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Oxovanadium(IV) Schiff base complexes encapsulated in zeolite-Y as catalysts for the liquid-phase hydroxylation of phenol

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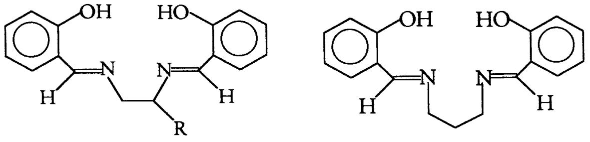
Liquid-phase hydroxylation of phenol with H_2O_2 to a mixture of catechol and hydroquinone in acetonitrile has been reported using oxovanadium(IV) Schiff base complexes encapsulated in zeolite-Y as catalysts. Reaction conditions have been optimized by considering the concentration of substrate and oxidant, amount of catalyst, volume of solvent and temperature. Under the optimized reaction conditions, [VO(sal-1,3-pn)]-Y (H_2sal-1,3-pn = *N*,*N*′-bis(salicylidene)propane-1,3-diamine) has shown the highest conversion of 34.3% after 6 h, [VO(salen)]-Y (H_2salen = *N*,*N*′-bis(salicylidene)ethane-1,2-diamine) and [VO(saldien)]-Y (H_2saldien = *N*,*N*′-bis(salicylidene)- diethylenetriamine) have comparable catalytic activity (~33% conversion) while [VO(sal-1,2-pn)]-Y (H_2sal-1,2-pn = *N*,*N*′-bis(salicylidene)propane-1,2-diamine) has the poorest performance (10.6% conversion). All these catalysts are more selective (90%) toward catechol formation except [VO(sal-1,3-pn)]-Y, which only gives ~68% selectivity.

KEY WORDS: selective hydroxylation of phenol; Schiff bases; vanadium complexes; zeolite-Y.

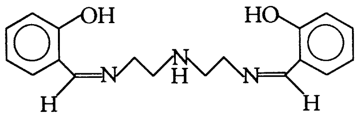
1. Introduction

Schiff base and related complexes of vanadium have attracted attention in recent years in the context of the role of vanadium in living organisms [1]. The catalytic activities of vanadium complexes, most of them based on enzymatic activities [2,3], is another intriguing and promising feature that has further stimulated such chemistry [4–9]. These homogeneous catalysts face the problem of separation from substrate and products. Encapsulation of metal complexes in the cavity of zeolite provides the advantages of heterogeneous catalysts, shares many advantageous features of homogeneous catalysts and minimizes the disadvantages of both.

Oxovanadium(IV) picolinate, [VO(pic)$_2$], encapsulated in zeolite-Y has been studied for the catalytic oxidation of cyclohexane, isopropanol and benzene using H_2O_2 [10]. Leaching of [VO(pic)$_2$] has, however, been noticed in the presence of H_2O_2 as an oxidant. It is, therefore, desirous to encapsulate oxovanadium(IV) complexes with bulky but flexible ligands and study their catalytic properties. In the present investigation, we have prepared and characterized oxovanadium(IV) complexes of ligands **I**, **II** and **III** (scheme 1) encapsulated in super cages and tested their catalytic activity for the oxidation of phenol. Suitable reaction conditions have been optimized to give maximum hydroxylation. Encapsulation of [VO(salen)] (H_2salen = **I**) in zeolite-Y has been reported by Ulagappan *et al.* [11] and Balkus *et al.* [12]. This catalyzes epoxidation of cyclohexane as well as oxidation of phenol but details of the oxidation of phenol have not been reported. [VO(salphen)] (H_2salphen = *N*,*N*′-bis(salicylidene)-*o*-phenylenediamine) bonded on carbamate-modified silica gel has also been synthesized recently and used for the liquid-phase oxidation of cyclohexane to cyclohexanol under moderate conditions [13].



I (R = H, H_2salen; R = CH_3, H_2sal-1,2-pn) **II** (H_2sal-1,3-pn)



III (H_2saldien)

Scheme 1.

2. Experimental

2.1. Materials

Vanadyl sulfate and phenol were obtained from Loba Chemie, India. Salicylaldehyde, 1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminopropane, diethylenetriamine and H_2O_2 (30%) were purchased from E. Merck, India. Y-zeolite (Si/Al ~10) was obtained from

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Indian Oil Corporation (R & D), Faridabad, India. Solvents and other reagents were also of AR grade.

2.2. Physical methods and analyses

IR spectra were recorded as KBr pellets using a Perkin-Elmer model 1600 FTIR spectrophotometer. Electronic spectra were recorded in Nujol using a Shimadzu 1601 UV–vis spectrophotometer by putting a layer of mull sample inside one of the cuvettes 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 a Philips PW 1140/90 X-ray powder diffractometer with a CuKα target at the Scientific Instrumentation Centre of our Institute. The metal contents were measured using inductively coupled plasma (ICP; Labtam 8440 plasmalab). All catalyzed reaction products were analyzed using a Nucon 5700 chromatograph fitted with an FID detector, an OV-17 (S.S.) column (2 m × 2 mm i.d.) and ORACLE2 computer software.

2.3. Preparations

2.3.1. Preparation of ligands

Ligands N,N'-bis(salicylidene)ethane-1,2-diamine (H_2salen) [14], N,N'-bis(salicylidene) propane-1,3-diamine (H_2sal-1,3-pn) [15], N,N'-bis(salicylidene)propane-1,2-diamine (H_2sal-1,2-pn) [15], N,N'-bis(salicylidene)-diethylenetriamine (H_2saldien) [16] were prepared as reported in the literature.

2.3.2. Preparation of OV-Y (oxovanadium exchanged zeolite)

An amount of 5.0 g of Na-Y zeolite was suspended in 300 ml of distilled water and to this was added $VOSO_4 \cdot 5H_2O$ (3.0 g, 12 mmol) with stirring. The reaction mixture was then heated with stirring at 90 °C for 24 h. The solid was filtered, washed with hot distilled water until the filtrate was free from any vanadyl ion content, and dried for 12 h at 150 °C in air.

2.3.3. Preparation of [VOL]-Y: a general method

All encapsulated complexes were prepared using a general flexible ligand method. Therefore, the preparation of one specific complex, [VO(sal-1,3-pn)]-Y, is outlined here. An amount of 1.0 g OV-Y and 2.5 g H_2sal-1,3-pn were mixed in a round-bottomed flask. The reaction mixture was heated at 150 °C overnight (~14 h) in an oil bath with stirring. The melted ligand acted as solvent as well as reactant. The resulting material was taken out and extracted with methanol until the complex was free from unreacted H_2sal-1,3-pn. The uncomplexed VO(IV) ions present in the zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. The resulting solid was then washed with hot distilled water until no precipitation of AgCl occurred on treating the filtrate with $AgNO_3$. The pale blue-green solid was dried at 120 °C for several hours to constant weight.

2.3.4. Oxidation of phenol

Catalytic experiments were carried out in a 50 ml reaction flask fitted with a water condenser. A general procedure was applied for all reactions. In a typical reaction, phenol (4.7 g, 0.05 mol) and 30% aqueous H_2O_2 (5.67 g, 0.05 mol) were mixed in 2 ml of MeCN and the reaction mixture was heated in an oil bath with continuous stirring at 80 °C. The catalyst to be tested (0.010 g) was added to it and the reaction was considered to begin. The reaction products were analyzed using a gas chromatograph after a specific interval of time by withdrawing a small aliquot.

The effects of various parameters, such as H_2O_2 concentration (moles of H_2O_2 per mole of phenol), phenol concentration (moles of phenol per mole of H_2O_2), amount of catalyst, temperature, volume of MeCN solvent, etc., have been studied in detail for the catalyst [VO(sal-1,3-pn)-Y]; however, the basic procedure is the same as outlined above.

Results and discussion

Stirring of $VOSO_4$ with Na-Y in aqueous solution leads to the formation of oxovanadium(IV) exchanged zeolite. Heating of this metal exchanged zeolite in excess of ligands (cf. scheme 1) at 100 °C for ~14 h under stirring allows the insertion of ligands in the cavity of the zeolite followed by their complexation with vanadium. The complexation of oxovanadium(IV) species with ligands was accompanied by a color change from light blue of exchanged zeolite to pale blue-green. Soxhlet extraction using methanol finally purified the impure materials. The remaining uncomplexed metal ions in zeolite were removed by exchanging back with aqueous 0.01 M NaCl solution. The percentage of encapsulated complexes along with the original loading (i.e. percentage of metal exchanged) is presented in table 1. These data reflect the variation in the insertion of vanadium complexes in the order [VO(sal-1,3-pn)]-Y < [VO(salen)]-Y < [VO(saldien)]-Y < [VO(sal-1,2-pn)]-Y. This order is understandable as H_2sal-1,3-pn has a lower melting point and greater flexibility than H_2salen. The H_2saldien ligand is relatively flexible but has a long chain while H_2sal-1,2-pn faces steric hindrance, which ultimately affect their insertion in the super cages of the zeolite-Y. The Si/Al ratio of 9.67 corresponds to a unit cell of formula $Na_{18}(AlO_2)_{18}(SiO_2)_{174}$. If we consider ~250 water

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

No.	Catalyst	Metal content (wt%)	No. of metal complexes per unit cell
1	[VO(salen)]-Y	0.76	2.0
2	[VO(sal-1,3-pn)]-Y	2.24	7.2
3	[VO(sal-1,2-pn)]-Y	0.32	1.0
4	[VO(saldien)]-Y	0.92	3.0
5	OV-Y	4.58	–

molecules associated with this, then, from the vanadium estimated, the metal complexes per unit cell can be approximated (table 1).

An attempt has been made to characterize these complexes by studying their IR and UV–vis spectra, and thermal as well as XRD patterns (see below). The formulation of the encapsulated complexes presented in table 1 are based on these studies.

3.1. Thermal decomposition studies

The TGA pattern together with DTA of one of the catalysts, [VO(sal-1,3-pn)]-Y, are shown in figure 1. The thermal decomposition of [VO(sal-1,3-pn)]-Y proceeds in two major steps. First, endothermic loss of 16% occurs between 100 and 250 °C due to the presence of at least 17 intra-zeolite water molecules. The presence of several water molecules in encapsulated complexes has been observed previously even after drying samples at 100–150 °C for several hours [15–17]. The second step of the thermogram involves exothermic loss, as expected, over a wide range (250–657 °C) of temperature on account of the slow decomposition of the chelating ligand. A weight loss of 12% matches with the theoretical value of 11.6%, if we consider 2.24% vanadium content as observed by atomic absorption spectroscopy. Other encapsulated complexes have similar decomposition patterns, but the two decomposition steps are difficult to estimate separately. This may be due to the presence of smaller amounts of intra-zeolite water molecules.

3.2. Spectral studies

The electronic spectra of all catalysts are presented in figure 2 and the relevant data are collected in table 2. As shown in the table, all complexes, except [VO(sal-1,2-pn)]-Y, exhibit one broad band between 348 and 380 nm, which is assigned to a ligand to metal charge transfer (LMCT) transition. A weak band usually appears in the ~600 nm region in oxovanadium(IV) complexes [18]. This band is visible only for [VO(sal-1,2-pn)]-Y as a very weak band. The absence of this band in other complexes may be due to partial oxidation of oxovanadium(IV) complexes to oxovanadium(V) ones. The EPR silent nature of [VO(salen)]-Y, as observed earlier by Ulgappan and Krishnasamy [11], also suggests the oxidation of these complexes to oxovanadium(V) in the cavities. Other bands appearing at 283–317, 233–277 and 204–215 nm for all complexes arise due to intra-ligand n–π^*, π–π^* and ϕ–ϕ^* transitions, respectively.

A partial list of IR spectral data of all catalysts is also presented in table 2. The intensity of the peaks of the encapsulated complexes is weak due to the low concentration of the complexes in zeolite. However, the IR spectra of the complexes exhibit two bands at 1539–1556 and 1627–1637 cm^{-1} due to ν(C=N) stretch of the coordinated nitrogen and ν(C=C) stretch of the benzene ring of the ligand. The appearance of two to

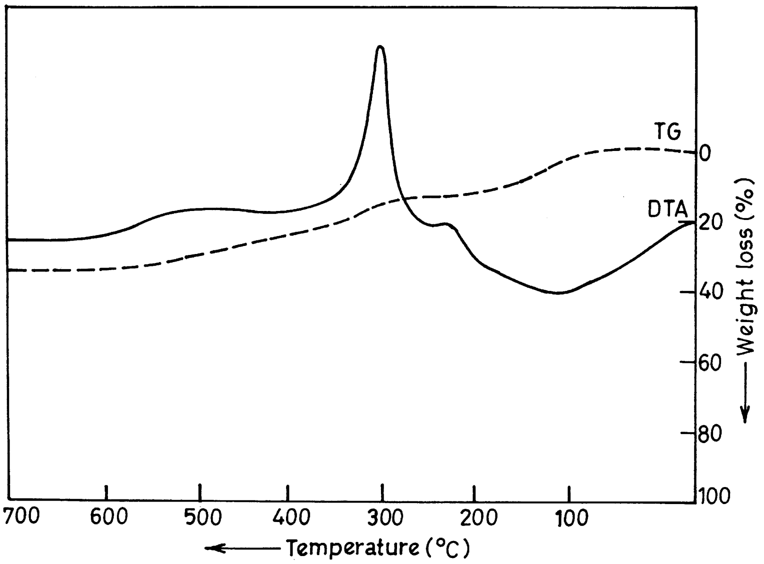


Figure 1. TGA and DTA profiles of [VO(sal-1,3-pn)]-Y.

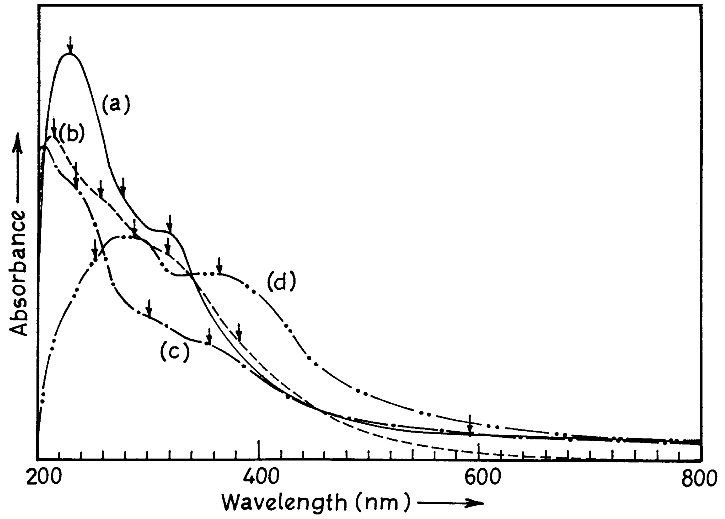


Figure 2. Electronic spectra of (a) [VO(sal-1,2-pn)]-Y (—), (b) [VO(salen)]-Y (- - -), (c) [VO(saldien)]-Y (—·—) and (d) [VO(sal-1,3-pn)]-Y (—··—).

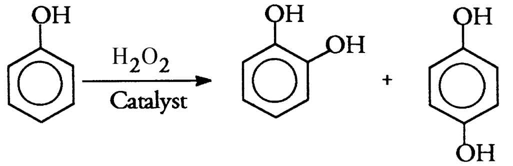
three bands in the low-frequency region of 404–472 cm^{-1} also suggests coordination of azomethine nitrogen as well as phenolic oxygen to the metal after deprotonation. The band due to $\nu(V{=}O)$ could not be located due to the appearance of a strong and broad band of the zeolite framework in the ~1000 cm^{-1} region. Thus, IR and UV–vis data indicate the encapsulation of complexes in the super cages of zeolite-Y.

3.3. X-ray powder diffraction studies

The X-ray powder diffraction patterns of Na-Y and OV-Y along with all encapsulated complexes were recorded at 2θ values between 10 and 70° to study their crystallinity. The XRD patterns of Na-Y, OV-Y and [VO(sal-1,3-pn)]-Y are shown in figure 3. The XRD patterns of vanadium exchanged zeolite and its encapsulated complexes are essentially similar to that of Na-Y, although a slight change in intensity of the peaks has been noticed. These observations suggest that the super cages are able to accommodate these complexes without any loss in crystallinity and morphology of the zeolite-Y. No new peaks could be observed in encapsulated samples probably due to low loading of the complexes present in the zeolite framework.

3.4. Catalytic activity

The catalytic oxidation of phenol using [VO(salen)]-Y], [VO(sal-1,3-pn)]-Y, [VO(sal-1,2-pn)]-Y and [VO(saldien)]-Y as catalysts and H_2O_2 as oxidant was studied as a function of time. As the hydroxyl group of phenol is *ortho-* and *para*-directing, the oxidation of phenol is expected to give two major products, i.e. catechol and hydroquinone as shown by equation (1):



(1)

The experimental results confirmed the presence of these two major products with a mass balance of >95%. Polymeric material or other products, if any, present as minor constituents could not be detected by gas chromatography and were neglected. During catalytic oxidation, vanadium complexes react with H_2O_2 to give oxoperoxo complexes, which ultimately transfer oxygen to the substrate.

In order to achieve suitable reaction conditions for a maximum oxidation of phenol, the following parameters

Table 2
IR and electronic spectral data

Catalyst	IR (cm^{-1})		λ_{max} (nm)
	ν(C=N), ν(C=C)	ν(M–O)/(M–N)	
[VO(salen)]-Y	1553, 1633	411, 451, 472	380, 316, 256, 213
[VO(sal-1,3-pn)]-Y	1544, 1632	423, 454	360, 285, 250
[VO(sal-1,2-pn)]-Y	1556, 1637	404, 458	600, 317, 277, 215
[VO(saldien)]-Y	1539, 1627	428, 447	348, 283, 233, 204

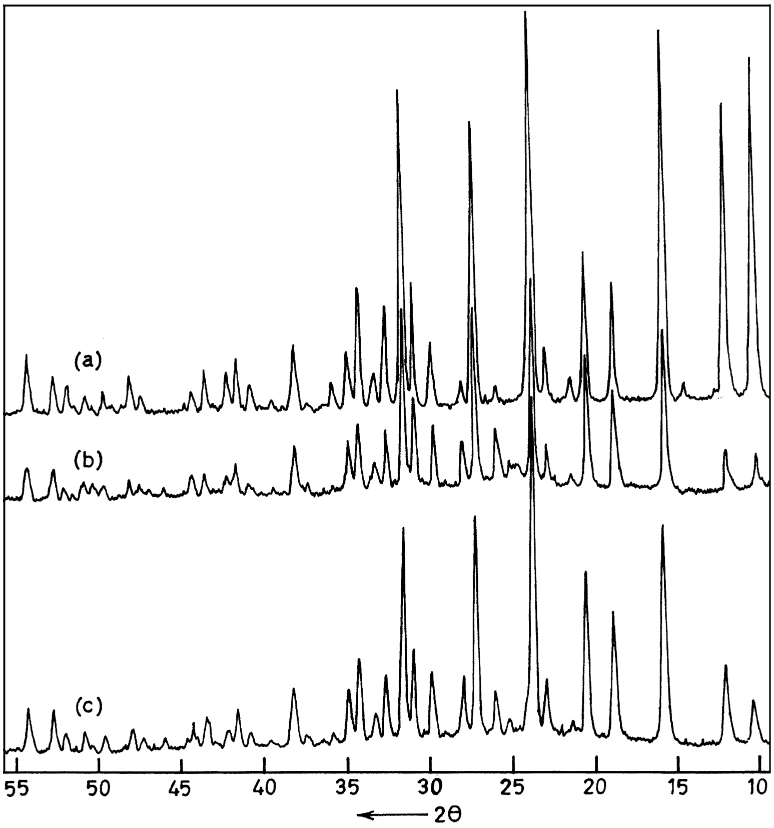


Figure 3. XRD patterns of (a) Na-Y, (b) OV-Y and (c) [VO(sal-1,3-pn)]-Y.

were studied in detail using [VO(sal-1,3-pn)]-Y as a representative catalyst:

- Effect of H_2O_2 concentration (moles of H_2O_2 per mole of phenol).
- Effect of phenol concentration (moles of phenol per mole of H_2O_2).
- Effect of amount of catalyst per unit weight of phenol.
- Effect of volume of solvent (keeping other parameters fixed).
- Effect of temperature.

The results of all these effects and possible explanations are summarized below.

3.4.1. *Effect of H_2O_2 concentration*

The effect of H_2O_2 concentration on the oxidation of phenol is illustrated in figure 4. Three different molar ratios of H_2O_2/phenol, 0.5 : 1, 1 : 1 and 2 : 1, were considered while keeping a fixed amount of phenol (4.7 g, 0.05 mol) and catalyst (10 mg) in 2 ml of MeCN. It is clear that the 1 : 1 molar ratio is the best to obtain

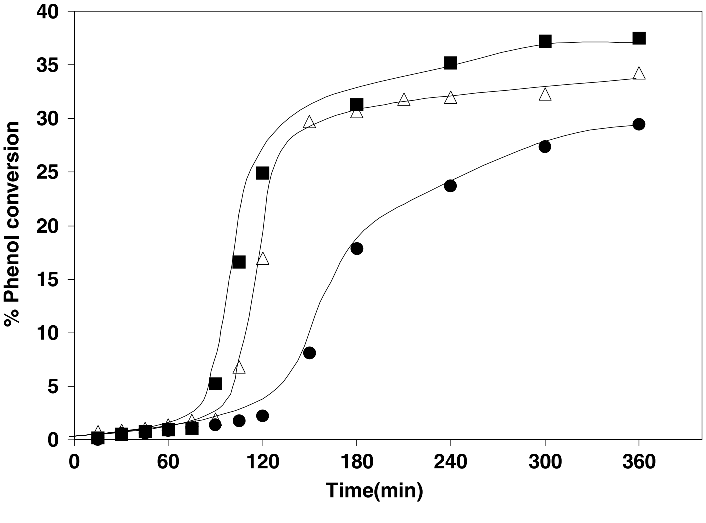


Figure 4. Effect of H_2O_2 concentration on phenol oxidation: (■) 0.1 mol, (△) 0.05 mol, (●) 0.025 mol.

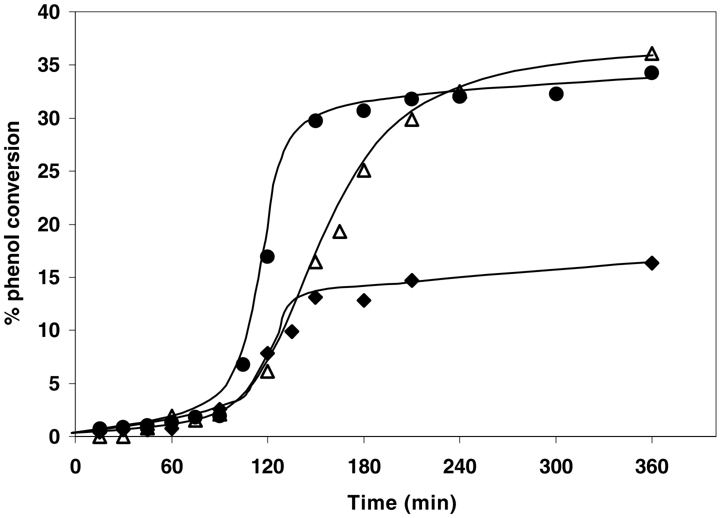


Figure 5. Effect of phenol concentration on phenol oxidation (◆) 0.1 mol, (●) 0.05 mol, (△) 0.03 mol.

the maximum phenol conversion of 34% at 80 °C in 6 h. Increasing the H_2O_2 concentration to 2 : 1 causes only partial improvement of phenol conversion to 37.5%, while decreasing the H_2O_2 concentration to 0.5 : 1 causes a decrease in phenol conversion (~29%). Even the addition of oxidant divided into three equal batches for a 1 : 1 molar ratio at every 1 h interval did not improve the transformation of phenol. For the above concentrations of H_2O_2, the selectivity of H_2O_2 conversion follows the order: 18.8 (2:1) < 34 (1:1) < 58 (0.5:1). These results suggest that, although selectivity of H_2O_2 conversion for 0.5 : 1 ratio is high as H_2O_2 is effectively consumed, 1 : 1 ratio is the minimum required condition for the effective oxidation of phenol (see below).

3.4.2. *Effect of phenol concentration*

In order to optimize the concentration (molar ratio) of phenol to give maximum oxidation, different molar ratios of phenol to H_2O_2 (0.5 : 1, 1 : 1, 2 : 1) were used while keeping other conditions fixed. Figure 5 shows the results. It is clear that molar ratios 0.5 : 1 and 1 : 1 gave 36–37% phenol conversions while 2 : 1 ratio showed lower conversion (15%). The selectivity of H_2O_2 conversion decreases considerably for the 0.5 : 1 ratio while for 1 : 1 ratio it is better. Thus, the molar ratio of phenol to H_2O_2 must be kept at 1 : 1 to give maximum phenol conversion along with better selectivity of H_2O_2 conversion. The rate of hydroxylation is also fast with the 1 : 1 ratio as it reaches a steady state within 120 min.

3.4.3. *Effect of amount of catalyst*

The amount of catalyst also has an influence on the phenol conversion. It was observed that increasing the amount of catalyst from 5 to 10 mg increases the conversion from 29.7 to 34.3% within 6 h of reaction time. Further increase of the amount of catalyst up to 25 mg resulted in only a negligible increase in phenol

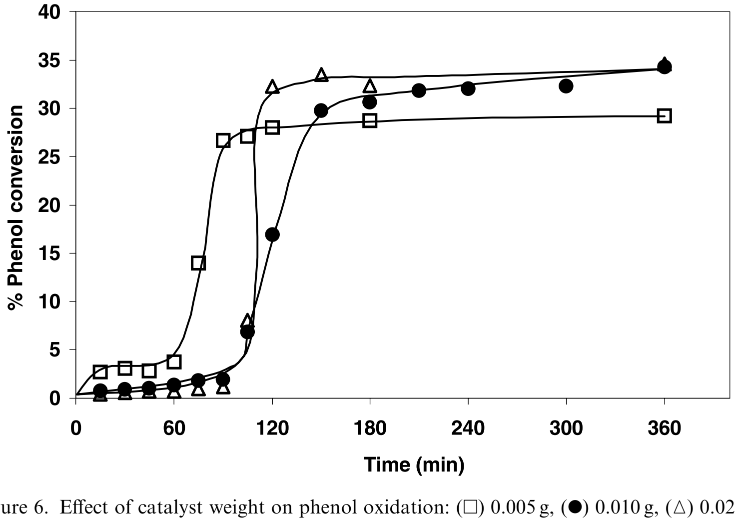


Figure 6. Effect of catalyst weight on phenol oxidation: (□) 0.005 g, (●) 0.010 g, (△) 0.025 g.

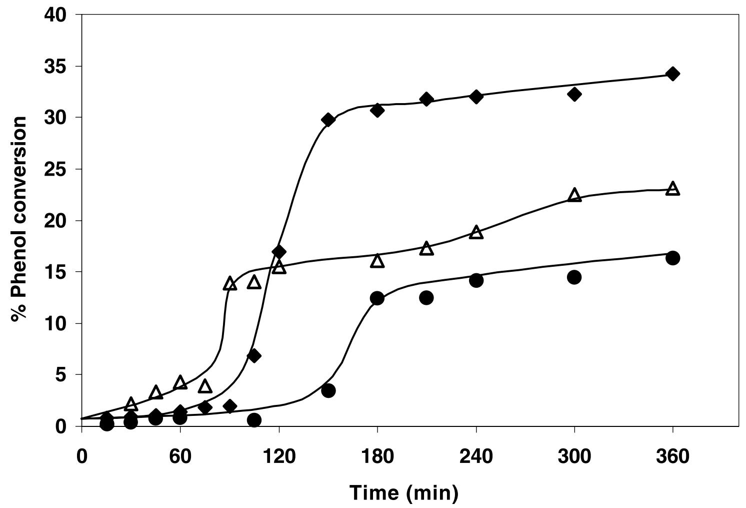


Figure 7. Effect of volume of solvent used on phenol oxidation: (◆) 2 ml, (△) 4 ml, (●) 6 ml.

conversion. Figure 6 illustrates the effect of the amount of catalyst on the conversion of phenol as a function of time. Such a phenomenon has also been observed by us [15,16,19] previously and has been interpreted in terms of thermodynamic and mass transfer limitations at higher reaction rate.

3.4.4. Effect of solvent volume

The volume of solvent has a great influence on the reaction rate as shown in figure 7. It is clear that 2 ml of MeCN is sufficient to give maximum production of catechol and hydroquinone for a fixed amount of catalyst (10 mg), phenol (4.7 g) and oxidant (5.67 g) at 80 °C. Increasing or decreasing the volume of MeCN from 2 ml always results in poorer performance of the catalyst. Excess of solvent may decrease the reactant concentration in the reaction mixture while less than 2 ml of solvent would not be sufficient to dissolve the reaction mixture.

3.4.5. Effect of temperature

Figure 8 illustrates the oxidation of phenol at temperatures of 50, 65 and 80 °C as a function of time while keeping fixed the optimized conditions for other parameters as concluded above (i.e. 4.7 g phenol, 5.67 g H_2O_2 and 0.01 g catalyst in 2 ml of MeCN). It is clear from the plot that 80 °C is the best temperature to perform the reaction with maximum conversion of phenol (34%) in 6 h. The performance of the catalyst is poor at 65 °C (23.3%) while a 50 °C reaction temperature facilitates only ~3% conversion after 3 h and ~16% after 24 h. Thus 80 °C is the minimum required temperature to maximize the transformation of phenol in minimum time.

3.5. Catalytic activity of other catalysts

After determining the optimized reaction conditions for [VO(sal-1,3-pn)]-Y, the other catalysts, [VO(salen)]-Y,

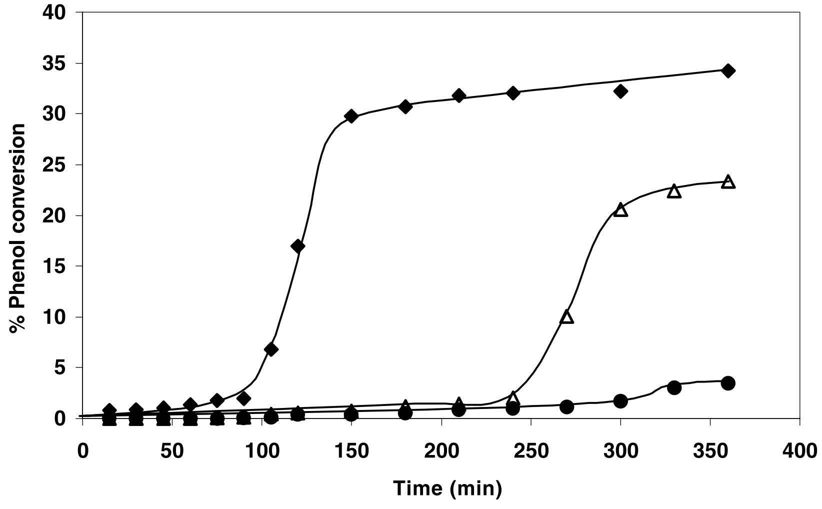


Figure 8. Effect of temperature on phenol oxidation in acetonitrile: (◆) 80 °C, (△) 65 °C, (●) 50 °C.

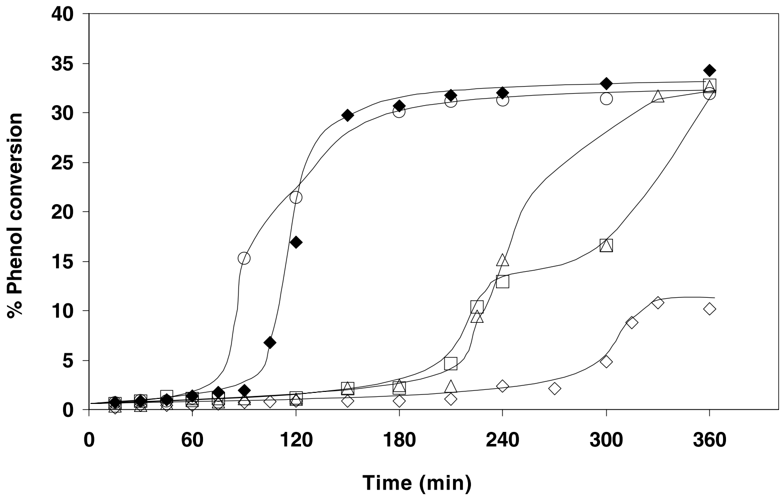


Figure 9. Phenol oxidation: (□) [VO-(saldien)]-Y, (◆) [VO-(sal-1,3-pn)]-Y, (◇) [VO-(sal-1,2-pn)]-Y, (△) [VO-(salen)]-Y and (○) OV-Y.

[VO(sal-1,2-pn)]-Y and [VO(saldien)]-Y including OV-Y, were also tested under the same reaction conditions (i.e. 4.7 g phenol, 5.67 g H_2O_2, 10 mg catalyst and 2 ml MeCN at 80 °C) for the oxidation of phenol. Figure 9 shows the performance of all catalysts together, including OV-Y. Under the optimized reaction conditions, [VO(sal-1,2-pn)]-Y has the poorest performance (10.6% conversion) while [VO(salen)]-Y and [VO(saldien)]-Y have comparable activity. For these catalysts, though, the reaction is very slow in the first 3 h; they perform much better in the next 3 h and catalyze the oxidation of phenol with a maximum of ~32% conversion. Catalyst [VO(sal-1,3-pn)]-Y shows the highest conversion of 34.3%. It is interesting to note that even OV-Y has catalytic activity comparable with that of [VO(salen)]-Y and [VO(saldien)]-Y. However, for OV-Y leaching of the vanadyl ion is always possible. Increasing the reaction time from 6 to 24 h does not show any appreciable change in oxidation products. Table 3 gives data for phenol conversion along with the selectivity of catechol and hydroquinone formation for these catalysts after 6 h of reaction time, while figure 10 summarizes all these results.

Table 3
Phenol conversion and the corresponding selectivity of catechol and hydroquinone after 6 h of reaction time

Compound	Phenol conversion (%)	TOF[a] (h^{-1})	Selectivity (%)	
			Catechol formation	Hydroquinone formation
[VO(salen)]-Y	32.6	1940	92.7	7.3
[VO(sal-1,3-pn)]-Y	34.3	665	67.7	32.3
[VO(sal-1,2-pn)]-Y	10.6	1472	96.8	3.2
[VO(saldien)]-Y	32.7	1514	91.6	8.4
OV-Y	31.5	295	90.2	9.8

[a] TOF (turnover frequency): moles of substrate converted per mole of metal (in the solid catalyst) per hour.

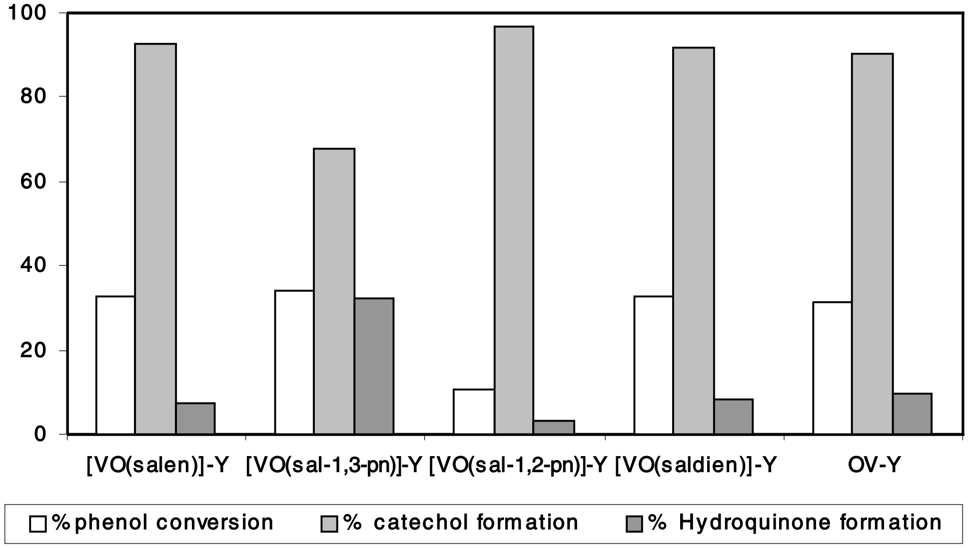


Figure 10. Bar diagram showing phenol conversion and catechol and hydroquinone formation for various catalysts.

It is clear from the data presented in table 3 that lengthening of the backbone of the ligand from $-CH_2-CH_2-$ to $-CH_2CH_2CH_2-$ or $-CH_2CH_2NHCH_2CH_2-$ in the catalysts hardly affects their performance while increasing the branching of the backbone to $-CH_2CH(CH_3)-$ has a considerable effect. This is reasonable as [VO(sal-1,2-pn)]-Y may not be able to expand the coordination number effectively for forming a peroxo coordinated intermediate to transfer oxygen to the substrate. It is also clear from table 3 that the selectivity for catechol formation, in general, is higher than for hydroquinone. Catechol formation for all the catalysts including OV-Y has 90–97% selectivity, except [VO(sal-1,3-pn)]-Y which gives only 68% selectivity.

4. Conclusion

Oxovanadium(IV) complexes [VOL; $LH_2 =$ **I**, **II** and **III**) have been encapsulated in the super cages of zeolite-Y. Chemical analyses, spectroscopic studies and XRD as well as thermogravimetric patterns present clear evidence for the encapsulation. These encapsulated complexes catalyze the oxidation of phenol effectively. The TOF values for all these catalysts are high, except for [VO(sal-1,3-pn)]-Y, further showing their effective catalytic activity. The low TOF value for [VO(sal-1,3-pn)]-Y is only due to high loading of the vanadium complex. However, the selectivity of phenol oxidation to catechol and hydroquinone depends on various factors. Under the optimum reaction conditions (i.e. 0.05 mol phenol, 0.05 mol of H_2O_2, 0.01 g catalyst and 2 ml MeCN at 80 °C), the selectivity toward catechol formation is 90–97%. The only exception is the catalyst [VO(sal-1,3-pn)]-Y, which shows 68% selectivity toward catechol formation under similar reaction conditions.

Acknowledgment

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