Model Molecules with Oxygenated Groups Catalyze the Reduction of Nitrobenzene: Insight into Carbocatalysis

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The role of different oxygen functional groups on a carbon catalyst was studied in the reduction of nitrobenzene by using a series of model molecules. The carbonyl and hydroxyl groups played important roles, which may be ascribed to their ability to activate hydrazine. In comparison, the ester, ether, and lactone groups seemed to be inactive, whereas the carboxylic group had a negative effect. The reaction occurred most likely through a direct route, during which nitrosobenzene may be converted directly into aniline.

For a long time, carbon was mainly used as a support for metal catalysts,^[1] but it is in fact also a catalyst in its own right.^[2] Recent years have witnessed the rapid development of

carbon-catalyzed reactions. Besides gas-phase reactions, such as the oxidative dehydrogenation of ethylbenzene and light alkanes,^[3] carbon materials have shown potential applications in several important liquid-phase reactions that were conventionally catalyzed by metal or metal oxide.^[3] Bielawski and coworkers found that graphite oxide was an efficient catalyst for some oxidation and hydration reactions.^[4] The Kakimoto group developed a nitric acid assisted nanoshell carbon-catalyzed method for the oxidation of alcohols.^[5] In addition, carbon materials also played an important role in reactions such as the ring opening of epoxides,^[6] oxidative coupling,^[7] and oxidation of cyclohexane.^[8]

Selective reduction of nitroarenes represents an important method for the preparation of the corresponding aromatic amines from both an industrial and a scientific point of view. It was reported that natural graphite,^[9] fullerene,^[10] and reduced graphene oxide^[11] could effectively catalyze the reduction of nitrobenzene. However, the detailed catalytic roles of

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	Supporting information for this article is available on the WWW under

http://dx.doi.org/10.1002/cctc.201402070.

the carbon catalysts in the reactions and especially the actual identities of the active sites are still under discussion. Mechanistic research over carbon catalysts remains a challenge because of their complex surface structure and the co-existence of various kinds of functional groups. In addition, undetermined impurities may also contribute to the catalytic activity of carbon materials.^[12] Consequently, the application of a model catalyst could be an effective method.^[13]

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Carbon materials such as graphite oxide, graphene, carbon nanotubes, and active carbon can be considered as carbon atoms grouped into layers of fused aromatic rings, and there are commonly many kinds of oxygenated groups on their surface. To study the role of various oxygenated groups in the selective reduction of nitrobenzene, we selected a series of



Scheme 1. Structures of different model catalysts.

model catalysts with different functional groups to mimic carbocatalysis (Scheme 1).

The performance of each model catalyst is summarized in Table 1. Phenanthraquinone exhibited the best performance as far as nitrobenzene conversion was concerned. However, poor selectivity for aniline was observed, and there was no clear improvement in the selectivity with a prolonged reaction time (Table 1, entries 1 and 2). Surprisingly, a large amount of hydroxylamine was formed ($\approx 60\%$). The other byproducts were mainly azoxybenzene and azobenzene (not shown). If the reaction was catalyzed by 9,10-anthraquinone, the aniline selectivity increased sharply to over 98%, although with relatively mild conversion (Table 1, entries 3 and 4). The results of these two model catalysts indicated that the oxygen functional groups

Table 1. Performance of the model catalysts in the reduction of nitrobenzene. $^{\left[a\right] }$						
Entry	Catalyst	Conv. [%]	Sel. [%]	Yield [%]		
1 ^(b)	A	99.0	22.0	21.8		
2	Α	100	22.1	22.1		
3 ^[b]	В	82.7	98.5	81.4		
4	В	97.7	98.4	96.1		
5	с	76.7	94.2	72.3		
6	D	56.0	98.7	55.3		
7	E	54.7	99.1	54.2		
8	F	76.1	80.2	61.0		
9	G	25.2	99.9	25.2		
10	н	22.0	99.9	22.0		
11	I	21.0	100	21.0		
12	J	15.6	100	15.6		
13 ^[c]	-	24.8	100	24.8		
14 ^[d]	В	96.1	99.2	95.3		

[a] General conditions: Functional groups (0.3 mmol), nitrobenzene (1.2 g), hydrazine monohydrate (6.0 equiv.), ethanol (2.0 mL), 100 °C, 5 h. [b] 3 h. Unless otherwise noted, the reaction temperature was the temperature of the oil bath. [c] No catalyst was used. [d] Under a helium atmosphere.

on anthraquinone-type catalysts were more suitable for the aimed reaction under the selected conditions. However, the results also suggested that not only the identity of the oxygenated groups but also their chemical environments were critical to the reaction, including the product distribution. Upon using anthrone as the catalyst, which has only one carbonyl group, both the conversion and aniline selectivity were lower than that obtained with the use of 9,10-anthraquinone (Table 1, entry 5). As the same amount of functional groups were added in the reactions for the two catalysts, these results revealed that conjugated carbonyl groups were more effective than two isolated ones.

1,4-Benzoquinone and 1,4-benzenediol exhibited almost the same conversion as well as the same aniline selectivity (Table 1, entries 6 and 7). Analysis by NMR spectroscopy showed that after hydrazine was added, 1,4-benzoquinone gave the same ¹H NMR and ¹³C NMR spectra as 1,4-benzenediol (Figure S1, Supporting Information). Given that 1,4-benzenediol is a weak acid and that hydrazine served as the base, the former could be mainly dissociated and converted into $[C_6H_4O_2]^{2-}$. In addition, UV/Vis spectroscopy (Figure S2) also confirmed this transformation. 9-Phenanthrenol was used to study the role of the hydroxyl group further, and the results showed that the hydroxyl group was indeed active for this reaction (Table 1, entry 8).

Benzyl benzoate, benzyl ether, phthalide, and terephthalic acid were chosen to mimic the ester, ether, lactone, and carboxylic acid groups, respectively (Table 1. entries 9–12). Benzyl benzoate, benzyl ether, and phthalide were not active relative to the blank test within experimental error, but terephthalic acid exhibited the lowest activity, and no improvement was achieved at higher catalyst loading (Figure S4). The low activity of the carboxylic group may be ascribed to the fact that this hydrophilic group hinders the adsorption of nitrobenzene.





Figure 1. Plot of the catalytic performance against the loading of 9,10-an-thraquinone. Reaction conditions: Nitrobenzene (2.4 g), hydrazine monohydrate (6.0 equiv.), ethanol (4.0 mL), 100 °C, 20 min.

Aiming to gain more insight into these model catalysts mimicking carbocatalysis, we then mainly studied 9,10-anthraquinone-catalyzed reactions owing to the excellent performance of this catalyst. A relatively good linear correlation between the catalyst loading and the initial catalytic activity was observed (Figure 1); this indicated again that the carbonyl group played an important role and that it was one type of active species.

We assumed that hydrazine was first activated by the oxygenated groups. Taking the carbonyl group as an example, the oxygen atom that has unpaired electrons can interact with the hydrogen atom of a hydrazine molecule. As a result, the N-H bond is weakened, which is beneficial to its decomposition. It was found that the activity improved notably if the reaction was performed in DMSO (Table S1, entries 12 and 13), possibly because the S=O group in DMSO interacted well with the hydrogen atoms of hydrazine thus to weaken the N-H bonds. The activity was further improved upon performing the reaction in [Bmim]Cl (Bmim = 1-butyl-3-methylimidazolium), which was reported to have good ability to dissolve cellulose because the chloride ions can interact with the hydrogen atoms in the cellulose molecules (Table S1, entries 14 and 15).^[14] This result confirmed the importance of the formation of hydrogen bonds in the activation of hydrazine. However, as the hydrazine decomposition tests indicated, the active sites may only activate hydrazine. Hydrazine started to decompose if both the catalyst and nitrobenzene existed in the mixture (Figure S5).

For reduction of C=C bonds by using hydrazine as the reducing agent, the actual reducing agent is diimide, which is generated by oxidation of hydrazine.^[15] However, for the reduction of the nitro group in the present study, the reaction proceeded under an atmosphere of helium as well as in air (Table 1, entry 14), which suggests that the active hydrogen resulting from hydrazine decomposition was the real reducing species and not diimide.

We further studied the reaction routes in this metal-free catalyzed reduction process. The reaction routes included direct and condensation pathways, which are generally accepted for the reduction of nitroarenes.^[16] For the direct pathway, nitro-

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benzene is reduced to nitrosobenzene, hydroxylamine, and aniline, successively, whereas for the condensation pathway, nitrosobenzene reacts with hydroxylamine to form azoxybenzene, which is then reduced to azobenzene, hydrazobenzene, and aniline, successively.

A plot of the reaction products as a function of reaction time is depicted in Figure 2, and it shows that the aniline selectivity was maintained at approximately 98% over the whole



Figure 2. Evolution of nitrobenzene and aniline. Reaction conditions: 9,10-Anthraquinone (0.15 mmol), nitrobenzene (1.2 g), hydrazine monohydrate (6.0 equiv.), ethanol (2.0 mL), $100 \,^{\circ}$ C (six experiments were performed for reactions at 1, 2, 3, 4, 5, and 6 h).

process. Even at the beginning stage, the selectivity of aniline was already above 90%, which is indicative of the quick formation of aniline. In addition, first-order reaction kinetics were observed for the overall reaction (Figure S6).

Although there was only a small portion of azoxybenzene and related products, we still could not exclude the possibility that azoxy-, azo-, and hydrazobenzene served as intermediates, because they may be converted very fast into aniline. To clarify this, we used these suspected intermediates as the initial reactants (Figure 3). It was shown that even after 5 h, there was still a large portion of azoxybenzene (27.9%) and azobenzene (66.9%) that remained. The dominant product was hydrazobenzene, and no aniline was detected. Then, we used hydrazobenzene as a substrate and found that its concentration was slightly increased, which probably resulted from the reduction of azobenzene, because the reagent we obtained contained approximately 10% azobenzene (Table S2, entry 1). The aforementioned results indicated that the three suspected intermediates could not be converted into aniline; thus, the condensation route could be neglected.

Nitrosobenzene was then used as a substrate. After hydrazine was added to the nitrosobenzene solution (ethanol was used as the solvent) at room temperature, the mixture was analyzed immediately by HPLC, and no nitrosobenzene was detected, but the aniline selectivity was 98.6% (Table S2, entry 3). We further found that nitrosobenzene was also completely converted and that the same aniline selectivity was observed if no catalyst was used. In comparison, only 33.7% of hydroxylamine was converted (with an aniline selectivity of 94.3%)



Figure 3. Evolution of azoxybenzene and azobenzene. Reaction conditions: 9,10-Anthraquinone (0.15 mmol), substrate (0.3 g), hydrazine monohydrate (12.0 equiv.), ethanol (2.0 mL), 100 °C. *C* is the concentration of the reactant, whereas C_0 is the initial concentration of the reactant (five experiments were performed for each substrate).

even at 100 °C for 30 min (Table S2, entry 5); this indicated that hydroxylamine was converted much more slowly than nitrosobenzene. This phenomenon suggested that nitrosobenzene was converted very fast, nitrosobenzene may be reduced directly to aniline without the formation of intermediate hydroxylamine, and the conversion of nitrosobenzene was a noncatalytic process. On the basis of these findings, we proposed a possible reaction pathway, as shown in Scheme 2.



Scheme 2. Proposed reaction route for the reduction of nitrobenzene catalyzed by 9,10-anthraquinone $(r_{3\gg}r_1, r_{3\gg}r_2)$.

Notably, nitrobenzene may also be converted directly into hydroxylamine under certain conditions considering that a large amount of hydroxylamine was formed if phenanthraquinone was used as the catalyst. As a matter of fact, nitrobenzene could be reduced directly to hydroxylamine by using a metal catalyst.^[16,17]

On the basis of these findings, we thus proposed a simple mechanism for the reduction of nitrobenzene catalyzed by carbon model catalysts. Scheme 3 shows the formation mechanism of nitrosobenzene. Taking one carbonyl group of 9,10-an-thraquinone as an example, the oxygen that has unpaired electrons interacts with the hydrogen atom of a hydrazine molecule. As a result, a hydrogen bond is formed, and the N–H bond is weakened. As nitrobenzene approaches the benzene ring of the catalyst through π - π interactions, the two oxygen atoms of the nitro group abstract the two activated hydrogen atoms. Then, the nitro group is reduced to a nitroso group. After nitrosobenzene is formed, it is converted into aniline directly through a noncatalytic process. 1,4-Benzoquinone- and 1,4-benzenediol-catalyzed reactions proceed through a similar

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Scheme 3. Supposed mechanism for the formation of nitrosobenzene catalyzed by 9,10-anthraquinone.

mechanism (Figure S7). Upon using phenanthraquinone as the catalyst, because the two carbonyl groups are located on the same side, the nitro group may abstract four hydrogen atoms at one time and be directly converted into hydroxylamine, but hydroxylamine is converted very slowly; as a result, a large amount of hydroxylamine accumulates (Figure S8).

In summary, we studied the role of different oxygen functional groups by using a series of model molecules, and the reduction of nitrobenzene was selected as a probe reaction. The carbonyl and hydroxyl groups played important roles, whereas the carboxylic group had a negative effect. Other oxygenated groups seemed to be inactive. The reaction occurred most likely through a direct route, during which nitrosobenzene could be converted directly into aniline. Considering that the carbon surface as well as its working mechanism could be rather complicated, these findings are of some significance for further investigations of carbon-catalyzed reactions and will direct the design and synthesis of carbon catalyst for organic and polymer chemistry.

Experimental Section

Nitrobenzene reduction

A flask was charged with the catalyst, nitrobenzene (1.2 g), hydrazine monohydrate (6.0 equiv.), and ethanol (2 mL). The mixture was immersed in an oil bath, which was set at 100 °C, and the product was quantified by HPLC.

Characterization

Characterization by NMR spectroscopy was performed with a Bruker 400 MHz NMR spectrometer with tetramethylsilane as an internal reference. UV detection was performed with a Cary 5000 UV/Vis/NIR spectrophotometer.

Acknowledgements

The authors acknowledge the financial support from the Ministry of Science and Technology (2011CBA00504), the National Natural

Science Foundation of China (21133010, 51221264, 21261160487), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA09030103), and the Doctoral Starting up Foundation of Liaoning Province, China (20121068).

Keywords: active sites · carbocatalysis · model catalyst · reaction mechanisms · reduction

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Received: February 23, 2014 Published online on ■■ ■, 0000

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ChemCatChem 0000, 00, 1-4

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Modeling carbon: Thanks to model molecules, the carbon-catalyzed reduction of nitrobenzene is mimicked. The role of different oxygen functional groups on a carbon catalyst is studied, and the carbonyl and hydroxyl groups seem to be the most important moieties, which may be ascribed to their ability to activate hydrazine. The reaction occurs more likely through a direct route, during which nitrosobenzene may also be converted directly into aniline.



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