Transition Metals Supported on Activated Carbon as Benzene Hydroxylation Catalysts

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Abstract. The direct conversion of benzene to phenol by hydroxylation with hydrogen peroxide was carried out over catalyst containing various transition metals impregnated on activated carbon. Iron and vanadium impregnated catalysts gave better yields of phenol compared to copper impregnated catalysts. The activity of transition metals supported on activated carbon catalyst in the production of phenol was V > Fe > Cu. In addition to the role of transition metals in catalyzing the hydroxylation reaction, the hydrophobic nature of the activated carbon surface and also the surface acidity and basicity seems to have enhanced the performance of these catalysts.

Keywords: activated carbon, transition metals, hydroxylation of benzene, phenol

1. Introduction

Carbon materials have been found useful in heterogeneous catalysis [1]. They can either act as catalysts by themselves or can act as supports to other catalytically active phases. The performance of these materials depends on their texture and surface chemistry.

The surface area and porosity describe the texture of these materials. Larger surface area and higher porosity help in higher dispersion of active phases. The surface chemistry of carbon materials can be ascribed to the surface oxygen containing chemical groups, which can be acidic, basic or neutral. The interaction between the surface groups and the active phase could also have a synergetic effect on the catalytic activity of these materials.

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In recent years, there has been a growing research interest to find a suitable solid catalyst for the selective oxidation of benzene to phenol under mild reaction conditions, with clean oxidants like O_2 and H_2O_2 [2–23]. Recently, we had reported the use of activated carbon as supports for transition metals to produce phenol from benzene with H_2O_2 as the oxidant [24]. Our results indicated that activated carbons could be a good alternative to MCM-41 as catalyst support for this reaction.

In the present study, we have investigated the effect of loading amount of transition metals like Cu, Fe and V on phenol yields. The influence of various solvents used during reaction also has been studied.

2. Experimental

2.1. *Preparation of Activated Carbon Supported Catalysts*

Commercially available China coal based activated carbon materials were used as support for preparing catalysts containing transition metals for the hydroxylation of benzene to phenol. Activated carbon was dried and evacuated and were impregnated with transition metals using appropriate metal salts. For impregnating copper on activated carbon, copper acetate monohydrate salt was used as metal precursor. For impregnating iron, iron nitrate monohydrate (Fe_NT) and iron acetylacetonate (Fe_AcAc) were used. The impregnation of vanadium was carried out with vanadyl acetylacetonate (V_AcAc). The salts were dissolved in appropriate solvents. The salt solution and activated carbon were mixed together using a rotary equipment (Temperature: 70°C). After contacting the metal salt solution and activated carbon for half an hour, vacuum evaporation of the excess solvent was done. The catalyst samples were then dried at 80°C in an air oven overnight and calcined in a rotary kiln in nitrogen atmosphere at 550°C for 5 h.

2.2. *Catalysts Characterization*

XRD for all Cu, Fe and V-impregnated catalysts were obtained on Rigaku (D/Max2000-Ultima plus; X-ray radiation, Cu Kα) X-ray diffractometer. Nitrogen adsorption—desorption isotherms were obtained at 77K on a Micrometrics ASAP 2010 apparatus. From these studies, BET surface area, pore size distribution and pore volume were obtained. The amount of

benzene and methanol adsorbed were measured gravimetrically at 60°C using a magnetic suspension balance (MSB), (Rubotherm, Germany). Cu, Fe and V-impregnated AC catalysts were analyzed by FE-SEM (LEO-1530FE).

2.3. *Benzene Hydroxylation*

Benzene hydroxylation reactions were carried out in a jacketed stainless steel reactor and the reactor contents were thoroughly mixed with the help of a magnetic stirrer. Reactions were carried out at a temperature of 65°C by circulating hot water in the jacket. Acetone was used as solvent (unless stated specifically otherwise) and H_2O_2 (30 wt%) as oxidant. The molar ratio of reactants benzene:H_2O_2:solvent was $1:3:8$. In all the experimental runs 0.1 g of catalyst was used. The reaction time was 5 hours. The products were analyzed by HPLC (Waters 2690), using a reverse phase C18 column, UV detector at 254 nm and a mobile phase consisting of 42 vol% water and 58 vol% acetonitrile.

3. Results and Discussion

3.1. *Characterization of Catalysts*

The BET surface area, pore volume and pore size of all the catalysts used in this study are presented in Table 1. Nitrogen adsorption experiments showed a typical type *I* isotherm for activated carbon catalysts. The specific surface area of the catalysts decreased with increased amount of metal loading, indicating that some micropore blockage by metal deposition on pore mouth. In the case of Cu-impregnated catalysts the specific surface area decreased from 1182 m^2/g (0.5 wt% Cu) to 1027 m^2/g (5.0 wt% Cu). For iron impregnated catalysts the specific surface area decreased from 1088 m^2/g (0.5 wt% Fe) to 1020 m^2/g (5.0 wt% Fe). Vanadium impregnated catalysts showed almost a 20% reduction in surface area. The specific surface area decreased from 1045 m^2/g (0.5 wt% V) to 852 m^2/g (5.0 wt% V).

The XRD patterns of activated carbon supported copper, iron and vanadium catalysts are shown in Fig. 1, 2 and 3, respectively. In the case of copper impregnated catalysts the XRD patterns indicate the presence of copper in the form of copper oxide and metallic copper. Similarly iron and vanadium were present as oxides on the catalyst surface, as can be seen from the

Table 1. BET surface area, pore volume and size by nitrogen adsorption.

Metal/ catalyst	Loading (wt%)	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Median pore radius (Å)*
Cu (metal precursor	0.5	1182	0.50	3.0
copper acetate)	1.0	1120	0.47	2.8
	2.0	1057	0.45	2.8
	5.0	1027	0.43	2.8
Fe (metal precursor	0.5	1088	0.53	2.8
iron nitrate)	1.0	1167	0.61	3.0
	2.0	993	0.45	2.8
	5.0	1020	0.49	2.8
Fe (metal precursor iron acetyl acetonate)	5.0	756	0.34	2.8
V (metal precursor vanadyl	0.5	1045	0.47	2.8
acetyl acetonate)	1.0	1005	0.45	2.8
	2.0	956	0.42	2.8
	5.0	852	0.39	2.8

*Median pore radius were calculated by Horvath-Kawazoe method.
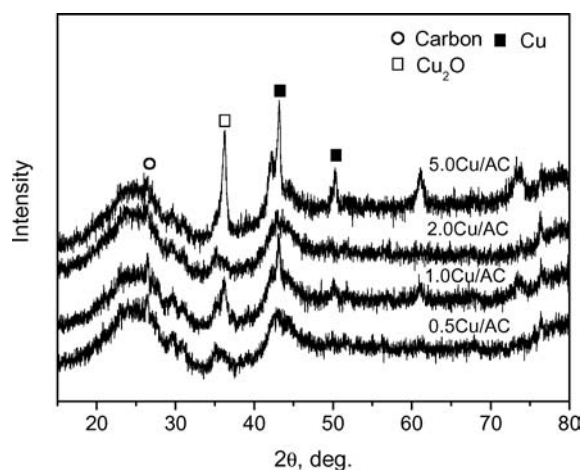

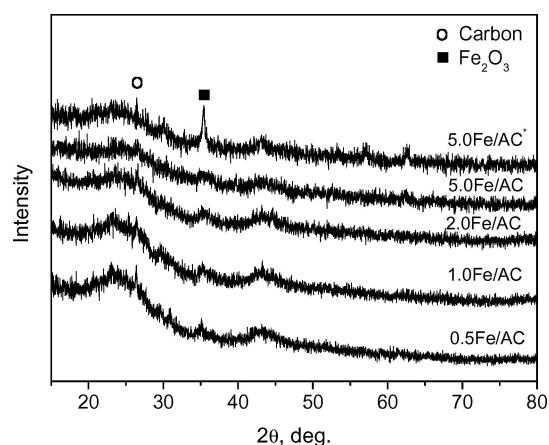*Figure 1*. The XRD patterns of Cu/AC catalysts.

Figure 2. The XRD patterns of Fe/AC catalysts (5.0Fe/AC*:iron acetylacetonate).

X-Ray diffractions of these catalysts given in Fig. 2 and 3.

The scanning electron micrograph (SEM) of various copper, iron and vanadium impregnated activated carbon catalysts is presented in Fig. 4 (Cu/AC), Fig. 5 (Fe/AC) and Fig. 6 (V/AC). As the impregnated amount of copper increased from 0.5 (wt%) to 5.0 (wt%) an increased amount of copper can be noticed on the surface of activated carbon. In the case of iron and vanadium impregnated catalysts, it can be seen that as the metal

loading increased, more metal deposition took place on the surface of the catalyst.

Benzene and methanol adsorption studies were conducted on activated carbon catalysts to determine the surface hydrophobicity and hydrophilicity of these materials and the results are presented in Table 2. The ratio of adsorbed benzene to adsorbed methanol on activated carbon catalysts indicate that the vanadium impregnated catalysts (vanadium acetyl acetonate precursor) were slightly more hydrophobic compared
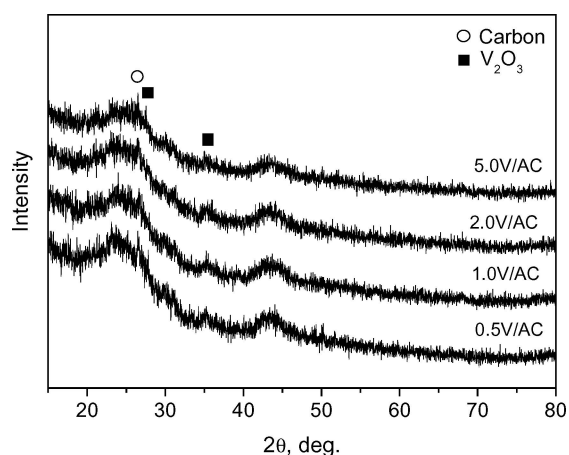
Figure 3. The XRD patterns of V_AcAc/AC catalysts.

to iron impregnated catalysts. Copper impregnated catalysts showed a higher degree of hydrophobicity compared to both iron and vanadium impregnated catalysts.

3.2. Performance Evaluation of Various Transition Metal Impregnated Activated Carbon Catalysts

Choi and coworkers [24] have reported that the activated carbon supported transition metal catalysts give a higher yield of phenol compared to that of transition metal impregnated on MCM-41 catalysts. In that study only catalysts containing 0.5 wt% transition metals were compared and the results of these studies are presented in Fig. 7.

It was also found that Cu, Fe and V containing catalysts gave higher yield of phenol. Hence, for this study catalysts containing Cu, Fe and V were chosen. To study the effect of metal loading of Cu, Fe and V on activated carbon, catalysts were prepared with 0.5, 1.0, 2.0 and 5.0 wt% of Cu, Fe and V on activated carbon. The results of reactions carried out with these catalysts are presented in Table 3.

From these results, it can be seen that the catalysts containing, Fe and V performed better than Cu containing catalysts. In the case of Fe containing
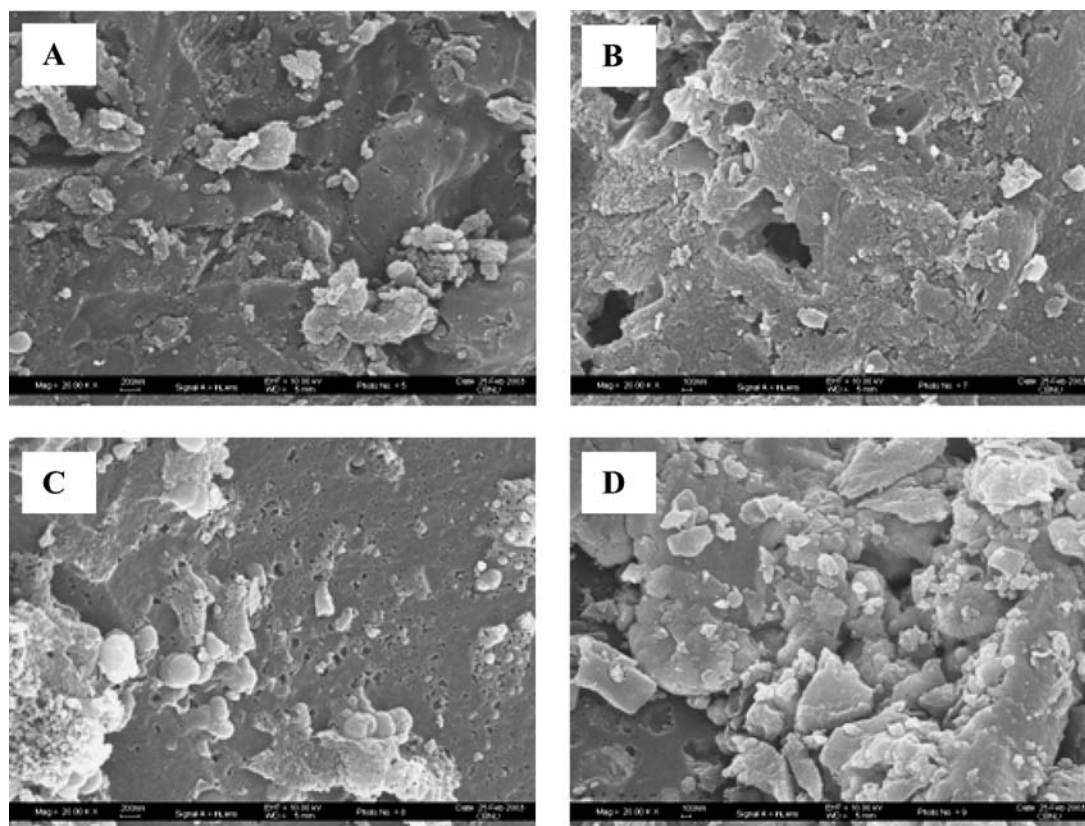

Figure 4. SEM images of Cu/AC catalysts (×20 K) (A-0.5 wt% Cu/AC; B-1.0 wt% Cu/AC; C-2.0 wt% Cu/AC; D-5.0 wt% Cu/AC).
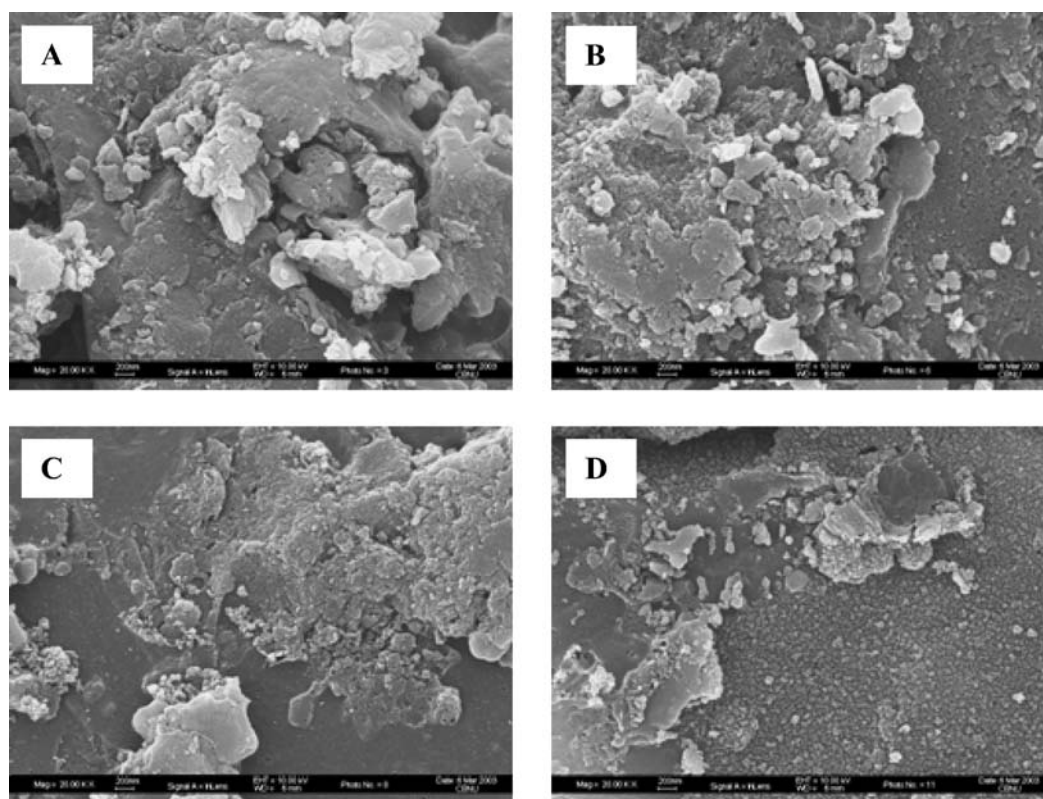
Figure 5. SEM images of Fe/AC catalysts ($\times$20 K) (A-0.5 wt% Fe/AC; B-1.0 wt% Fe/AC; C-2.0 wt% Fe/AC; D-5.0 wt% Fe/AC).

catalysts, the catalyst with Fe precursor Iron nitrate, gave a higher yield of phenol compared to catalyst made with iron acetylacetonate. In the case of Fe impregnated catalysts, the change in catalytic activity could be attributed to the lower surface area of the catalyst prepared with iron acetylacetonate as precursor (756 m^2/g) compared to the one prepared with iron nitrate as precursor (1019 m^2/g). In the case of iron nitrate as the precursor, the salt was dissolved in water, where as iron acetylacetonate was dissolved in acetone. It is well known that with water as solvent, the surface of activated carbon being hydrophobic, the distribution of metal on the surface becomes non uniform and it has also been reported that cluster formation takes place. When acetone was used as the solvent, it could have easily entered the pores of carbon, leading to uniform distribution of metal all over the surface. As acetone could penetrate smaller pores and deposit iron, probably more pore blocking took place (as indicated by lower surface area of these catalysts). In the case of iron nitrate precursor, being in aqueous solution, its penetration and deposition in smaller pores

Table 2. Benzene-methanol adsorption by the MSB.

Catalyst	Bz (mmol/g)	Me (mmol/g)	Bz/Me
0.5Cu/AC	4.6098	3.3009	1.3965
1.0Cu/AC	4.1823	3.3500	1.2485
2.0Cu/AC	4.1312	1.5982	2.5849
5.0Cu/AC	3.9802	1.3932	2.8568
0.5 Fe/AC[#]	4.8767	10.9260	0.4463
1.0 Fe/AC[#]	5.2285	11.7275	0.4458
2.0 Fe/AC[#]	3.9133	10.4008	0.3762
5.0 Fe/AC[#]	4.4546	9.5977	0.4641
5.0 Fe /AC[$]	3.2833	6.5074	0.5045
0.5 V /AC	4.4797	9.4116	0.4760
1.0 V /AC	4.4474	8.9717	0.4957
2.0 V /AC	4.0260	8.7898	0.4580
5.0 V /AC	3.7597	7.6011	0.4946

[#]metal precursor : Iron Nitrate; [$]metal precursor : Iron acetylacetonate.

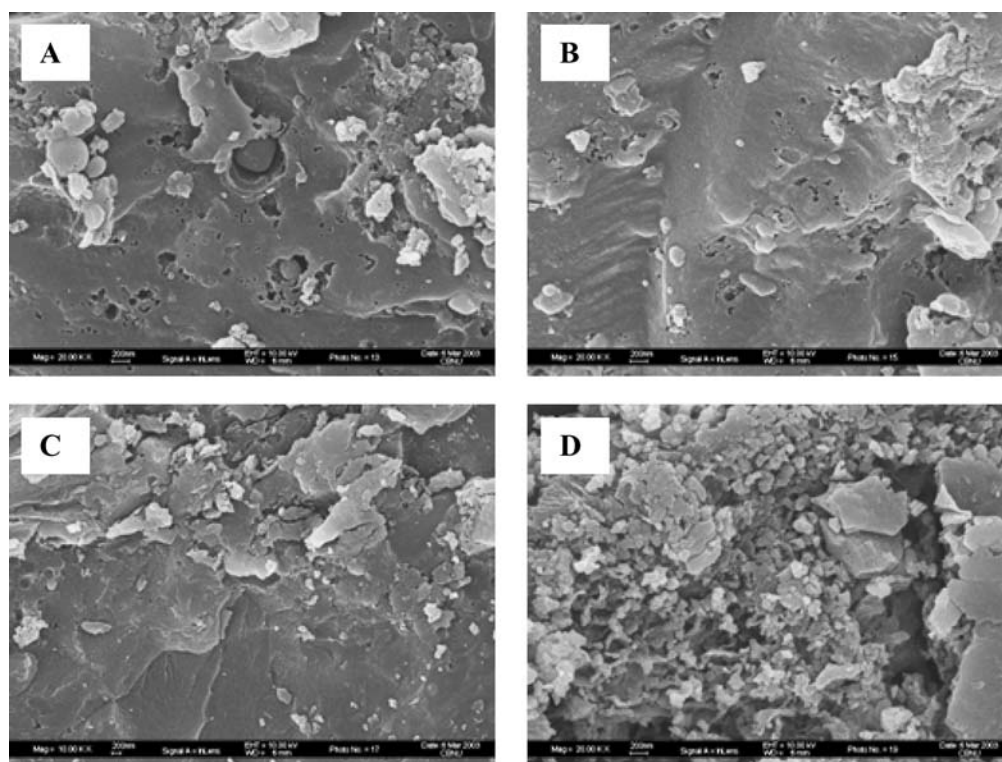might have been prevented by the hydrophobicity of the surface.

Figure 6.   SEM images of V/AC catalysts. (× 20 K) (A-0.5 wt% V/AC; B-1.0 wt% V/AC; C-2.0 wt% V/AC; D-5.0 wt% V/AC).
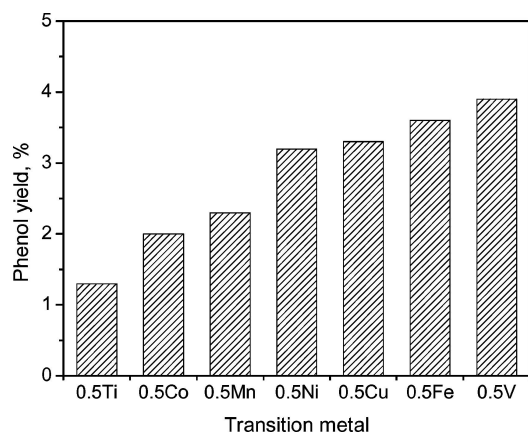

Figure 7.   Phenol yield on various transition metals loaded AC catalysts.

3.3.   *Effect of Solvents and Solvent Ratios on the Reactivity and Yield of Phenol*

Benzene hydroxylation with hydrogen peroxide in the presence of a solid catalyst is a three-phase reaction system. To enhance the rate of chemical reaction it is necessary to bring about an intimate contact between the reactants and the catalyst. One way to achieve this would be to increase the speed of agitation and also to bring the reactants into a single phase. To bring the reactants to a single homogeneous phase, an appropriate solvent like acetone, acetonitrile or methanol could be used. For an initial study of the effect of solvents on the yield of phenol, acetone and acetonitrile were chosen. The results of reactivity of benzene and yield of phenol for vanadium impregnated activated carbon catalyst (benzene : solvent = 1 : 6.58) are presented in Table 3. It was found that acetonitrile as solvent gave better yield of phenol compared to acetone as solvent.

To study the effect of solvents further, reactions were carried out with acetonitrile (benzene:acetonitrile = 1 : 4.65 mole ratio) and methanol (benzene : methanol = 1 : 6.58 mole ratio) as solvents on 5.0 wt% vanadium (metal precursor : vanadyl acetylacetonate) impregnated activated carbon catalyst were compared. The results are presented in Fig. 8(A) and (B). It can be seen that acetonitrile as a solvent leads to more yield of phenol on these catalysts.

Table 3.   Catalyst performance.

Catalyst	Loading (wt%)	Solvent used in reaction	Phenol Yield (%)	Phenol selectivity (%)
Cu impregnated on	0.5	Acetone	3.4	54.1
Activated carbon	1.0	Acetone	3.5	37.4
(metal precursor	2.0	Acetone	3.8	48.2
copper acetate)	5.0	Acetone	3.1	57.2
Fe impregnated on	0.5	Acetone	3.6	45.5
Activated carbon	1.0	Acetone	2.6	44.6
(metal precursor	2.0	Acetone	3.7	58.1
iron nitrate)	5.0	Acetone	7.0	60.7
Fe impregnated on Activated carbon (metal precursor iron acetyl acetonate)	5.0	Acetone	5.4	51.5
V impregnated on	0.5	Acetone	3.1	38.7
Activated carbon (metal	1.0	Acetone	2.8	42.3
precursor vanadyl	2.0	Acetone	3.3	53.5
acetyl acetonate)	5.0	Acetone	4.2	64.5
V impregnated on	0.5	Acetonitrile	8.0	74.5
Activated carbon (metal	1.0	Acetonitrile	9.7	67.8
precursor vanadyl	2.0	Acetonitrile	10.6	55.1
acetyl acetonate)	5.0	Acetonitrile	13.2	49.4

The varied performance of solvents can be explained with the role of these solvents in the reaction. These solvents help in keeping both benzene and hydrogen peroxide in one phase. This helps in the easy transport of both the reactants to the active sites of the catalyst. The acetonitrile, acetone and methanol adsorption data on these catalysts (Fig. 9), suggests that acetonitrile has a greater affinity to the catalytic surface than acetone. This greater affinity of acetonitrile could lead to more effective transport of the reactants to the catalyst active sites. At the same time, they also help the products in desorbing and vacating the active sites. In the case of methanol, it is known that it is a scavenger of hydroxyl ions [13]. Benzene and methanol have to compete to react with the hydroxyl ions. Methanol being in excess (benzene : methanol = 1 : 6.58 mole ratio) in the re-action mixture, it would have greater chance to react with hydroxyl ions than benzene molecules, leading to reduction in the yield of phenol. Even though methanol had a higher specific adsorption on the catalyst (Fig. 9), its ability to transport reactants to the catalytic sites are greatly neutralized by its scavenging action on hydroxyl ions. Therefore the effectiveness of methanol as solvent to a great extent was reduced, leading to lesser yields of phenol.

A comparison of the results obtained for acetonitrile (various substrate : solvent ratio), shows that a higher yield of phenol was obtained for the case where the benzene : acetonitrile ratio was 1 : 4.65, compared to that of 1 : 6.58. This is because of the fact that the larger the quantity of solvent, greater is the dilution effect and thereby limited access of the reactants to active sites.

Similar studies were carried out with iron impreg-nated catalysts and it was found that a trend similar to that of vanadium impregnated catalysts was obtained. The results are presented in Fig. 10.

A comparison of iron and vanadium impregnated catalysts is given in Fig. 11. It shows that the iron im-pregnated catalyst gave a slightly higher yield com-pared to that of vanadium impregnated catalyst.

It is known that the catalytic activity of the transition metal sites is dependent on the outer *d* electron density. Lesser the electron density, greater is the capacity of these transition metals to activate oxidant species like hydrogen peroxide. From the point of view of electron density the catalyst activity should be V > Fe > Cu. It was also seen from the benzene-methanol adsorp-tion studies that vanadium impregnated catalysts were slightly more hydrophobic than iron impregnated cat-alysts, there by again indicating that the activity of
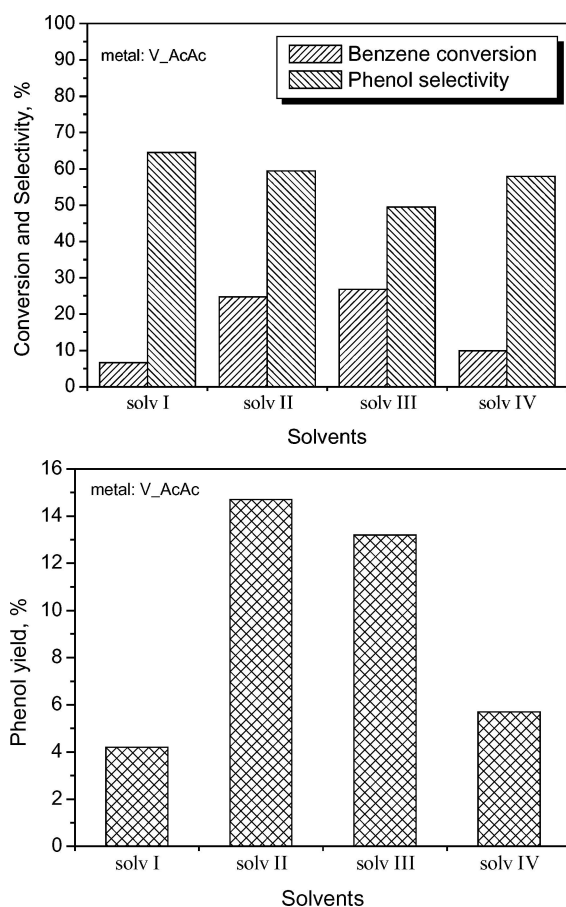
Figure 8. A. The effect of different solvents and V/AC (V_AcAc, vanadyl acetylacetonate) *solv I, acetone (20.8g); solv II, acetonitrile(14.7g), solv III, acetonitrile(20.8g);solv IV, MeOH(20.8g) B. The effect of different solvents and V/AC (V_AcAc, vanadyl acetylacetonate) *solv I, acetone(20.8g); solv II, acetonitrile(14.7g), solv III, acetonitrile(20.8g);solv IV, MeOH(20.8g).

Figure 9. The adsorption trends of 5.0V/AC with acetone, acetonitrile and methanol.

Figure 10. The effect of different solvents and two precursors of Fe/AC (Fe_NT, iron nitrate; Fe_AcAc, iron acetylacetonate) *solv I, acetone(20.8g); solv II, acetonitrile(14.7g), solv III, acetonitrile(20.8g).

vanadium impregnated catalyst would be higher to that of iron containing catalyst.

Additional surface characterization in the form of the surface acidity and basicity of the catalysts were carried out and the results are presented in Table 4. The surface of 5 wt% iron containing catalyst in comparison to 5 wt% vanadium containing catalyst appears to be more basic and less acidic in nature.

Phenol being slightly acidic in nature would adsorb on basic sites on the catalyst more strongly. This would lead to further hydroxylation of phenol to higher hydroxylated products like hydroquinone and benzoquinone. The acidic nature of the surface of V 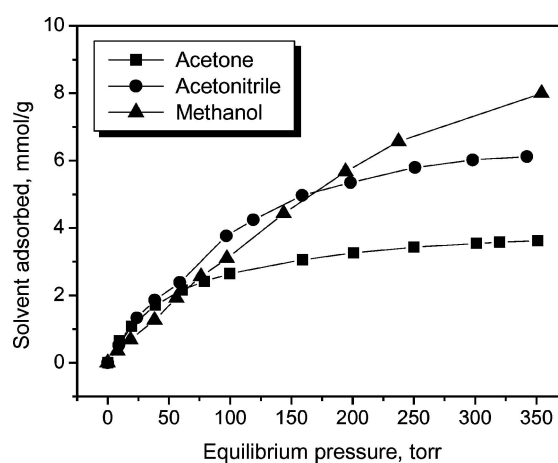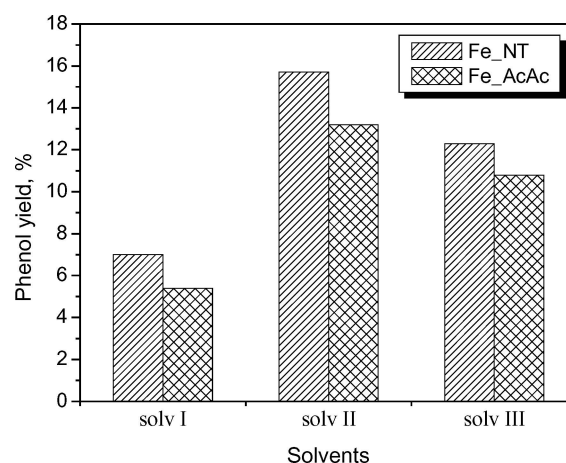containing catalyst is more preferred compared to Fe containing catalyst, which is more basic, in the hydroxylation of benzene to phenol.

The electronic configuration, surface hydrophobicity and surface acidity indicate that V impregnated activated carbon catalysts should be more active than Fe impregnated activated carbon catalysts. In spite of this, it was found that Fe impregnated activated carbon catalysts yielded more phenol compared to V impregnated activated carbon catalysts. The comparison of phenol yields given in Fig. 11 indicate that the iron containing catalyst yielded more phenol than vanadium containing catalyst. This contradictory behavior of these catalysts

Table 4. Acidity and basicity of AC catalysts by the titration method.

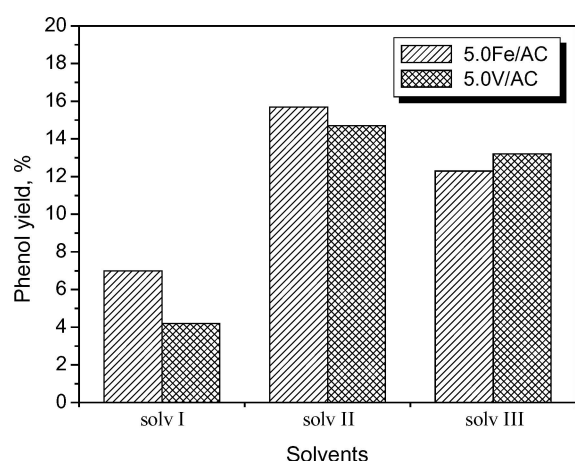| Catalysts	Acidity (m_{eq})	Basicity (m_{eq})
0.5Fe/AC	0.0634	0.0693
5.0Fe/AC	0.0640	0.0508
0.5V/AC	0.0746	0.0693
5.0V/AC	0.1759	0.0185

Figure 11. The effect of different solvent with Fe/AC and V/AC catalyst. *solv I, acetone(20.8g); solv II, acetonitrile(14.7g), solv III, acetonitrile(20.8g).*

could be resolved by comparing the surface areas of these catalysts.

A comparison of surface areas of 5.0 wt% Fe catalyst (1019.9 m^2/g) and 5.0 wt% V catalyst (841.4 m^2/g) indicates that the lesser activity of V containing catalyst is due to lesser surface area. If phenol yield were to be calculated on the basis of available surface area, it would clearly indicate that the V containing catalysts to be more reactive than the Fe containing catalysts.

4. Conclusions

Activated carbon supported catalysts containing 0.5, 1, 2 and 5 wt% Cu, Fe and V were tested for their catalytic activity in the hydroxylation of benzene to phenol using hydrogen peroxide. It was found that iron and vanadium containing catalyst (with 5.0 wt% loading) gave phenol yields over 15%. This could be attributed to the d orbital electron density of the transition metals and their ability to activate the oxidant and also the sur-

face hydrophobicity of these catalysts. In addition the surface acidity and basicity was also found to influence the yield of phenol. The results of reactions carried out with various solvents, acetonitrile as solvent and the substrate to solvent ratio of 1 : 4.65 gave higher yields of phenol.

Even though the 5.0 wt% iron containing catalyst had a larger surface area, 17% more than 5.0 wt% vanadium containing catalyst, its yield of phenol was only marginally higher (about 1%), indicating that the 'd'' orbital electron density of the transition metal, the hydrophobicity of the catalyst surface and also its acidity had an important role in the direct hydroxylation of benzene to phenol. The results obtained with iron and vanadium showed an encouraging trend in the yield of phenol. Further studies are on to enhance the yield of phenol by modifying the catalysts.

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