Hydrothermal Carbon Enriched with Oxygenated Groups from Biomass Glucose as an Efficient Carbocatalyst

Guodong Wen, Bolun Wang, Congxin Wang, Jia Wang, Zhijian Tian, Robert Schlögl, and Dang Sheng Su*

Abstract: Metal-free carbocatalysts enriched with specific oxygenated groups with different morphology and size were synthesized from glucose by hydrothermal carbonization, in which cheap and widely available biomass could be converted into functionalized carbon using an environmentally benign process. The hydroxy- and carbonyl-enriched hydrothermal carbon (HTC) could be used in nitrobenzene reduction, and higher conversion was obtained on the sphere morphology with smaller size. In the Beckmann rearrangement of cyclohexanone oxime, carbonyl-enriched HTC exhibited superior performance compared with conventional solid acid (such as HY and HZSM-5), on which the strong acid sites and weak Lewis acid sites lead to high selectivity for the side product. Although the intrinsic acidity of carbon is weak, the carboxyl-enriched carbon was used in weak β-ketosteroid acid-catalyzed reactions, such as the Beckmann rearrangement.

Carbon-based structures (for example, carbon spheres and graphene) have aroused great attention in a wide variety of applications, such as catalysis, adsorbents, and electrode materials. Recently, it has been shown that carbon could be also used as important metal-free catalysts for many kinds of heterogeneous catalysts for sustainable chemistry, including thermocatalysis (for example, dehydrogenation of ethylbenzene and light alkanes), oxidation of alcohol, epoxidation of styrene, and reduction of nitrobenzene, electrocatalysis, and photocatalysis. However, the understanding of catalytic mechanism has been restricted because of the complicated surface structures (for example, defects, functional groups, and metal impurities).

The oxygenated groups have been assumed to be the active sites in many carbon-catalyzed reactions, and the synthesis of carbon materials with specific oxygenated groups is regarded as an efficient and direct route to confirm the active site and study the mechanism. For example, we have confirmed that carbonyl groups are the active sites in the oxidative dehydrogenation reaction by synthesis of carbonyl groups enriched phenanthrenequinone cyclotrimer. This cyclotrimer exhibited obviously higher activity than other commercial carbon materials and even metal phosphates and oxides. These results indicated that the synthesis of carbon enriched with specific functionalized groups is not only critical to study the mechanism, but is also important to prepare highly efficient carbon catalysts.

The morphology of the HTC samples derived directly from glucose is shown in Figure 1 and the Supporting Information, Figure S1. It can be seen from these SEM and TEM images that carbon microspheres (ca. 558 nm) are uniformly formed when the initial glucose concentration was 10 wt%, and the average size of the spheres could be decreased to 227 nm as the initial glucose concentration was reduced to 2.5 wt%. The addition of PVA could change the carbon sphere to small flake. All of the HTC samples except the PVA dispersed HTC (denoted as HTC-10GPVA) showed similar I_D/I_G ratios (derived from Raman spectra; Supporting Information, Figure S2), which were as high as about 1.8, indicating that the graphitization degree of the HTC was low. It is well-known that biomass glucose is rich in oxygenated groups. As expected, the glucose derived HTC was also enriched with oxygenated groups, it was found from the XPS analysis that the oxygen atom concentration on the surface of HTC is as high as 13.0 at%. After deconvolution, we can see that the surface of HTC was enriched with OH and C=O groups.

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Reduction of nitrobenzene over HTC and other carbon catalysts.

Table 1: Reduction of nitrobenzene over HTC and other carbon catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv.%</th>
<th>Aniline selectivity [%]</th>
<th>S_{BET} [m^2 g^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank[3]</td>
<td>21.8</td>
<td>98.8</td>
<td></td>
</tr>
<tr>
<td>HTC-10G</td>
<td>47.1</td>
<td>100</td>
<td>6.5</td>
</tr>
<tr>
<td>HTC-5G</td>
<td>50.2</td>
<td>100</td>
<td>7.8</td>
</tr>
<tr>
<td>HTC-2.5G</td>
<td>61.5</td>
<td>94.1</td>
<td>17.0</td>
</tr>
<tr>
<td>HTC-5GPVA</td>
<td>43.5</td>
<td>100</td>
<td>19.8</td>
</tr>
<tr>
<td>UDD</td>
<td>21.1</td>
<td>100</td>
<td>313.0</td>
</tr>
<tr>
<td>Graphite</td>
<td>37.7</td>
<td>96.1</td>
<td>10.8</td>
</tr>
<tr>
<td>HHT</td>
<td>19.5</td>
<td>100</td>
<td>33.8</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>62.5</td>
<td>98.2</td>
<td>883.3</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 20 mg catalyst, 1.2 g nitrobenzene, 6.0 equivalent hydrazine monohydrate (3.4 g), 100°C, 4 h. [b] The blank experiment was conducted in the absence of any catalyst.

It is assumed that smaller sphere size is beneficial for exposing more active sites, thus leading to superior conversion. This assumption is supported by the N_2 physical adsorption analysis, which shows that the specific surface area increased from 6.5 to 17.0 m^2 g^{-1} when the initial glucose concentration decreased from 10 to 2.5 wt%. It seems that the small flake morphology owing to the addition of PVA did not show positive influence on the reduction reaction. Four model molecules (cyclohexanol, cyclohexanone, 9-phenanthrol, and anthrone) were used as model catalysts to study the effect of chemical environment on the activity of C=O and OH. It seems that the carbonyl and hydroxy groups attached to a sp^3 carbon skeleton were not favorable for the reaction (Supporting Information, Table S2). Apart from OH and C=O groups, the COOH group is also important among the various oxygenated groups. The carbonyl group can not only enhance the dispersion of carbon-supported metals,[13] but can also be used as active center in some carbon-catalyzed reactions (for example, acid-catalyzed reactions[14] and oxidative coupling of amines to imines[15]). However, the concentration of carboxyl groups on HTC derived directly from glucose is low. Titirici and co-workers showed that carbonyl group could be enriched on HTC by adding acrylic acid in the carbonization process,[16] however the carboxyl content was not quantified and correlated with the adding amount of acrylic acid. Besides, they did not test the carbonyl-enriched HTC as catalysts. Therefore, further study especially the quantification is necessary to optimize this process and resulting HTC. In this study, the content of carboxyl was quantified by Boehm titration (Table 2).

Table 2: Beckman rearrangement of cyclohexanone oxime over carboxyl-enriched HTC.[4]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv. [%]</th>
<th>Lactam selectivity [%]</th>
<th>Cyclohexanone selectivity [%]</th>
<th>Content of carboxyl [mmol g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank[4]</td>
<td>10.3</td>
<td>72.8</td>
<td>27.2</td>
<td></td>
</tr>
<tr>
<td>HTC-10G</td>
<td>13.9</td>
<td>94.5</td>
<td>5.5</td>
<td>0.3</td>
</tr>
<tr>
<td>HTC-10G1A</td>
<td>24.5</td>
<td>76.3</td>
<td>23.7</td>
<td>0.5</td>
</tr>
<tr>
<td>HTC-10G3.3A</td>
<td>29.1</td>
<td>74.5</td>
<td>25.5</td>
<td>0.6</td>
</tr>
<tr>
<td>HTC-10G10A</td>
<td>35.6</td>
<td>77.3</td>
<td>22.7</td>
<td>1.5</td>
</tr>
<tr>
<td>HTC-10G10A300</td>
<td>49.1</td>
<td>89.1</td>
<td>10.9</td>
<td>2.0</td>
</tr>
<tr>
<td>HTC-10G10A300m</td>
<td>20.2</td>
<td>81.3</td>
<td>18.7</td>
<td>2.0</td>
</tr>
<tr>
<td>HY</td>
<td>53.3</td>
<td>26.2</td>
<td>58.9</td>
<td>20.0</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>22.8</td>
<td>0</td>
<td>52.0</td>
<td></td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 115 mg cyclohexanone oxime, 10 mL benzonitrile, 50 mg catalyst, 130°C, 1.5 h. [b] Determined by Boehm titration. [c] The blank experiment was conducted in the absence of any catalyst.

Figure 1. SEM images of HTC derived directly from glucose. a) HTC-10G, b) HTC-5G, c) HTC-2.5G, d) HTC-10G:PVA.
oxidation for the functionalization of carbon materials with carboxyl groups.

The surface of the carbon sphere is no longer smooth owing to the addition of acrylic acid (Figure 2; Supporting Information, Figure S8). The carboxyl-enriched HTC was used as acid catalysts in Beckmann rearrangement of cyclohexanone oxime. This reaction is the key process for the production of caprolactam, which is an important intermediate for the manufacture of nylon-6. The industrial route for the reaction involves the application of concentrated H₂SO₄, which leads to pollution and corrosion. Therefore, a greener process is urgently needed. It was found that the conversion increased with the addition of acrylic acid from 0 to 10 wt% because of the increase of carboxyl content (Table 2). It was reported that the carboxyl content on HTC could be increased by the treatment at 300°C in air in a muffle furnace.[17] Unfortunately, the conversion severely decreased from 35.6 to 20.2% (HTC-10G10A300m), which is possibly due to the large microporous surface area (Supporting Information, Table S1). The formation of microporosity is caused by the loss of strongly micropore-bound decomposition products during the heat treatment.[18] We showed that the carboxyl groups could also be introduced by treatment in an open tube furnace (HTC-10G10A300). Fortunately, it seems that the formation of microporosity was suppressed when large amount of oxygen was introduced in this open tube furnace system. HTC-10G10A300 exhibited not only high conversion but also extremely high lactam selectivity as high as 89.1%, which is even higher than some conventional solid acid catalysts such as HY and HZSM-5. Solid acid zeolite catalysts have been widely studied in Beckmann rearrangement reactions.[19] The HTC-10G10A300 is relatively stable (Supporting Information, Figure S9), and the reaction order for cyclohexanone oxime concentration is pseudo first order (Supporting Information, Figure S10).

Although HY gave a bit higher conversion than HTC-10G10A300, much lower lactam selectivity was observed. A NH₃-TPD experiment was performed to compare the acidity between HTC sample and zeolite samples, the results are shown in Figure 3. A peak with extremely high intensity could be found on HTC-10G10A300 at low temperature (centered around 120°C), indicating that large number of weak acid sites are presented on the HTC sample. However, strong acid sites on this HTC sample are generally negligible as almost no desorption signal was detected at higher temperature range. Although the peaks for HY and HZSM-5 at low temperature are much weaker than that on HTC, obvious peaks at higher temperatures were found, indicating the presence of strong acid sites on the two zeolites, which lead to the high selectivity for side product such as dimers or high-molecular weight by-products.[19c] Moreover, extremely high selectivity for side product cyclohexanone was also observed on the two zeolites, which is most likely caused by the known weak Lewis acid sites.[19c] These results demonstrated that carboxyl, which is a typical type of Brønsted acid site, could act as efficient and selective active center in the Beckmann rearrangement reaction.

Four model molecules (acetic acid, benzoic acid, 2-naphthalene-carboxylic acid, and 1-pyrene-carboxylic acid) were chosen to study the influence of chemical environment on the activity of carboxyl group. It seems that the carboxyl group attached to the sp³ carbon skeleton is not favorable for the formation of lactam (Supporting Information, Table S3), and the large π-conjugation system is not favorable for the rearrangement either because the formation of lactam was suppressed with the increase of the benzene ring based on model molecules studies (Supporting Information, Table S3). The graphitization degree of carboxyl-enriched HTC is low, which could be demonstrated by the high \( I_{D1}/I_{G} \) ratios from the Raman spectra (Supporting Information, Figure S11). It could be found from the TPD profiles that the desorption peak of carboxyl shifted to higher temperatures after treat-

![Figure 2](image1.png)

![Figure 3](image2.png)
ment in air (Supporting Information, Figure S12), indicating that the thermo stability of carboxyl increased after the treatment, thus the increase of the activity after treatment in air could be partially ascribed to the enhancement of the carboxyl stability.

In summary, oxygenated-group-enriched HTC with different size and morphology could be successfully synthesized by hydrothermal carbonization. Hydroxy- and carbonyl-group-enriched HTC could be used in nitrobenzene reduction reaction, and higher conversion could be obtained on carbon spheres with smaller size. Carbonyl-enriched HTC could be applied in Beckmann rearrangement of cyclohexanone oxime. The number of surface carbonyl groups could be obviously increased by treatment in air in an open tube furnace. The performance of carbonyl-enriched HTC is even better than conventionally used solid acids (for example, HY and HZSM-5), which could be attributed to the significantly lower concentration of acid sites on these solid acids. For weak Brønsted acid sites on these solid acids are prone to lead to high selectivity of side product. Although the intrinsic acidity of carbon materials is weak, these results demonstrated that these weak Brønsted acid sites on carbon could exhibit significant advantages to other conventionally used solid acids in some weak Brønsted acid-catalyzed reactions such as the Beckmann rearrangement.

**Experimental Section**

All chemicals used were analytical grade. D-Glucose, anisole, hydrazine monohydrate (85%), acetic acid, and activated carbon were supplied from Sinopharm Chemical Reagent Co., Ltd. Nitrobenzene and graphite (particle size 7–10 μm) were purchased from Alfa Aesar. Ultradispersed nanodiamond (UDD) was bought from Beijing Grish Hitech Co. (China). HHT was supplied from Pyrograf Products, Inc. HZSM-5 (SiO₂/Al₂O₃ = 60) and HY (SiO₂/Al₂O₃ = 4.8) were provided from Dalian Institute of Chemical Physics, CAS.

To obtain hydrothermal carbon, 26 mL glucose aqueous solution was sealed into a Teflon inlet (volume 34 mL) in an autoclave and treated in an oven at 190°C for 16 h. Then, the carbonaceous materials were washed with ethanol and dried at 80°C overnight. The obtained hydrothermal carbon was denoted as HTC-xG, where x represents the weight percentage of glucose in the initial solution. For the synthesis of carbonyl-group-enriched HTC, we added acetic acid to the glucose aqueous solution. The glucose weight percentage was 10 wt%, while the acetic acid percentages were 1, 3, and 5 wt%. The mixture was also transferred into the Teflon inlet, treated at 190°C for 16 h and dried at 80°C overnight. The obtained carbonyl-group-enriched HTC was marked as HTC-10Gx, where x is the weight percentage of the acetic acid in the initial mixture. The HTC-10G10A sample was then calcined in air at 300°C for 5 h in an open tube furnace or in a muffle furnace. The obtained samples were denoted as HTC-10G10A300 and HTC-10G10A300m, respectively.

The surface area and pore volume were measured on Micrometrics ASAP 2020. Transmission electron microscopy (TEM) images were recorded on Tecnai T12 (FEI) with a 120 kV accelerating voltage. The particle size and morphology of the HTC was visualized from scanning electron microscopy (SEM) images by FEI Quanta FEG 250. The X-ray photoelectron spectroscopy (XPS) experiments were performed on ESCALAB 250 with a monochromatized Al Kα X-ray source. Raman experiments were conducted on LabRam HR 800 using 633 nm laser. The deconvolution of the spectra was similar to our previous work. Temperature-programmed desorption (TPD) was tested in He (50 mL·min⁻¹) at a heating rate of 10°C·min⁻¹ from 80 to 900°C, the gas effluent was detected online with mass spectrometry (Omnistar GSD 300). NH₃-TPD was carried out in He (50 mL·min⁻¹) with 10°C·min⁻¹ from 30 to 900°C, the gas effluent was also analyzed online with mass spectrometry. Before the NH₃ desorption, the samples were saturated adsorbed with 10% NH₃/Ar (50 mL·min⁻¹) for 40 min at room temperature. The carboxyl group was quantified by Boehm titration. Specifically, 0.1 g sample was immersed in 30 mL 0.01 mol·L⁻¹ NaHCO₃ solution. After slowly stirred at room temperature for 24 h, 10 mL filtrate was pipetted, and the excess base was titrated with 0.01 mol·L⁻¹ HCl.

The nitrobenzene reduction was performed in the presence of 1.2 g nitrobenzene and 3.4 mL hydrazine monohydrate over 20 mg catalyst at 100°C for 4 h. The products were determined by GC (Agilent 7890) with HP-5 column, and anisole (0.5 g) was added as internal standard. Beckmann rearrangement of cyclohexanone oxime was conducted with 115 mg cyclohexanone oxime and 10 mL benzonitrile over 50 mg catalysts at 130°C for 1.5 h. The products were analyzed by GC with HP-5 column, and DMF (50 μL) was added as internal standard. The products were also identified with GC-MS (GC7890B-MS5977, Agilent).

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