

Direct synthesis of phenol from benzene on iron-impregnated activated carbon catalysts

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Abstract

The direct conversion of benzene to phenol by hydroxylation with hydrogen peroxide was carried out over catalysts containing iron impregnated on activated carbon. Iron was impregnated on various surface modified activated carbons. The catalyst that was made by treating activated carbon with nitric acid, that was treated thermally in the presence of nitrogen at 600 °C and impregnated with 5 wt.% iron, gave a phenol yield of 20%. It was found that the synergistic interactions of surface groups and the impregnated iron have enhanced the performance of these catalysts.

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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 of 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 helps 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 interactions between the surface groups and the active phase could also have a synergetic effect on the catalytic activity of these materials.

In recent years, there has been a growing research interest in finding a suitable solid catalyst for the selective oxidation of benzene to phenol under mild reaction conditions, with clean oxidants like O₂ and H₂O₂ [2–23]. Recently, we reported the use of activated carbon as supports for transition metals to produce phenol from benzene with H₂O₂ as the oxidant [24]. Our results indicated that activated carbons could be a good alternative to MCM-41 as catalyst support for this reaction.

Choi et al. [24] have reported that the activated carbon supported transition metal catalysts gave 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. In continuation of that work, Choi et al. [25] studied the performance of copper-, iron- and vanadium-impregnated activated carbon catalysts on phenol yield by varying the metal loading and also the solvent used. They concluded that 5 wt.% iron containing activated carbon catalyst gave the highest yield of phenol of 15.8%.

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In the present work, in order to enhance the performance of iron-impregnated activated carbon catalysts, we have investigated the effect of surface modification of the activated carbon support on phenol yields. For reaction studies, activated carbons with modified surface chemistry were loaded with 5 wt.% iron and used as catalysts.

2. Experimental

2.1. Preparation of activated carbon supported catalysts

Commercially available Norit activated carbon materials were used as support for preparing catalysts containing iron for the hydroxylation of benzene to phenol. Activated carbon was dried and evacuated. Then the activated carbon was refluxed with 5 M nitric acid for 3 h and the material was washed until neutral pH was attained. Various samples of the nitric acid-treated activated carbon were kept in a rotary kiln and it was heat treated for 3 h in nitrogen atmosphere at temperatures of 873, 1023 or 1373 K. These activated carbons were then impregnated with 5 wt.% iron using iron nitrate monohydrate. The salt solution and activated carbon were mixed together using a rotary instrument (temperature 343 K). After contacting the metal salt solution and activated carbon had been in contact for half an hour, vacuum evaporation of the excess solvent was done. The catalyst samples were then dried at 353 K in an air oven overnight and calcined in a rotary kiln in nitrogen atmosphere at 823 K for 5 h.

The following abbreviations have been used for catalysts used in this study.

NAC	Norit activated carbon, as obtained.
NACH	NAC refluxed in 5 M nitric acid for 3 h.
NACH-600N	NACH heat-treated at 873 K in flowing nitrogen for 3 h.
NACH-750N	NACH heat-treated at 1023 K in flowing nitrogen for 3 h.
NACH-1100N	NACH heat-treated at 1373 K in flowing nitrogen for 3 h.
5.0Fe/NAC	5 wt.% iron impregnated on NAC.
5.0Fe/NACH	5 wt.% iron impregnated on NACH.
5.0Fe/NACH-600N	5 wt.% iron impregnated on NACH-600N.
5.0Fe/NACH-750N	5 wt.% iron impregnated on NACH-750N.
5.0Fe/NACH-1100N	5 wt.% iron impregnated on NACH-1100N.

2.2. Catalyst characterization

XRD for all Fe-impregnated catalysts were obtained on a Rigaku (D/Max2000-Ultima plus; X-ray radiation, Cu K α) X-ray diffractometer. Nitrogen adsorption–desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 apparatus. From these studies, BET surface area, pore size distribution and pore volume were obtained. Fe-impregnated AC catalysts were also analyzed by FE-SEM (LEO-1530FE).

2.3. Benzene hydroxylation

Benzene hydroxylation reactions were carried out in a jacketed stainless steel reactor. The reactor contents were thoroughly mixed with the help of a magnetic stirrer. Reactions were carried out at a temperature of 336 K by circulating hot water in the jacket. Acetonitrile was used as solvent and H₂O₂ (30 wt.%) as oxidant. The molar ratio of the reaction mixture of benzene:H₂O₂:solvent was 1:3:4.65. In all the experimental runs, 0.1 g of catalyst was used. The reaction time was 5 h. The products were analyzed by HPLC (Waters 2690), using a reverse phase C18 column, a 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. A sample nitrogen adsorption isotherm for 5 wt.% iron loaded, nitric acid-treated Norit activated carbon (5.0Fe/NACH) is shown in Fig. 1. The specific surface area of the activated carbon support increased after treatment with nitric acid. The surface area of NAC was 861.5 m²/g; the value rose to 964.3 m²/g for NACH. The heat treatment of NACH at temperatures of 873, 1023 and 1373 K modified the surface properties and also led to the decrease of surface areas of NACH-600N, NACH-750N and NACH-1100N to 749.5, 828.1 and 863.7 m²/g, respectively. There was further reduction in surface areas with metal loading, indicating that some micro pore blockage occurred due to metal deposition on the pore mouths.

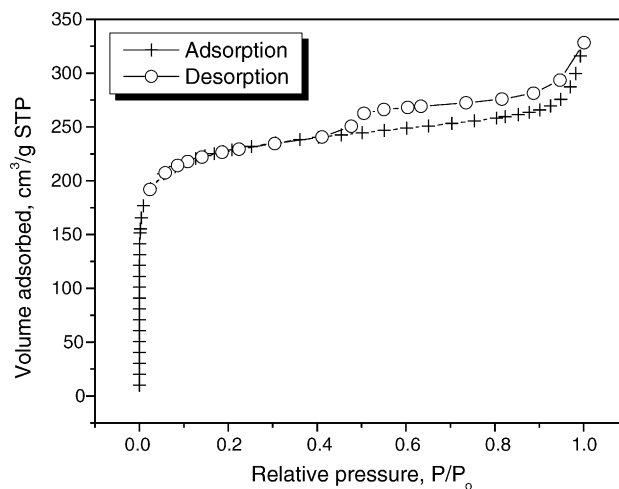


Fig. 1. Typical nitrogen adsorption and desorption isotherm at 77 K with 5.0Fe/NACH catalyst.

Table 1
Properties of used catalysts by nitrogen adsorption in the reaction

Catalysts	BET surface area (m ² /g)	Average pore radius (2V/A by BET) (Å)	Median pore radius (Horvath-Kawazoe) (Å)
NAC	861.5	11.9	2.5
NACH	964.3	28.1 ^a	2.6
NACH-600N	749.5	12.8	2.6
NACH-750N	828.1	11.2	2.5
NACH-1100N	863.7	11.3	2.5
5.0Fe/NAC	829.7	12.2	2.5
5.0Fe/NACH	858.6	28.7 ^a	2.6
5.0Fe/NACH-600N	607.2	11.0	2.5
5.0Fe/NACH-750N	823.3	10.8	2.5
5.0Fe/NACH-1100N	839.6	10.6	2.5

^a BJH adsorption average pore radius (2V/A by BET).

The XRD patterns of various activated carbon and iron-impregnated activated carbons are shown in Figs. 2 and 3, respectively. In the case of iron-impregnated catalysts, the XRD patterns indicate the presence of iron in the form of iron oxide.

The scanning electron micrographs (SEM) of some typical samples of activated carbons (NAC, NACH and NACH-600N) and iron-loaded activated carbon (5.0Fe/NACH-600N) are shown in Fig. 4. The SEM micrographs clearly indicate the surface modifications that have taken place on the surfaces of activated carbon (NAC) by nitric acid treatment (NACH) and heat treatment of NACH at 873 K, and changes due to iron-loaded NACH-600N activated carbon. It can be seen from Fig. 4A and B, that the surface pore openings have increased due to treatment of NAC with nitric acid. This is also supported by the BET surface areas determined for the catalysts NAC and NACH. The surface area changed from 861.5 to 964.3 m²/g, indicating more pore openings. A comparison of Fig. 4B and C indicates that there has been some structural collapse due to heat treatment of NACH at 873 K in nitrogen atmosphere. This is supported by the observation of lower BET surface area of NACH-600N compared to NACH

(749.5 m²/g from 964.3 m²/g). A comparison of Fig. 4C and D indicates that the impregnation of 5 wt.% iron has led to some loss in surface area due to pore blocking (surface area decreased from 749.5 to 607.2 m²/g).

3.2. Temperature programmed desorption studies

To understand the nature of surface groups on the various activated carbon samples used in this study, we carried out temperature programmed desorption studies. The CO and CO₂ evolution curves for NAC and NACH activated carbons are shown in Figs. 5 and 6, respectively. Both these figures indicate the enhancement of surface oxygen groups on the activated carbon treated with nitric acid (NACH), in comparison with the original activated carbon (NAC). These figures also indicate the decrease in carboxylic anhydride groups (peak at 800 K) on treatment with nitric acid [26].

Figs. 7 and 8 show the CO and CO₂ evolution curves of various heat-treated NACH activated carbon, respectively. It is very clearly seen from these figures that, as the thermal treatment temperature increased from 873 to 1023 to 1373 K, the surface oxygen groups got removed from the

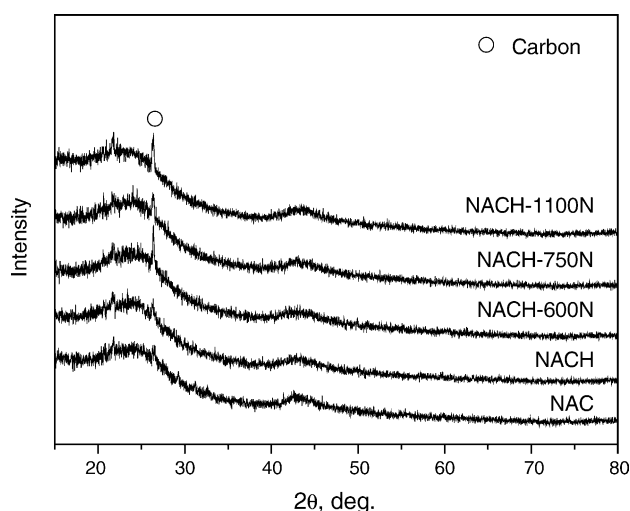


Fig. 2. XRD patterns of Norit AC catalysts.

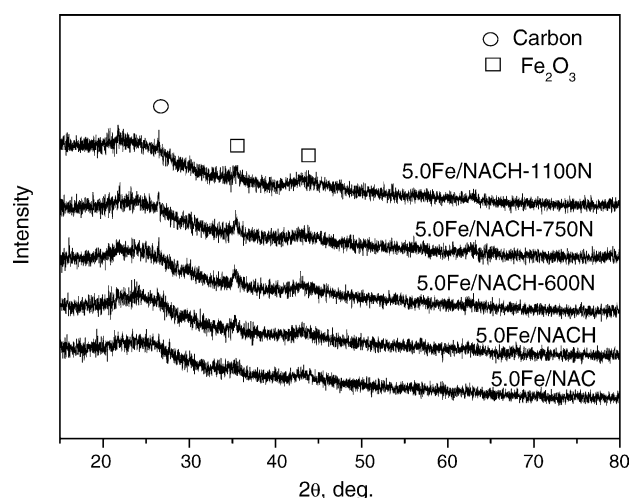


Fig. 3. XRD patterns of Fe-loaded Norit AC catalysts.

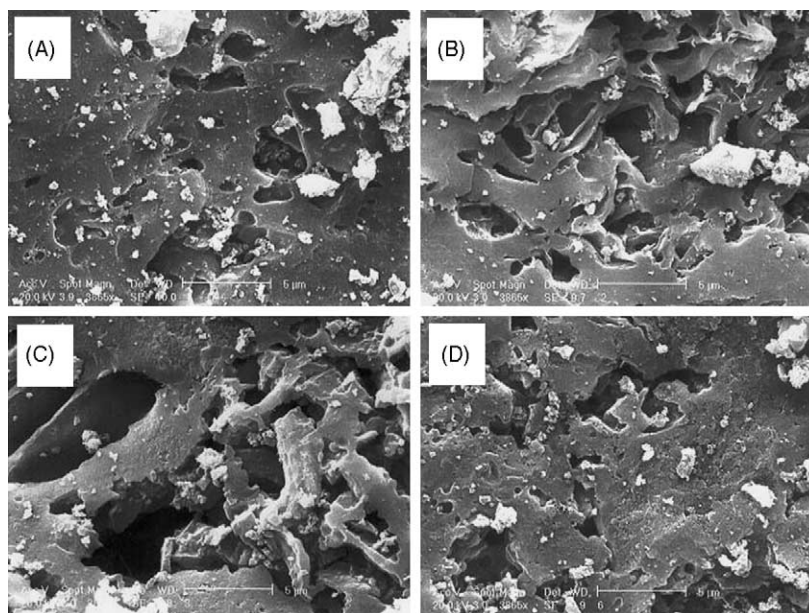


Fig. 4. SEM images of Norit AC catalysts ($\times 5$ K): (A) NAC; (B) NACH; (C) NACH-600N; (D) 5.0Fe/NACH-600N.

surface of the activated carbon, thereby leading to reduction in CO and CO₂ evolution.

The CO and CO₂ evolution curves for 5.0Fe/NACH-600N, 5.0Fe/NACH-750N and 5.0Fe/NACH-1100N are given in Figs. 9 and 10, respectively. The CO evolution curves indicate a sharp peak at 800 K and the CO₂ evolution curves show reduced peak intensities at 400, 600 and 775 K, and a sharp peak at 800 K, indicating the uniform spreading of iron on the activated carbon support.

3.3. Performance evaluation of various iron-impregnated activated carbon catalysts

Benzene conversion and phenol selectivity on various surface modified activated carbons are shown in Fig. 11. The phenol yield obtained on these catalysts is shown in Fig. 12.

From these figures it can be seen that activated carbon treated with nitric acid and heat treated at 873 K gave the highest phenol yield of 9.2%.

The TPD results shown earlier indicate a good distribution of surface oxygen groups on NACH-600N, in comparison with the distributions on NAC, NACH, NACH-750N and NACH-1100N.

Figs. 5–8 show TPD spectra of the activated carbon before and after the different oxidative and thermal treatments. In all cases, an increase in the amount of surface oxygen groups is evidenced by the increase of the CO and CO₂ peaks. The liquid phase treatment with nitric acid (Fig. 6) has enhanced the CO₂ evolution at low temperatures (from 375 to 675 K), while there is an enhancement of CO evolution (Fig. 5) at higher temperatures (from 750 to 1000 K).

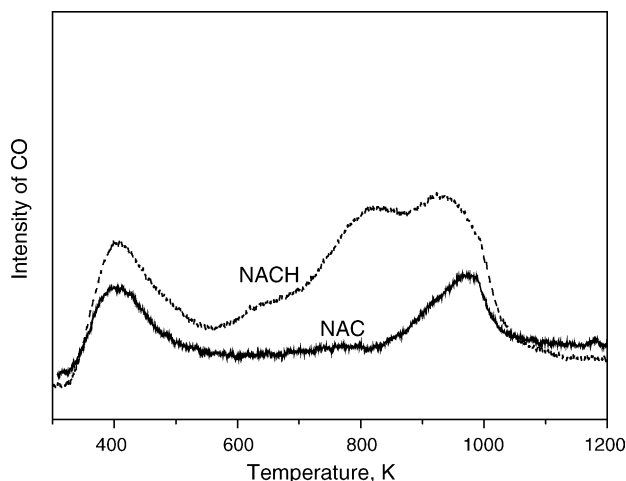


Fig. 5. CO evolutions of NAC and NACH by TPD-MS.

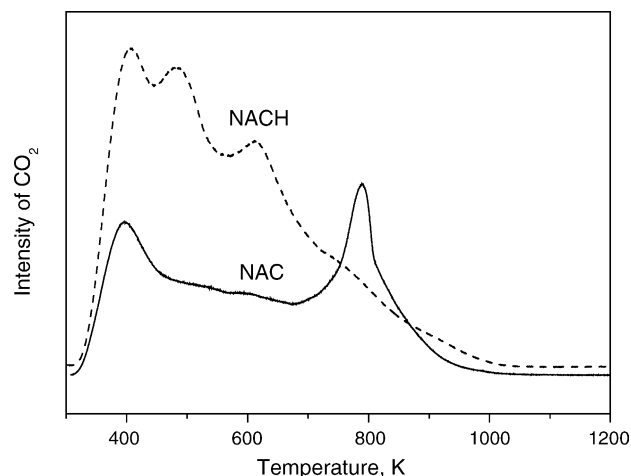


Fig. 6. CO₂ evolutions of NAC and NACH by TPD-MS.

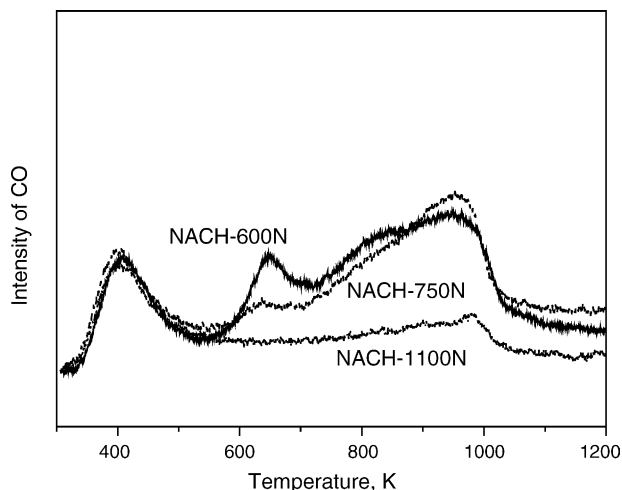


Fig. 7. CO evolutions of several AC catalysts by TPD–MS after acid and thermal treatment.

The first CO_2 peak may undoubtedly be attributed to carboxylic acid functional groups, while the higher temperature CO_2 peak, having a maximum around 800 K, may result from carboxylic anhydrides and lactones.

The liquid phase treatment has enhanced the surface groups that could be attributed to phenols, ethers, carbonyl/quinone, as evidenced by the enhancement of CO evolution at higher temperatures (from 800 to 1000 K) [26].

Figs. 7 and 8 show the TPD of activated carbon (NACH) after heat treatment at temperatures of 873, 1023 and 1373 K. It is clearly seen that the CO evolution drastically decreased with increase in heat treatment temperature, indicating the removal of surface oxygen groups. A similar trend is also observed in the CO_2 evolution, confirming the removal of surface oxygen groups.

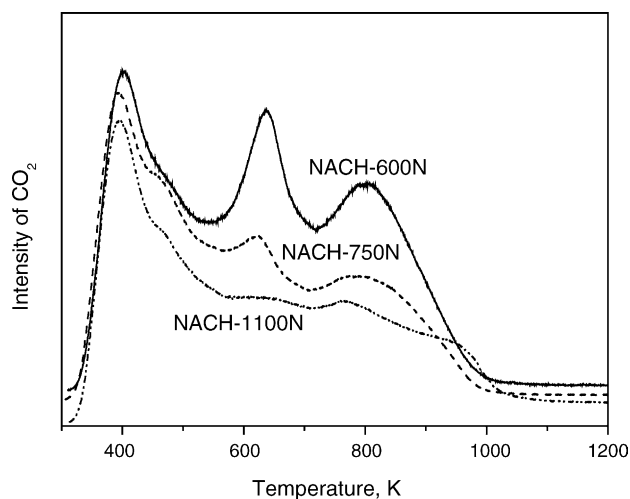


Fig. 8. CO_2 evolutions of several AC catalysts by TPD–MS after acid and thermal treatment.

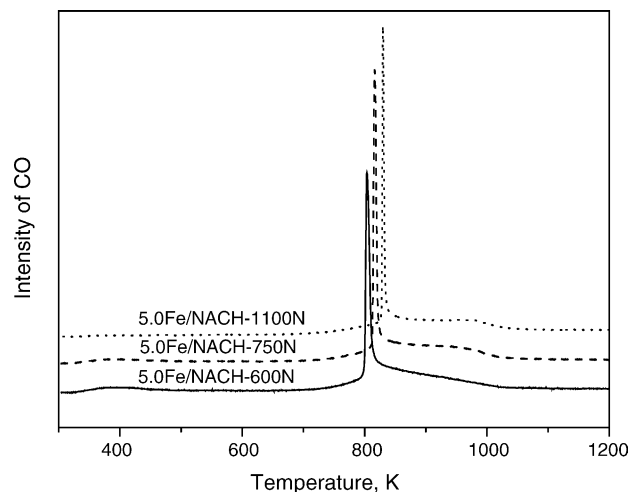


Fig. 9. CO evolutions of 5.0 wt.% Fe-loaded Norit AC catalysts by TPD–MS.

In the CO evolution from NACH catalyst (Fig. 5), it can be seen that there are distinct peaks at 400, 800 and 950 K, and there is also a peak at 650 K. In the CO evolution from NACH-600N catalyst, it can be seen that there are distinct peaks at 400, 650, 800 and 950 K. That is the peak seen for NACH catalyst at 650 K has become sharper in the case of NACH-600N catalyst.

Similarly by comparing the CO_2 evolution curves (Figs. 6 and 8), it can be seen that for NACH catalyst, there are sharp peaks at 400, 500 and 650 K and shoulders at 800 and 900 K. Whereas in the case of NACH-600N catalyst it can be seen that there are sharp peaks at 400, 650 and 800 K and a shoulder at 500 K.

This indicates that there has been a definite alteration to the nature of surface oxygen groups between NACH and

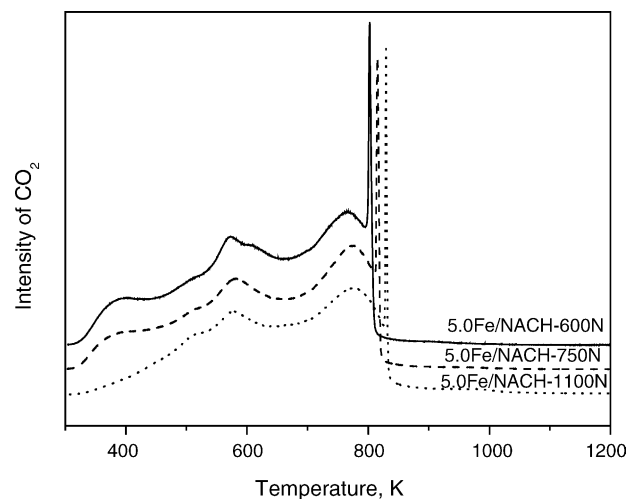


Fig. 10. CO_2 evolutions of 5.0 wt.% Fe-loaded Norit AC catalysts by TPD–MS.

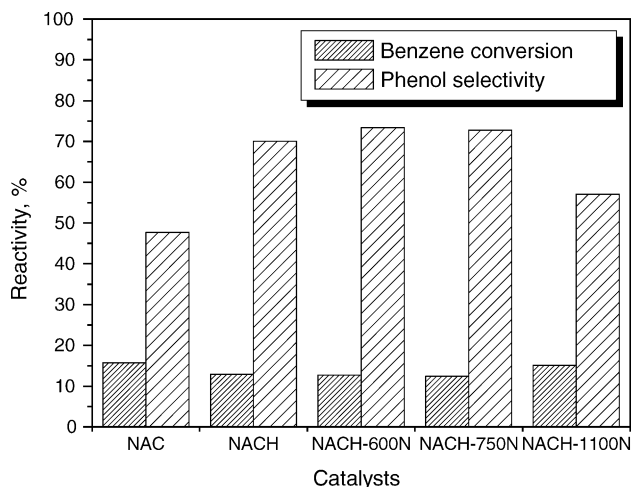


Fig. 11. Catalytic reactivity of Norit AC catalysts in acetonitrile as a solvent.

NACH-600N, and this has been brought about by the heat treatment at a higher temperature in flowing nitrogen.

It is well known that carbon materials by themselves can act as catalysts [1]. It is also known that carbon materials can activate molecules during reactions [27]. These qualities of activated carbon materials have been found to be influenced by the surface oxygen groups that are present in them. The results of benzene hydroxylation reactions shown in Figs. 11 and 12 clearly indicate that there has been some influence of these surface groups on this reaction, even though they appear to be marginal.

Figs. 13 and 14 show the reactivity (conversion of benzene and selectivity to phenol) and yield of phenol, respectively, on 5.0Fe/NAC, 5.0Fe/NACH, 5.0Fe/NACH-600N, 5.0Fe/NACH-750N and 5.0Fe/NACH-1100N. It can be seen from these results that the benzene conversion and the yield of phenol were the highest on 5.0Fe/NACH-600N

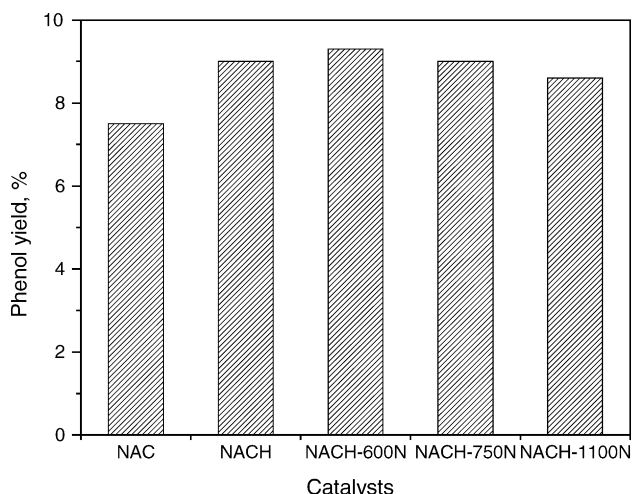


Fig. 12. Phenol yield of Norit AC catalysts in acetonitrile as a solvent.

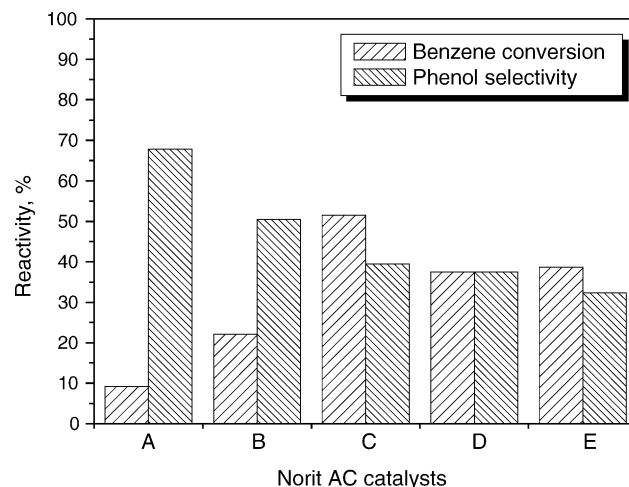


Fig. 13. Catalytic reactivity of Fe-loaded Norit AC catalysts (solvent: acetonitrile): (A) 5.0Fe/NAC; (B) 5.0Fe/NACH; (C) 5.0Fe/NACH-600N; (D) 5.0Fe/NACH-750N; (E) 5.0Fe/NACH-1100N.

catalyst. The yield of phenol, which was 9.2% on NACH-600N, increased to 20% in the case of 5.0Fe/NACH-600N. This clearly indicates the catalyzing effect of iron impregnated on activated carbons. The reasons for the increased yields can be sought from the TPD and carbon monoxide adsorption study results on these catalysts.

Fig. 9 shows TPD of iron-impregnated activated carbons. It can be seen that, except for a sharp peak at about 800 K, no other peaks for CO are observed. Fig. 10 shows CO₂ evolution of iron-impregnated activated carbons. A comparison with unloaded catalysts indicated a sharp reduction in CO₂ evolution of iron-impregnated catalysts, except for a sharp peak at 800 K similar to what was observed for CO evolution.

The peak at about 800 K is attributed to the decomposition of iron carbonate and indicates that the impregnated iron has occupied the surface more evenly irrespective of the

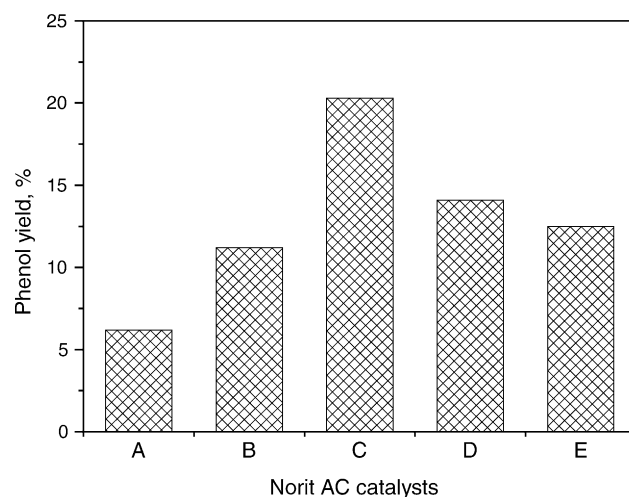


Fig. 14. Phenol yield of Fe-loaded Norit AC catalysts (solvent: acetonitrile): (A) 5.0Fe/NAC; (B) 5.0Fe/NACH; (C) 5.0Fe/NACH-600N; (D) 5.0Fe/NACH-750N; (E) 5.0Fe/NACH-1100N.

surface oxygen groups present. These results only indicate that the activated carbons have provided a good base for the impregnation of iron.

The impregnated metal ions are known to act as catalytically active sites. These metals being electron acceptors, they are able to act as Lewis acid centers. Their electrostatic fields are also thought to be responsible for the activation and reactivity of the adsorbed reactant molecules. Several techniques are used in order to characterize the surface acidity, most of them based on the adsorption of typical probe molecules [28].

Of the probe molecules that can be used to characterize surface acidity, carbon monoxide meets many criteria. Such suitability has promoted its extensive use during the last decade. Carbon monoxide has a smaller molecular size, in addition to having a small dipole moment. It is also highly polarizable leading to its use as an adsorbent for studying surface acidity of many different materials [29,30,31].

CO adsorption studies were carried out in a PCT (volumetric adsorption test equipment) apparatus. The catalysts were degassed for 30 min at 423 K. After each catalyst was cooled to 298 K, CO was passed over it for 30 min, and thus the adsorption isotherms were obtained. The CO adsorbed at equilibrium for NAC, NACH, NACH-600N, NACH-750N and NACH-1100N are shown in Table 2. It can be seen that about 1.1 mmol of CO was adsorbed on 1 g of NACH-1100N catalyst. About 1, 0.96, 0.91 and 0.45 mmol of CO were adsorbed on 1 g of NAC, NACH, NACH-750N and NACH-600N catalysts, respectively.

The CO adsorbed at equilibrium of 5.0Fe/NAC, 5.0Fe/NACH, 5.0Fe/NACH-600N, 5.0Fe/NACH-750N and 5.0Fe/NACH-1100N are presented in Table 2. It can be seen that about 0.95, 0.9, 0.89, 0.85 and 0.64 mmol of CO were adsorbed on 1 g of 5.0Fe/NACH-750N, 5.0Fe/NAC, 5.0Fe/NACH, 5.0Fe/NACH-600N and 5.0Fe/NACH-1100N, respectively.

In the case of NAC, NACH and NACH-1100N activated carbons, there was a reduction in CO adsorption with the impregnation of 5 wt.% iron on them, whereas there was a marginal increase in CO adsorption capacity between NACH-750N and 5.0Fe/NACH-750N. In the case of

5.0Fe/NACH-600N catalyst, its CO adsorption capacity went up by about 90% to 0.85 mmol/g compared to the support NACH-600N, whose adsorption capacity was only 0.45 mmol/g.

Of all the activated carbon catalysts (with out impregnation of iron) tested, NACH-600N had the least BET surface area of 749.5 m²/g. The heat treatment at 873 K seems to have brought about a modification on the pore structure of this material. This could be the reason for the small amount of CO adsorbing on it. This indicates that the increase in CO adsorption capacity of 5.0Fe/NACH-600N over NACH-600N is only due to the presence of iron in the catalyst, whereas in the case of other catalysts the effect of iron has been negative, in that the CO adsorption capacity of the activated carbon supports decreased with the addition of iron.

The CO adsorption results indicate that iron on 5.0Fe/NACH-600N catalyst is finely dispersed. From Figs. 13 and 14 it can be seen that this catalyst gave the highest conversion for benzene; the yield of phenol was also the highest, around 20%, in comparison with the yields on other catalysts.

It is well known that neither the surface area nor its pore structure are sufficient to explain many of the properties of carbon supported catalysts. Oxygen surface groups are considered to be of much importance in the preparation of carbon supported catalysts, since the common methods of excess solution and incipient-wetness impregnation entail contacting the carbon with a solution of the catalyst precursor. Rodriguez-Reinoso [1] have indicated that, to obtain iron-impregnated activated carbon catalysts prepared using iron nitrate precursor, the carboxyl groups of the activated carbon supports were essential to facilitate the access of aqueous solution to small pores, thereby enhancing the dispersion of iron. Szymanski and Rychliki [32] have reported that the treatment of activated carbon with nitric acid resulted in the formation of carboxylic groups. The TPD studies have also indicated that there has been an enhancement of surface carboxyl groups in addition to other surface groups. Pereira et al. [33] have reasoned that heating activated carbon (treated with nitric acid) at high temperatures under a flow of nitrogen leads to generation of active sites by the decomposition of carboxylic, lactone and phenol groups. When this material is exposed to oxygen at room temperature, oxygen fixation takes place on these sites giving rise to different type of oxygen surface groups. The modified surface groups on NACH-600N and its synergistic interaction with impregnated iron could be the reason for the better performance of 5.0Fe/NACH-600N catalyst compared to 5.0Fe/NACH catalyst.

The results obtained on the surface modified catalysts indicate that there has been a synergistic effect of surface oxygen groups and the impregnated iron in catalyzing the benzene hydroxylation reaction, for the synthesis of phenol. A comparison of yields of phenol on various catalysts cited in the literature is presented in Table 3.

Table 2
CO adsorption at equilibrium

Catalyst	CO adsorbed at equilibrium (mmol/g)
NAC	1.0
NACH	0.96
NACH-600N	0.45
NACH-750N	0.91
NACH-1100N	1.1
5.0Fe/NAC	0.9
5.0Fe/NACH	0.89
5.0Fe/NACH-600N	0.85
5.0Fe/NACH-750N	0.95
5.0Fe/NACH-1100N	0.64

Table 3

Comparison of performance of various catalysts in the open literature for the hydroxylation of benzene to phenol (liquid phase reaction)

Catalyst	Reaction temperature (°C) (oxidant)	Conversion, selectivity and yield (%)	Reference
Cu-zeolite	30 (O ₂)	Y = 1.69	[7]
Pd/SiO ₂	45 (O ₂ and H ₂)	X = 7.0, S = 88.2, Y = 6.2	[8]
CuO–Al ₂ O ₃	30 (O ₂)	Y = 1.0	[11]
V/SiO ₂	30 (O ₂ and H ₂)	Y = 8.2	[13]
V/MCM-41	30 (O ₂ and H ₂)	Y = 8.6	[13]
Polymer bound vanayl acetylacetonate	70 (30% H ₂ O ₂)	Y = 10.0	[16]
TS-1	60 (30% H ₂ O ₂)	X = 74.4, S = 85.6, Y = 63.7	[17]
V/MCM-41	70 (30% H ₂ O ₂)	X = 1.39, S = 93, Y = 1.29	[21]
V/MCM-48	70 (30% H ₂ O ₂)	X = 0.44, S = 93, Y = 0.41	[21]
AMM catalyst Fe ₃ MeSi ₅₀ Si	60 (30% H ₂ O ₂)	X = 7.1, S = 63.86, Y = 10.6	[23]
AMM catalyst Cu ₃ Si	60 (30% H ₂ O ₂)	X = 7.1, S = 21.13, Y = 1.5	[23]
0.5 wt.% V on activated carbon	65 (30% H ₂ O ₂)	Y = 3.9	[24]
5 wt.% iron on activated carbon	65 (30% H ₂ O ₂)	Y = 15.8	[25]
5.0Fe/NACH-600N	65 (30% H ₂ O ₂)	X = 50.0, S = 40.0, Y = 20.0	Present work

4. Conclusions

Commercially available Norit activated carbon was treated with nitric acid and was also thermally treated to modify the surface functional groups. These materials were impregnated with 5 wt.% iron and were used for the synthesis of phenol from benzene. TPD studies indicated the extent of surface modification of these catalysts. The carbon monoxide adsorption studies indicated that, in the case of 5.0Fe/NACH-600N catalyst, there was a 90% increase in the carbon monoxide adsorption capacity over NACH-600N activated carbon. This indicated a fine dispersion of iron and a synergistic interaction between the surface and the impregnated iron, leading to a yield of 20% phenol on this catalyst.

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