

Low temperature hydroxylation of benzene to phenol by hydrogen peroxide over Fe/activated carbon catalyst

Yongke Zhong, Guiying Li^{*}, Liangfang Zhu, Yun Yan, Gang Wu, Changwei Hu^{*}

*Key Laboratory of Green Chemistry and Technology (Sichuan University), Ministry of Education,
College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, PR China*

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Abstract

A series of Fe-based catalysts were prepared by impregnating activated carbon with the aqueous solution of ferric sulfate. These catalysts were employed to the hydroxylation of benzene to phenol using hydrogen peroxide as the oxidant. Boehm titration and X-photoelectron spectroscopy (XPS) were used to characterize the catalysts. It was found that ferric species were mainly anchored on activated carbon via its interaction with surface carboxylic oxygen group. These supported ferric species was found catalytically active for the titled reaction. A benzene conversion of 19.6%, a phenol yield of 17.5% with a selectivity of 89.3% was obtained under optimized conditions: 303 K, atmospheric pressure, and using acetonitrile as the solvent.

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1. Introduction

The commonly used cumene process for the production of phenol suffers mainly from low atom utilization, low phenol yield, high energy consumption, and the production of equal amount of acetone as the by product [1–3]. The study of the direct hydroxylation of benzene to phenol has attracted increasing interests [1–9]. Traditionally, Fenton reagent was used to oxidize benzene to phenol, where Fe^{2+} acted as the catalyst, and H_2O_2 acted as the oxidant [10–11]. Very recently, Choi et al. [12,13] used iron-impregnated activated carbon catalysts to directly convert benzene to phenol. It was found that the hydrophobic nature of the activated carbon surface, the surface acidity or basicity, or the synergistic interactions of the surface groups and the impregnated iron enhanced the performance of these catalysts. In the present work, the hydroxylation of benzene was performed over Fe/activated carbon catalyst operated at ambient temperature to further explore the catalytic performance of these catalysts, and the interaction between ferric species and activated carbon.

2. Experimental

2.1. Preparation of the catalysts

The catalysts were prepared by incipient impregnation of the activated carbon to the aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$ with desired concentrations. The activated carbon was coal based and purchased from Jiangsu Nantong Activated Carbon Cooperation (China). It was grounded to 40–80 mesh and pretreated with 12 M nitric acid before impregnation. The impregnation of activated carbon with $\text{Fe}_2(\text{SO}_4)_3$ solution was endured for 30 min, and the sample was dried at 380 K before use. The as-prepared catalysts were denoted as AC-Fe03, AC-Fe08, AC-Fe11, AC-Fe15, AC-Fe30, AC-Fe43, AC-Fe51, and AC-Fe55, respectively, according to the amount of Fe loaded, as shown in Table 1a.

2.2. Boehm titration of activated carbon

The Boehm titration of the samples was carried out according to [14]. The aqueous solution of NaHCO_3 , Na_2CO_3 , or NaOH with a concentration of about 0.05 mol/L was used in the titration. Spectroscopically pure ethanol was used to dissolve $\text{CH}_3\text{CH}_2\text{ONa}$ in preparing the solution needed for titration.

^{*} Corresponding authors. Tel.: +86 28 88835525; fax: +86 28 85411105.
E-mail addresses: gchem@scu.edu.cn, chwehu@mail.sc.cninfo.net (C. Hu).

2.3. Characterizations of the catalysts

X-ray photoelectron spectroscopies (XPS) of the catalysts were collected in a Krotos-XSAM 800 Multifunctional Electron Spectrometer using monochromatic Al K α radiation. The anode was operated at 12 kV and 20 mA. The spectrometer was equipped with a DS300 unit for data acquisition. And the binding energies were referenced to the C1s peak at 284.5 eV. The software XPS Peak Processing was used to deconvolute the peaks to separate different species of the same element. The texture of the samples was characterized by Brunauer, Emmett and Teller (BET) method using ZXF-5 equipment (China).

2.4. The adsorption of benzene

The benzene adsorption capacity of the catalysts was carried out according to [15]. The catalysts were dried at 380 K for 10 h, cooled to room temperature in degassing, and then immersed to acetonitrile solution of benzene for 12 h at 393 K. The amount of benzene adsorbed was calculated according to the variation of the concentration of the solution.

2.5. Activity measurement

The oxidation of benzene to phenol was carried out in a two-necked 50 mL round bottom flask placed in a water bath. In a typical procedure, 0.5 g catalyst and 1 mL (11.3 mmol) benzene were added into 20 mL acetonitrile, and then 5 mL (48.5 mmol) H₂O₂ (30%) was added into the above mixture. The reaction was performed without stirring for about 7 h. Then, the liquid products were separated from the catalyst by filtration and analyzed by HPLC (Waters 1525P). *O*-Cresol was used as an internal substance to quantify the phenol formed. The main product of the reaction was further identified by coupled gas chromatography and mass spectroscopy (GC–MS, Agilent 5973 Network 6890N) to be phenol, with a very small amount of benzoquinone. The yield of phenol was calculated as (mmol phenol)/(mmol initial benzene). The selectivity of phenol was calculated as (mmol phenol)/(mmol all products) [9]. The catalytic turnover number (TON) was estimated as (mmol phenol)/(mmol initial ferrum added).

3. Results and discussion

3.1. The influence of Fe loading on the texture of the catalyst and on its benzene adsorption

The variation of the surface area and the pore volume of the catalysts with their Fe loadings were shown in Fig. 1. It was found that both the surface area and the pore volume showed a tendency of decrease with the increase of Fe loading. When the Fe loading increased from 0 to about 0.1 mmol/g, the pore volume decreased drastically, while it kept almost constant as Fe loading increased from 0.1 to 0.3 mmol/g and decreased obviously again with further increase of Fe loading. This variation implied that the ferric species entered and blocked up firstly (when Fe loading <0.1 mmol/g) the micro-pores of the acti-

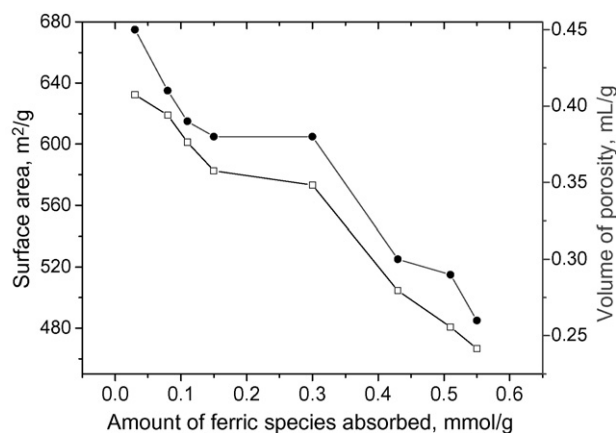


Fig. 1. The dependence of surface area and pore volume on Fe loading. (●) Pore volume of the catalysts; (□) surface area of the catalysts.

vated carbon, then coated the surface of meso- and macro-pores, and blocked up the meso- or macro-pores when sufficient ferric species were loaded. The variation of the surface area showed almost the same tendency, although it was not as obvious as that of the pore volume. This confirmed the above deduction. Thus, in the present aqueous system, ferric species also tended to distribute on the interior of the porosity. It was summarized that the metal precursor would be mostly located at the external surface of the carbon particle when using water as the solvent for impregnation, but it would penetrate to the interior of the porosity when using acetone [16]. The difference of the above results from [16] might be caused by different metal precursor used.

The dependence of the amount of benzene adsorbed on the surface area was shown in Fig. 2. It was indicated that the amount of benzene adsorbed decreased almost linearly with the decrease of the surface area as the loading of Fe increased. The amount of benzene adsorbed was much lower than that reported previously [15]. This small amount of benzene adsorption comparing to [15] might be originated from the fact that different activated carbon and impregnating solvents were used. The reported [15] amount

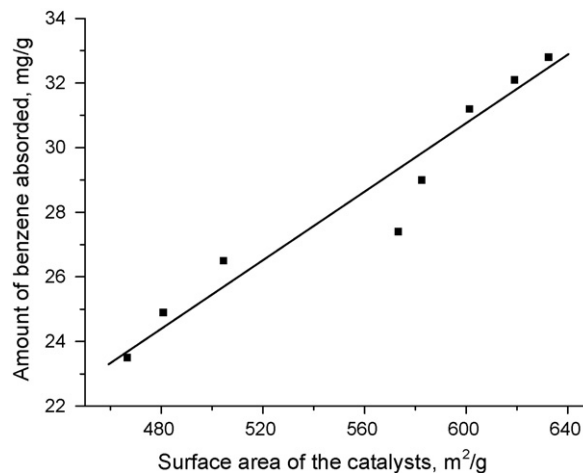


Fig. 2. The dependence of the amount of benzene adsorbed on the surface area.

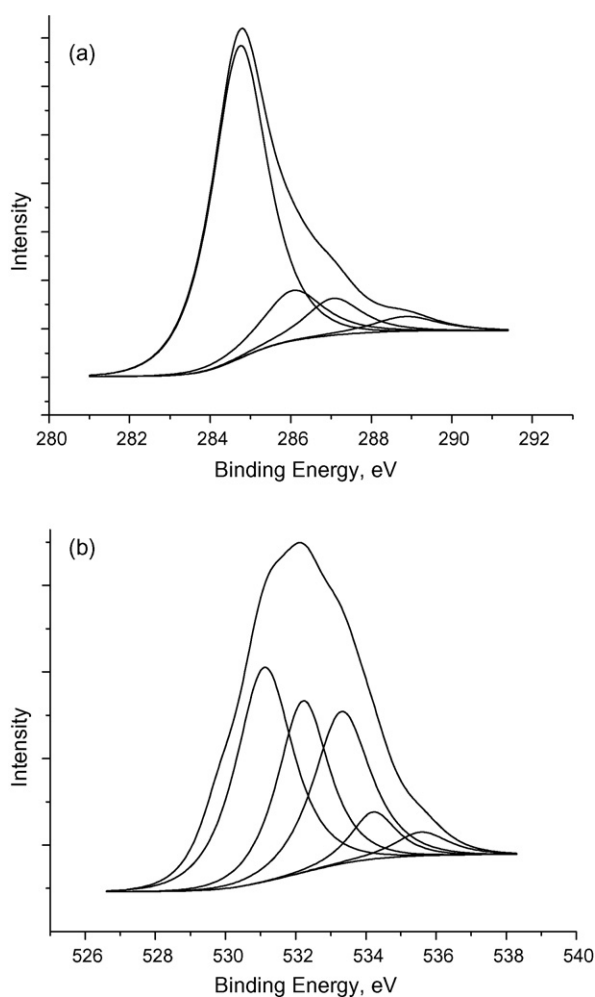


Fig. 3. X-ray photoelectron spectra of AC-Fe03. (a) C1s peak; (b) O1s peak.

of benzene absorbed was much higher, because the activated carbon used in Ref. [15] had much higher surface area. The hydrophobic nature of benzene in aqueous solvent also resulted in a higher benzene absorption than in acetonitrile solvent in the present work [15,17].

3.2. The interaction of ferric species with the surface groups of activated carbon

The catalyst samples were characterized by XPS technique, and the representative XPS peaks were shown in Fig. 3. Fig. 3 showed that both the C1s peak and O1s peak of the catalysts were asymmetric, indicating the convolution of different surface carbon and oxygen species. The surface carbon could be assigned to graphite carbon and the contaminant carbon, phenol carbon, carbonyl carbon, and carboxylic carbon according to the bonding energy of 284.5, 286.0, 287.1, and 288.9 eV, respectively, after deconvolution. And the O1s bonding energies of 529.8, 531.1, 532.2, 533.3, 534.2, and 535.5 eV, respectively, could be assigned to hydrolyzed oxygen of ferric species, carbonyl oxygen, phenol oxygen, lactonic oxygen, carboxylic acid oxygen, and water oxygen, [18,19]. It should be noted that the O1s peak of O in SO_4^{2-} overlapped with that of carbonyl oxygen at

Table 1a

The relative concentration of different surface carbon species after deconvolution with the increase of $\text{Fe}_2(\text{SO}_4)_3$ loaded

Sample	Fe content (mmol/g)	Binding energy (eV) and the composition (%)			
		284.5	286.0	287.0	288.9
AC	0.0	66.5	18.2(54.4) ^a	8.7(25.9)	6.6(19.8)
AC-Fe03	0.03	70.5	16.6(56.2)	8.7(29.5)	4.2(14.3)
AC-Fe08	0.08	71.2	16.3(56.6)	8.6(29.7)	3.9(13.7)
AC-Fe11	0.11	73.4	14.9(56.2)	8.3(31.3)	3.4(12.5)
AC-Fe15	0.15	77.1	12.9(56.0)	7.5(32.5)	2.6(11.5)
AC-Fe30	0.30	81.8	11.9(65.3)	3.8(20.7)	2.6(14.0)
AC-Fe43	0.43	85.2	9.3(62.6)	3.4(23.2)	2.1(14.2)
AC-Fe51	0.51	86.0	9.2(65.5)	3.4(24.1)	1.5(10.4)
AC-Fe55	0.55	89.3	7.8(72.8)	2.6(24.3)	0.3(3.0)

^a The values in parentheses were obtained by renormalization of the three species (phenol carbon, carbonyl carbon, and carboxylic carbon).

about 531.1 eV [20]. The relative concentration of each species deconvoluted was shown in Tables 1a and 1b.

The variation of the relative concentration of different surface carbon and oxygen species with the increase of Fe loading might indicate the interaction of ferric species with the activated carbon. Since the C1s XPS peaks of graphite carbon and of contaminant carbon overlapped, and so did the O1s XPS peaks of SO_4^{2-} oxygen and carbonyl oxygen, it was not apparent to compare the variation of different carbon and oxygen species directly from the deconvoluted values. In order to compare the variation of phenol carbon, carbonyl carbon and carboxylic carbon, as well as that of phenol oxygen, lactonic oxygen and carboxylic oxygen, a renormalization of both the three carbon and oxygen species was made and the results were shown in the parentheses of Tables 1a and 1b. It was clear that with the increase of Fe loading from 0 to 0.11 mmol/g, the relative concentration of phenol carbon, carbonyl carbon, as well as phenol oxygen and lactonic oxygen varied slightly, while that of carboxylic carbon and carboxylic oxygen decreased drastically. This implied that ferric species anchored firstly on the carboxylic site, with further increase in Fe loading, the ferric species interacted with or covered the lactonic or carbonyl surface groups. This was in good

Table 1b

The relative concentration of different surface oxygen species after deconvolution with the increase of $\text{Fe}_2(\text{SO}_4)_3$ loaded

Sample	Binding energy (eV) and the corresponding composition (%)				
	531.1	532.2	533.3	534.2	529.8
AC	15.4	34.4(40.6) ^a	32.9(38.9)	17.3(20.6)	
AC-Fe03	21.0	33.6(42.7)	31.2(39.6)	14.1(17.6)	
AC-Fe08	25.5	31.9(45.1)	28.3(39.9)	10.9(15.1)	
AC-Fe11	32.1	30.8(45.3)	27.7(40.8)	9.3(13.9)	
AC-Fe15	37.4	28.6(45.8)	26.5(42.4)	7.5(11.8)	
AC-Fe30	41.9	25.5(46.0)	24.1(43.4)	5.8(10.6)	2.7
AC-Fe43	53.3	21.1(55.2)	13.8(36.1)	3.3(8.8)	8.6
AC-Fe51	58.2	18.3(63.1)	9.7(33.3)	1.3(3.7)	12.8
AC-Fe55	65.5	13.8(65.2)	7.5(33.8)	0.2(1.0)	15.1

^a The values in parentheses were obtained by renormalization of the three species (phenol oxygen, lactonic carbon, and carboxylic oxygen).

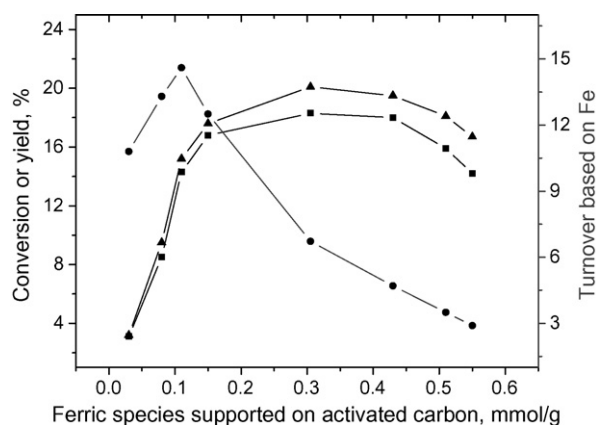


Fig. 4. Effect of iron amount loaded on AC on the activity of hydroxylation of benzene. Condition: catalyst, 0.5 g; acetonitrile, 20 mL; benzene, 11.2 mmol; H_2O_2 , 48.5 mmol; T , 303.2 K; t , 7.0 h. (▲) Conversion of benzene; (■) yield of phenol; (●) catalytic turnover based on Fe added.

agreement with [16] that carboxylic groups were essential for the support of iron nitrate. That is to say, the carboxylic groups were also essential for the support of iron sulfate. When the Fe loading was higher than 0.3 mmol/g, a new oxygen species at 529.8 eV was observed. This new species could be attributed to oxygen species in the hydrolyzed product of ferric sulfate, indicating the formation of new ferric species.

3.3. The effect of Fe loading on the activity of hydroxylation of benzene

The results of activity test were shown in Fig. 4. It was shown that the conversion of benzene increased with increasing Fe loading firstly, reached a maximum value at Fe loading of about 0.3 mmol/g, and then decreased slightly with further increment of Fe loading. The yield of phenol varied in a similar trend as the benzene conversion with the increase of Fe loading. The catalytic turnover in terms of phenol produced per Fe used varied similarly, with the highest value at a Fe loading of 0.11 mmol/g (AC-Fe11). The highest benzene conversion and highest phenol yield obtained were 19.6% and 17.5%, respectively, over AC-Fe30, with a selectivity of 89.3%. This yield of phenol is a little lower than that reported by Choi et al. (20%) [12], while the selectivity of phenol was much higher than the reported value (75%) in [12]. This might be caused by much lower temperature and different ferric precursor used in the present work. Control experiments carried out at 318, 333 and 348 K gave reduced selectivities as 88.1, 84.4 and 81.1%, respectively, confirming the above deduction.

It was interesting to note that the highest catalytic turnover was observed on AC-Fe11. As mentioned above, the ferric species interacted mainly with surface carboxylic groups below the Fe loading of 0.11 mmol/g, and beyond this loading, ferric species might interact with other surface oxygen groups. The drastic decrease of both carboxylic oxygen and carboxylic carbon, as well as the appearance of new inactive ferric species might be responsible for the decrease of catalytic activity. Those facts revealed that the ferric species interacted with carboxylic groups was mainly active for the target reaction.

Table 2

Surface oxygen species (by Boehm titration) on surface of AC before and after heat treatment (mmol/g)

Activated carbon	Carboxylic	Lactonic	Phenol	Carbonyl	Total carbon
AC	0.96	0.14	1.10	0.46	2.64
573 K	0.64	0.18	1.07	0.46	2.35
713 K	0.38	0.26	0.71	0.44	1.79
733 K	0.11	0.18	0.54	0.37	1.21

3.4. The effect of surface composition on the hydroxylation activity

In order to confirm the contribution of carboxylic species on the catalytic performance to the titled reaction, the activated carbon was pretreated by heating in nitrogen flow at different temperatures to change the amount of the different groups before catalyst preparation. The variation of the amount of groups was determined by Boehm titration. The results were shown in Table 2. It was indicated that the heat pretreatment at 573 K in nitrogen flow reduced mainly the amount of carboxylic groups, and at 713 K the amount of phenolic groups decreased further, while the amount of lactonic groups increased slightly, indicating that there was some lactonic groups formed during the heat pretreatment. At 773 K, the amount of lactonic was also reduced. It was in accordance with the results obtained by temperature programmed desorption [21]. Obviously, the reduction of some of phenolic groups at 713 K was due to the formation lactonic groups.

As shown in Fig. 5, the catalyst prepared using the heat-treated activated carbon as the support showed reduced activity because of the decrease of the surface carboxylic groups on the support. This further confirmed the importance of carboxylic groups for the preparation of hydroxylation catalyst.

To further confirm the above deduction, a control experiment using different modeled complexes of Fe as the catalysts was carried out. Salicylic acid, catechol and phthalic acid were

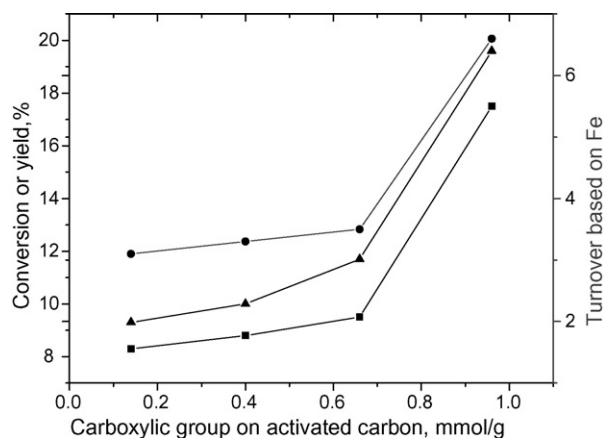


Fig. 5. Effect of surface carboxylic groups on AC on catalytic activity of AC-Fe. Condition: catalyst, 0.5 g; acetonitrile, 20 mL; benzene, 11.2 mmol; H_2O_2 , 48.5 mmol; T , 303.2 K; t , 7.0 h. (▲) Conversion of benzene; (■) yield of phenol; (●) catalytic turnover of catalysis based on Fe added.

used to coordinate to ferric species. The reaction of $\text{Fe}_2(\text{SO}_4)_3$ with phthalic acid gave a yellow precipitant which showed no activity. The homogeneous solution of the salicylic acid coordinated ferric species and catechol coordinated ferric species showed a phenol yield of 16.3% (TON 6.1, which was close to the AC-Fe30 catalyst) and 5.5% (TON 2.1), respectively. This showed that the coordination of salicylic acid to ferric species gave a much higher activity. That is, the interaction of both the carboxylic group and the hydroxyl group of salicylic acid with ferric species favored the catalytic performance of the ferric species for the titled reaction. This might be why activated carbon acted well as a support for it provided both carboxylic and phenol groups for the interaction with ferric species.

4. Conclusion

Activated carbon supported ferric sulfate catalyst showed good catalytic performance for the direct hydroxylation of benzene to phenol by hydrogen peroxide under moderate condition. The ferric species anchored firstly to carboxylic groups providing high performance catalytic phase for the titled reaction. The synergistic effect of activated carbon for the titled reaction might be provided by the coexistence of carboxylic and phenol surface groups.

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