Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Nitrobenzene reduction catalyzed by carbon: If the reaction really belongs to carbocatalysis?

Shuchang Wu,[a] Guodong Wen,[a] Jia Wang,[a] Junfeng Rong,[b] Baoning Zong,[b] Robert Schlögl[c] and Dang Sheng Su*[a]

[a] Dr. S. C. Wu, Dr. G. D. Wen, J.Wang, Prof. D. S. Su
Shenyang National Laboratory for Materials Science
Institute of Metal Research, Chinese Academy of Sciences
72 Wenhua Road, Shenyang, 110016, China
[b] Prof. J. F. Rong, Prof. B. N. Zong
Research Institute of Petroleum Processing
18 Xueyuan Road, Haidian District, Beijing,100083, PR China
[c] Porf. R. Schlögl
Department of Inorganic Chemistry, Fritz Harber Institute of the Max Planck Society
Faradayweg 4-6, Berlin, 14195, Germany

* Corresponding author. E-mail: dssu@imr.ac.cn
Fax: (+86) 24-8397-0019

Synthesis of CMK-3

CMK-3 was synthesized according to previous report [1]. Briefly, 2 g of SBA-15 was added to a solution obtained by dissolving 2.5 g of sucrose and 0.3 g of H_2SO_4 in 10 g of H_2O. The mixture was placed in a drying oven for 6 h at 100 ^oC, and subsequently the mixture was placed in another drying oven at 160 ^oC and maintained for 6 h. The sample turned dark brown. After that, the sample containing partially polymerized and carbonized sucrose at the present step was treated again at 100 ^oC and 160 ^oC using the same drying oven after the addition of 1.6 g of sucrose, 0.18 g of H_2SO_4 and 10 g of H_2O. The carbonization was conducted by pyrolysis at 900 ^oC for 3 h under Ar atmosphere. The carbon-silica composite obtained after pyrolysis was treated with 10 wt % hydrofluoric acid at room temperature for 24 h, to remove the silica template. The final product obtained was filtered, washed with ethanol and dried at 110 ^oC for 12 h.

Catalytic reduction of nitrobenzene

Typically, a certain amount of catalyst, 1.2 g of nitrobenzene and 5.0 equivalent of hydrazine monohydrate were added in turn into a 25 ml round-bottom flask. The mixture was heated in an oil bath under a water-cooled condenser and kept for a period of time. Unless otherwise noted, the reaction temperature in this manuscript was the temperature of oil bath. When the reaction was finished, methanol/water (volume ratio 75:25) was added and the mixture was diluted exactly to 50 ml in a volumetric flask. The products were analyzed by HPLC (Elite, UV detector, mobile phase: 75/25 (v/v) methanol/water) with SinoChrom ODS-BP column.

Table S1 Metal contents (mg/ g) in carbon samples analyzed by ICP-AES

Catalyst	Fe	Al	Cu	Ni	Zn	Co
oCNT	4.36	0.74	1.20×10^{-3}	7.40×10^{-3}	0.28	0.80×10^{-3}
CMK-3	0.04	1.23	-	-	0.02	-

Table S2 XPS analyses of both the fresh and the used samples

Catalyst	C (at %)	O (at %)	C=O (at %)	O=C-O (at %)	C-O (H) (at %)	C/O ratio
oCNT	94.3	5.7	1.3	2.5	1.9	16.5
oCNT-used	94.2	4.6	0.9	1.9	1.8	20.5

Table S3 Nitrobenzene reduction in the presence of HHT related materials [a]

Entry	Catalyst	Conv. (%)	Sel. (%)
1[b]	-	12.0	98.5
2 [c]	-	14.0	98.0
3	HHT	23.3	99.9
4 [d]	HHT500	23.3	99.6
5 [d]	HHT800	26.4	99.9
6 [e]	HHT-*f*-800	22.7	99.5

[a] Condition: 20 mg of catalyst, 1.2 g of nitrobenzene, 5.0 equivalent of hydrazine monohydrate, 100 °C, 4 h. [b] No catalyst was added. [c] 2 mL of concentrated HCl and 2 mL of concentrated HNO_3 were firstly added into the round-bottom flask and then evaporated completely at 100 °C before adding reactants. The reaction condition is the same as reported in [a]. [d] 10 mL of concentrated HNO_3 was firstly added into the round-bottom flask and evaporated completely at 100 °C followed by the addition of 10 mL of concentrated HCl and 0.2 g of HHT. When the solution was completely vaporized, the obtained material was labeled as HHT-*imp*. HHT-*imp* was annealed in Ar flow at 500 °C and 800 °C to prepare HHT500 and HHT800, respectively. [e] HHT-*imp* was washed with concentrated HCl, after filtration and washing with distilled water, the obtained material was annealed at 800 °C in Ar flow, and was denoted as HHT-*f*-800.

The blank test showed that the activity was quite low (Table S2, entry 1). After intentionally introducing some metal impurities (if any), a slight increase of activity was observed (Table S2, entry 2). But this slight increase may also be due to experimental error. HHT which had hardly any oxygenated groups exhibited low activity (Table S2, entry 3). After introduction of some metal contaminants (from HCl and HNO_3) and the subsequent thermal annealing under noble gas, the obtained HHT500 provided no improved activity (Table S2, entry 4). Although HHT800 exhibited only a slight higher activity, this improvement could not be observed if the HHT-*imp* was washed with HCl followed by filtration process. These results suggested that the metal contaminants that were introduced by acid treatment and thermal annealing had negligible effect on the activity.

Table S4 Nitrobenzene reduction catalyzed by 9, 10-anthraquinone in the presence of carboxylic acids

Entry	Additive	Conv. (%)	Sel. (%)
1	no	77.1	98.8
2 [a]	Terephthalic acid	49.9	99.1
3 [b]	Formic acid	59.5	98.2
4 [b]	Acetic acid	57.2	98.6

Conditions: 20 mg of 9, 10-anthraquinone, 1.2 g of nitrobenzene, 5.0 equivalent of hydrazine monohydrate, 2 mL of ethanol, 100 ^{o}C, 5 h.

[a] 20 mg of additive. [b] 20 μL of additives.

Due to the basicity of the hydrazine and the acidity of the additives, some reductant would be consumed by the added acid. However, the amount of the reductant (50.93 mmol) used in the reaction was much higher than that of the additives (only 0.12 mmol for terephthalic acid), so the amount of hydrazine that was consumed by the additives could be neglected.

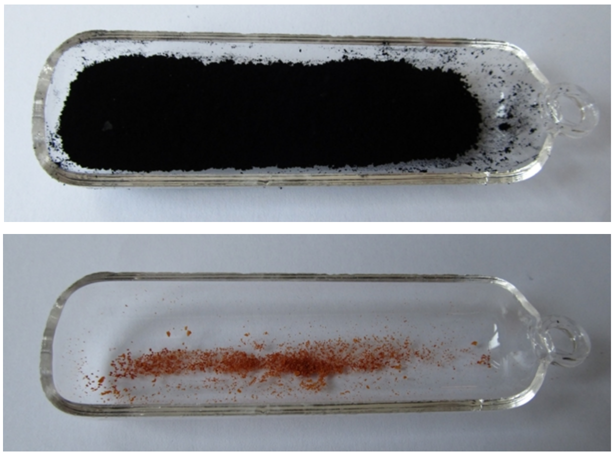

Figure S1 Digital photographs of oCNT before (top) and after (down) calcination under air

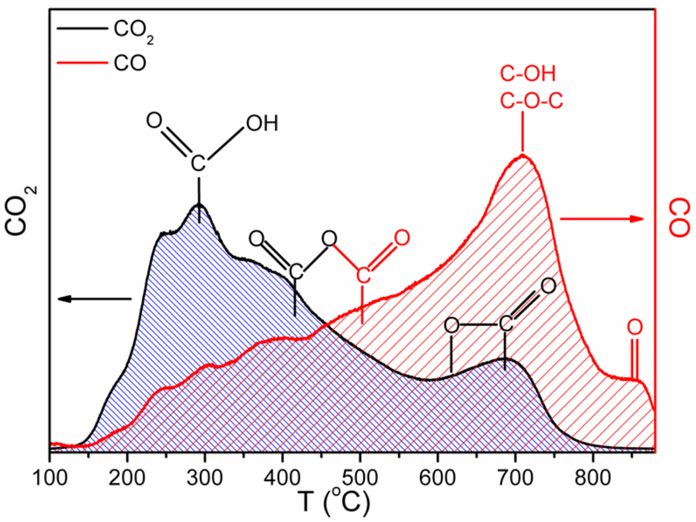

Figure S2 TPD profile of oCNT. Condition: 100 mg of oCNT, He, 50 ml/ min, 10 °C/ min, 900 °C [2-3]

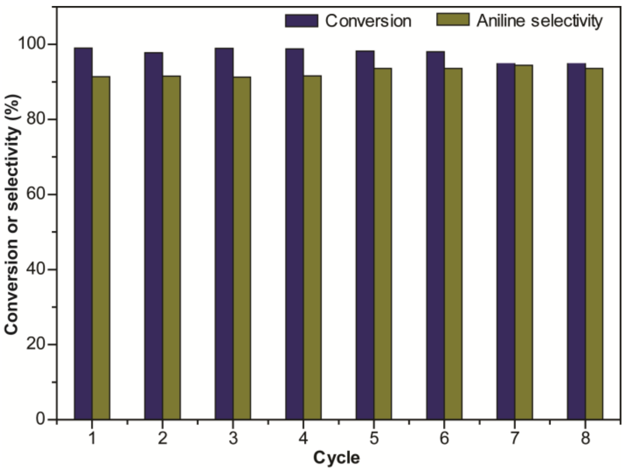

Figure S3 Recycling test of oCNT [3]

Reaction condition: 20 mg of oCNT, 1.2 g of nitrobenzene, 6.0 equivalent of hydrazine monohydrate, 100 °C, 4 h.

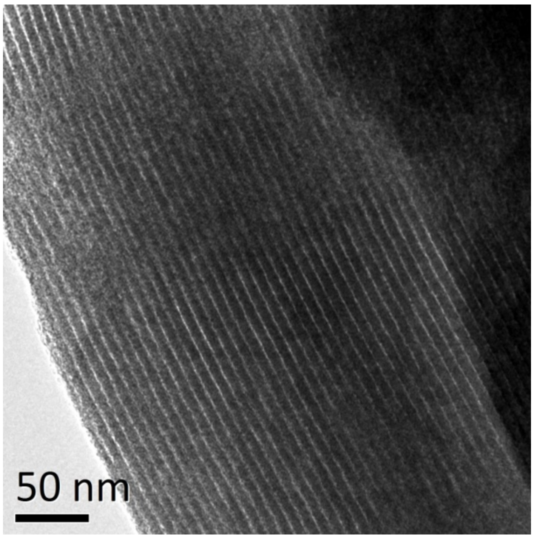

Figure S4 TEM image of CMK-3

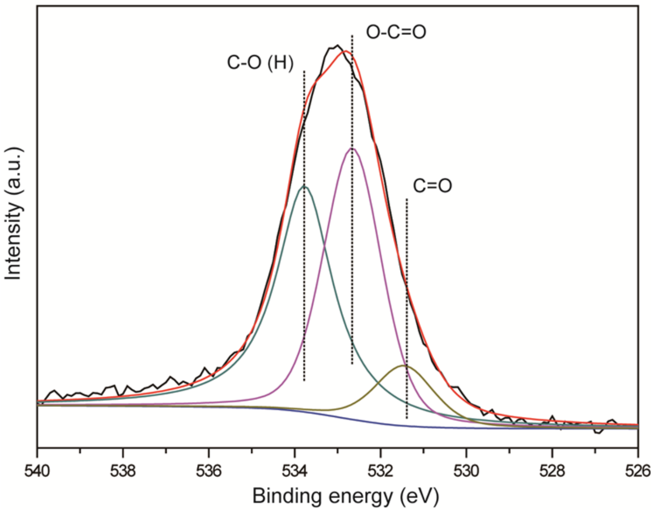

Figure S5 XPS O1s spectrum of CMK-3

[1] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.*, 2000, 122, 10712-10713.

[2] B.W. Zhong, H.Y. Liu, X.M. Gu, D.S. Su, *ChemCatChem*, 2014, 6, 1553-1557

[3] S.C. Wu, G.D. Wen, B.W. Zhong, B.S. Zhang, X.M. Gu, N. Wang, D.S. Su, *Chin. J. Catal.*, 2014, 35, 914-921.