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Direct Synthesis of Phenol from Benzene on an Activated Carbon Catalyst Treated with Nitric Acid

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Commercially available coal-based activated carbon was treated by nitric acid with different concentrations and the resultant samples were used as catalysts for the direct hydroxylation of benzene to phenol in acetonitrile. Boehm titration, X-ray photoelectron spectroscopy, scanning electron microscope coupled with an energy dispersive X-ray microanalyzer, and Brunauer-Emmett-Teller method were used to characterize the samples. The number of carboxyl groups on the surface was found to be the main factor affecting the catalytic activity. An optimum catalytic performance with a yield of 15.7% and a selectivity of 87.2% to phenol was obtained.

Key words: Activated carbon, Catalytic activity, Carboxyl group, Hydrogen peroxide, Phenol

I. INTRODUCTION

Phenol is a valuable intermediate in chemical industry and widely applied in agrochemicals, plastics, and petrochemicals [1–3]. Cumene process is the main route to produce phenol up to now. However, this process involves multiple steps and has many defects. Therefore, the one-step production of phenol by direct insertion of oxygen into the C–H bond of benzene becomes one of the most important intriguing tasks, while it is challenging in the field of organic synthesis [4–6]. To avoid over-oxidation, an oxygen species with mild reactivity seems to be necessary. Generally, the oxidants employed in the catalytic hydroxylation of benzene are hydrogen peroxide, molecular oxygen [4–7], and N₂O [8–11]. Expensive materials are often used in the preparation of the hydroxylation catalysts [12, 13]. The recycle of homogeneous catalyst and the leaching of active components from supported catalysts are still challenges for this reaction [3, 14].

Activated carbon has been extensively used not only as adsorbent but also as catalyst support or catalyst because of its stability under acidic and alkaline environments [15], such as, the removing of metallic ions and organic chemicals from liquid waste. Choi *et al.* and Zhong *et al.* used activated carbon containing iron as the catalyst for the direct hydroxylation of benzene and obtained good results [16, 17]. Moreover, activated carbon showed good catalytic performance in the selective

oxidation of cyclohexanone, PMIDA, and ethylbenzene [18, 19]. Carbonyl/quinone groups were shown to be the active phase for the oxidative dehydrogenation of ethylbenzene to styrene, and a linear correlation between the activity and the concentration of such sites was given in Ref.[19]. The unsaturated bonds and structural defects on the surface of activated carbon play important roles on its chemical properties. Since the solubility in water and the capacity of being adsorbed on activated carbon are different for benzene and phenol, it is expected that once phenol is formed over the activated carbon catalyst, it will dissolve in the reaction solution, leave the surface of the catalyst, thus shift the reaction equilibrium towards the formation of phenol.

In the present work, a cheap and easily-prepared catalyst was obtained by modification of coal-based activated carbon with nitric acid. The relationship between surface oxygen groups and catalytic activity of activated carbon on hydroxylation of benzene was explored.

II. EXPERIMENTS

A. Preparation of catalysts

Commercially available coal-based activated carbon from Jiangsu Nantong Activated Carbon Cooperation, China with a particle size of 0.42–0.84 mm was washed by distilled water and dried at 110 °C to obtain the sample named AC. AC was immersed in a 10.0 mol/L nitric acid solution at 90 °C for 10 h, and then washed by distilled water to reach a constant pH and finally dried at 110 °C. The resultant sample was denoted as AC10. The AC sample was also treated by nitric acid with the following different concentration via the pro-

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cedure above: 0.1, 0.5, 1.0, 2.0, 3.0, 5.0, 8.0, 12.0, 14.0, and 16.0 mol/L, and the samples obtained were named AC0.1, AC0.5, AC1, AC2, AC3, AC5, AC8, AC12, AC14, and AC16, respectively.

B. Characterization of the activated carbon catalysts

The Boehm titration of the samples was carried out according to Boehm method [20]. The aqueous solution of NaHCO_3 , NaOH with a concentration of about 0.1 mol/L, and Na_2CO_3 of 0.05 mol/L was used in the titration. 0.1 mol/L of $\text{CH}_3\text{CH}_2\text{ONa}$ was freshly prepared using chromatographically pure ethanol. Quadruplicate of each sample (0.5 g) was placed in 50 mL alkaline solutions above, respectively, and the vials were sealed and shaken under ultrasonic vibration for 24 h at room temperature. Superfluous hydrochloric acid solution (0.1 mol/L) was added into the filtrate and then back titrated by NaOH , using methyl red as the indicator. The values reported are the average obtained by at least three parallel experiments, and the deviation is less than 5 $\mu\text{mol/g}$.

To ascertain the surface oxygen groups with corresponding carbon species on the activated carbon, XPS characterization was carried out for the two typical samples, AC and AC10. XPS was operated on a XSAM800 spectrometer (KRATOS) using Al $K\alpha$ radiation (1486.6 eV), the source being operated at 12 kV and 12 mA. The binding energy (BE) was calibrated with C1s at 284.8 eV, and a linear background was subtracted from all spectra. Then peak fitting was performed with 80/20 Lorentz-Gauss function. The resolution of the spectrometer is within 0.5 eV.

The textural characterization of the carbon materials was based on BET method using ZXF-6 equipment (China) by nitrogen adsorption at 77 K. Prior to measurement, the samples were pretreated at 373 K for 3 h under vacuum.

Scanning electron microscope (SEM) coupled with an energy dispersive X-ray microanalyzer (EDX) was used to quantitatively measure the amount of several elements on the surface of the activated carbon. The samples were measured by an FEI Inspect F SEM. Analyses were performed directly in the SEM by the Oxford INCA Penta FET \times 3 EDX microanalyser. The voltage for the energy dispersive analysis was 20 kV, and the time of X-ray collection was 100 s.

C. Activity test

The hydroxylation of benzene was carried out in a two-necked 50 mL round flask placed in water bath. The typical reaction conditions were as the following: 0.1 g catalyst, 1 mL (11.25 mmol) benzene, 10 mL acetonitrile, 3 mL (29.44 mmol) hydrogen peroxide (30%), 70 $^\circ\text{C}$ for 6 h. The reaction mixture was filtered and analyzed by HPLC (Waters 1525P) equipped with a UV detector at 225 and 254 nm using a reverse phase C18

column. The main product and by-products were quantified using *o*-cresol as internal standard, while 50% water and 50% acetonitrile was used as the mobile phase. All products have been firstly identified by coupled gas chromatography and mass spectroscopy (GC-MS, Agilent 5973 Network 6890N). The amount of dihydric phenols formed was only to a minor extent and no tar was observed to form. The yield of phenol was calculated as phenol/initial benzene, and the selectivity to phenol was calculated as phenol/(phenol+benzoquinone) [7]. All the activity tests are repeated at least three times, and the average values are reported. The deviation for the yield to phenol is about 0.5%.

III. RESULTS AND DISCUSSION

A. The effect of nitric acid concentration on the surface property of AC

The amount of different surface oxygen groups on the samples obtained from Boehm titration is listed in Table I. It indicates that the amount of surface oxygen groups increases significantly after nitric acid treatment, and the amount of carboxyl groups on the sample increases monotonically with the increase of nitric acid concentration in the treatment, which is in agreement with the previous reports [15, 21]. The amount of carbonyl groups increases gradually when the nitric acid concentration increases from 0.1 mol/L to 2.0 mol/L, and reaches the maximum value of 1.09 mmol/g by 2.0 mol/L nitric acid treatment, and then goes down with further increase in the nitric acid concentration. The variation of the amount of lactone groups shows no regularity, while the amount of total surface oxygen groups has the same trend as carboxyl groups. Though the removal of impurities may increase the amount of surface oxygen groups, the significant increase should be originated from oxidation, that is, during the treatment by nitric acid, the surface of AC is oxidized to form different kinds of oxygen groups generally, resulting in significant increase of these species and the oxidation is affected by the concentration of nitric acid.

Both the C1s peaks and O1s peaks of catalyst AC10 are shown in Fig.1. High resolution XPS profiles of C1s and O1s exhibit asymmetric character, indicating the existence of different kinds of surface C and O species on the samples, which is in accordance with the results of Boehm titration. According to the reports in Ref.[22–25], for surface carbon, the deconvoluted peaks at the binding energy of 284.7–284.9, 286.0–286.1, 287.2–287.4, 288.6–288.8, and 290.5–290.8 eV were ascribed to graphitic carbon and contaminative carbon, alcohol and/or ether groups, carbonyl groups, carboxyl and/or ester groups, and carbonate groups, respectively. For the surface oxygen, the peaks at 530.3–531.8, 531.9–533.4, 533.4–533.6, and 535.1–536.3 eV corresponded to carbonyl groups, alcohol and/or ether groups, carboxyl and/or ester groups,

TABLE I Boehm titration results of the samples treated by nitric acid with different concentrations.

Catalyst	Amount of different surface oxygen groups/(mmol/g)				Total oxygen/(mmol/g)
	Carboxyl	Lactone	Phenolic hydroxyl	Carbonyl	
AC	0.10	0.06	0.09	0.37	0.62
AC0.1	0.32	0.25	0.13	0.79	1.49
AC0.5	0.37	0.38	0.22	0.95	1.92
AC1	0.41	0.41	0.12	0.81	1.75
AC2	0.64	0.28	0.04	1.09	2.05
AC3	0.66	0.36	0.32	0.95	2.29
AC5	0.78	0.35	0.48	0.92	2.53
AC10	1.03	0.38	0.62	0.81	2.84
AC12	1.00	0.66	0.55	0.68	2.89
AC14	1.12	0.68	0.58	0.80	3.18
AC16	1.36	0.54	0.88	0.71	3.49

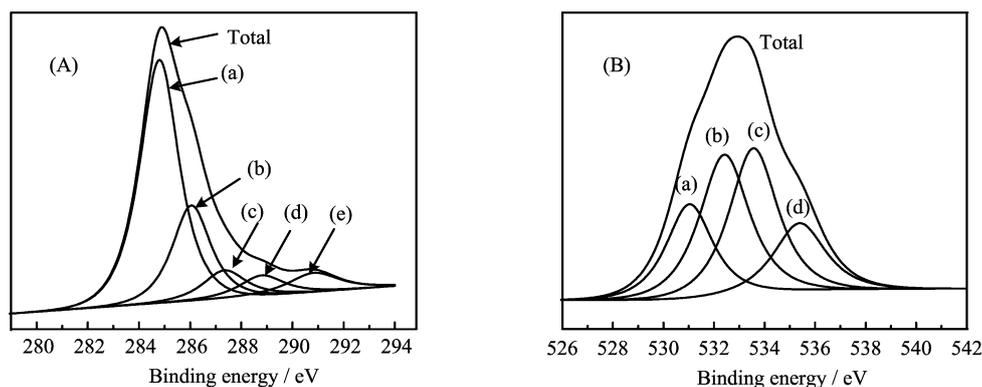


FIG. 1 (A) C1s XPS spectra of AC10. (a) Graphitic carbon and contaminative carbon, (b) alcohol and/or ether groups, (c) carbonyl groups, (d) carboxyl and/or ester groups, and (e) carbonate groups. (B) O1s XPS spectra of AC10. (a) Carbonyl groups, (b) alcohol and/or ether groups, (c) carboxyl and/or ester groups, and (d) chemisorbed oxygen.

and chemisorbed oxygen, respectively.

The relative amount of different surface species is given in Table II. It is observed that the variation tendency in surface oxygen groups obtained by XPS is the same as that obtained by Boehm titration. The increase of carboxyl groups is the most significant.

By N_2 adsorption at 77 K, we got the variation in BET surface area S_{BET} and pore structure R_{mean} of the samples. As shown in Table III, the S_{BET} of activated carbon samples decreases monotonically with the increase of nitric acid concentration, and no significant changes in other textural parameters are observed, which is consistent with the results reported in Ref.[26, 27].

The nitrogen adsorption isotherms of the samples are shown in Fig.2. All the samples treated with nitric acid have mainly micropores (type I isotherms) according to IUPAC. As the concentration of nitric acid gets higher, the knee of the adsorption isotherm becomes narrow, implying that the samples modified with nitric acid of higher concentration have more micropores on the whole [28]. When the concentration of nitric acid

for modification is as low as 0.1 mol/L, the surface area of treated AC increases because of more pore openings [16], that is, ashes and some other impurity in pore canal were removed by nitric acid. The anchor of oxygen groups on the inner surface of pores by oxidation might also contribute to the increase of the number of micropores. However, when the concentration of nitric acid continues to increase, the surface area of samples starts to decrease because of macropores collapsing or maybe there are more and more $-COOH$ stretching from the wall of slit-shaped pores. In addition, there is another possibility that the increased oxygen groups make carbon surface more hydrophilic and attract water clusters to blockage [29].

B. Catalytic activity

The catalytic activity in terms of phenol yield increases with the increase of reaction temperature, as shown in Table IV. This is in agreement with the results obtained over other catalysts [30, 31]. The amount of benzoquinone also increases with the reaction temper-

TABLE II The deconvolution of C1s and O1s XPS spectra for AC and AC10.

Catalyst	Surface carbon (C1s)/%				
	Graphitic	Alcohol and/or ether	Carbonyl	Carboxyl and/or ester	Carbonate groups
AC	56.03	27.39	5.28	5.17	6.13
AC10	58.88	22.53	7.28	5.46	5.83
Catalyst	Surface oxygen (O1s)/%				
	Carbonyl	Phenolic hydroxyl/ether	Carboxyl and/or ester	Chemisorbed	
AC	24.49	39.51	23.91	12.09	
AC10	20.12	32.12	32.10	15.67	

TABLE III BET textural characteristics of activated carbon samples.

Catalyst	$S_{\text{BET}}/(\text{m}^2/\text{g})$	$V/(\text{mL}/\text{g})$			$R_{\text{mean}}/\text{nm}$
		Total	Meso.	Mic.	
AC	870	0.53	0.11	0.42	13.29
AC0.1	881	0.55	0.08	0.47	11.92
AC1	843	0.59	0.11	0.48	12.48
AC3	831	0.48	0.09	0.39	12.63
AC5	786	0.49	0.09	0.39	12.65
AC10	780	0.54	0.14	0.40	13.09
AC12	646	0.38	0.08	0.30	13.02
AC14	652	0.44	0.10	0.34	13.40
AC16	624	0.47	0.12	0.35	13.85

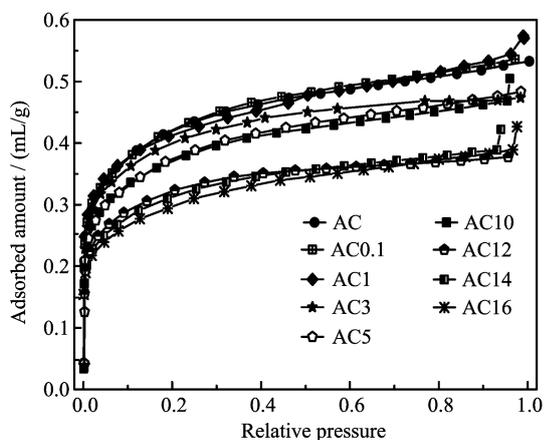


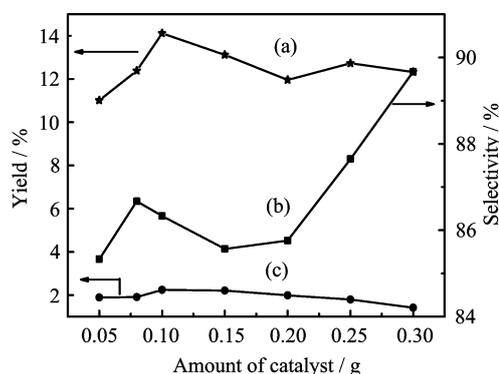
FIG. 2 Nitrogen adsorption isotherms of activated carbon modified by nitric acid with different concentrations.

ature, while the selectivity to phenol has the opposite tendency. Since the boiling point of benzene is 80.1 °C, reaction temperature higher than 70 °C will cause serious volatilization loss of benzene. Thus the reaction temperature was kept 70 °C in the following experiments.

The optimum amount of catalyst was tested and the results are illustrated in Fig.3. It is shown that the yield of phenol increases initially with the amount of catalyst, and reaches the maximum value of 14.1% with 0.10 g

TABLE IV Effect of temperature on the catalytic activity. Reaction conditions: 0.1 g AC10, 1 mL (11.25 mmol) benzene, 3 mL (29.44 mmol) H₂O₂, 10 mL acetonitrile, 6 h.

	Temperature/°C		
	50	60	70
Yield of phenol/%	7.3	10.9	15.2
Yield of benzoquinone/%	0.6	1.7	3.0
Selectivity to phenol/%	92.0	86.7	83.6

FIG. 3 The catalytic performance with the different amount of catalyst AC10. (a) Yield of phenol, (b) selectivity of phenol, and (c) yield of benzoquinone. Reaction conditions: 1 mL (11.25 mmol) benzene, 3 mL (29.44 mmol) H₂O₂, 10 mL acetonitrile, 70 °C, 6 h.

catalyst used, and then decreases slightly with further increase in catalyst amount, which is in accordance with the tendency reported in Refs.[7, 32]. The yield of benzoquinone has the same variation tendency as phenol. It is interesting to note that with more amount of catalyst used, the yield of phenol decreases slightly while the selectivity increases significantly. To explain this fact, the escaped oxygen under the reaction conditions was collected. Figure 4 shows that the amount of oxygen formed from the self-decomposition of hydrogen peroxide increases monotonically with the amount of catalyst used. That is to say, with more amount of catalyst used, the increased self-decomposition of hydrogen peroxide reduces both the target reaction and the over oxidation of phenol, thus the selectivity of phenol increases and

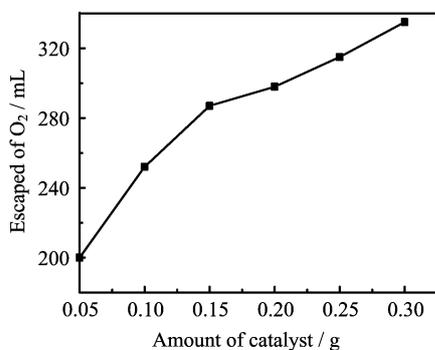


FIG. 4 The amount of oxygen escaped with the different amount of catalyst AC10. Reaction conditions: 1 mL (11.25 mmol) benzene, 3 mL (29.44 mmol) H₂O₂, 10 mL acetonitrile, 70 °C, 6 h.

the yield decreases.

The effect of reaction time on the yields of phenol and benzoquinone is shown in Fig.5. The yield of phenol increases from about 11.0% to about 13.8% as the reaction time increases from 2 h to 6 h. Later, along with the increase of reaction time, the yields decrease. It indicates that the optimized reaction time is 6 h, which resembles the results in Ref.[33].

The effect of the amount of H₂O₂ was tested, and the results are shown in Fig.6. It is seen that the yield of phenol increases with the amount of H₂O₂ used firstly, and reaches the maximum value of 15.7% with 3.5 mL H₂O₂ used, and then decreases monotonically, which has also the same tendency with that in previous reports [32–34]. It is interesting to note that the yield of benzoquinone also increases with the amount of H₂O₂ used, and keeps at about 2.1% when the amount of H₂O₂ used is more than 3 mL. It should be noted that when 3.5 mL H₂O₂ was used, violent boiling was observed. So, 3 mL H₂O₂ was selected in the present work for optimization.

The above optimization gives out the following optimum conditions: 0.1 g AC10, 1.0 mL benzene, 3.0 mL hydrogen peroxide (30%), 10.0 mL acetonitrile, 70 °C for 6 h, the highest yield 15.7% of phenol was obtained with the selectivity of 87.2% to phenol.

C. The origin of the catalytic performance

To probe the origin of the catalytic performance of the catalyst, several controlled experiments were carried out.

The impurities such as iron oxides, silica, calcium carbonate might be catalytically active for the target reaction. The two typical samples, AC and AC10, were characterized by SEM/EDX, and the results are listed in Table V. It is indicated that after being treated by nitric acid, the contents of these impurities decreased significantly. A comparison of the catalytic activity with these data shows that these impurities are not the main

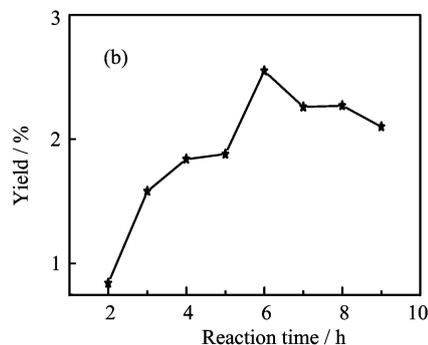
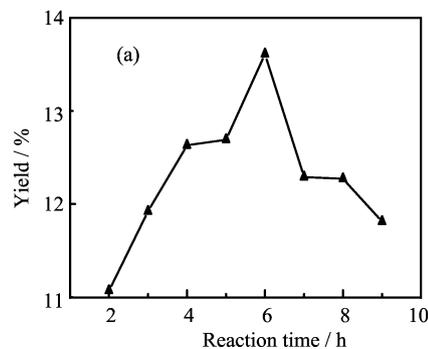


FIG. 5 Dependences of yield of phenol (a) and benzoquinone (b) on reaction time. Reaction conditions: 0.1 g AC10, 1 mL (11.25 mmol) benzene, 3 mL (29.44 mmol) H₂O₂, 10 mL acetonitrile, 70 °C.

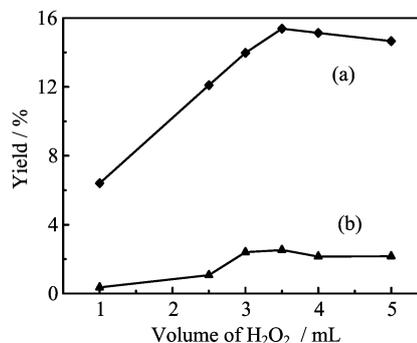


FIG. 6 The catalytic performance with the amount of peroxide hydrogen. Reaction conditions: 0.1 g AC10, 1 mL (11.25 mmol) benzene, 10 mL acetonitrile, 70 °C, 6 h. (a) Phenol and (b) benzoquinone.

reason for the catalytic performance. Then the correlation of catalytic performance with the amount of surface carboxyl groups is also studied.

The quantitative relative amount of different carbon species obtained by XPS may be affected by the contaminated carbon in XPS measurement, so the amount of acid surface groups obtained by Boehm titration is used in the following discussion. To correlate the catalytic activity with the surface groups, the variation of the amount of carboxyl groups on samples A0.1–A16 (as mentioned before) with the activity is summarized

TABLE V The elemental composition on the surface of AC and AC10 by SEM/EDX.

	Element	Weight/%	Atom/%
AC	C K	78.34	88.42
	O K	7.84	6.64
	Al K	2.00	1.00
	Si K	4.92	2.38
	Ca K	0.36	0.12
	Fe K	1.43	0.35
	Cu K	5.12	1.09
AC10	C K	69.03	77.15
	O K	24.42	20.49
	Si K	3.65	1.75
	Cu K	2.91	0.61

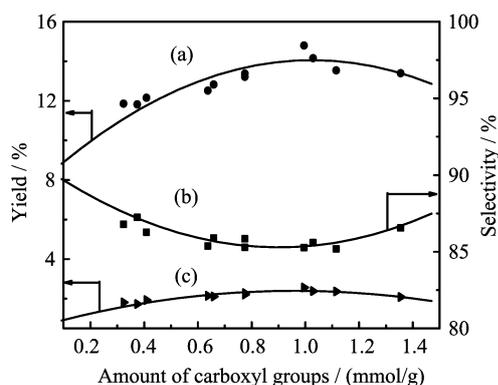


FIG. 7 The dependence of catalytic performance on the amount of carboxyl groups. Reaction conditions: 0.1 g catalyst, 1 mL (11.25 mmol) benzene, 3 mL (29.44 mmol) H_2O_2 , 10 mL acetonitrile, 70 °C, 6 h. (a) Yield of phenol, (b) the selectivity to phenol, and (c) yield of benzoquinone.

in Fig.7. As shown in Fig.7, at the beginning, the yield of phenol goes up with the increase of carboxyl groups. After going around the maximum, the yield of phenol goes down in spite of the high carboxyl group content, and the yield of benzoquinone has the same variation trend as that of phenol, while the selectivity to phenol exhibits the opposite tendency. The dependence of phenol yield on the amount of other surface oxygen groups was also studied, but no intimate correlation was observed. It is indicated that the surface carboxyl groups might be important for the target reaction.

To ascertain the contribution of the surface oxygen groups, AC and AC10 were treated in nitrogen flow at 1000 °C for 3 h to remove the surface oxygen groups, and then the catalytic activity of the obtained samples, named AC-1000 and AC10-1000, respectively, was tested under the same reaction conditions. The result of Boehm titration showed that the oxygen groups were actually removed by the calcinations in N_2 flow at 1000 °C. It is observed that after being treated at 1000 °C, their activity decreases drastically, as shown

TABLE VI Changes of surface area and catalytic performance of the two typical catalysts before and after being treated at 1000 °C. Reaction conditions: 0.1 g catalyst, 1 mL (11.25 mmol) benzene, 3 mL (29.44 mmol) H_2O_2 , 10 mL acetonitrile, 70 °C, 6 h.

Catalyst	$S_{\text{BET}}/(\text{m}^2/\text{g})$	Yield/%	Selectivity/%
AC	870	5.8	95.9
AC10	624	15.7	87.2
AC-1000	648	2.8	99.3
AC10-1000	591	5.6	95.3

TABLE VII The reusability of AC10 for the hydroxylation of benzene. Reaction conditions: 0.1 g catalyst; 1 mL (11.25 mmol) benzene, 3 mL (29.44 mmol) H_2O_2 , 10 mL acetonitrile, 70 °C, 6 h.

Run	Yield/%	Selectivity/%
1	15.3	86.6
2	11.1	90.9
3	11.1	88.6
4	10.2	93.3

in Table VI. These data confirmed that surface oxygen groups contributed mainly to the catalytic activity. However, it could not explain the decrease of the yields of both phenol and benzoquinone with higher carboxyl content. It was reported that the amount of benzene adsorbed on activated carbon decreases almost linearly with the decrease of the surface area of the samples [17]. When treated with nitric acid of lower concentration, the surface area of modified carbon increases, but when the concentration of nitric acid continues to increase, the surface area of samples starts to decrease, thereby lead to a decline of benzene adsorption. Moreover, when the concentration of nitric acid getting higher, there will be more oxygen groups especially carboxyl groups formed on the carbon materials. As hydrophilic groups, they may affect the competition adsorption of water and benzene on activated carbon surface. The reduced π -electronic density in the basal planes of the carbon reduces benzene and phenol adsorption [26, 35, 36]. These factors may inhibit the formation of phenol.

The stability of the catalyst was also tested and the results are listed in Table VII. It is shown that the activity decreases slightly after the first run, and keeps almost constant in the following runs. It indicates that the catalyst is rather stable for the target reaction.

IV. CONCLUSION

Modified activated carbon shows good catalytic performance for the direct hydroxylation of benzene to phenol. The amount of carboxyl groups is found to be the main factor which affects the catalytic performance. The highest activity is obtained over AC10 with proper

surface area and high amount of carboxyl groups, giving a yield of 15.7% with 87.2% selectivity to phenol.

V. ACKNOWLEDGMENTS

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