

Supplementary Information

Direct hydroxylation of benzene to phenol using H₂O₂ as an oxidant over vanadium-containing nitrogen doped mesoporous carbon catalysts†

Liya Hu, Cheng Wang, Bin Yue,* Xueying Chen and Heyong He*

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433, China.

E-mail addresses: yuebin@fudan.edu.cn (B. Yue), heyonghe@fudan.edu.cn (H. He); Tel.: +86 21 65643916.

Table S1 Optimization of various reaction conditions over 4.2V/NC-600 catalyst.

Entry	Catalyst amount (g)	nH ₂ O ₂ : nbenzene	Temperature (°C)	Time (h)	Solvent	Benzene conversion (%)	Phenol selectivity (%)	Phenol yield (%)
1	0.02	3	70	1	80 % acetic acid	21.6	92.5	20.0
2	0.02	3	70	2	80 % acetic acid	29.3	94.0	27.5
3	0.02	3	70	3	80 % acetic acid	31.0	97.2	30.1
4	0.02	3	70	4	80 % acetic acid	29.3	96.9	28.4
5	0.02	3	50	3	80 % acetic acid	14.4	90.0	13.0
6	0.02	3	60	3	80 % acetic acid	21.8	92.6	20.2
7	0.02	3	80	3	80 % acetic acid	30.5	96.3	29.4
8	0.01	3	70	3	80 % acetic acid	27.0	96.5	26.1
9	0.03	3	70	3	80 % acetic acid	26.8	98.1	26.3
10	0.02	1	70	3	80 % acetic acid	11.1	98.5	10.9
11	0.02	2	70	3	80 % acetic acid	20.5	98.1	20.1
12	0.02	4	70	3	80 % acetic acid	32.4	94.1	30.5
13	0.02	3	70	3	100 % acetic acid	17.7	98.3	17.4
14	0.02	3	70	3	90 % acetic acid	23.4	98.2	23.0
15	0.02	3	70	3	70 % acetic acid	29.4	94.2	27.7
16	0.02	3	70	3	acetone	3.2	99.3	3.2
17	0.02	3	70	3	acetonitrile	24.3	94.2	22.9

Reaction conditions: 0.4 mL of benzene, 5 mL of solvent, 30 wt% H₂O₂ as the oxidant.

The optimum reaction conditions: 0.02 g of catalyst amount, 70 °C of reaction temperature, 3 h of reaction time, 3 to 1 of H₂O₂ to benzene molar ratio, and 80 wt% of acetic acid solvent.

Table S2 Carbon balance closure.

Catalysts	Carbon in (mmol)	Carbon out (mmol)			Carbon balance closure (%) ^b
		Unreacted benzene	Phenol	Byproducts ^a	
- ^c	27.0	27.0	0	0	>99
NH ₄ VO ₃	27.0	24.3	2.2	0.5	>99
1.4V/NC-400	27.0	23.9	2.6	0.5	>99
1.4V/NC-500	27.0	22.5	4.0	0.5	>99
1.4V/NC-600	27.0	21.4	5.1	0.5	>99
1.4V/NC-700	27.0	23.5	3.2	0.3	>99
2.8V/NC-600	27.0	19.6	6.9	0.5	>99
4.2V/NC-600	27.0	18.6	8.1	0.2	>99
5.6V/NC-600	27.0	20.5	6.3	0.2	>99
4.2V/C-hexa	27.0	19.5	7.2	0.2	>99
NC-600	27.0	27.0	-	-	>99
C-hexa	27.0	27.0	0	0	>99

^a The total amount of hydroquinone and catechol.

^b The carbon balance closure was calculated as the molar ratio of carbon out to carbon in.

^c The blank experiment without any catalyst.

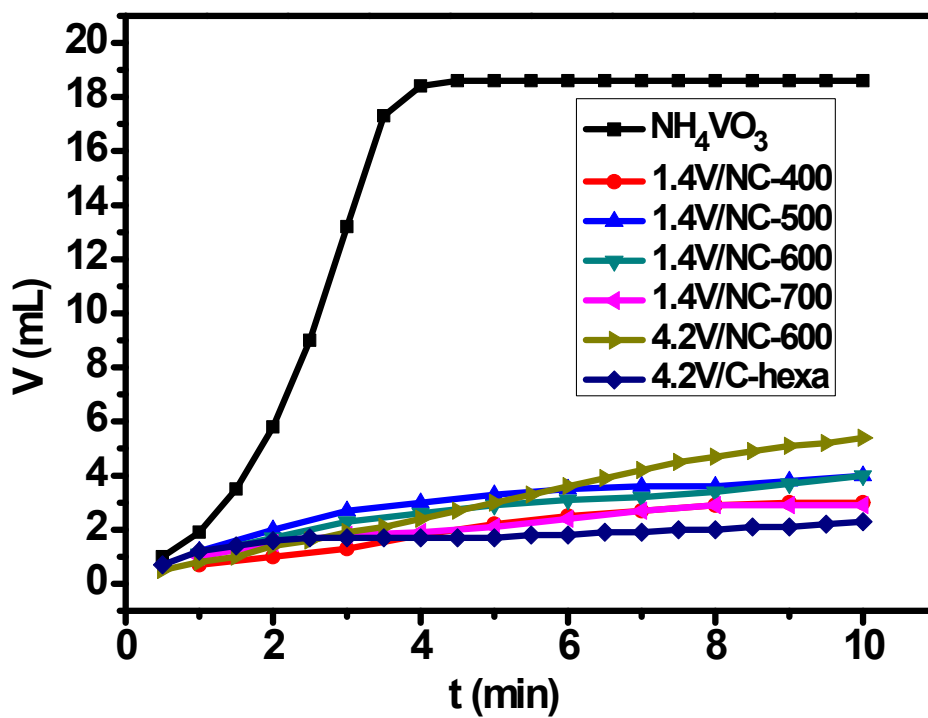


Fig. S1. Released oxygen volume as a function of reaction time.

Reaction conditions: 0.01 g catalyst, 5 mL of 80 wt% acetic acid, 0.2 mL of 30 wt% H₂O₂, 70 °C.