Supporting information

Facile One-pot Synthesis of V_xO_y@C Catalysts Using Sucrose for Direct Hydroxylation of Benzene to Phenol

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Table S1 The V $2P_{3/2}$ of V_xO_y@C catalysts.

Entry	**Catalysts**	**V $2P_{3/2}$**
1	V_xO_y@C-0.293-120	516.5
2	V_xO_y@C-0.195-120	516.9
3	V_xO_y@C-0.098-120	516.9
4	V_xO_y@C-0.05-120	516.0
5	V_xO_y@C-0.025-120	515.5

Table S2 Catalytic performances of the V_xO_y@C catalysts prepared from different V precursors

Entry	**Catalysts**	**V% (ICP)**	**V $2P_{3/2}$**	**Phenol selectivity [%]**	**Phenol yield [%]**
1	V_xO_y@C-Cl	0.91	----[a]	96.6	5.9
2	V_xO_y@C-A	4.19	516.7	91.6	8.9

Reaction conditions: catalyst, 25 mg; ascorbic acid, 0.8 g; acetonitrile, 2.0 g; benzene, 1.0 mL; O_2 pressure, 3.0 MPa; temperature, 80 ^{o}C, time, 10 h.
[a] The V content was too low to be detected.

The vanadium content (4.19 wt%) and vanadium species (516.7 eV) of the V_xO_y@C-A detected from the XPS were similar to those of the V_xO_y@C-0.195-120 (Table 2 entry 2, 4.38 wt%; Table S1 entry 2, 516.9 eV). Therefore, the yield of phenol over the V_xO_y@C-A (8.9%) was similar to that over V_xO_y@C-0.195-120 (Table 2, 9.2%). The low vanadium content of the V_xO_y@C-Cl (0.91 wt%) was the main reason for that V_xO_y@C-Cl gave the low yield of phenol (5.9%).

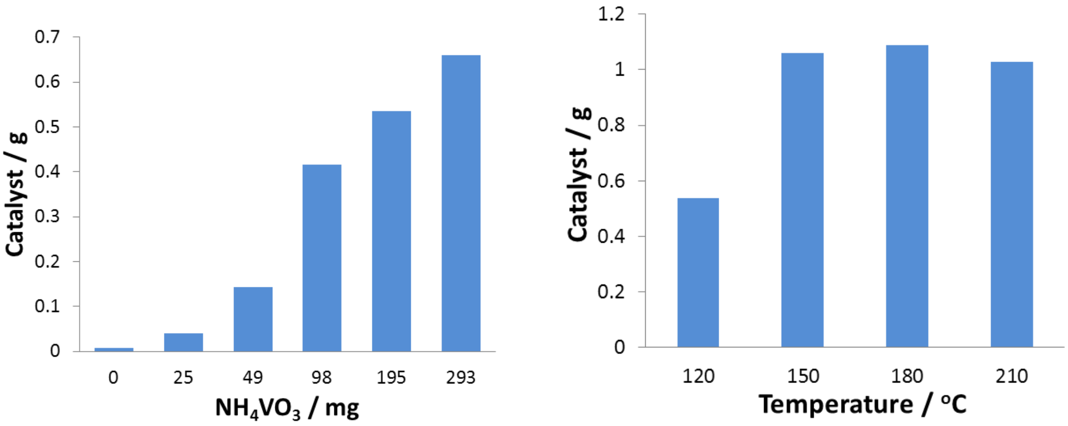

Fig. S1 The dependence of amount of catalysts obtained on the amount of NH_4VO_3 and the hydrothermal temperature.

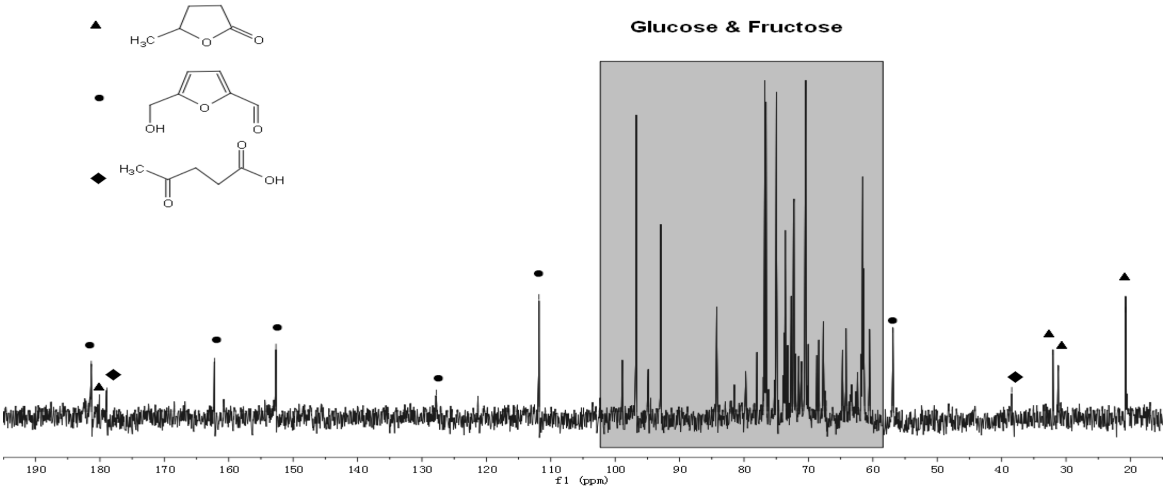

Fig. S2 ^{13}C NMR spectrum of the reaction solution of the hydrothermal process.

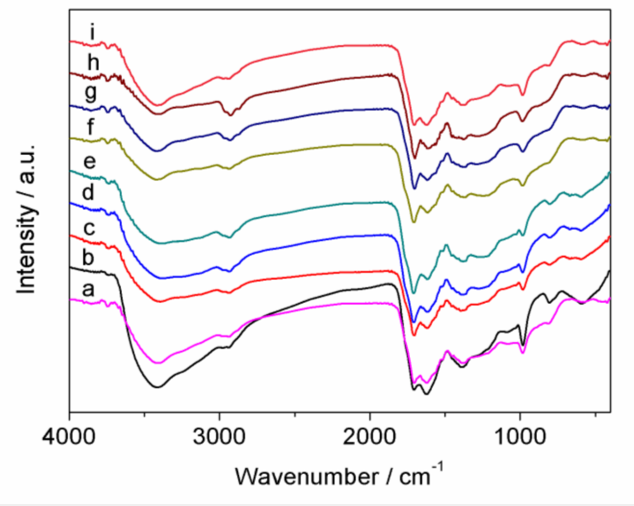

Fig. S3 FT-IR spectra of the catalysts
(a) V_xO_y@C-0.293-120, (b) V_xO_y@C-0.195-120, (c) V_xO_y@C-0.0.098-120,
(d) V_xO_y@C-0.05-120, (e) V_xO_y@C-0.025-120, (f) V_xO_y@C-0.195-150,
(g) V_xO_y@C-0.195-180, (h) V_xO_y@C-0.195-210, (i) V_xO_y@C-0.025-180.

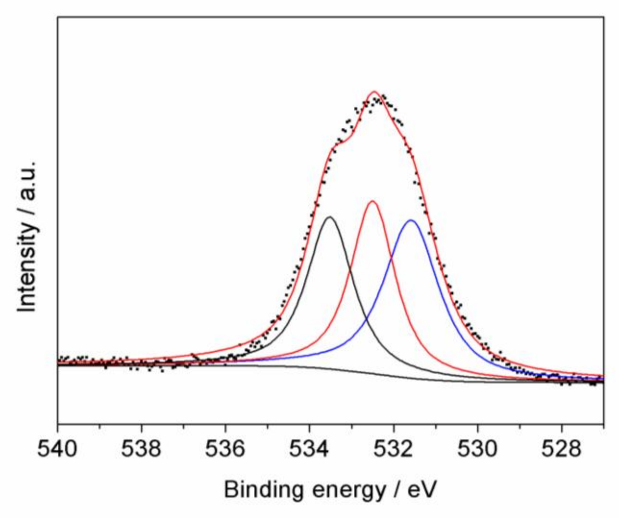

Fig. S4 O1s XPS spectrum of the V_xO_y@C-0.195-120.

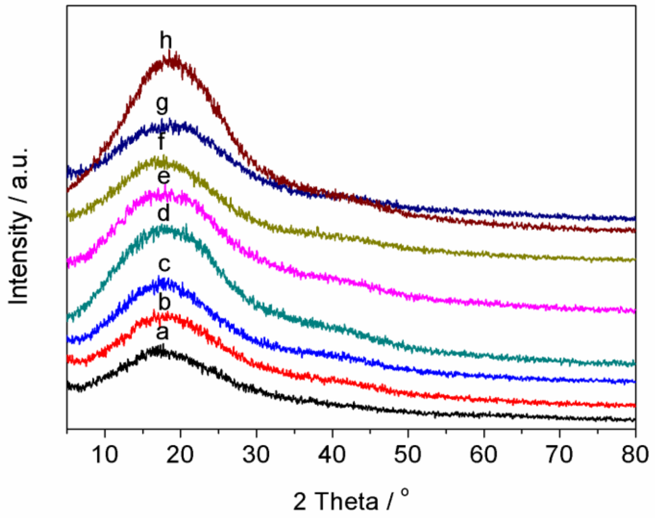

Fig. S5 XRD patterns of the catalysts
(a) V_xO_y@C-0.293-120, (b) V_xO_y@C-0.195-120, (c) V_xO_y@C-0.098-120,
(d) V_xO_y@C-0.025-120, (e) V_xO_y@C-0.195-150, (f) V_xO_y@C-0.195-180,
(g) V_xO_y@C-0.195-210, (h) V_xO_y@C-0.025-180.

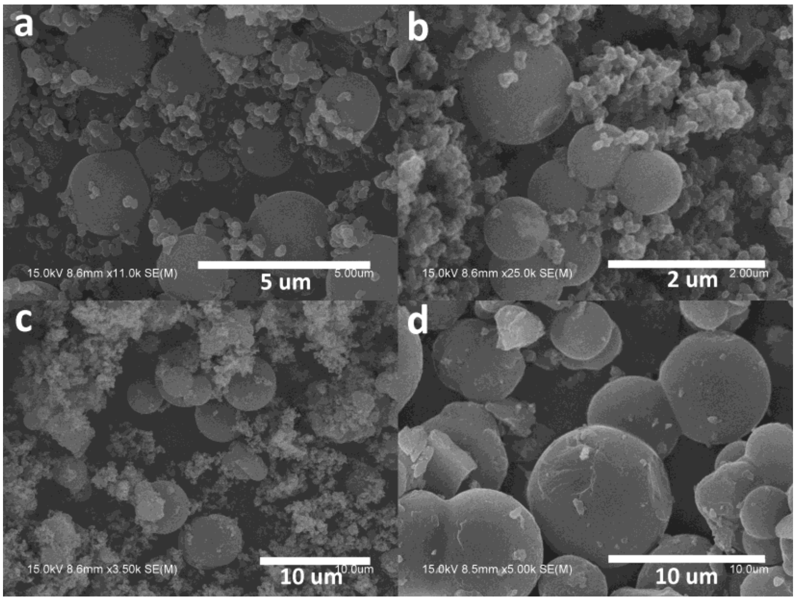

Fig. S6 The SEM images of V_xO_y@C catalysts. (a) V_xO_y@C-0.025-120, (b) V_xO_y@C-0.195-120,
(c) V_xO_y@C-0.195-180, (d) V_xO_y@C-0.025-180.

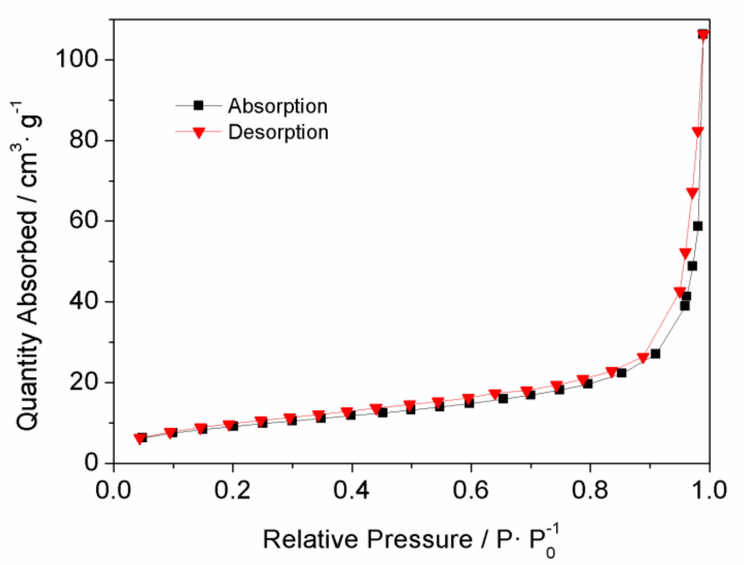

Fig. S7 Nitrogen adsorption-desorption isotherm of the V_xO_y@C-0.195-120.

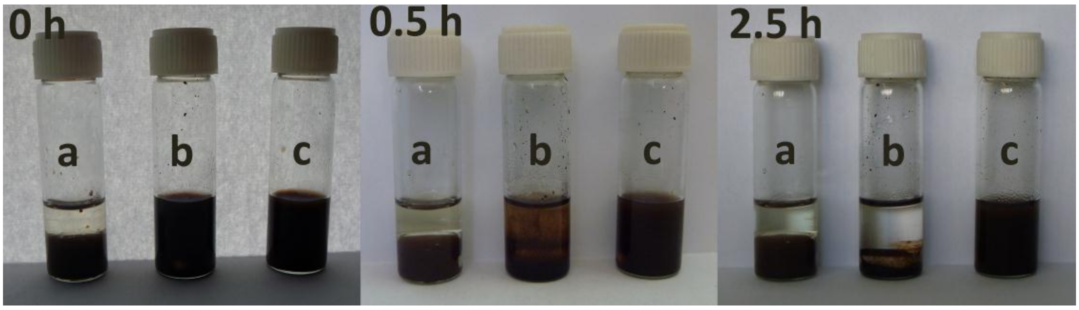

Fig. S8 The catalyst V_xO_y@C-0.195-120 dispersion mixtures stood for 0 h, 0.5 h and 2.5 h after stirring.

a, water+benzene; b, benzene; c, acetonitrile+benzene

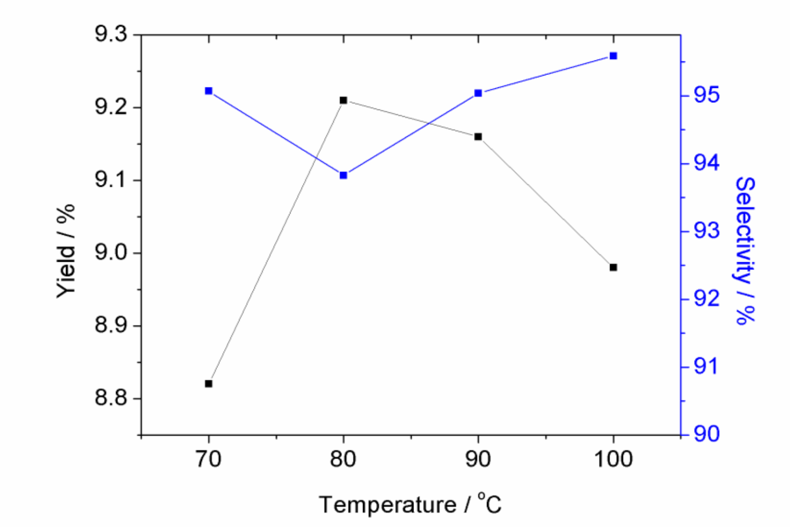

Fig. S9 The influence of reaction temperature on the hydroxylation of benzene to phenol over the V_xO_y@C-0.195-120 catalyst.

Reaction conditions: catalyst, 25 mg; ascorbic acid, 0.8 g; acetonitrile, 2.0 g; benzene, 1.0 mL; O_2 pressure, 3.0 MPa; reaction time, 10 h.

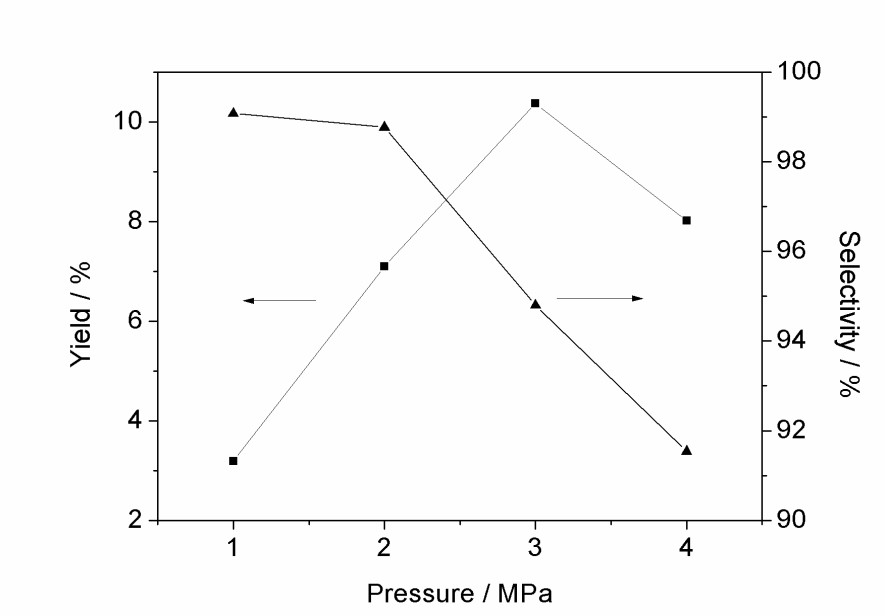

Fig. S10 The influence of oxygen pressure on the hydroxylation of benzene to phenol over the V_xO_y@C-0.195-120 catalyst.

Reaction conditions: catalyst, 25 mg; ascorbic acid, 0.8 g; acetonitrile, 2.0 g; benzene, 1.0 mL; temperature, 80 °C, reaction time, 10 h.

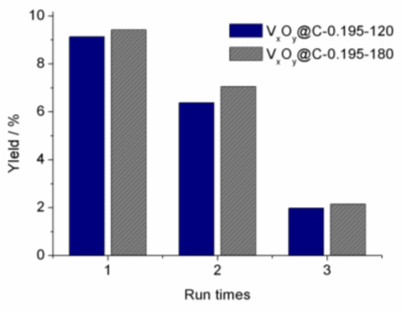

Fig. S11 Reuse of the catalysts for benzene hydroxylation

Reaction conditions: catalyst, 25 mg; ascorbic acid, 0.8 g; acetonitrile, 2.0 g; benzene, 1.0 mL; O_2 pressure, 3.0 MPa; temperature, 80 ^{o}C; reaction time, 10 h.

The reuse results of the V_xO_y@C catalysts are shown in Fig. S11. It can be found that the activity of the catalysts gradually declined, which may be due to the leaching of V. The supported vanadium catalysts for oxidation usually faced the situation of V leaching. Further investigation is required to improve the stability of the catalysts.