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Short communication

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

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ABSTRACT

In this communication, N-doped multiwall carbon nanotube (N-MWCNT) supported Pt NPs (1.8 nm) were prepared via a facile routine under microwave irradiation and tested in the selective oxidation of glycerol in an aqueous base-free solution. Characterizations confirmed that N-MWCNTs could improve the dispersion of Pt through strengthened metal-support interactions and donate its electron to metallic Pt. This electron-enriched Pt NPs on the surface of N-MWCNTs is active and stable for the selective oxidation of glycerol.

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 cuboctahedral Pt NPs [22] and Pt_9Sn_1/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

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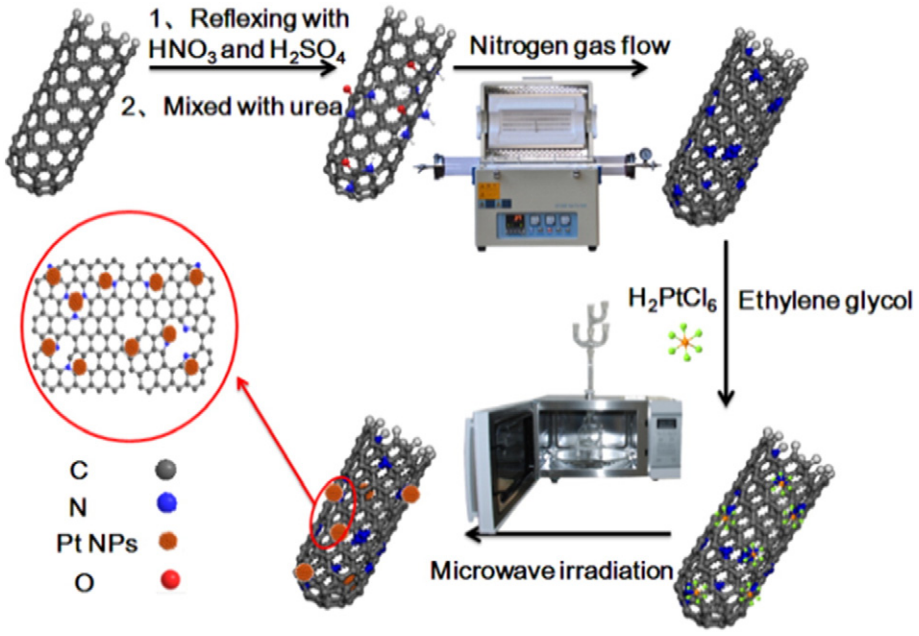

Scheme 1. Preparation routine of Pt/N-MWCNTs.

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_2PtCl_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.

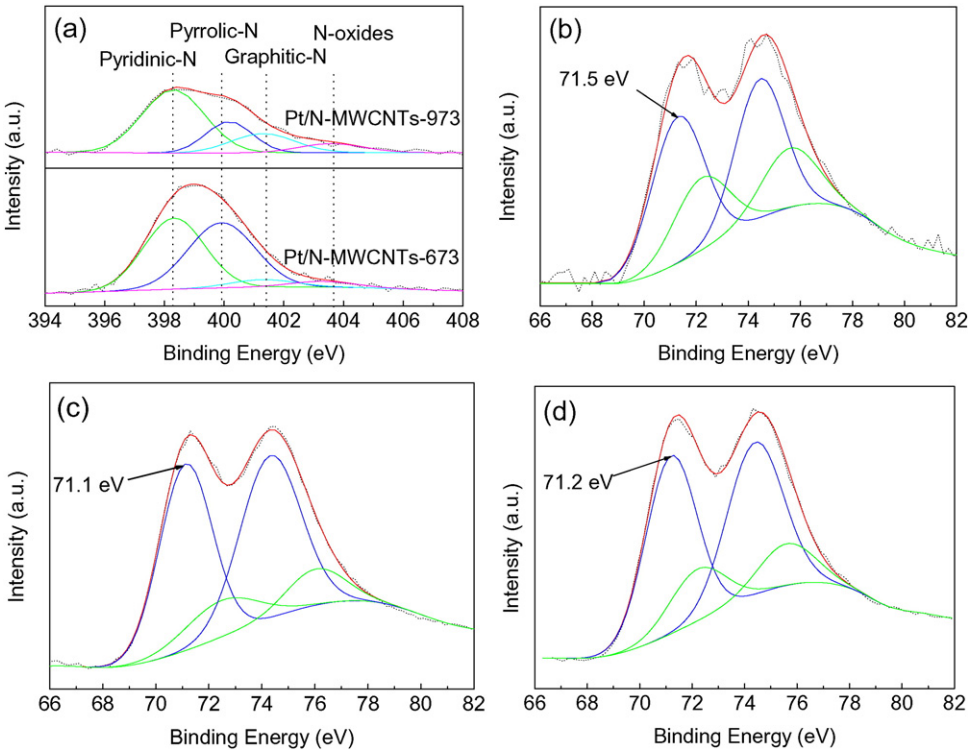

Fig. 1. High resolution XPS analysis of N 1 s signals (a), Pt 4f spectra in Pt/MWCNTs (b), Pt/N-MWCNTs-673 (c) and Pt/N-MWCNTs-973 (d).