuK_α target at Institute Instrumentation Center. The metal contents were measured by using Perkin-Elmer model 3100 Atomic Absorption Spectrometer. All catalyzed reaction products were analyzed using Nucon 5700 gas chromatograph fitted with FID detector, a 2 m × 2 mm (ID) OV-17 (SS) column and ORACLE 2 computer software. Scanning electron micrographs of catalysts were recorded on a Leo instrument model 435 VP. For this, the samples were dusted on alumina and coated with a thin film of gold to prevent surface change and to protect the surface material from thermal damage by the electron beam. In all analyses a uniform thickness of about 0.1 mm was maintained.

2.3. Preparations

2.3.1. Preparation of Na—NH_4VO_3—Y (1)

About 5.0 g Na—Y zeolite was suspended in 200 mL distilled water containing NH_4VO_3 (4.09 g, 35 mmol) and the reaction mixture was heated while stirring at 90 °C for 24 h. The solid was filtered, washed with hot distilled water till the filtrate was free from NH_4VO_3 and dried at 150 °C for 12 h in an air oven.

2.3.2. Preparation of $NH_4[VO_2$(sal-inh)]—Y (2)

About 2.4 g (10 mmol) H_2sal-inh was dissolved in 1:1 NH_4OH (100 mL) with occasional heating at 50 °C and filtered to remove any insoluble ligand; usually small amount of ligand remains insoluble during dissolution. An amount of 1.0 g Na—NH_4VO_3—Y was added to the above solution while stirring the reaction mixture. During this period ligand slowly enter through the zeolite pores and formed complex with vanadium. After 2 h, the pH of the reaction mixture was slowly adjusted to 7.5 with 4 M HCl and stirring continued for next 2 h. The resulting material was filtered, washed thoroughly with water and dried at 150 °C. Finally the crude mass was extracted with methanol till the complex was free from any free H_2sal-inh. The uncomplexed metal ions present in the zeolite were then removed by exchanging with aqueous 0.01 M NaCl (200 mL) solution for 8 h and filtered. Finally, the solid product obtained was washed with hot distilled water till no precipitation of AgCl on treating filtrate with $AgNO_3$ and dried at 150 °C for several hours to a constant weight.

2.3.3. Preparation of $NH_4[VO_2$(sal-oap)]—Y (3)

Catalyst $NH_4[VO_2$(sal-oap)]—Y was prepared following essentially the above procedure, replacing H_2sal-inh with H_2sal-oap.

2.4. Catalytic activity study: oxidation of phenol

The catalytic activity study towards the hydroxylation of phenol was carried out in a 50 mL flask fitted with a water cooled condenser. In a typical reaction, an aqueous solution of 30% H_2O_2 (5.67 g, 0.05 mol) and phenol (4.7 g, 0.05 mol) were mixed in 2 mL of MeCN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. An appropriate catalyst (0.025 g) was added to the reaction mixture and with this the reaction was considered to begin. During the reaction, the products were analyzed using a gas chromatograph after specific interval of time by withdrawing small aliquot. The effects of various parameters such as amounts of oxidant and catalyst as well as the temperature of the reaction were studied in order to see their effect on the reaction product pattern.

3. Results and discussion

Synthesis of dioxovanadium(V) complexes of H_2sal-inh and H_2sal-oap encapsulated in the super cages of zeolite-Y was carried out by the flexible ligand method where ammonium salt of ligands reacted with pre-exchanged Na—NH_4VO_3—Y in aqueous solution at pH ca. 7.5. The crude mass was subjected to Soxhlet extraction in methanol to remove excess ligand that remained uncomplexed in the cavities of the zeolite as well as located on the surface of the zeolite along with neat complexes formed, if any. The remaining uncomplexed metal ions in zeolite were removed by exchanging back with aqueous 0.01 M NaCl solution. The percent metal contents estimated by atomic absorption spectroscopy suggest the encapsulation of the metal complexes inside the super cages of the zeolite-Y. This is further supported by the scanning electron micrographs (SEM) recorded for Na—NH_4VO_3—Y and its encapsulated complexes. The micrographs indicate the presence of well-defined crystals free from any shadow of the metal ions or complexes present on the external surface.

Various physico-chemical technique e.g., IR and electronic absorption spectroscopy and XRD as well as thermal analysis pattern characterized the resulting catalysts. A comparison of the physico-chemical properties of these catalysts with that of the simple complex

Table 1
Chemical composition, physical and analytical data of encapsulated catalysts

S. No.	Catalyst	Colour	Vanadium content (wt%)	No. of vanadium per unit cell
1	Na—NH_4VO_3—Y	Colourless	1.5	4.8
2	$NH_4[VO_2$(sal-inh)]—Y	Yellow	0.81	3.2
3	$NH_4[VO_2$(sal-oap)]—Y	Brown	0.62	1.96

$NH_4[VO_2$(sal-inh)$\cdot H_2O]$, prepared by the reaction of sodium salt of H_2sal-inh with NH_4VO_3, were also carried out [32]. The formulations of the encapsulated complexes are, thus, based on the simple complex and conclusion drawn from various studies (vide infra). The formula, colour, vanadium per unit cell and the percentage of vanadium content of various catalysts (i.e. encapsulated one) along with Na—NH_4VO_3—Y are presented in table 1.

3.1. Spectral studies

IR spectra of H_2sal-inh and H_2sal-oap exhibit ν(C=N) stretch at 1616 and 1630 cm^{-1}, respectively [31,32]. A significant shift of this band to lower wave number (10–16 cm^{-1}) indicates the coordination of azomethine nitrogen to the vanadium. The ligand H_2sal-inh exhibits ν(C=O) at 1685 cm^{-1} but band due to coordination of enolized oxygen of this ligand could not be observed due to appearance of ν(Si—O) stretch as strong band in this region. Similarly, bands due to ν(O=V=O) stretches could not be located as these bands appear underneath the Si—O band. However, appearance of at least three bands in the low frequency region (400–500 cm^{-1}) indicates the coordination of nitrogen and oxygen of the metal. A partial list of IR spectral data is presented in table 2.

Table 2
IR and electronic spectral data of ligands and encapsulated complexes

Compound	IR frequency (cm^{-1})		λ_{max} (nm)[a]
	ν(C=N)	ν(M—N)/(M—O)	
H_2sal-inh[b]	1616		214, 234.5 (sh) 289, 333
$NH_4[VO_2$(sal-inh)]—Y[c]	1600	441, 480, 530	215, 268, 318, 405
$NH_4[VO_2$(sal-inh)$\cdot H_2O]$[b]	1601	420, 463, 477	229, 280, 323, 402.5
H_2 sal-oap[b]	1630		207, 268.5, 348, 442
$NH_4[VO_2$(sal-oap)]—Y[c]	1620	433, 487, 537	258, 320, 432

[a] sh = Shoulder band.
[b] Recorded in methanol.
[c] Recorded in nujol.

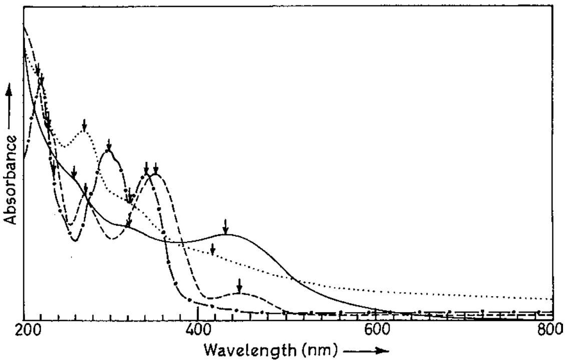


Figure 1. Electronic spectra of H_2sal-inh (–•–), H_2sal-oap (- - -), $NH_4[VO_2$(sal-inh)]—Y (···) and $NH_4[VO_2$(sal-oap)]—Y (—).

The electronic spectral studies of ligands along with neat $NH_4[VO_2$(sal-inh)$\cdot H_2O]$ (recorded in methanol) and encapsulated complexes (recorded in nujol) are also presented in table 2 and spectra of encapsulated complexes are reproduced in figure 1. The UV spectrum of H_2sal-inh exhibits three spectral bands at 214, 289 and 333 nm and these are due to ϕ–ϕ*, π–π* and n–π* transitions, respectively. A weak shoulder associated with the second band at 234.5 nm is also arising due to hydrogen bonding and association present in the ligand. The absence of band due to hydrogen bonding and association indicates that the hydrogen bond is broken after complex formation. Other intra-ligand bands are still present in the $NH_4[VO_2$(sal-inh)] —Y where 289 and 333 nm bands shift towards lower nm while 214 nm band appears at nearly constant position. In addition, a new band appears at 405 nm, which is assigned as ligand to metal charge transfer (LMCT) transition from the phenolate oxygen atom to an empty d-orbital of the vanadium atom. As dioxovanadium(V) has d° configuration, d–d band is not expected. The spectral features of this encapsulated complexes is similar to that recorded for neat $NH_4[VO_2$(sal-inh)$\cdot H_2O]$ (table 2). The ligand H_2sal-oap exhibits ϕ–ϕ*, π–π* and n–π* bands at 207, 268.5 and 348 nm, respectively. Another band appearing at 442 nm seems to be a splitted band of n–π* transition. The band corresponding to last two transitions appear at 258 and 320 nm, respectively, while band due to ϕ–ϕ* transition could not be located. A broad band at 432 nm is assigned to LMCT transition. Thus, electronic spectral data support the encapsulation of these complexes in the cavity of zeolite-Y.

3.2. TGA studies

The TGA data with the percent weight loss at different temperature ranges are presented in table 3. It is clear from the data that removal of trapped water

Table 3
TGA data

Catalysts	% Weight loss		
	50–170 °C	170–350 °C	350—800 °C
NH_4VO_3—Y	21	4	5
$NH_4[VO_2$(sal-oap)]—Y	20	4	4
$NH_4[VO_2$(sal-inh)]—Y	15	5	5

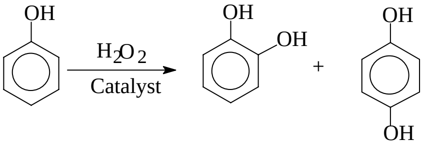
occurs up to 170 °C while loss of intra-zeolite water occurs in the temperature range 170–350 °C. A weight loss of ca. 5% between temperature range 350–800 °C in all catalysts suggests the decomposition of encapsulated NH_4VO_3/complexes in this temperature range, though, loss of NH_4^+ group is expected to occur at lower temperature. The low percent weight loss indicates the presence of only small amount of vanadium complexes/ NH_4VO_3 in the cavities of zeolite. This is in agreement with the low percent vanadium content estimated by atomic absorption spectrometer.

3.3. XRD studies

The X-ray diffraction patterns of Na—Y, Na—NH_4-VO_3—Y, $NH_4[VO_2$(sal-oap)]—Y and $NH_4[VO_2$(sal-inh)]—Y were recorded at 2θ values between 5 and 70°. The peaks observed in all patterns are essentially similar and no new peaks were detected which is probably due to poor loading of the metal complexes during encapsulation. Observation of patterns also indicates that zeolite framework has not undergone any significant structural change during encapsulation of complexes and thus crystallinity of the zeolite is preserved. The molecular dimensions of the known structures of [VO(OMe)(MeOH)(sal-oap)] [33] and [VO(OMe)(-MeOH)(sal-inh)] [32] at any angle are less than 12 Å and thus zeolite-Y can accommodate these complexes well in its super cages.

3.4. Oxidation of phenol

Liquid phase hydroxylation of phenol catalyzed by encapsulated complexes using H_2O_2 as an oxidant has been studied in CH_3CN. As hydroxyl group present on phenol is *ortho* and *para* directing, the hydroxylation of phenol is expected to give two products viz. catechol and hydroquinone as shown by equation (1). The presence of these two products in the reaction mixture was also observed with a mass balance of about 96%. Minor products (e.g., polymeric materials), if any, were not detectable in GC under the reaction conditions, used here in.



(1)

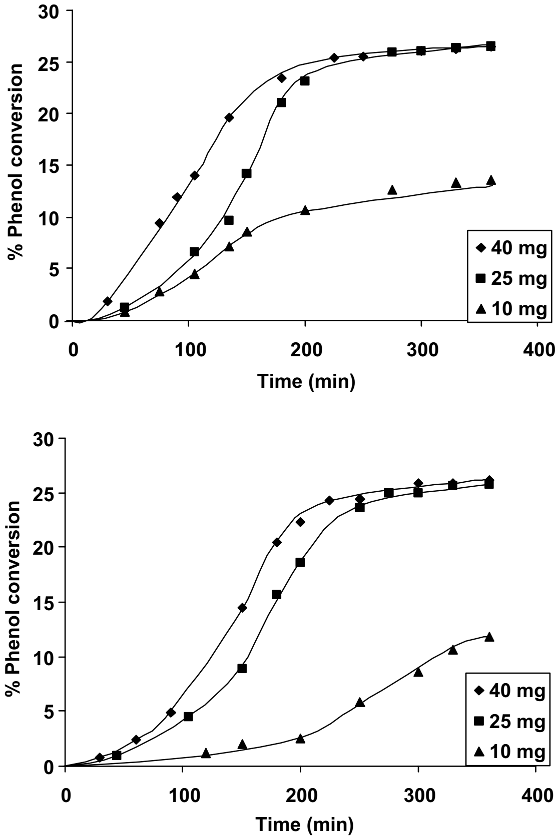


Figure 2. Effect of catalyst weight on phenol oxidation in $NH_4[VO_2$(sal-inh)]—Y (above) and $NH_4[VO_2$(sal-oap)]—Y (below).

In order to acquire suitable reaction conditions for maximum transformation of phenol both the catalysts were studied in detail by considering the following reaction parameters:

- effect of amount of catalyst,
- effect of temperature, and
- effect of H_2O_2 concentration.

3.4.1. Effect of amount of catalyst

The effect of amount of catalyst on the rate of reaction is illustrated in figure 2a and b. Three different amounts (e.g. 10, 25, 40 mg) of both catalysts were used for the fixed amount of phenol (4.7 g) and oxidant (5.67 g) in 2 mL CH_3CN. An amount of 25 or 40 mg gave comparable results in both cases with ca. 26% phenol conversion in 6 h of reaction time at 80 °C. Lowering the amount of catalyst resulted in the poor conversion. Such phenomenon has been interpreted in terms of thermodynamic and mass transfer limitations at high reaction rate. These factors are also applicable here. Thus, 25 mg of catalyst may be considered to be sufficient enough to give best performance.

3.4.2. Effect of temperature

The influence of temperature on the performance of catalyst for phenol conversion is illustrated in figure 3a

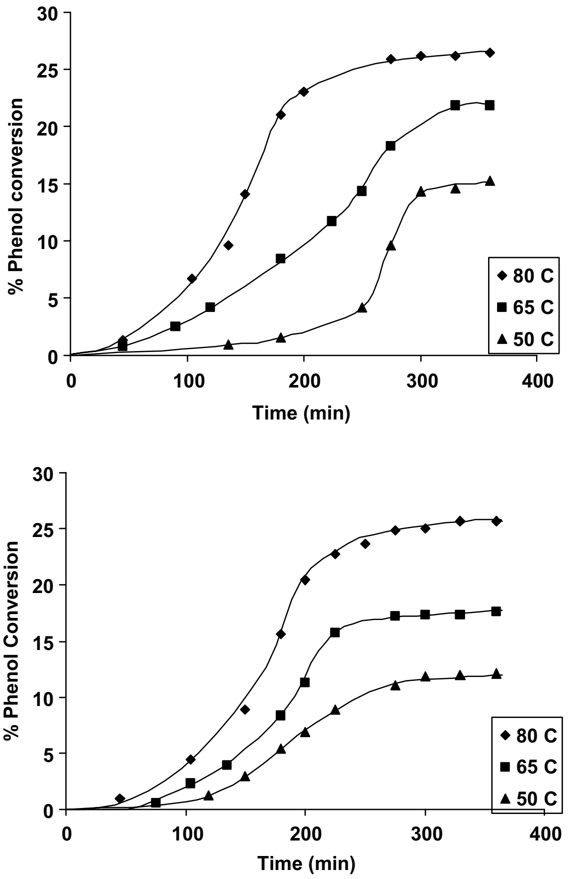


Figure 3. Effect of temperature on phenol conversion in $NH_4[VO_2(sal\text{-}inh)]$—Y (above) and $NH_4[VO_2(sal\text{-}oap)]$—Y (below).

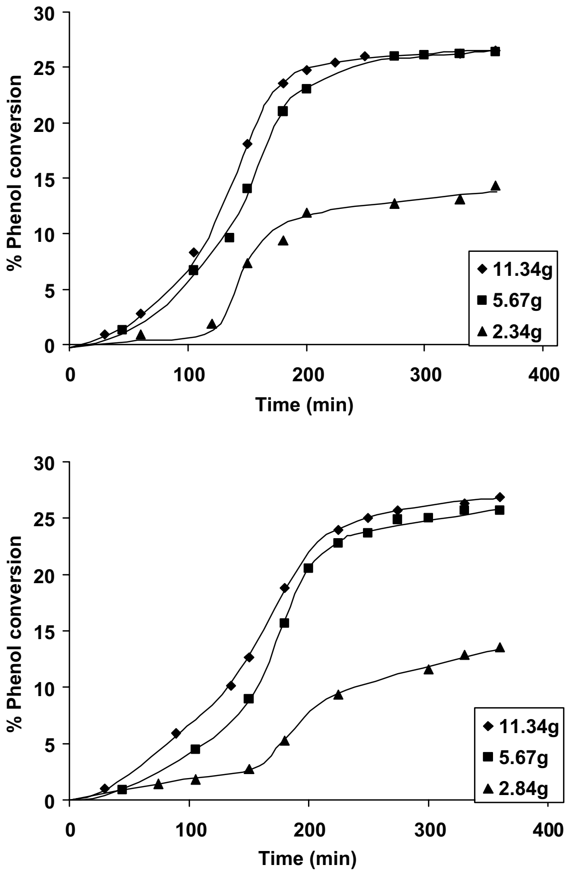


Figure 4. Effect of H_2O_2 concentration on phenol conversion in $NH_4[VO_2(sal\text{-}inh)]$—Y (above) and $NH_4[VO_2(sal\text{-}oap)]$—Y (below).

and b. Three different temperatures (50, 65 and 80 °C) were considered, while keeping other parameters as mentioned above (i.e., 4.7 g phenol, 5.67 g H_2O_2 and 25 mg catalyst) for the catalytic performance in 2 mL of CH_3CN. It is clear from the plots that both the catalysts have comparable performance and increasing the temperature from 50 to 80 °C causes increase in phenol transformation. The hydroxylation of phenol is maximum at 80 °C and ca. 60% of total conversion was achieved in 3 h. Thus, 80 °C is the minimum required temperature to supply sufficient energy to reach the energy barrier of phenol transformation.

3.4.3. *Effect of H_2O_2 concentration*

Amount of H_2O_2 concentration has great influence on reaction rate. Such influence as a function of time is illustrated in figure 4a and b using three different amounts of aqueous 30% H_2O_2 viz. 2.84, 5.67 and 11.34 g for a fixed amount of phenol (4.7 g) and catalyst (25 mg) in 2 mL CH_3CN. The lowest H_2O_2 concentration results in only ca. 14% phenol hydroxylation. Other two concentrations (i.e., 1:1 and 2:1 H_2O_2/phenol ratios) give comparable results of ca. 26% conversion. The percent conversion of phenol for these amounts of H_2O_2 follow the order: 1:1 > 0.33:1 > 2:1. This information suggests that H_2O_2/phenol ratio of 1:1 is ideal for the maximum conversion as well as maximum efficiency. Thus, the larger concentration of oxidant is not an essential condition to maximize phenol conversion.

3.5. *Catalytic activity comparison for $NH_4[VO_2(sal\text{-}inh)]$—Y and $NH_4[VO_2(sal\text{-}oap)]$—Y and Na—$NH_4VO_3$—Y*

All conditions and requirements as concluded above were considered essential for the maximum hydroxylation of phenol to a mixture of catechol and hydroquinone. It is clear from the data that both the catalysts have comparable catalytic activities. The catalyst $NH_4[VO_2(sal\text{-}inh)]$—Y with a phenol conversion of 26.5% is only slightly better than $NH_4[VO_2(sal\text{-}oap)]$—Y (25.7%) while Na—$NH_4VO_3$—Y gives 31% conversion of phenol. However, in terms of turn over frequency (TOF), $NH_4[VO_2(sal\text{-}oap)]$—Y is better catalyst than $NH_4[VO_2(sal\text{-}inh)]$—Y as TOF for these catalysts are 762 and 477, respectively. In all cases, the phenol conversion increases slowly in the beginning and reaches to a steady state in ca. 6 h. The presence of induction period in these catalysts indicates either slow formation of peroxo species or taking long time to transfer oxygen to the substrate due to mass transfer

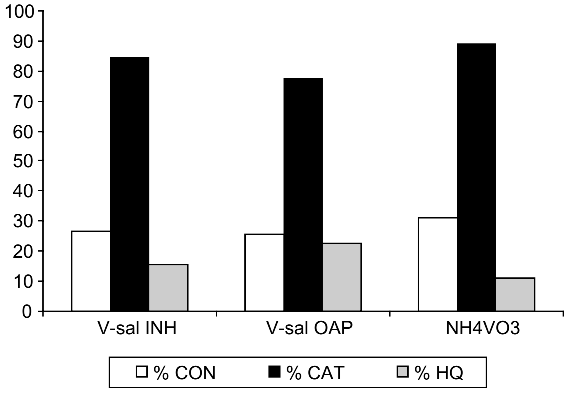


Figure 5. Bar diagram showing percent phenol conversion and percent selectivity of catechol and hydroquinone formation for catalysts.

limitations. The hydroxylation of phenol with H_2O_2 over TS-1 (Si/Ti = 23), though, gives better result, the formation of *p*-benzoquinone in addition to catechol and hydroquinone using solvents 2-butanone and acetonitrile was also observed [16]. Figure 5 presents phenol conversion and selectivities of catechol and hydroquinone formation as bar diagram. The selectivity of catechol formation varies in the order: Na—NH_4VO_3—Y (89%) > $NH_4[VO_2$(sal-inh)]—Y (84.6%) > $NH_4[VO_2$(sal-oap)]—Y (77%). This high selectivity of catechol formation and transformation of phenol are maintained even after 24 h of reaction time. These selectivities are comparable with that of other vanadium(IV) complexes encapsulated in zeolite-Y [11]. In general metal complexes encapsulated in zeolite-Y are reported to yield catechol in much higher proportion in comparison to hydroquinone. The product selectivity of such molecular sieve based catalysts is based on the shape and size of the product molecules.

Leaching or decomposition of the catalysts was tested by filtering the catalyst during the reaction and studying the catalytic activity of the filtrate. The filtrate obtained from Na—NH_4VO_3—Y show further catalytic activity to some extent in the transformation of phenol, indicating slow leaching of NH_4VO_3 in solution from the cavity of the zeolite during reaction. However, no appreciable transformation of phenol from other solutions suggests negligible leaching or decomposition of complexes $NH_4[VO_2$(sal-inh)] and $NH_4[VO_2$(sal-oap)] under reaction conditions. Recovered catalysts are also reusable after regeneration. For example $NH_4[VO_2$(sal-inh)]—Y, a representative catalyst was reused for phenol hydroxylation after refluxing in acetonitrile for 2 h followed by drying at 150 °C. A nearly identical activity of the recovered catalyst suggests its reusability and stability. Comparable IR and electronic spectral patterns of fresh and used catalysts also suggest their further reusability and stability.

4. Conclusion

Dioxovanadium(V) complexes, $NH_4[VO_2$(sal-inh)] and $NH_4[VO_2$(sal-oap)] have been encapsulated in the super cages of zeolite-Y. Chemical analyses, spectroscopic, SEM, XRD as well as thermogravimetric patterns present clear evidence for the encapsulation. Encapsulation of the complexes is, though, low in zeolite-Y matrix these are good catalysts for the oxidation of phenol to a mixture of catechol and hydroquinone with high TOF. No leaching of complexes from matrix and their reusability after regeneration has added advantages of using them. The selectivity of $NH_4[VO_2$(sal-inh)]—Y towards catechol formation is 86.6%, while that of $NH_4[VO_2$(sal-oap)]—Y is 77% under optimized reaction conditions.

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References

1. A. Butler, in: *Bioinorganic Catalysis*, 2nd edn. eds. J. Reedijk and E. Bouwman (Marcel Dekker, New York, 1999) ch. 5.
2. A. Butler, Coord. Chem. Rev. 187 (1999) 17.
3. C. Slebodnick, B.J. Hamstra and V.L. Pecoraro, Struct. Bonding (Berlin) 89 (1997) 51.
4. A. Butler and A.H. Baldwin, Struct. Bonding (Berlin) 89 (1997) 109.
5. V. Conte, F. Di Euria and G. Licini, Appl. Catal. A: Gen. 157 (1997) 335.
6. F. Van der Velde, I.C.W.E. Arends and R.A. Sheldon, J. Inorg. Biochem. 80 (2000) 81.
7. A.G.J. Ligtenbarg, R. Hage and B.L. Feringa, Coord. Chem. Rev. 237 (2003) 89.
8. A. Kozlov, K. Asakura and Y. Iwasawa, J. Chem. Soc. Faraday Trans. 94 (1998) 809.
9. N. Ulagappan and V. Krishnasamy, Indian J. Chem. 35A (1996) 787.
10. K.J. Balkus Jr., A.K. Khanmamedova, K.M. Dixon and F. Bedioui, Appl. Catal. A: Gen. 143 (1996) 159.
11. M.R. Maurya, M. Kumar, S.J.J. Titinchi, H.S. Abbo and S. Chand, Catal. Lett. 86 (2003) 97.
12. G.S. Mishra and A. Kumar, Catal. Lett. 81(2002) 113.
13. T. Joseph, D. Srinivas, C.S. Gopinath and S.B. Halligudi, Catal. Lett. 83 (2002) 209.
14. R.A. Sheldon and R.A. Vansanten, *Catalytic Oxidation*: *Principles and Applications* (World Scientific, Singapore, 1995).
15. *Industrial Organic Chemicals*: *Starting Materials and Intermediates*, *An Ullamann's Encyclopaedia*, Vol. 6 (Wiley-VCH, New York, 1999).
16. A. Thangaraj, R. Kumar and P. Ratnasamy, J. Catal. 131 (1991) 294.
17. V. Rives, A. Dube and S. Kannan, Phys. Chem. Chem. Phys. 3 (2001) 4826.
18. H. Zhang, X. Zhang, Y. Ding, L. Yan, T. Ren and J. Suo, New J. Chem. 26 (2002) 376.

19. R.J. Mahalingam, S. Bodamali and P. Selvam, Chem. Lett. 11 (1999) 1141.
20. K. Takai, Y. Shimashaki, T. Shishido and K. Takehira, Bull. Chem. Soc. Jpn. 75 (2002) 311.
21. K.J. Balkus Jr. and A.G. Gabrielov, J. Incl. Phenom. Mol. Recog. Chem. 21 (1989) 159.
22. R. Raja and P. Ratnasamy, Stud. Surf. Sci. Catal. 101 (1996) 181.
23. R. Raja and P. Ratnasamy, Appl. Catal. A: Gen. 143 (1996) 145.
24. C.R. Jacob, S.P. Varkey and P. Ratnasamy, Appl. Catal. A: Gen. 168 (1998) 353.
25. C.R. Jacob, S.P. Varkey and P. Ratnasamy, Micropor. Mesopor. Mater 22 (1998) 465.
26. T. Joseph, C.S. Sajanikumari, S.S. Deshpande and S. Gopinathan, Indian J. Chem. 38A (1999) 792.
27. S. Deshpande, D. Srinivas and P. Ratnasamy, J. catal. 188 (1999) 261.
28. S. Chavan, D. Srinivas and P. Ratnasamy, J. catal. 192 (2000) 286.
29. S. Seelan, A.K. Sinha, D. Srinivas and S. Sivasanker, Bull. Catal. Soc. India 1 (2002) 29.
30. K.N. Srivastava, S. Das and R.A. Lal, Indian J. Chem. 25A (1986) 85.
31. A. Syamal and M.R. Maurya, Indian J. Chem. 25A (1986) 934.
32. M.R. Maurya, S. Khurana, C. Schulzke and D. Rehder, Eur. J. Inorg. Chem. (2001) 779.
33. M.J. Clague, N.L. Keder and A. Butler, Inorg. Chem. 32 (1993) 4754.