Short communication

Selective oxidation of glycerol over nitrogen-doped carbon nanotubes supported platinum catalyst in base-free solution

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1. Introduction

Glycerol is a by-product during the production of biodiesel, and the rapidly rising production of biodiesel has led to a serious surplus of glycerol [1,2], which makes it one of the most attractive platform chemicals. In the past years, catalytic oxidation of glycerol to valuable products has become a hot research topic [3–6]. In published works, Au-based catalysts were reported intensively for this reaction, but the performance of Au depends strongly on the basicity of reaction mixture [7–14]. Mechanism investigation showed that oxygen atoms incorporated into glyceric acid (GLYA) over Au catalyst originated mainly from water solvent when NaOH was added [14,15], and NaOH in the reaction mixture would catalyze the cleavage of C–C in glycerol [10].

Taken the potential industrial application into consideration, selective oxidation of glycerol in a base-free aqueous solution is more favorable. Kimura et al. found that Pt–Bi/C can catalyze the oxidation of glycerol to dihydroxyacetone (DHA) without the addition of base [16], Gallezot et al. confirmed that Bi can prevent the over-oxidation of Pt and favor the oxidation of secondary alcohol [17]. Recently, it was reported that H-mordenite supported Au–Pt nanoparticles (NPs) [18,19] and Mg(OH)2 supported Au–Pt and Au–Pd NPs [20] can catalyze the oxidation of glycerol to free GLYA without the addition of base, and CuO supported Au NPs is active for the selective oxidation of glycerol to DHA without NaOH [21]. At the same time, more recent works found that cubicoctahedral Pt NPs [22] and PtSn/C [23] are more active for the selective oxidation of glycerol than tetrahedral Pt NPs.

Previous works in our laboratory also showed that mono-metal Pt was capable for the selective oxidation of glycerol to GLYA in a base-free condition [24], and micropore-free multiwall carbon nanotubes (MWCNTs) and carbon nanofibers supported Pt catalysts were more active than traditional Pt/carbon for this reaction because of the easier accessibility of Pt on the outer wall [25,26]. But the oxidation rate of glycerol over Pt catalysts decreased during time on stream, which might be caused by over-oxidation of surface metal NPs to oxides, and/or the decarboxylation of aldehyde intermediates to form CO that strongly adsorbed on Pt [27,28]. How to increase the stability and resistance to poisoning of Pt catalyst becomes an urgent problem [14].

Latest papers show that the properties of supports significantly affect the selectivity of product, and weaker basic site can increase the selectivity of GLYA and prevent GLYA from over oxidation [29]. N-doped supports [30,31] and mesoporous carbon nitride [32] can improve the performance and stability of Pt NPs due to the electron donation from nitrogen to Pt. In this communication, N-doped MWCNTs (N-MWCNTs) was prepared via a facile calcinations of mixed MWCNTs and urea, Pt NPs were loaded on N-MWCNTs in ethylene glycol (EG) under microwave irradiation (see Scheme 1). The performance of Pt/N-MWCNTs for the selective oxidation of glycerol in a base-free solution was tested and compared with the nitrogen-free Pt/MWCNTs.

2. Experimental

2.1. Catalysis Preparation

MWCNTs (purity >97%, diameter 30 ± 10 nm, and length less than 2 μm) were purchased from Shenzhen Nanotech Port Co. Ltd. (China). MWCNTs were pre-treated in a mixture of concentrated nitric and...
sulfuric acids (1:1, v/v) at 80 °C for 5 h, and then, washed with distilled water until the pH of effluent solution reached 6.7, the solid was dried in vacuum overnight and denoted as H-MWCNTs.

Two grams of H-MWCNTs and urea (the mass ratio of urea/H-MWCNTs is 10:1) were mixed in water under stirring, and then the solvent was subsequently evaporated in a rotary evaporator. The resulting material was carbonized in nitrogen at different temperature for 2 h, and denoted as N-MWCNTs − x, x means calcination temperature in K.

One gram of N-MWCNTs-673 (or N-MWCNTs-973) and 4.0 mL aqueous solution of H$_2$PtCl$_6$ (0.01 g·Pt/mL) were mixed in 50 mL EG under stirring for 1 h. Subsequently, the pH of above suspension was adjusted to 11–12 using NaOH/EG. Above mixture was then subjected to microwave irradiation at 145 °C for 7.5 min (Sineo, MAS-II, 600 W, 2.45 GHz). After irradiation, the suspension was cooled, solid product was isolated, washed with distilled water until free of Cl, and further dried in vacuum at 40 °C for 10 h.

**Fig. 1.** High resolution XPS analysis of N 1 s signals (a), Pt 4f spectra in Pt/MWCNTs (b), Pt/N-MWCNTs-673 (c) and Pt/N-MWCNTs-973 (d).
2.2. Catalysts characterization

X-ray diffraction (XRD) was performed on RIGAKUD/MAX2550/PC diffractometer using Cu Kα radiation at 40 kV and 100 mA. The morphologies and dimensions of catalysts were observed by transmission electron microscopy (TEM, JEOL-2010 F) using an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were recorded on Perkin-Elmer PHI ESCA System, the X-ray source was Mg standard anode 146 (1253.6 eV) at 12 kV and 300 W. Actual content of Pt in prepared catalysts was determined on inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Plasma-Spec-II spectrometer).

2.3. Glycerol oxidation

Glycerol oxidation was carried out in a 50 mL custom designed stainless autoclave with a glass inner layer, which contains 10 mL glycerol solution (0.1 g/mL) and 0.1 g catalyst. The reactor was sealed, filled with 0.5 MPa O2 and placed in an oil bath preheated to required temperature and maintained at that temperature for a given time under vigorously stirring. After reaction, catalyst was removed by centrifugation and the aqueous solution was analyzed using an Agilent 1100 series high-performance liquid chromatograph (HPLC) equipped with a refractive index detector (RID) and a Zorbax SAX column (4.6 mm × 250 mm, Agilent). The turnover frequency (TOF) on the basis of surface Pt atoms was calculated as: TOF = (number of glycerol molecular converted) / (surface Pt atoms × reaction time).

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (h⁻¹)b</th>
<th>Conv. (%)</th>
<th>Selectivity (%)c</th>
<th>GLYA</th>
<th>GLYHD</th>
<th>DHA</th>
<th>GLYCA</th>
<th>Others</th>
<th>GLYA</th>
<th>GLYHD</th>
<th>DHA</th>
<th>GLYCA</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pt/C</td>
<td>–</td>
<td>43.9</td>
<td>82.8</td>
<td>1.7</td>
<td>13.6</td>
<td>1.9</td>
<td>0.0</td>
<td>–</td>
<td>43.9</td>
<td>82.8</td>
<td>1.7</td>
<td>13.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Pt/MWCNTs</td>
<td>116.4</td>
<td>29.0</td>
<td>78.6</td>
<td>3.1</td>
<td>15.0</td>
<td>3.2</td>
<td>0.1</td>
<td>–</td>
<td>29.0</td>
<td>78.6</td>
<td>3.1</td>
<td>15.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt/N-MWCNTs-673</td>
<td>–</td>
<td>39.9</td>
<td>82.8</td>
<td>1.4</td>
<td>13.6</td>
<td>1.7</td>
<td>0.5</td>
<td>–</td>
<td>39.9</td>
<td>82.8</td>
<td>1.4</td>
<td>13.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Pt/N-MWCNTs-973</td>
<td>354.2</td>
<td>54.9</td>
<td>83.0</td>
<td>4.2</td>
<td>7.3</td>
<td>5.5</td>
<td>0.0</td>
<td>–</td>
<td>54.9</td>
<td>83.0</td>
<td>4.2</td>
<td>7.3</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 1 Oxidation of glycerol using different Pt catalysts.  

- Reaction conditions: catalyst 0.1 g, aqueous solution of glycerol 10 mL (0.1 g/mL), 60°C, 0.5 MPa O2, 3 h.  
- TOF was calculated on the basis of surface Pt at beginning of the reaction (% conversion of glycerol).  
- Selectivity was calculated as: (mmol of product in reaction mixture) × (the number of carbon atoms in product) / (initial mmol of glycerol − mmol of glycerol left) × 3) × 100%. GLYA: glyceric acid, DHA: 1,3-dihydroxyacetone, GLYCA: glycolic acid, GLYHD: glyceraldehyde.  
- 5% Pt/C, purchased from Sigma-Aldrich.
(number of surface Pt atoms) / (reaction time, h). The selectivity of each product was calculated as: (mmol of product in reaction mixture) / (the number of carbon atoms in product) / ((initial mmol of glycerol – mmol of glycerol left) × 3) × 100%.

3. Results and discussion

3.1. The structure of catalysts

XPS spectra of Pt/MWCNTs, Pt/N-MWCNTs-673 and Pt/N-MWCNTs-973 were shown in Fig. S1. It was confirmed that the content of N in Pt/N-MWCNTs-673 and Pt/N-MWCNTs-973 are 4.4 and 2.5 at%, respectively (see Table S1). High resolution of N 1 s spectra disclosed that mainly graphitic N (N\textsubscript{G}), pyridinic N (N\textsubscript{p}), pyrrolic N (N\textsubscript{pyr}), and pyridine oxide (N-oxides) formed on the surface of MWCNTs (see Fig. 1a, Fig. S2 and Table S2) [31,33]. These results indicated that N atoms were incorporated into carbon skeletal of N-MWCNTs, and the relative percentage of graphitic N increased from 5 to 16.7% when the calcination temperature was raised from 673 to 973 K because of the rearrangement of nitrogen groups under high temperature (Table S2) [34].

XRD patterns of Pt/MWCNTs, Pt/N-MWCNTs-673 and Pt/N-MWCNTs-973 were shown in Fig. S3. The strong (002) diffraction of hexagonal graphite at 2θ \approx 26.5° indicates that the graphite structure of MWCNTs is stable. The diffraction peaks of Pt in Pt/MWCNTs are broad, and these peaks become weaker and obscure in Pt/N-MWCNTs-673 and Pt/N-MWCNTs-973, indicating that Pt highly dispersed on these supports. The average crystalline size of Pt that calculated from the half-width of Pt (111) in Pt/MWCNTs, Pt/N-MWCNTs-673 and Pt/N-MWCNTs-973 are 2.2, 1.9 and 1.7 nm, respectively.

TEM images of Pt/N-MWCNTs-673 and Pt/N-MWCNTs-973 with particle size distributions (insert) were shown in Fig. 2. Pt NPs dispersed homogeneously on the surface of N-MWCNTs, only limited aggregated particles (larger than 3 nm) was detected in the counted 800 particles. The calculated mean size of Pt NPs in Pt/N-MWCNTs-673 and Pt/N-MWCNTs-973 are 2.0 ± 0.5 and 1.8 ± 0.5 nm, respectively. Elemental linescans of a single nanotube (Fig. 2e and f) shows that there is a good spatial correspondence of C and N with the intensities of their K\textsubscript{α} lines, indicating that N was successfully doped into the carbon skeleton of MWCNTs. At the same time, high-resolution of Pt 4f spectra (see Fig. 1b–d) also revealed that the amount of metallic Pt on the surface of N-MWCNTs is higher than that on pristine MWCNTs, and the detected ratio of Pt\textsuperscript{0}/Pt\textsuperscript{4+} increased with the content of N, which could be attributed to the strong electron donating effect of N-dopants in carbon skeleton [30–32]. But Pt NPs dispersed unevenly on the surface of N-free MWCNTs. Some aggregated particles (larger than 4 nm) were detected in Pt/MWCNTs, and the mean size of counted 800 particles is 2.4 ± 0.8 nm (Fig. S4). These results could be attributed to that incorporation of N in MWCNTs can promote the electronic conductivity of MWCNTs via the donating electron of N, and N-MWCNTs are more favorable for immobilization of Pt through the strengthened metal-support interactions [30,31]. Besides the defects caused by N incorporation, N dopants in N-MWCNTs (especially for N\textsubscript{p} and N\textsubscript{pyr}) can also increase the electron enrichment and the dispersion of neighboring Pt NPs, N\textsubscript{p} with high charge density can endow carbon with a metal-like electronic structure to host the reactive oxygen species.

3.2. Selective oxidation of glycerol

The activity and product distribution of selective oxidation of glycerol over these catalysts in base-free aqueous solution at 60 °C were summarized in Table 1. It can be found that GLYA is the main product in all experiments. The conversion of glycerol and selectivity of GLYA over Pt/MWCNTs is 29.0 and 78.6%, respectively. When Pt NPs were supported on N-MWCNTs, the detected conversion of glycerol over Pt/N-MWCNTs-673 and Pt/N-MWCNTs-973 increased to 39.9 and 54.9%, respectively, and the selectivity of GLYA over these catalysts was higher than 82%. Time-on-stream data confirmed that the selectivity of GLYA over Pt/N-MWCNTs-973 remains higher than 80% (see Fig. S5), and the calculated initial turnover frequency (TOF, at 10% conversion of glycerol) of surface Pt atom reached 354.2 h\textsuperscript{-1}.

At the same time, time-on-stream experiments over Pt/N-MWCNTs-973 and Pt/MWCNTs (see Fig. S6) indicated that the oxidation rate of glycerol over Pt/MWCNTs decreased obviously with the increasing time, and the detected conversion of glycerol only increased slightly from 29.0% (at 3 h) to 40.4% (at 6 h). On the other hand, the conversion of glycerol over Pt/N-MWCNTs-973 increased continuously. These results indicated that the deactivation of Pt during the glycerol oxidation process can be partially retarded when nitrogen was added into the support. That is, the Pt/N-MWCNTs-973 was stable for the oxidation of glycerol, which could be attributed to that electron-enriched Pt NPs would protect itself from over-oxidation. Recycling experiments (Fig. S7) also confirmed that Pt/N-MWCNTs-973 is stable as the conversion of glycerol only decreased slightly from 40.8 to 36.0% in the 5th cycle, and the selectivity of GLYA remained stable.

4. Conclusion

We found that N-doped MWCNT supported Pt NPs is highly active, selective and stable for the oxidation of glycerol with molecular oxygen in an aqueous base-free solution. Characterization results disclosed that nitrogen in the framework of MWCNTs can modify the electronic structure of the carbon matrix, donate its electron to metallic Pt NPs, and strengthen the interaction between carbon and metals.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.08.002.

References