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## Nitrobenzene reduction catalyzed by carbon: does the reaction really belong to carbocatalysis?†

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The reduction of nitrobenzene could proceed in the presence of carbon. The activity mainly originated from carbonyl groups on the carbon surface instead of metal impurities which were embedded in the carbon.

Reactions catalyzed by carbon are an interesting topic, and attract an increasing amount of attention. The past several years have witnessed the rapid development of carbon-catalyzed reactions (carbocatalysis) in both gas phase<sup>1–5</sup> and liquid phase.<sup>6–11</sup> For example, carbon nanotubes (CNTs) or nanodiamond showed good to excellent performance in oxidative dehydrogenation of ethylbenzene and *n*-butane;<sup>1–4</sup> graphite oxide was tested to be an efficient catalyst for oxidation of various alcohols;<sup>6</sup> nitrogen doped graphene played an important role in the reduction of 4-nitrophenol.<sup>11</sup>

One critical task during carbocatalysis is to determine the activity of carbon material in the presence of metal impurities, and ascertain that the metal impurities have no or negligible effect on the reaction. For example, during the synthesis of CNTs, in spite of the post-purification such as acid or base treatment, a low content of residual metal catalyst was still unavoidable.<sup>12</sup> There were several reports on the reactions in which even a trace amount of metal impurities had a significant effect. It was suggested that trace quantities of copper were critical in some arylation reactions;<sup>13</sup> van Bokhoven and co-workers found that the residual nickel

instead of fullerene was the real active species in the hydrogenation of nitrobenzene,<sup>14</sup> which contradicted the conclusion from Xu's group.<sup>9</sup> CNTs containing residual Co and Fe were quite active for NH<sub>3</sub> decomposition.<sup>15</sup> In addition, metal contaminants also played a great part in some electrocatalytic reactions.<sup>16,17</sup>

Although confusing in some cases, the study of carbocatalysis was important from both a scientific and a practical point of view. The high activity of metal impurities could not rule out the possibility that carbon was an efficient catalyst in some reactions. Three methods were generally used to detect if a reaction was a true carbocatalysis process: deliberately loading the possible metal onto carbon; removing functional groups; and using a model catalyst. For oxidative dehydrogenation of *n*-butane or liquid phase oxidation of cyclohexane, the loading of Fe had negligible effect on the reaction, suggesting that the activity actually originated from carbon.<sup>2,8</sup> For thiophenol oxidation catalyzed by graphite oxide (GO), it was difficult to exclude the contributions from metal impurities, but graphite and hydrazine-reduced GO which have only a small amount of oxygen functional groups exhibited quite low activity, confirming that the activity was mainly attributed to the oxygenated groups on GO.<sup>18</sup> In addition, the application of a model catalyst was also an efficient method. For example, the good performance of 1-pyrenecarboxylic acid in the oxidative coupling reaction of amines confirmed that the carboxylic group was the active site on GO catalysts.<sup>19</sup> The reduction of nitroarenes is an important process, and there were instances where different carbon materials were used as catalysts, but few of them excluded the effect of metal impurities.<sup>9,20–23</sup> It was reported that metals such as Fe were highly active for this reaction.<sup>24–27</sup> Unfortunately, Fe was commonly used as a growth catalyst in the preparation of carbon materials such as CNTs and graphene. So it was necessary to find out if the reaction was a real carbocatalysis process when carbon was used as catalyst. We have found that aromatic compounds with carbonyl or hydroxyl groups could serve as good catalysts for nitrobenzene

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† Electronic supplementary information (ESI) available: Digital photographs of oCNT before and after calcination, nitrobenzene reduction catalyzed by HHT related materials as well as by 9,10-anthraquinone in the presence of carboxylic acids, recycling test and TPD profile of oCNT, TEM image of CMK-3 and XPS analyses of fresh and used oCNT and O1s spectrum of CMK-3. See DOI: 10.1039/c4cy00811a

reduction,<sup>28</sup> while carbon was also active for the reaction in which the carbonyl groups provided an important kind of active site.<sup>29</sup> Herein, more convincing information is provided on the carbon-mediated reduction of nitrobenzene. This approach includes intentionally masking certain oxygenated groups as well as using both model catalysts and carbon which was synthesized under metal-free conditions. The results confirmed that carbon was indeed active in the reaction, and the activity mainly originated from carbonyl groups.

We first studied nitrobenzene reduction in the presence of CNTs. The commercial CNTs were synthesized by chemical vapor deposition using Fe as a growth catalyst. After washing with concentrated HCl at room temperature for 24 h, the purified sample was denoted as rCNT. To obtain the oxidized sample (oCNT), rCNT was treated with concentrated HNO<sub>3</sub> in a 120 °C oil bath for 2 h, and the product was rinsed with distilled water, followed by drying at 110 °C. HCl could remove the exposed Fe catalyst, while HNO<sub>3</sub> could not only remove the exposed Fe contaminants, but also introduces oxygen functional groups on the CNT surface. However, as the TEM image showed, there was still residual Fe after acid treatment (Fig. 1). To demonstrate the existence of Fe, we calcined the oCNT at 800 °C under air atmosphere. After calcination, the 1.0 g of black oCNT powder transformed into about 7 mg of red iron oxide (Fig. S1†), suggesting that Fe indeed existed even after treatments of two kinds of acid. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis also showed that metal impurities existed in the oCNT (Table S1†). These Fe nanoparticles were embedded in the channels of CNT, and could not come into contact with the acid. As a result, these particles may also be unable to interact with reactants during the reaction.

The surface oxygen functional groups could be removed by thermal treatment under a noble gas atmosphere. X-ray photoelectron spectroscopy (XPS) characterizations were carried out to detect the oxygen bonding configurations as well as

elemental contents in CNT samples. C=O was attributed to carbonyl group, and O=C-O was assigned to carboxylic group, anhydride, lactone and ester (Fig. 2). On the other hand, hydroxyl group and ether were labeled as C-O (H). The total content of oxygen on oCNT was 5.7 at%, in which O=C-O was found to be the dominant kind of functionality (Table 1).

After calcination under Ar flow at 500 °C for 2 h, there was decrease in the total content of oxygen as well as different oxygen containing functional groups on the obtained oCNT500. However, O=C-O seemed to be most unstable, a large amount of it having been stripped due to thermal treatment, while about 50% of the other two kinds of oxygen functionalities were still present. When oCNT was calcined at 800 °C (oCNT800), the oxygen functional groups further decreased: only about 1.0 at% of oxygen was left on the surface. In addition, the result from temperature programmed desorption (TPD) revealed similar information (Fig. S2†). These results suggested that surface oxygenated groups could be easily introduced or to some extent selectively removed by oxidation or calcinations. In comparison, the thermal treatment at or below 800 °C could not remove Fe impurities, as the melting point and boiling point of iron are 1537 °C and 2862 °C, respectively.

The catalytic performances of different samples were summarized in Table 2. oCNT revealed moderate activity in the reduction of nitrobenzene (Table 2, entry 1). However, after the decomposition of a large amount of O=C-O, the activity notably improved from 40.2% to 95.5%, although there was a slight decrease in aniline selectivity (Table 2, entry 2).

The total content of oxygen and carbonyl groups was quite low for oCNT800. As expected, an obvious deactivation was observed when oCNT800 was used as the catalyst (Table 2, entry 3). The performance of each catalyst suggested that the oxygenated groups and not the Fe impurities were mainly responsible for the activity. oCNT was taken as an example to

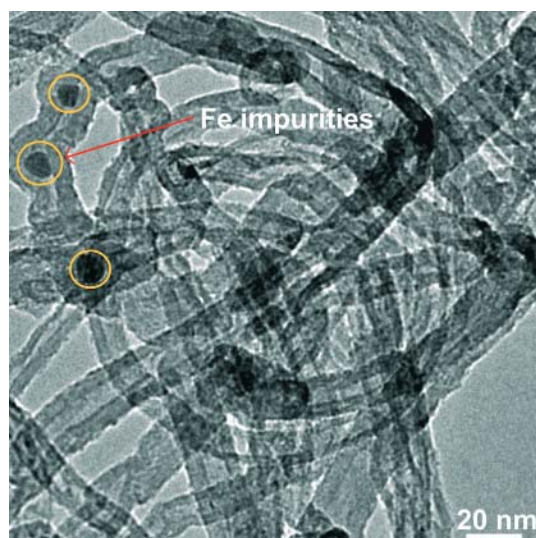


Fig. 1 TEM image of oCNT.

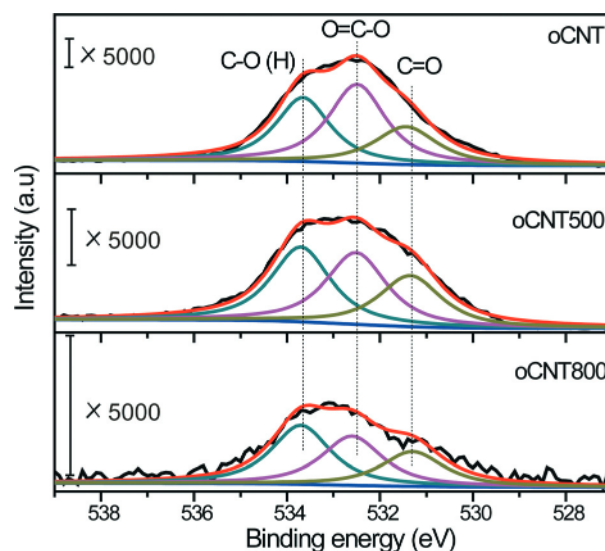


Fig. 2 XPS O1s spectra of CNT samples.

**Table 1** Oxygen content of different CNT samples

Catalyst	O (at%)	C=O (at%)	O=C-O (at%)	C-O (H) (at%)
oCNT	5.7	1.3	2.5	1.9
oCNT500	2.4	0.6	0.9	0.9
oCNT800	1.0	0.2	0.4	0.4

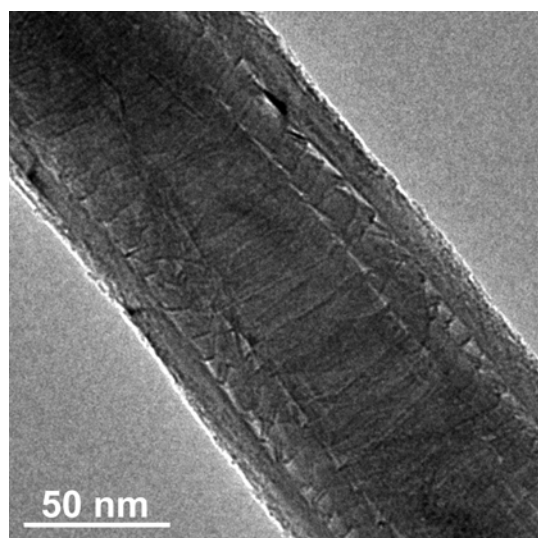
**Table 2** Nitrobenzene reduction in the presence of different catalysts<sup>a</sup>

Entry	Catalyst	Conv. (%)	Sel. (%)
1	oCNT	40.2	97.5
2	oCNT500	95.5	91.9
3	oCNT800	22.2	99.8
4	oCNT800 <sup>b</sup>	49.7	96.9
5	No <sup>c</sup>	5.9	100
6	oCNT <sup>d</sup>	21.9	96.5
7	PH-oCNT <sup>d</sup>	6.2	99.9
8	oCNT500 <sup>d</sup>	78.9	94.6
9	PH-oCNT500 <sup>d</sup>	36.5	95.1

<sup>a</sup> Reaction conditions: 20 mg of catalyst, 1.2 g of nitrobenzene, 5.0 equivalent of hydrazine monohydrate, 90 °C, 3 h. <sup>b</sup> 60 mg of catalyst. <sup>c</sup> No catalyst. <sup>d</sup> 100 mg of catalyst, 60 °C.

study the stability of the carbon catalyst, the results showing that oCNT was still very active for the 8th run (Fig. S3†), and a small change was observed for the content of oxygen functional groups (Table S2†).

It was necessary to note that most of the chemicals contained metal impurities, and different treatments may have led to different, new contaminants, and may have changed the chemical state of existing contaminants. In order to ascertain that the main activity did not originate from these newly formed impurities, we performed some more tests. We used highly graphitized multiwalled carbon nanofibers (labeled as HHT) as a catalyst due to its simplified structure (Fig. 3). There were hardly any oxygen functional groups on the surface, and the amount of structure defects was quite low. As a

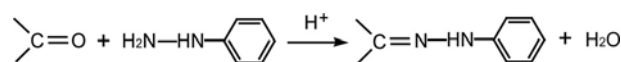
**Fig. 3** TEM image of HHT.

result, we could easily study the effect of possible impurities that may be introduced during different treatments. The catalytic results showed that the contribution of the potential contaminants could be neglected (Table S3†).

We previously proposed that the carbonyl group was critical to the reaction, while the carboxylic group and anhydride had a negative effect. In addition, the surface area, morphology, structure defects and other kinds of oxygenated groups played insignificant roles,<sup>29</sup> but more convincing proof was still needed. Masking the carbonyl group was considered a good method. If the catalyst exhibited suppressed activity, that would suggest an important role for the carbonyl group. On the other hand, the carbonyl group would be shown to have no positive effect if the activity is improved or remained the same. We used phenylhydrazine to mask the carbonyl group as reported previously.<sup>30</sup> This method was based on the reaction between the carbonyl group and phenylhydrazine, during which HCl served as catalyst (Scheme 1). After the carbonyl groups on oCNT and oCNT500 were masked, the obtained materials were denoted as PH-oCNT and PH-oCNT500, respectively (for more detailed information including the characterization of the catalyst, please refer to ref. 30). The activity decreased notably after the carbonyl group was masked compared to the fresh sample (Table 2, entries 6–9), which confirmed that the carbonyl group indeed played an important role in the reaction. The residual activity of both PH-oCNT and PH-oCNT500 may be derived from structural defects, edges and other oxygenated groups such as hydroxyl groups.

To further illustrate the important role of carbonyl groups as well as the fact that the reaction could proceed readily under metal-free conditions, we used 9,10-anthraquinone and anthracene as two model catalysts (Fig. 4a).

We have studied the performances of a series of model catalysts with different oxygenated groups in nitrobenzene reduction,<sup>28</sup> and here the catalyst without any functional group was also investigated to make a comparison. Only about 22% of nitrobenzene conversion was obtained after 5 h when anthracene was used as catalyst, suggesting that anthracene, which has no oxygenated groups, was inactive (Fig. 4b). In comparison, the reaction proceeded very well in the presence of 9,10-anthraquinone: 47.8% of the nitrobenzene was converted within 1 h, and after 5 h only 3% of the substrate was left. In addition, the aniline selectivity was above 97% during the whole process. As the same molar amount of each catalyst was loaded during the reaction, the results strongly demonstrated that the carbonyl group was of paramount importance for the reaction and the reaction could occur without metal or metal oxide. If carboxylic acids were added to the reaction system, an obvious decrease in conversion of nitrobenzene was observed (Table S4†),

**Scheme 1** Reaction between a carbonyl group and phenylhydrazine.

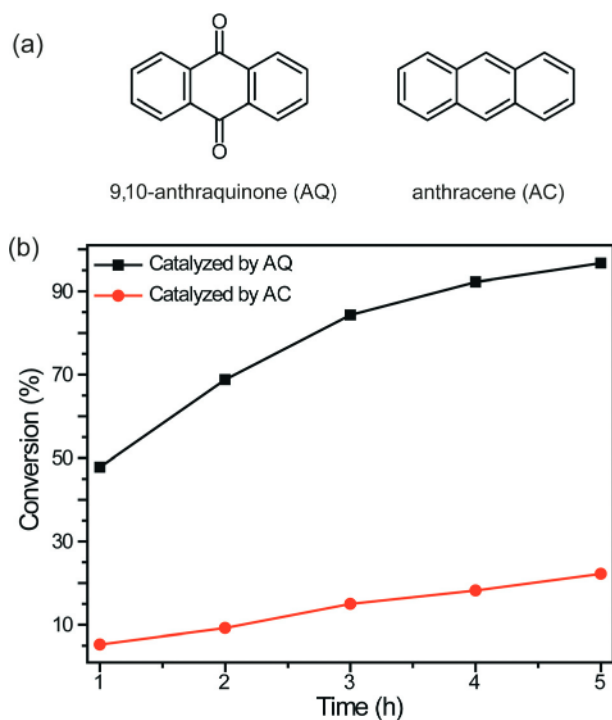


Fig. 4 Structure of (a) two model catalysts and (b) their catalytic performances. Reaction conditions: 14.4 mmol of catalyst, 1.2 g of nitrobenzene, 6 equivalents of hydrazine monohydrate, 2 mL of ethanol, 100 °C.

revealing the negative role of carboxylic groups, which was in accordance with the results when CNT samples worked as catalysts. These results suggested that the activity was dominated not only by the active groups (carbonyl groups), but also the negative functionalities (such as carboxylic groups). So there was no linear correlation between the activity and the content of carbonyl group. This was the reason that the conversion of nitrobenzene was about 50% rather than around 95% when 60 mg of oCNT800 was added in the reaction (Table 2, entry 4).

We then used CMK-3 as catalyst. The CMK-3 was synthesized by a hard-templating method,<sup>31</sup> during which no metal was added, and as a result, there may be no metal contaminant in the catalyst. The obtained carbon had an ordered mesoporous structure (Fig. S4†), with carbonyl groups on the surface and a total oxygen content of about 3.0 at% (Fig. S5†). The catalytic tests demonstrated that the CMK-3 showed moderate activity in nitrobenzene reduction (Table 3, entries 1–3), suggesting that the reaction could indeed proceed readily in the absence of a metal catalyst. In order to improve the activity, the CMK-3 was oxidized by nitric acid during which different kinds of oxygen-containing groups were introduced on the carbon surface. It was shown that the nitric acid oxidation played an important role in enhancing the activity of the carbon catalyst, although the aniline selectivity decreased to some extent (Table 3, entries 4–5).

In conclusion, we have studied nitrobenzene reduction in the presence of carbon materials as well as aromatic model

Table 3 Nitrobenzene reduction catalyzed by CMK-3<sup>a</sup>

Entry	Loading (mg)	Conv. (%)	Sel. (%)
1	20	50.6	99.2
2	50	75.3	96.3
3	80	88.3	91.2
4 <sup>b</sup>	20	87.6	87.6
5 <sup>b,c</sup>	15	95.0	89.3

<sup>a</sup> Reaction conditions: the respective loading of catalyst, 1.2 g of nitrobenzene, 5.0 equivalents of hydrazine monohydrate, 100 °C, 3 h.

<sup>b</sup> The CMK-3 was oxidized by nitric acid at 120 °C for 2 h. <sup>c</sup> 5 h.

catalysts. It was revealed that the reaction could occur under metal-free conditions, and the activity was mainly derived from carbonyl groups. As far as oCNT was concerned, Fe still remained as an impurity, but had no or marginal effect on the reaction, because it was embedded in the carbon and could not interact with the reactants. By calcination of the oCNT at different temperatures together with masking certain groups, the carbonyl group was also tested to be a critical active site. These findings provide a method to test whether a reaction belongs to carbocatalysis or not and pave a way for designing efficient metal-free catalysts.

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## Notes and references

- G. Mestl, N. I. Maksimova, N. Keller, V. V. Roddatis and R. Schlögl, *Angew. Chem., Int. Ed.*, 2001, **40**, 2066.
- J. Zhang, X. Liu, R. Blume, A. H. Zhang, R. Schlögl and D. S. Su, *Science*, 2008, **322**, 73.
- D. S. Su, N. I. Maksimova, G. Mestl, V. L. Kuznetsov, V. Keller, R. Schlögl and N. Keller, *Carbon*, 2007, **45**, 2145.
- X. Liu, B. Frank, W. Zhang, T. P. Cotter, R. Schlögl and D. S. Su, *Angew. Chem., Int. Ed.*, 2011, **50**, 3318.
- J. Zhang, D. S. Su, R. Blume, R. Schlögl, R. Wang, X. G. Yang and A. Gajović, *Angew. Chem., Int. Ed.*, 2010, **49**, 8640.
- D. R. Dreyer, H. P. Jia and C. W. Bielawski, *Angew. Chem., Int. Ed.*, 2010, **49**, 6813.
- H. Huang, J. Huang, Y. M. Liu, H. Y. He, Y. Cao and K. N. Fan, *Green Chem.*, 2012, **14**, 930.
- H. Yu, F. Peng, J. Tan, X. W. Hu, H. J. Wang, J. Yang and W. X. Zheng, *Angew. Chem., Int. Ed.*, 2011, **50**, 3978.
- B. J. Li and Z. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 16380.
- Y. B. Kuang, N. M. Islam, Y. Nabaee, T. Hayakawa and M. Kakimoto, *Angew. Chem., Int. Ed.*, 2010, **49**, 436.

- 11 X. K. Kong, Z. Y. Sun, M. Chen, C. L. Chen and Q. W. Chen, *Energy Environ. Sci.*, 2013, 6, 3260.
- 12 P. R. Chen, L. M. Chew and W. Xia, *J. Catal.*, 2013, 307, 84.
- 13 S. L. Buchwald and C. Bolm, *Angew. Chem., Int. Ed.*, 2009, 48, 5586.
- 14 L. Pacosová, C. Kartusch, P. Kukula and J. A. van Bokhoven, *ChemCatChem*, 2011, 3, 154.
- 15 J. Zhang, M. Comotti, F. Schüth, R. Schlögl and D. S. Su, *Chem. Commun.*, 2007, 1916.
- 16 C. E. Banks, A. Crossley, C. Salter, S. J. Wilkins and R. G. Compton, *Angew. Chem., Int. Ed.*, 2006, 45, 2533.
- 17 M. Pumera and Y. Miyahara, *Nanoscale*, 2009, 1, 260.
- 18 D. R. Dreyer, H. P. Jia, A. D. Todd, J. X. Geng and C. W. Bielawski, *Org. Biomol. Chem.*, 2011, 9, 7292.
- 19 C. L. Su, M. Acik, K. Takai, J. Lu, S. J. Hao, Y. Zheng, P. P. Wu, Q. L. Bao, T. Enoki, Y. J. Chabal and K. P. Loh, *Nat. Commun.*, 2012, 3, 1298.
- 20 B. H. Han, D. H. Shin and S. Y. Cho, *Tetrahedron Lett.*, 1985, 26, 6233.
- 21 J. W. Larsen, M. Freund, K. Y. Kim, M. Sidovar and J. L. Stuart, *Carbon*, 2000, 38, 655.
- 22 Y. J. Gao, D. Ma, C. L. Wang, J. Guan and X. H. Bao, *Chem. Commun.*, 2011, 47, 2432.
- 23 H. Y. Zhou, L. Shi and Q. Sun, *Chin. J. Catal.*, 2012, 33, 1463.
- 24 S. Kim, E. Kim and B. M. Kim, *Chem. – Asian J.*, 2011, 6, 1921.
- 25 K. Junge, B. Wendt, N. Shaikh and M. Beller, *Chem. Commun.*, 2010, 46, 1769.
- 26 R. V. Jagadeesh, G. Wienhöfer, F. A. Westerhaus, A. E. Surkus, M. M. Pohl, H. Junge, K. Junge and M. Beller, *Chem. Commun.*, 2011, 47, 10972.
- 27 R. V. Jagadeesh, A. E. Surkus, H. Junge, M. M. Pohl, J. Radnik, J. Rabeah, H. M. Huan, V. Schünemann, A. Brückner and M. Beller, *Science*, 2013, 342, 1073.
- 28 S. C. Wu, G. D. Wen, X. M. Liu, B. W. Zhong and D. S. Su, *ChemCatChem*, 2014, 6, 1558.
- 29 S. C. Wu, G. D. Wen, B. W. Zhong, B. S. Zhang, X. M. Gu, N. Wang and D. S. Su, *Chin. J. Catal.*, 2014, 35, 914.
- 30 W. Qi, W. Liu, B. S. Zhang, X. M. Gu, X. L. Guo and D. S. Su, *Angew. Chem., Int. Ed.*, 2013, 52, 14224.
- 31 S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, 122, 10712.