Iron Promoted Sulphated Zirconia Systems As Efficient Catalysts For Phenol Hydroxylation

Suja.H and S.Sugunan
Department of Applied Chemistry
Cochin University of Science and Technology, Kochi-22, Kerala, India.

Abstract

The present work investigates on the applicability of metal promoted sulphated zirconia catalysts for the hydroxylation of phenol under mild conditions. The percentage conversion and product distribution was highly sensitive towards the reaction parameters like the catalyst composition, reaction temperature, H_2O_2/ phenol ratio and the solvent used.

Key words :- phenol hydroxylation, iron promoted sulphated zirconia, wet peroxide oxidation.

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1. Introduction

The developments in catalysis during the last few decades have been mandated mainly by the considerations related to the abatement and prevention of pollution, conservation of raw materials and efficient production of fine chemicals. With growing ecological concern chemical producers have been subjected to increasing pressure to minimise the dispersion of waste chemicals. The organic effluents containing phenolic compounds from pharmaceutical, fine chemical and petrochemical industries, on account of their poor biodegradability form a major threat to the ecological balance. The selective oxidation of phenol to industrially useful diphenols (catechol and hydroquinone) forms a convenient route to their efficient disposal. High temperatures and pressures involved in supercritical oxidation render it totally uneconomical for phenol oxidation [1,2]. Hydrogen peroxide constitutes a very efficient agent for the selective partial oxidation of organic compounds under mild conditions.

The homogeneous liquid phase hydroxylation of phenol catalysed by mineral acids [3], simple metal ions and their complexes [4,5] has been widely investigated. In spite of the potential catalytic activity, the inherent disadvantages associated with homogeneous catalysis demands their replacement with solid acids. The various catalysts employed for the process include molecular sieves like TS-1, TS-2, Ti-MCM-41, Ti-ZSM-48, V-ZSM-11 [6-15], hydrotalcite like compounds [16, 17], zeolite encapsulated metal salen complexes [18]. Santos *et al* reported the aqueous phase oxidation of phenol using a series of commercial copper containing catalysts at elevated temperatures and oxygen pressures [19, 20]. Simple and supported and complex metal oxides [21-25] have also been reported to catalyse phenol hydroxylation.

Zirconia has gained wide attention as a catalyst and as a catalyst support. The super acidic properties associated with sulphated zirconia have been utilized in several industrially important reactions including paraffin isomerization, paraffin cracking, isoparaffin alkylation and acylation of aromatics, esterification, etherification, nitration etc. [26,27]. The redox properties of afore mentioned

catalytic systems has been rarely exploited. We report the hydroxylation of phenol with hydrogen peroxide over iron promoted sulphated zirconia systems. The primary advantage with these systems lies in the fact that the reaction proceeds under atmospheric pressures and at relatively lower temperatures.

2. Experimental

2.1 *Preparation of catalyst*

The metal incorporated sulphated zirconia systems were prepared by a single step impregnation technique from zirconium hydroxide using 1 N H_2SO_4 (10 ml/g of hydrous zirconium oxide) and ferric nitrate solution. The iron content in the samples was varied from 2 to 10%. The samples after overnight drying at 120°C were calcined at 700°C for three hours.

2.2 *Catalyst characterization*

Characterization of the samples was carried out by BET surface area and pore volume measurements (Micromeritics Gemini Surface area analyzer), XRD (Rigaku D-max C X-ray diffractometer), TG (Shimadzu, TGA-50), IR (Shimadzu DR 8001) and Laser Raman spectroscopy (Dilor Jobin Spectrophotometer). The

surface acidity determination was carried out by ammonia TPD and perylene adsorption studies. The sulphate content in the samples was estimated by EDX analysis (Stereoscan 440).

2.3 *Catalytic activity*

The catalytic oxidation of phenol was conducted at atmospheric pressure in a 100ml R.B flask equipped with a condenser and a magnetic stirrer. The reactants (phenol, 30% H_2O_2 and solvent) in the required ratio were stirred with 0.1 g of the catalyst. The products were identified by comparison with authentic samples in a Chemito 8610 Gas Chromatograph equipped with a flame ionization detector and an SE-30 column. The conversions and product selectivities were scanned for different H_2O_2/ phenol ratios and reaction temperatures. The solvent effect was also investigated.

3. Results and Discussion

3.1 *Physico-chemical characterization*

A detailed investigation on the physico-chemical properties of the catalyst systems has been reported earlier [28] and is summarized in Table 1.

Table 1   Physico chemical properties – A comparative evaluation

Catalyst systems	Surface area (m^2/g)	Pore volume (cc/g)	Sulphate content (wt %)	% Sulphate retained	Total Acidity (Amount of NH_3 desorbed mmol/g)	Perylene adsorbed (10^{-6} mol/g)
ZrO_2	32.7	0.065	-	-	0.31	0.09
SZ	44.8	0.079	18.5	47.6	1.05	2.75
Fe(2)SZ	61.1	0.082	30.1	84.7	1.23	3.67
Fe(4)SZ	60.4	0.083	28.9	81.3	1.24	4.18
Fe(6)SZ	59.6	0.085	27.1	76.4	1.26	7.37
Fe(8)SZ	57.3	0.075	24.7	69.4	1.26	8.85
Fe(10)SZ	55.7	0.088	23.1	64.9	1.30	10.69

A clear enhancement in the surface area obtained for the iron promoted systems in comparison with the pure and simple sulphated systems can be explained on the basis of the higher resistance to sintering acquired *via* sulphation and metal doping [26,27]. XRD (Fig. 1) and Laser Raman techniques (Fig. 2) reveal the stabilization of the tetragonal phase in modified zirconia samples in spite of high calcination temperature employed [28]. Traces of monoclinic phase detected in the simple sulphated and low loaded iron systems may be
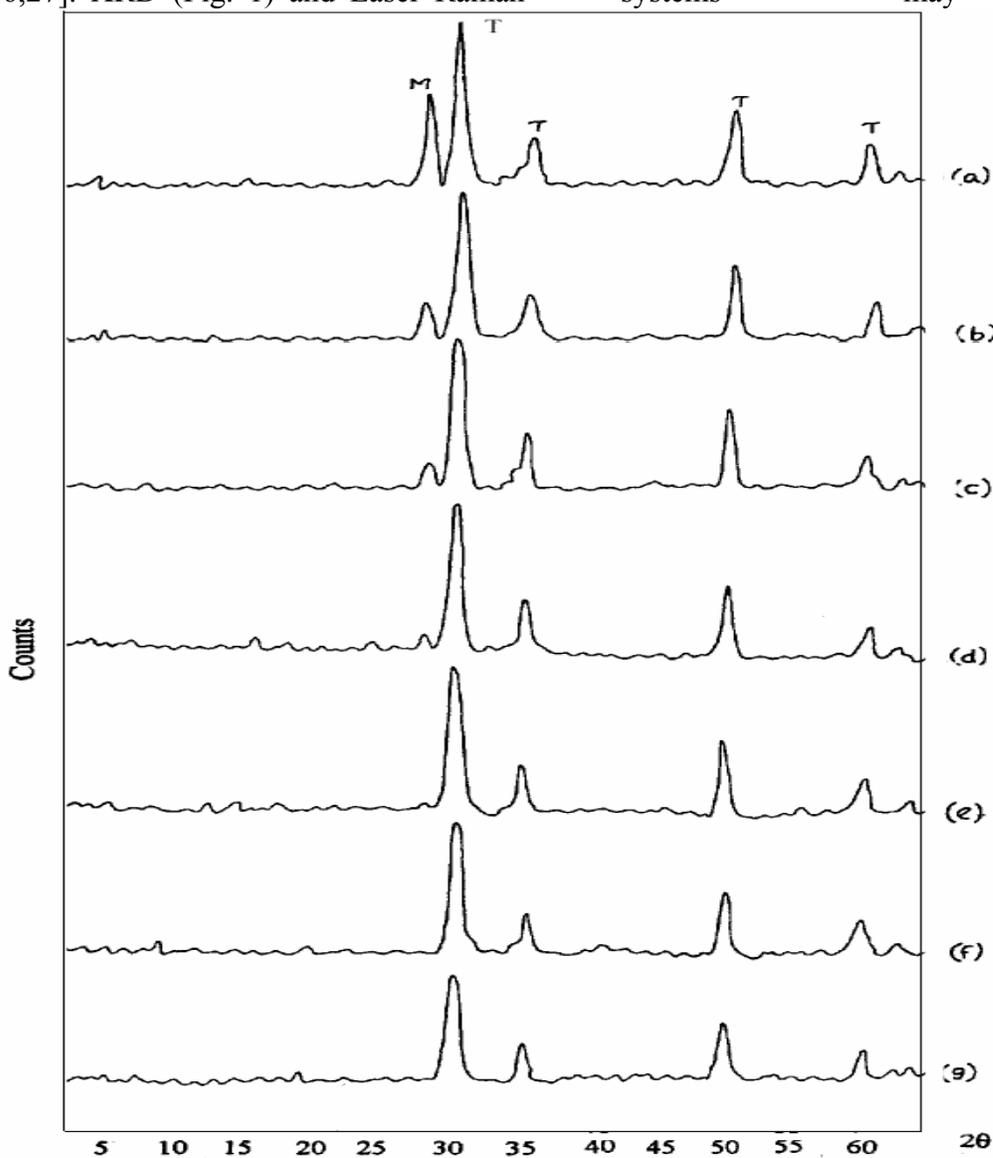

Fig. 1 XRD patterns of pure and modified zirconia systems
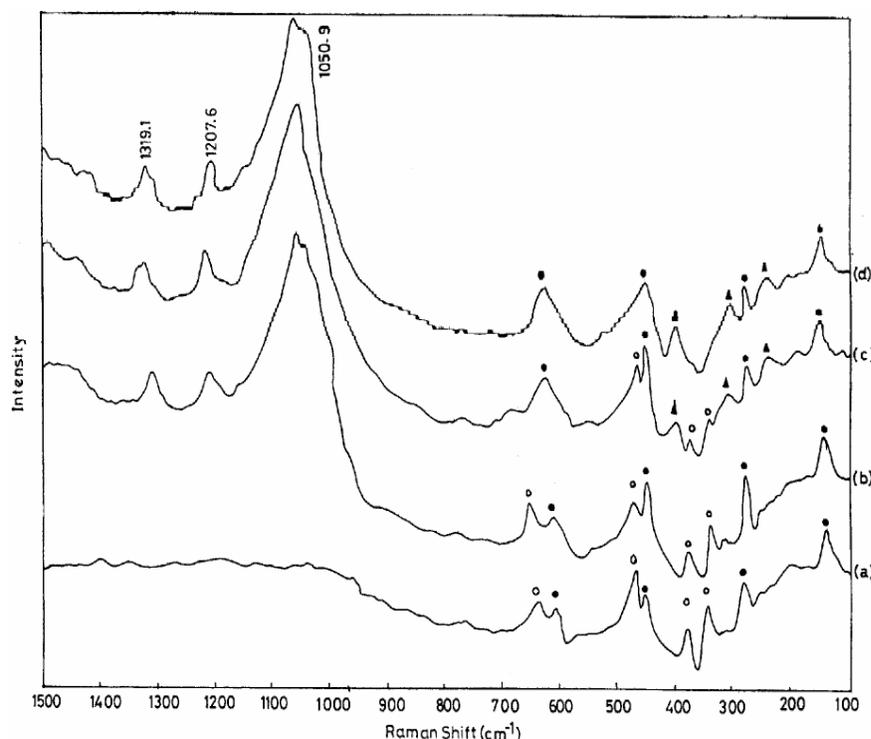a) ZrO_2; b) SZ; c) Fe(2)SZ; d) Fe(4)SZ
e) Fe(6)SZ; f) Fe(8)SZ; g) Fe(10)SZ

Fig. 2 Laser Raman Spectra of representative systems
a) ZrO_2 ;b) SZ; c) Fe(2)SZ; d) Fe(10)SZ,
○ Monoclinic ● Tetragonal ▲Fe_2O_3

ascribed to the high sulphate loading. At high iron loadings monoclinic phase completely disappeared indicating the stabilising effect of iron. Absence of characteristic peaks corresponding to Fe_2O_3 in the XRD pattern also suggests the existence of iron in highly dispersed form on the catalyst surface. Specific bands corresponding to sulphate groups could be located in the Infra red (Fig. 3) and Laser Raman spectrum. It was interesting to note that the polynuclear sulphates were absent (as evident from the lack of a peak in IR spectrum at around 1400 cm^{-1}) in our systems in spite of high sulphate loading reported. The thermogravimetric analysis confirms the thermal stability of the systems.

Ammonia TPD [29] method points out to a considerable enhancement of acidity for the modified zirconia samples in comparison with pure ZrO_2. The incorporation of promoters resulted in a rearrangement in the acid strength distribution in a direction favouring the formation of strong acid sites, while the total acidities were comparable (Fig. 4). The Lewis acidity enhancement obtained by perylene adsorption studies [30,31] can be ascribed to the increase in the electron acceptor properties of the three co-ordinate zirconium cations *via* the inductive effect of the sulphate anions, which withdraw electron density from the zirconium cations through the bridging oxygen atom. Incorporation of iron moieties resulted in a further increase in the Lewis acidity.

3.2 *Catalytic activity*

The pure and simple sulphated zirconia were totally inactive towards

phenol hydroxylation reaction. Incorporation of iron even in very low levels resulted in a drastic enhancement in the catalytic activity. This is quite reasonable as Fe^{3+} is one of the best-known oxidation-reduction catalysts. The reaction proceeded with high selectivity to catechol and hydroquinone when compared to the unidentified tarry products formed only in traces. A quantitative estimation of the tarry products was not attempted in the present survey. The catalyst composition, solvent and reaction parameters were found to have a vital influence on the phenol conversion and product distribution.
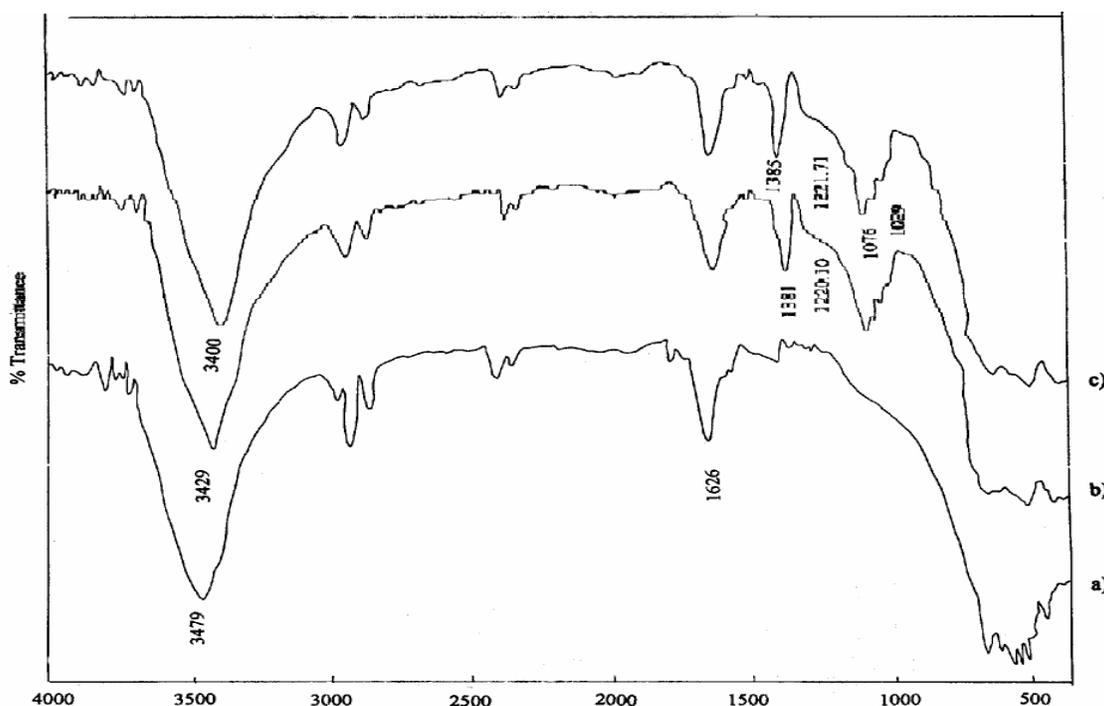

Fig. 3 Representative Infra Red spectra
a) ZrO_2; b) Fe(2)SZ;   c) Fe(10)SZ

Table 2 represents the variation in the phenol conversion and product selectivity with the catalyst composition. The reaction was performed at room temperature and atmospheric pressure. An increase in iron loading improved the phenol conversion. The conversion and catechol selectivity obtained was considerably high when compared with the earlier reports on other catalyst systems [15]. An increase in iron loading resulted in a gradual lowering of the selectivity towards catechol. At an iron loading of 10% the product selectivity approaches statistical ratio and the product selectivities were 65% catechol and 35% hydroquinone. There was no formation of benzoquinone at any stage of the reaction.

Table 2 Catalytic activity comparison of various systems for phenol hydroxylation

Catalyst	Conversion	Catechol	Hydroquinone	CAT/HQ
Fe(2)SZ	56.2	91.6	8.4	10.9
Fe(4)SZ	63.2	84.3	15.7	5.4
Fe(6)SZ	67.4	76.9	23.1	3.3
Fe(8)SZ	73.2	70.3	29.7	2.3
Fe(10)SZ	81.5	65.1	34.9	1.9

Reaction conditions: 0.1g Fe(2)SZ catalyst, Duration-1 hr, Reaction temperature-30°C, H_2O_2/Phenol ratio-5:1
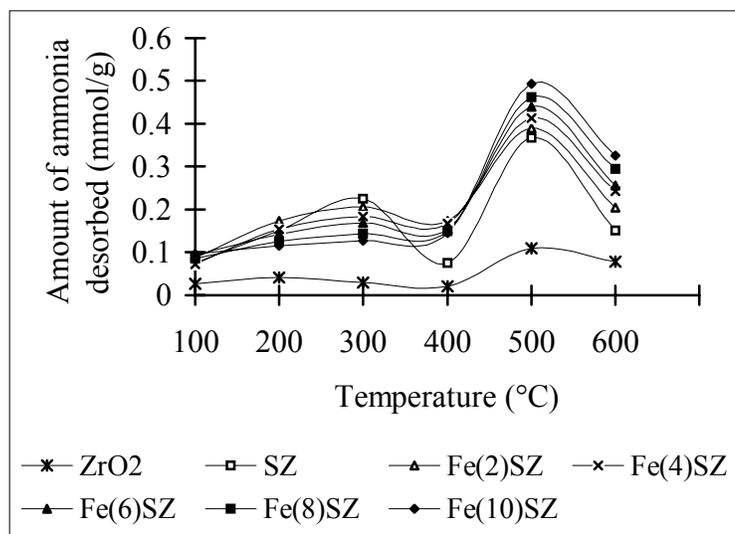

Fig. 4   Acid strength distribution profiles from Ammonia TPD studies

The dependence of the percentage conversion and product selectivity on the H_2O_2/phenol volume ratio is visible from Table 3. There seems to be an optimum value for the oxidant to phenol ratio, a further increase of which results in a drastic reduction in phenol conversion to desired products. This may be related to the over oxidation of phenol at high peroxide concentration. After a H_2O_2/phenol volume ratio of 5: 1 tarry product formation predominated. Actual phenol conversion at a H_2O_2 to phenol ratio of 10:1 was nearly 100%. However, the conversion to diphenols was only 6.5%.

Table 3 Dependence of phenol conversion and product selectivity on H_2O_2/phenol ratio

H_2O_2/Phenol ratio	Conversion to diphenols	Catechol	Hydroquinone	CAT/HQ
1:1	15.3	96.8	3.2	27.5
2:1	36.5	94.3	5.7	16.5
3:1	44.9	79.9	20.1	4.0
4:1	49.3	87.0	13.0	6.7
5:1	56.2	91.6	8.4	10.9
7:1	34.8	95.2	4.8	19.8
10:1	6.5	96.9	3.1	31.3

Reaction conditions: Fe(2)SZ catalyst - 0.1 g, Duration- 1 hour, Reaction temperature-30°C

The progress of the reaction monitored at regular intervals of time (Fig. 5) showed a progressive increase in the percentage conversion with time at the expense of selectivity. Initially, an induction period of 30 minutes was observed during which the percentage conversion was very low. After half an hour a sharp rise was observed in the yield of diphenols, which leveled off after one hour. Thereafter the continued stirring resulted in a sharp decline in the diphenol yield. It was quite interesting to note that there was no formation of benzoquinones, the further oxidation products of diphenols. A direct over oxidation to tarry products was observed in all the cases after an optimum reaction time. Thus, prolonged reaction time even though beneficial for the phenol conversion reduces the selectivity to diphenols. Darkening of the solution with time may be due to the formation of the tarry materials by the over oxidation of diphenols or the polymerization of the phenoxy radicals.
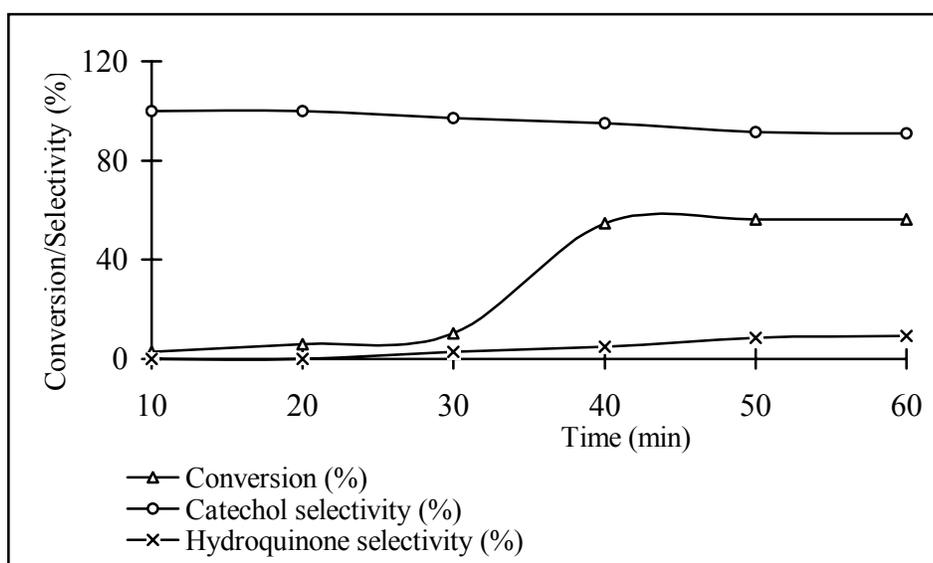

Fig. 5 Variation in conversion and percentage selectivity with time
Fe(2)SZ catalyst - 0.1 g, Room temperature, H_2O_2 / Phenol ratio-5:1

The reaction temperature plays a significant role in deciding the percentage conversion and selectivity (Table 4).
Maximum conversion to diphenols and selectivity to catechol was obtained at room temperature. The decrease in phenol conversion with increase in reaction temperature is consistent with the exothermic nature of the reaction. The accelerated decomposition of H_2O_2 at elevated temperatures may also contribute to the drop off in the conversion. The activation energy for the decomposition of H_2O_2 is lower than that for the hydroxylation of phenol [20, 21]. Above 90°C, over oxidation results in tarry products. The catalyst composition seems to counterbalance the influence of the reaction temperature. A decrease in the activity in the case of Fe(10)SZ system was rather trivial till 70°C, above which a perceptible decline in conversion was obtained. Reaction temperature also influenced the relative product selectivity. In the case of Fe(2)SZ, selectivity to catechol decreased with reaction temperature and finally the statistical ratio was attained at around 80°C. However, with Fe(10)SZ, the statistical ratio was

maintained irrespective of the reaction temperature.

Solvent effect was studied using water, methanol, acetonitrile and acetone with

Fe(2)SZ as the representative system (Table 5).

Table 4 Influence of catalyst composition in deciding the temperature effect on phenol hydroxylation.

Reaction Temp (°C)	Catalyst	Conversion (%)	Selectivity (%)		CAT/HQ
			Catechol	Hydroquinone	
RT	Fe(2)SZ	56.2	91.6	8.4	10.9
	Fe(10)SZ	81.5	65.1	34.9	1.9
50	Fe(2)SZ	50.4	84.4	15.6	5.4
	Fe(10)SZ	77.1	64.4	35.6	1.8
60	Fe(2)SZ	42.5	76.4	23.6	3.2
	Fe(10)SZ	73.6	65.3	33.7	1.9
70	Fe(2)SZ	36.0	70.1	29.9	2.3
	Fe(10)SZ	70.2	66.1	33.9	1.9
80	Fe(2)SZ	28.5	65.4	34.6	1.9
	Fe(10)SZ	48.5	65.1	33.9	1.9

Reaction Conditions: Fe(2)SZ catalyst - 0.1 g, H_2O_2 / Phenol ratio- 5:1, Duration- 1 hour.

Table 5 Solvent effect on phenol conversion and selectivity

Solvent	Reaction Temp (°C)	Time (Hrs)	Conversion (%)	Selectivity (%)	
				Catechol	Hydroquinone
Water	RT	1	56.2	91.6	8.4
	70	1	36.0	70.1	29.9
Methanol	RT	2.5	-	-	-
	70	1	28.5	98.5	1.5
Acetonitrile	RT	2.5	20.7	69.1	30.9
	70	1	12.4	65.2	34.8
Acetone	RT	2.5	-	-	-
	70	1	5.7	100	-

Reaction Conditions: Fe(2)SZ catalyst - 0.1 g, H_2O_2 / Phenol ratio- 5:1

The selection of the solvent had a vital influence on the phenol conversion and product selectivity. Water was found to be the best solvent for phenol hydroxylation at the temperatures studied. At room temperature only water and acetonitrile were effective as solvents. Acetonitrile showed low percentage conversion (20.7% in 2.5 hours), whereas methanol failed to give any reaction. High selectivity to catechol (91.8%) was observed when water was used as the solvent. At 70°C, the reactivity was in the order water > methanol >acetonitrile. Methanol gave high selectivity to catechol (98.5%) at elevated temperatures whereas selectivity was lower in the case of water (70.10%). With acetone as solvent there was no

reaction at all. The influence of solvent can be interpreted on the basis of polarity. Phenol conversion increases with solvent polarity. However this reasoning seems inadequate to explain the activity at room temperature since acetonitrile seemed to be a better solvent than methanol. The product distribution also seems to have a complex dependence on the solvent, which needs further investigation.

The redox property of iron may be considered to play a crucial role in the initiation of the reaction. The total inability of pure and simple sulphated system to bring about the phenol conversion points to the fact that Fe^{3+} is the active species involved in the reaction. The high reduction potential of Fe^{3+}/ Fe^{2+} system (0.78 V) favours the abstraction of hydrogen atom from phenol , Fe^{3+} being reduced into Fe^{2+}. Thus phenol conversion seems to be a function of the Lewis acidity (electron accepting capacity) of the systems. The increase in phenol conversion with iron loading is also in line with the Lewis acidity enhancement. The appearance of an induction period and the subsequent exponential increase in conversion suggests the involvement of a free radical mechanism for the reaction.

A homogeneous heterogeneous mechanism has been suggested for the reaction [32,33] according to which the generation of phenoxy radicals may occur on the catalyst surface. At the same time, the catalyst surface can also trigger the homolytic cleavage of H_2O_2 to $OH^{\cdot}$ radicals. The formation of catechol and hydroquinone is believed to occur via the attack of $OH^{\cdot}$ on the benzene ring. The formation of phenoxy radicals takes place at the catalyst surface after which the propagation of the reaction can occur either in liquid phase or on the catalyst surface. A typical homogeneous free radical mechanism predicts the formation of *ortho* and *para* isomer in either statistical or a 1:1 ratio. The preferential formation of the *ortho* isomer suggests some sort of an association between the phenoxy radicals and the catalyst surface which leaves the *ortho* position more prone to attack by hydroxyl species generated on the catalyst surface. Another possibility is that the diffusion of the radicals from the catalyst surface may be a slow process when compared with the attack of the hydroxyl radicals. Thus, before the radicals get sufficient time to drift apart the attack of $OH^{\cdot}$ occur preferentially at the ortho position.

Conclusions

Catalytic wet peroxide oxidation of phenol over iron promoted sulphated zirconia seems to be a function of the catalyst composition. Low iron loading leads to a preferential formation of catechol while at high iron loadings the product selectivity approaches statistical ratio. The H_2O_2 to phenol ratio and reaction temperature also influenced the catalytic activity and relative product selectivity. The solvent employed had a deciding effect on the phenol conversion and product distribution. The experimental results suggest the involvement of a free radical mechanism with the active involvement of Fe^{3+} species. However, a meticulous investigation of the reaction course is essential before a clear-cut prediction of the mechanism can be made. Whatever the case may be, the iron supported sulphated zirconia systems seem to be a promising catalyst for the disposal of phenolic wastes.

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