Supporting Information
For
Engineering surface groups of commercial activated carbon for benzene hydroxylation to phenol with dioxygen

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Supplementary Figures

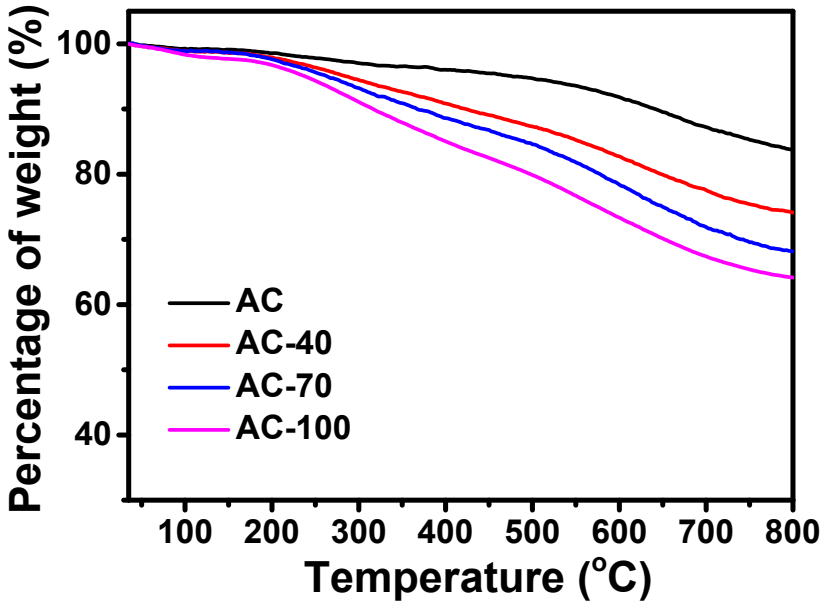

Figure S1. TG profiles of AC and AC-*x* series.

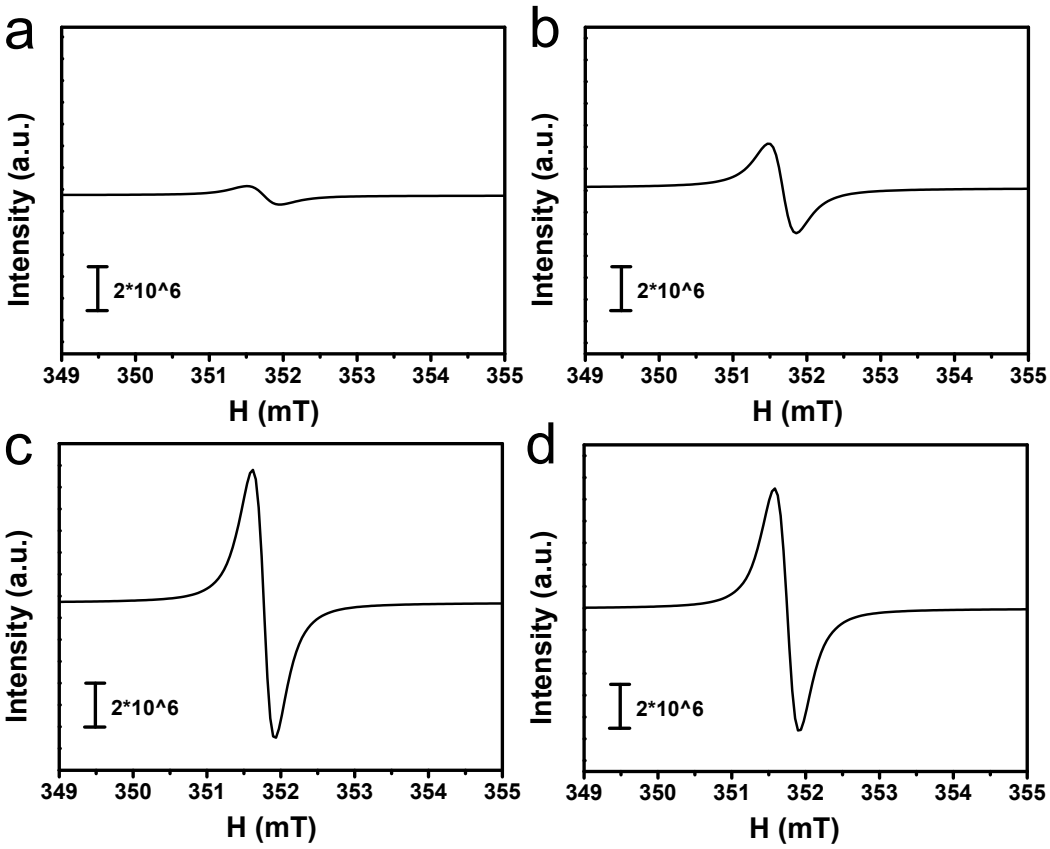

Figure S2. ESR spectrum of (a) AC, (b) AC-40, (c) AC-70 and (d) AC-100.

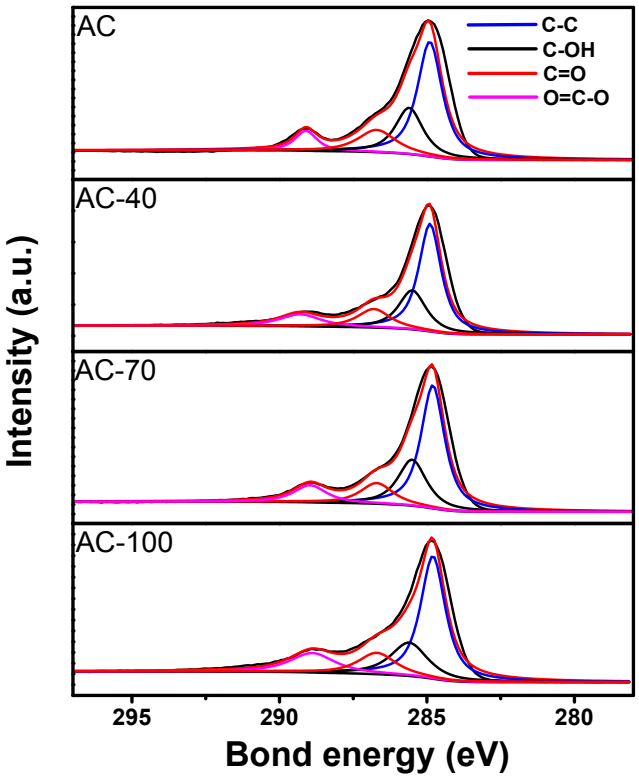

Figure S3. C 1s XPS spectra of AC and AC-*x* series.

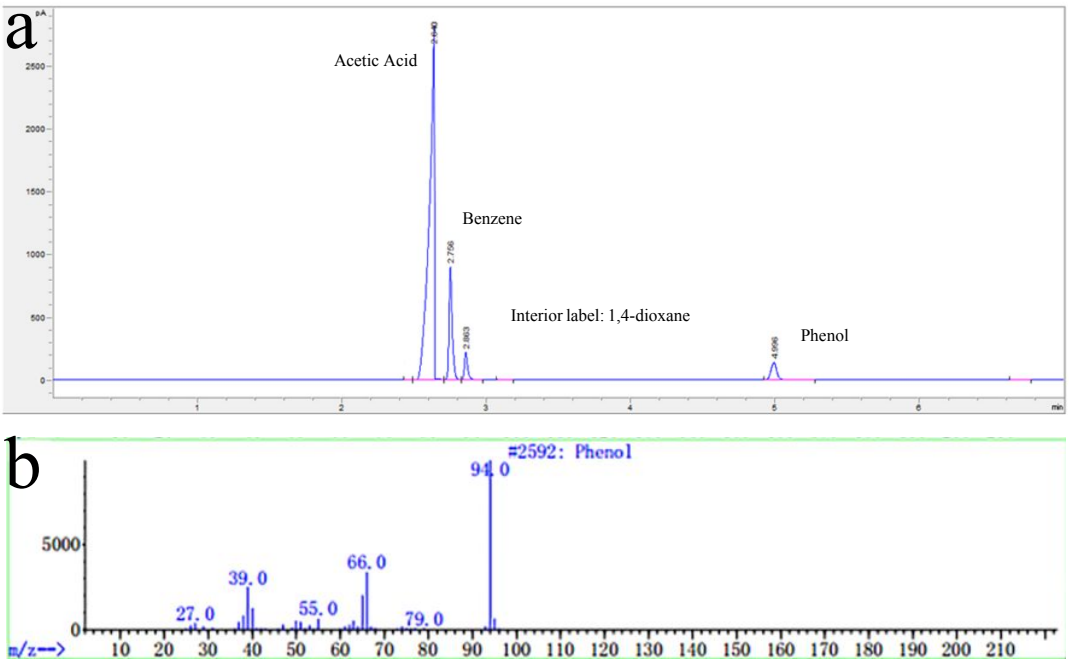

Figure S4. (a) The GC spectrum of reaction solution and (b) Mass spectrum of phenol obtained after 36 h in the AC-70 catalyzed benzene hydroxylation with O2. Reaction conditions: benzene (45 mmol), catalyst (0.2 g), LiOAc (0.6 g), acetic acid (15 mL), temperature (155 °C), water (10 mL) and oxygen pressure (2.2 MPa).

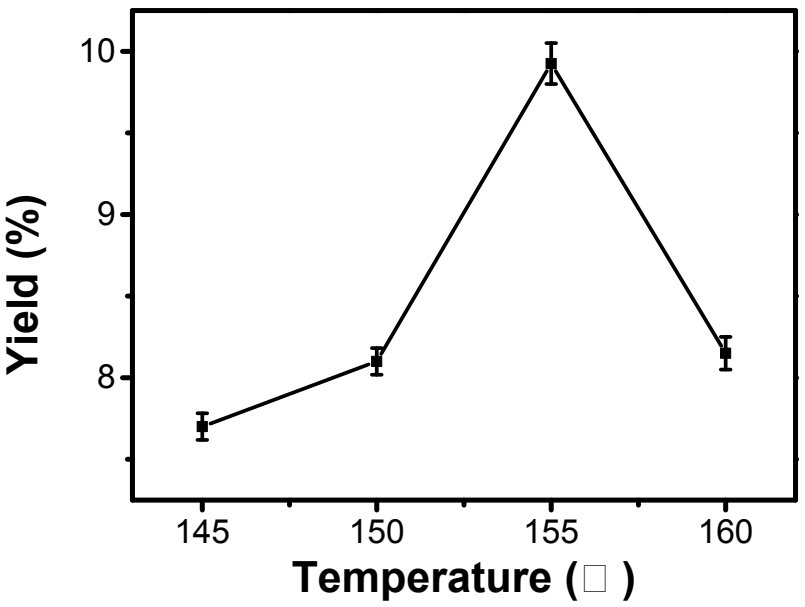

Figure S5. The phenol yield over AC-70 at different temperatures. Reaction condition: benzene (45 mmol), catalyst (0.2 g), LiOAc (0.6 g), acetic acid (15 mL), water (10 mL) and oxygen pressure (2.2 MPa).

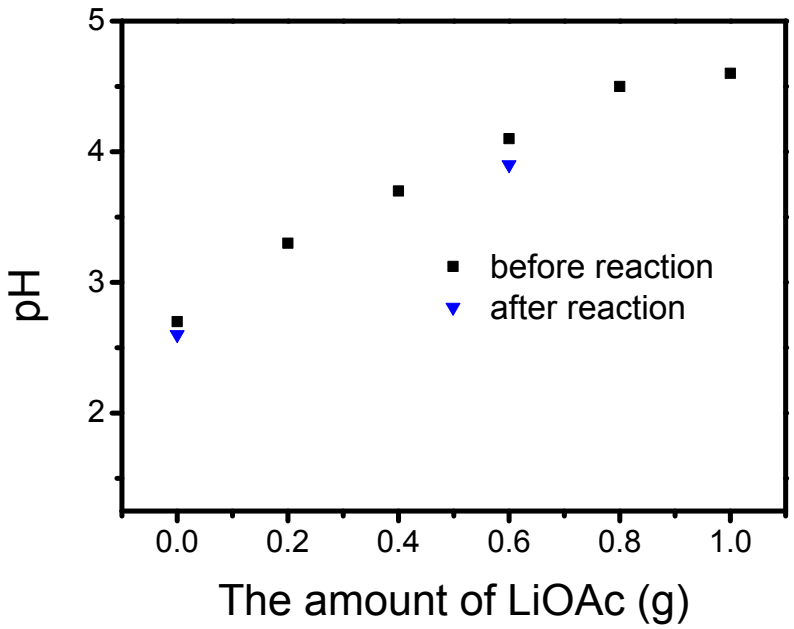

Figure S6. pH value of aqueous solution of acetic (60 vol.%, 25 mL) with different amounts of LiOAc.

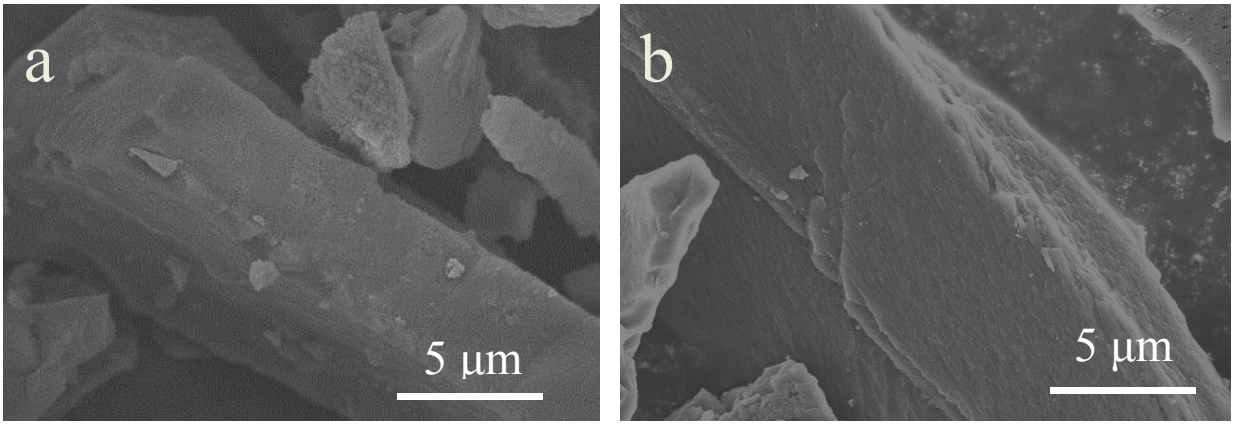

Figure S7. Comparison of SEM images of (a) fresh AC-70 and (b) recovered AC-70 after 5th run.

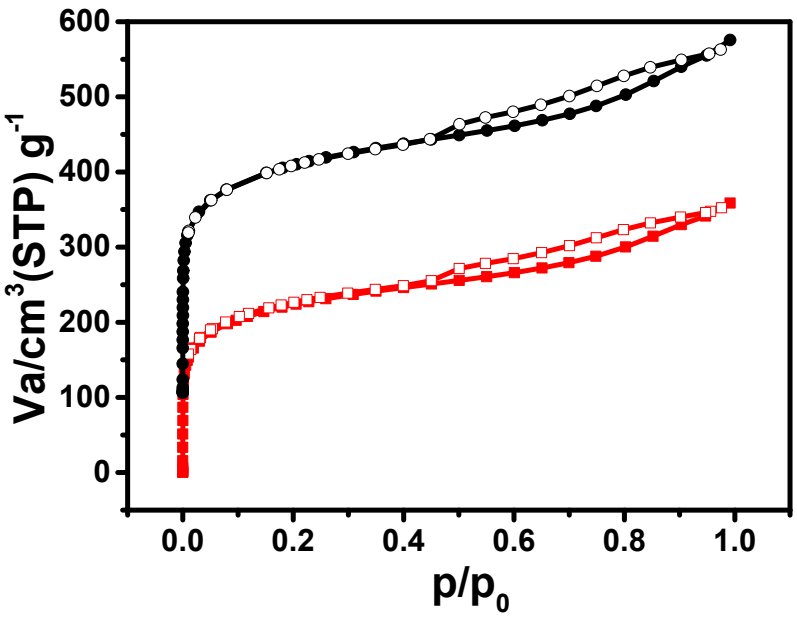

Figure S8. Comparison of N_2 sorption isotherms of fresh AC-70 (black line) and recovered AC-70 after 5th run (red line). The adsorption isotherm of fresh AC-70 is shifted by 100 cm^3 g^{-1}.

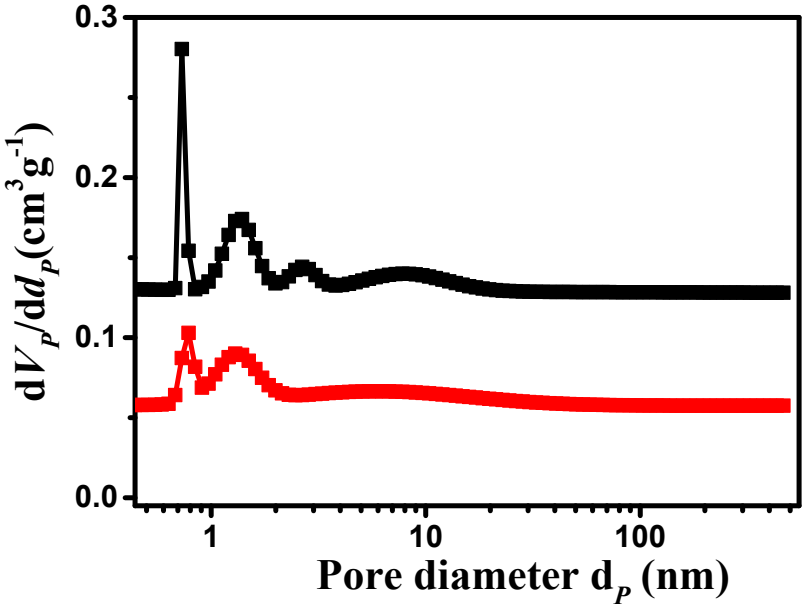

Figure S9. Comparison of pore size distribution curves of fresh AC-70 (black line) and recovered AC-70 after 5th run (red line). The pore size distribution curve of fresh AC-70 is shifted by 0.13 cm^3 g^{-1}.

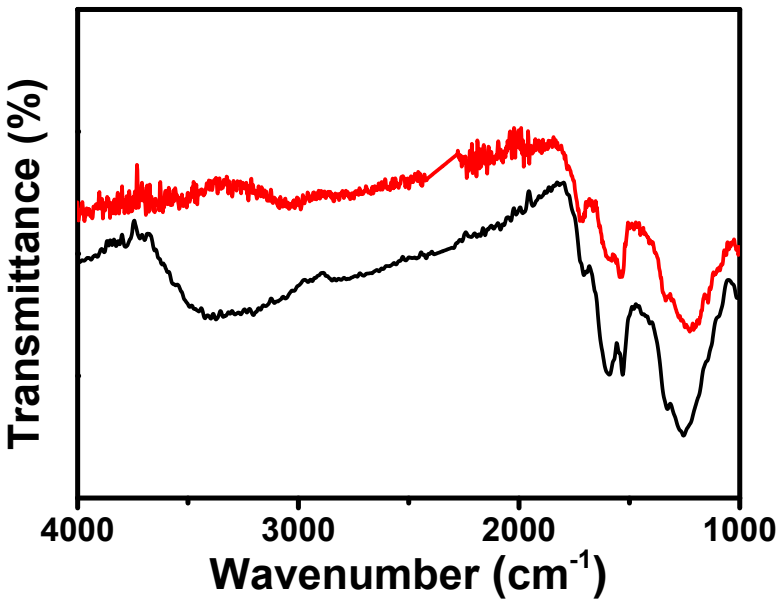

Figure S10. Comparison of FT-IR spectra of fresh AC-70 (black line) and recovered AC-70 after 5th run (red line).

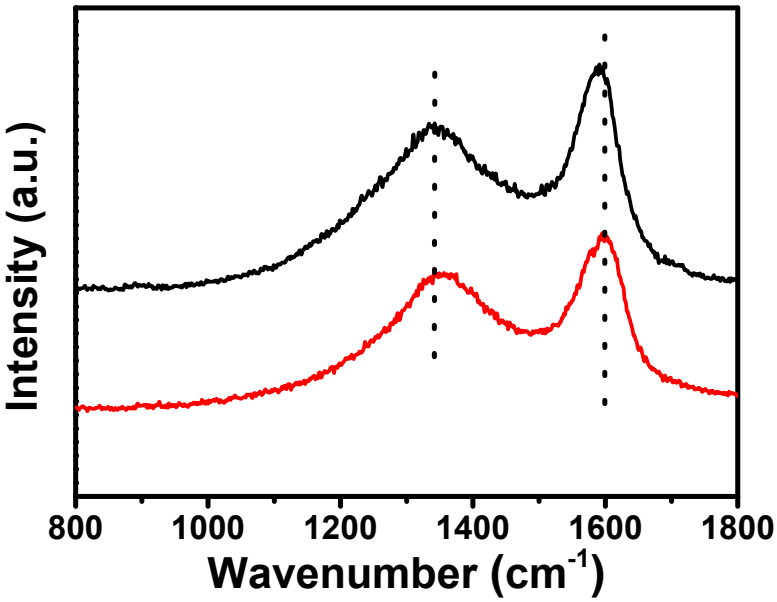

Figure S11. Comparison of Raman spectra of fresh AC-70 (black line) and recovered AC-70 after 5th run (red line).

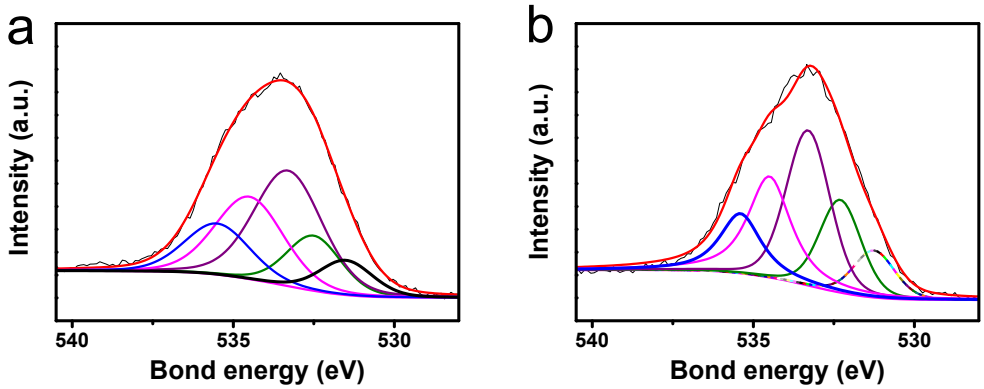

Figure S12. Comparison of O 1s XPS spectrum of (a) fresh AC-70 and (b) recovered AC-70 after 5th run.

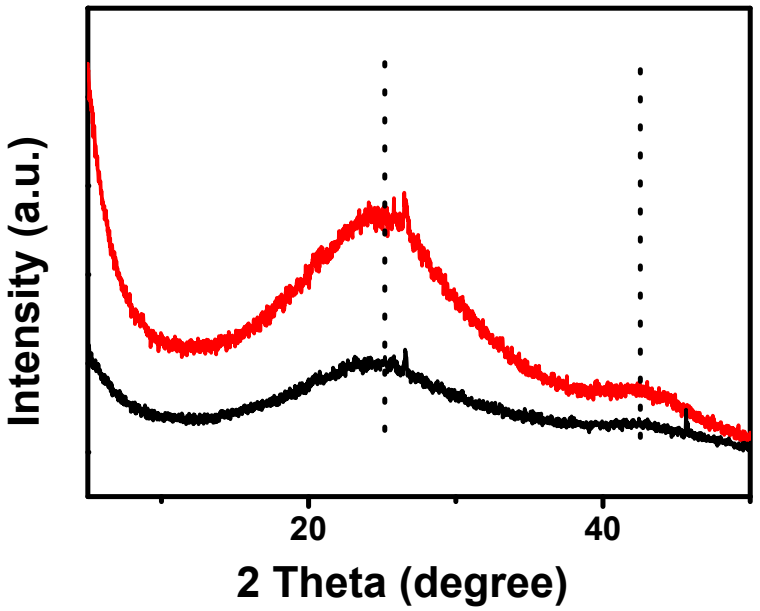

Figure S13. Comparison of XRD spectrum of AC-70 (black line) and recovered AC-70 after 5th run (red line).

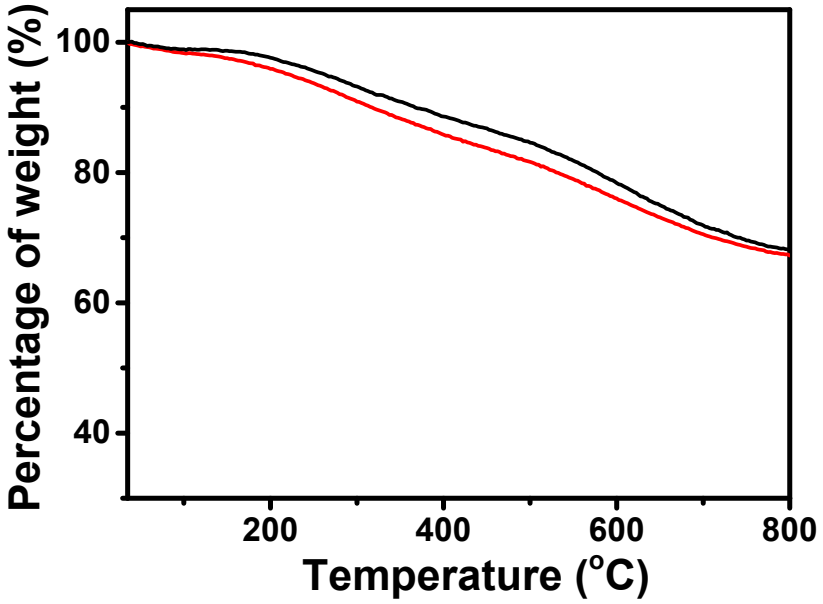

Figure S14. Comparison of TG profiles of recovered AC-70 (black line) and recovered AC-70 after 5th run (red line).

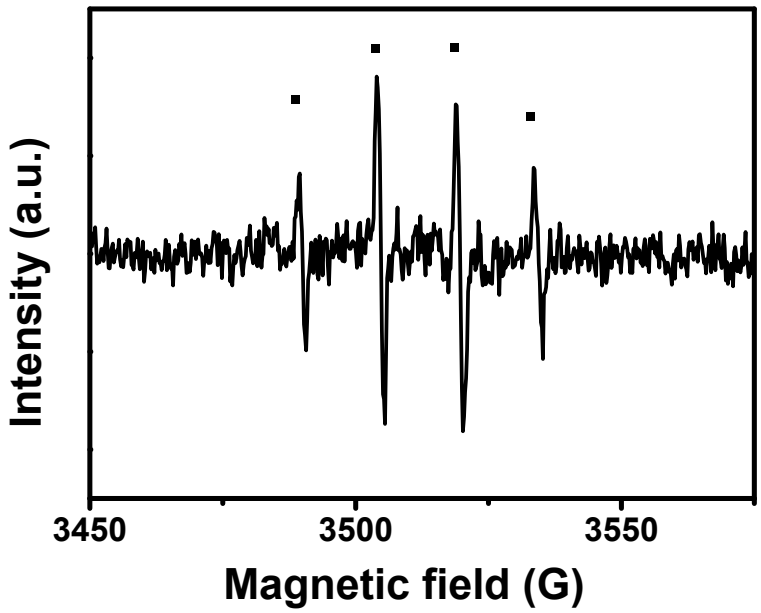

Figure S15. EPR spectrum of reaction mixture. Reaction conditions: DMPO (0.5mmol), catalyst (0.2 g), LiOAc (0.6 g), acetic acid (15 mL), water (10 mL), temperature (155 °C) and oxygen pressure (2.2 MPa).

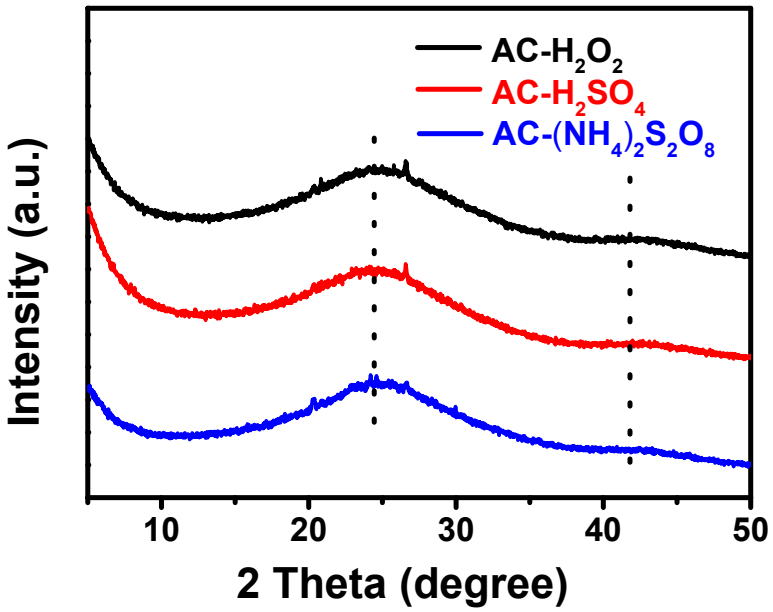

Figure S16. XRD patterns of modified AC samples.

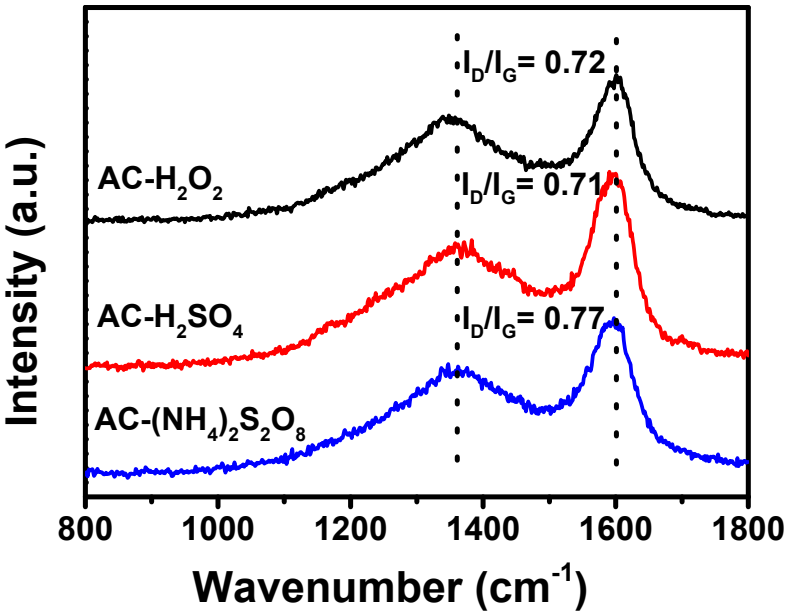

Figure S17. Raman spectra of modified AC samples.

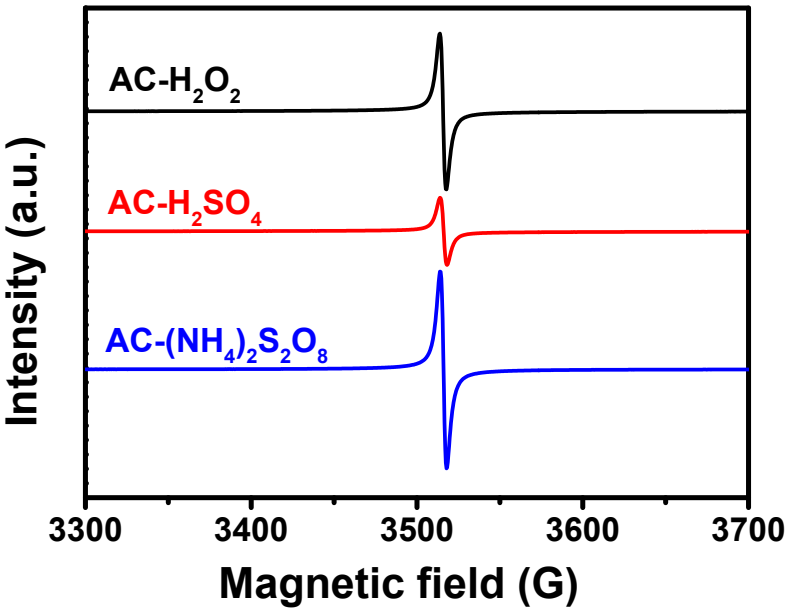

Figure S18. ESR spectra of modified AC samples.

Supplementary Tables

Table S1. Elemental analysis

Entry	Sample	C (wt.%)	H (wt.%)	N (wt.%)	Total O content[b] (wt%)
1	AC	74.1	3.2	0.6	22.2
2	AC-40	61.3	3.4	1.9	33.4
3	AC-70	58.3	3.2	2.1	36.5
4	AC-100	56.7	3.2	2.1	38.0
5[a]	AC-70	64.8	2.3	1.8	31.1

[a]Recovered AC-70 after 5th run. [b]The total oxygen content was evaluated by CHN elemental analysis, according to the following formula: O%=1−C%−H%−N% by assuming that there were mainly C, H, O and N element in AC and AC-*x* series.

Table S2. Summary of O 1s XPS result of AC-40, AC-70 and AC-100[a]

Sample	Surface O content (at%)	O1 (at%)	O2 (at%)	O3 (at%)	O4 (at%)	O5 (at%)
AC	13.9	0.34	2.72	4.41	4.17	2.26
AC-40	17.7	1.40	1.51	5.81	4.78	4.20
AC-70	22.2	1.90	3.08	8.07	5.76	3.39
AC-100	23.7	1.47	6.36	7.83	5.03	3.01
AC-70[b]	23.1	1.93	4.65	8.06	5.72	2.75

[a]O1: quinone carbonyl groups; O2: oxygen atoms in carboxyl groups; O3: ether functional groups; O4: oxygen atoms in phenol groups; O5: adsorbed water and/or oxygen.
[b]Recovered AC-70 after 5th run.

Table S3. Phenol yield at different reaction temperature over AC-70 catalyst [a].

Entry	Temperature (°C)	Yieldb (%)	Yieldc (%)	Yieldd (%)	Average yield (%)	Standard Deviation
1	145	7.6	7.8	7.7	7.7	0.082
2	150	8.2	8.1	8.0	8.1	0.082
3	155	10.1	9.8	9.9	9.9	0.13
4	160	8.3	8.1	8.1	8.15	0.10

[a]Reaction condition: benzene (45 mmol), catalyst (0.2 g), LiOAc (0.6 g), acetic acid (15 mL), water (10 mL) and oxygen pressure (2.2 MPa). [b]The yield in the 1st run. [c]The yield in the parallel 2nd run. [d] The yield in the parallel 3rd run.

Table S4. Benzene hydroxylation to phenol catalyzed by AC-70 under different reaction conditions[a]

Entry	Catalyst dosage (g)	P (MPa)	T (°C)	t (h)	Yield (%)
1[b]	0.2	2.2	155	36	1.2
2[c]	0.2	2.2	155	36	9.6
3[d]	0.2	2.2	155	36	1.7
4[e]	0.2	2.2	155	36	0.2

[a]Reaction conditions: benzene (45 mmol), acetic acid (15 mL) and water (10 mL). [b]LiOAc (0 g). [c]In the presence of 45 mmol BHT. [d]In the presence of 45 mmol DMSO. [e]Under N_2 atmosphere, N_2 pressure (2.2 MPa)

Table S5. Activity comparison of different catalysts in the benzene hydroxylation with O_2.

Entry	Catalyst	Catalyst type	Reaction system	Reducing agent	Phenol yield [%]	Ref.
1	V_xO_y@C-0.050–120	Transition metal	Heterogeneous	Ascorbic acid	9.4/2.2 (3rd recycle)	1
2	$Bipy_2PMoV_1$	Transition metal	Heterogeneous	Ascorbic acid	7.8/3.7 (4th recycle)	2
3	$[D\text{-}3\text{-}CNPy]_2HPMoV_2$	Transition metal	Heterogeneous	Ascorbic acid	13.0/6.8 (4th recycle)	3
4	$Pd(OAc)_2$	Noble metal	Homogeneous	none	10.5	4
5	C_3N_4-$PMoV_2$	Transition metal	Semi-Heterogeneous	none	13.6/2.1 (4th recycle)	5
6	C_3N_4-Ch_5PMoV_2	Transition metal	Semi-Heterogeneous	none	10.7/5.9 (4th recycle)	6
7	$HPA(V_2)$/HMS +$Pd(OAc)_2$	Noble metal	Heterogeneous	none	13.7/1.6 (3rd recycle)	7
8	VO–N–A	Transition metal	Heterogeneous	none	3.7/1.4 (5th recycle)	8
9	$[(C_3CNpy)_2Pd(OAc)_2]_2HPMoV_2$	Noble metal	Heterogeneous	none	9.8/2.1 (3rd recycle)	9
10	$[DiBimCN]_2HPMoV_2$@NC-560	Transition metal	Heterogeneous	none	10.5/6.1 (5th recycle)	10
11	FeC(5)	Transition metal	Heterogeneous	none	14.2/10.1 (5th recycle)	11
12	V-Zr/AC	Transition metal	Heterogeneous	none	8.67/7.78 (4th recycle)	12
13	NOC-0.15	Metal free	Heterogeneous	none	12.5/111.9 (6th recycle)	13
14	QAPs	Metal free	Heterogeneous	none	15.9/5.1(4th recycle)	14
15	AC-70	Metal free	Heterogeneous	none	10.1/9.4 (5th recycle)	This work

Table S6. Elemental analysis

Entry	Sample	C (wt.%)	H (wt.%)	N (wt.%)	Total O content[a] (wt%)
1	AC	74.1	3.2	0.6	22.2
2	AC-H_2O_2	68.6	4.2	0.3	26.9
3	AC-H_2SO_4	73.9	3.6	0.3	22.2
4	AC-$(NH_4)_2S_2O_8$	64.7	4.2	0.3	38.0

[a]The total oxygen content was evaluated by CHN elemental analysis, according to the following formula: O%=1−C%−H%−N% by assuming that there were mainly C, H, O and N element in modified AC samples.

Table S7. Summary of O 1s XPS result of AC-H_2O_2, AC-H_2SO_4 and AC-$(NH_4)_2S_2O_8$.[a]

Sample	Surface O content (at%)	O1 (at%)	O2 (at%)	O3 (at%)	O4 (at%)	O5 (at%)
AC-H_2O_2	18.8	1.74	2.78	4.86	5.20	4.22
AC-H_2SO_4	14.9	1.86	3.29	2.31	5.44	1.99
AC-$(NH_4)_2S_2O_8$	21.4	1.83	3.86	7.25	5.68	2.78

[a]O1: quinone carbonyl groups; O2: oxygen atoms in carboxyl groups; O3: ether functional groups; O4: oxygen atoms in phenol groups; O5: adsorbed water and/or oxygen.

Supplementary References

(1) Wang, W. T.; Ding, G. D.; Jiang, T.; Zhang, P.; Wu, T. B.; Han, B. X. Facile one-pot synthesis of VxOy@C catalysts using sucrose for the direct hydroxylation of benzene to phenol. *Green Chem.* **2013**, *15*, 1150.

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(12) Wang, W. T.; Li, N.; Shi, L. L.; Ma, Y. M.; Yang X. F. Vanadium-zirconium catalyst on different support for hydroxylation of benzene to phenol with O2 as the oxidant. *Appl. Catal. A-Gen.* **2018**, *553*, 117-125.

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(14) Wang, W. T.; Tang, H.; Jiang, X. L.; Huang, F. E.; Ma, Y. M. Quinone-amine polymers as metal-free and reductant-free catalysts for hydroxylation of benzene to phenol with molecular oxygen. *Chem. Commun.* **2019**, *55*, 7772.