

Preparation and characterization of PtPd-NiOx/CNTs ternary heterostructures catalyst

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Abstract. In this paper, using carbon nanotubes (CNTs) as the carrier, a new type of heterogeneous material Pt-PdNiOx/CNTs was prepared by impregnation reduction method. By means of XRD, TEM, XPS and electrochemical analysis, Pt-PdNiOx/CNTs catalyst of the structure and in the methanol oxidation catalytic mechanism are studied and analyzed the relationship between the structure and properties. The results show that with the increase of Ni content, the size of Pt-PdNi/CNTs catalyst particles was decreased. The average particle diameter of Pt-PdNi / CNTs was 2.4 nm. NiOx protected the relative content of Pt0 activity center, so that zero-valent Pt content in Pt-PdNi / CNTs reached 75.3%. This greatly improved the Pt-PdNiOx / CNTs catalyst anti-poisoning ability and catalytic properties.

1. Introduction

Supported catalyst as an important catalyst material, because it has excellent performance of heat and mass transfer, and other characteristics suitable for continuous reaction process in the petrochemical industry, especially in the selective hydrogenation of olefins, aromatics and other hydrocarbon substances, important reactions such as oxidation process has been widely used.

Carbon nanotubes (CNTs) have a unique nano hollow structure and closed topological configuration, which makes it has the nano hollow tubular structure. So CNTs in the catalyst carrier material has great potential for application [1]. Platinum has good catalytic performance, excellent high temperature oxidation resistance and other characteristics[2], making it become an indispensable precious metal material in the field of modern industry, science, medicine etc., it is widely used in petroleum, pharmaceuticals, automotive, chemical, aerospace and military and other fields, but platinum is a rare metal, and its storage capacity is limited[3,4]. In order to further improve the activity and stability of the catalyst, the ternary or quaternary heterostructure catalysts become research hotspot recently. Currently, there exist a variety of tri- or polyhydric heterostructure catalyst, especially Pt-PdM (M = Cu, Ni, Co, etc.) heterostructure catalyst become a research focus [5].

In this paper, CNTs as the carrier, by impregnation reduction method in the surface of the carrier base load Pd based (PdNiOx) nanoparticles, and epitaxial growth method in the Pt deposited on the surface of the nanoparticles, thereby forming PtPd-NiOx / CNTs ternary heterostructures catalyst. The catalytic performance of methanol oxidation was tested, and the relationship between the structure and properties of the catalyst was studied.

2. Experimental

2.1 Materials

Chloroplatinic Acid was purchased from Shanghai bojing chemical Co., Ltd.; PdCl₂ was purchased from Shanghai zhanyun chemical Co., Ltd.; NiCl₂·6H₂O was purchased from Tianjin jinhuitaiya chemical reagent Co., Ltd.; concentrated sulfuric acid and concentrated nitric acid was purchased from Tianjin jinhuitaiya chemical reagent Co., Ltd.; glycerol and glycol was purchased from Tianjin City Xin Dayu Chemical Co., Ltd.; carbon nanotube was purchased from Beijing Dk Nano technology Co., Ltd..

2.2 Process

2.2.1 Modification of CNTs carrier

Weighing CNTs were added to 50 mL of concentrated nitric acid and concentrated sulfuric acid, at 50 °C reflux reaction for 4 hours. Washed to neutral, dried, then ground to a powder, finally get oxidized CNTs.

2.2.2 Preparation of Pt-PdNiO_x/CNTs catalyst

Take the oxidation glycerol was added to the CNTs, followed by addition of PdCl₂, NiCl₂ · 6H₂O ultrasonic dispersion 1h. After magnetic stirring 0.5h, followed by heating up to 150 °C, constant temperature heating reaction 4h, then naturally cooled and filtration, dried for 10 h at 70 °C, and finally get PdNi/ CNTs.

Take PdNi/ CNTs was added to the glycol, and then added H₂PtCl₆·6H₂O, adjusted pH = 12 by adding dropwise 0.5mol/L KOH-EG solution. After magnetic stirring 1.5h, constant temperature heating reaction for 24h at 120 °C, then naturally cooled and filtration, dried for 10 h at 70 °C, and finally get Pt-PdNiO_x/CNTs.

2.3 Instrumental

Monochromatic powder X-ray diffraction spectra were recorded with an XRD-6100 (Shimadzu Corporation), diffractometer (Cu K α radiation, $\lambda = 1.54 \text{ \AA}$) over a 2θ range of 5–70° (step size, 0.028; time per step, 1.0 s). X-ray photoelectron spectroscopy were recorded with VG ESCALAB250 x-ray photoelectron spectrometers (U.S.A Thermo Company), vacuum test 2×10^{-9} Pa. TEM images were obtained on a H-800 transmission electron microscope (Japan Hitachi Company), using an accelerating voltage of 200 kV. Electrocatalytic properties were recorded with CS354 electrochemical workstation (China wuhan corrtest instruments Co.Ltd.), scanning speed is 50 mV/s and the potential range is -0.2 ~ 1 V.

3. Results and Discussion

3.1 Crystal Structure Analysis

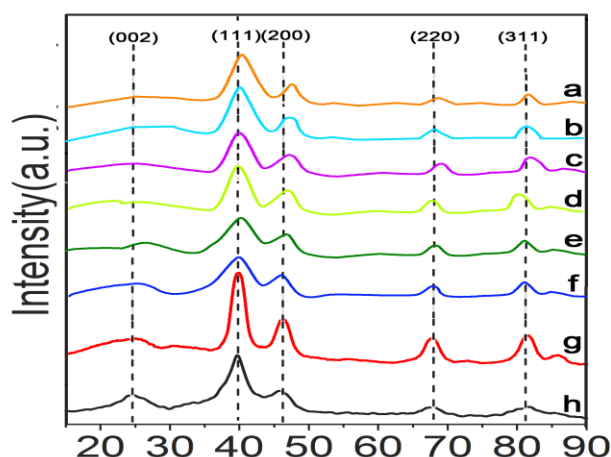


Fig. 1 XRD pattern of Pd₃Ni₁/CNTs(a)Pt₁-Pd₃Ni₁/CNTs(b)Pd₃Ni₃/CNTs(c)Pt₁-Pd₃Ni₃/CNTs(d)Pd₃Ni₆/CNTs(e)Pt₁-Pd₃Ni₆/CNTs(f)Pt/CNTs(g)and (h)Pt/C (JM)

In the figure 1, each sample in 2θ of 40.0 °, 47.4 °, 67.7 ° and 81.9 ° emerged platinum face-centered cubic structure (111), (200), (220) and (311) diffraction peaks characteristic. This was consistent with the standard spectrum of platinum (04-0802 JCPDS) and with the reference catalyst Pt / CNTs (g) and Pt / C (JM) (h) of the peaks. Nickel oxide was not found in the catalyst, and the oxide of nickel was existed in amorphous form. Compared with PdNi/ CNTs, Pt-PdNi/ CNTs (111) crystal diffraction peak shifts to the left. Pt-PdNi/ CNTs planes spacing was 0.224 nm, slightly less

than the Pt / C (JM) crystal interplanar spacing (0.227 nm), indicating that Pt particles covered on the surface of the Pd particles, which contributed to the increase in the Pt atomic exposure rate.

3.2 Morphology Analysis

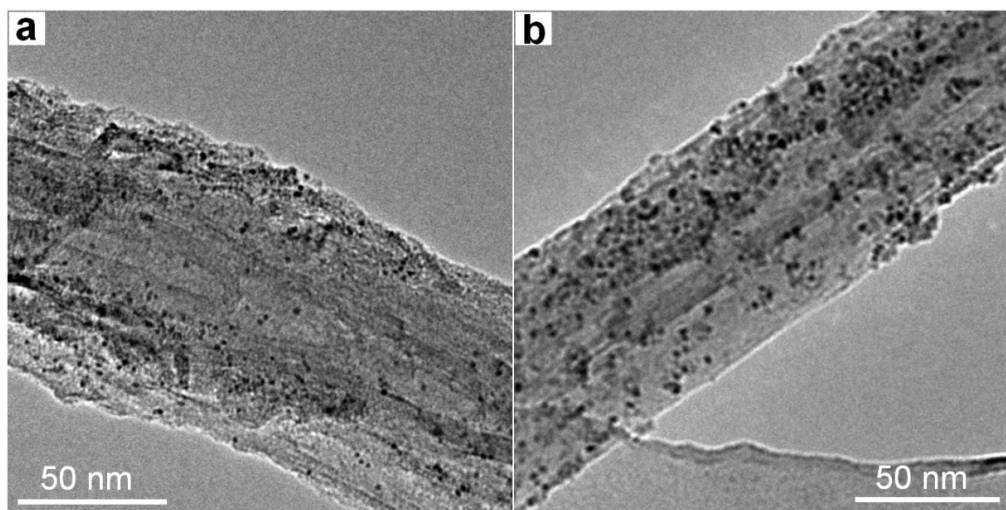


Fig. 2 TEM images of Pt-PdNi/CNTs and Pt-Pd/CNTs

From the above figure showed that the average particle diameter of Pt-PdNi / CNTs is 2.4 nm, much less than the Pt-Pd / CNTs of 5.2 nm. The particles Pt-Pd / CNTs catalyst appeared agglomeration, and Pt-PdNi/CNTs catalyst particles distribution was uniform. Moreover, with the increase of Ni content, the particle size of Pt-PdNi/CNTs catalyst decreased gradually. The reason may be the carrier surface amorphous form NiO_x as nucleation centers, so that the particle size is reduced.

3.3 XPS Fine Spectrum Analysis

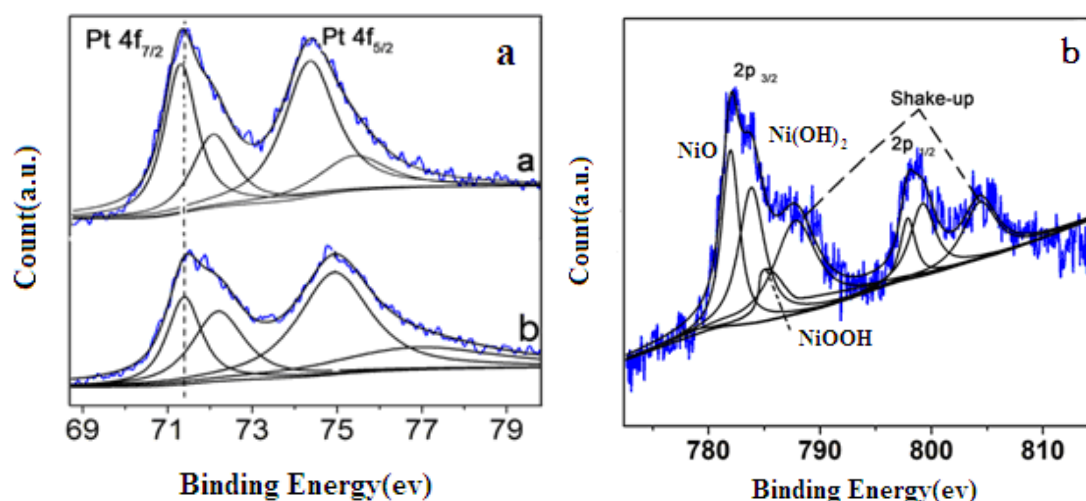


Fig. 3 XPS images of Pt-PdNi/CNTs and Pt/C (JM)

Figure 3 showed XPS images of Pt4f, Pd3d and Ni2p on the Pt-PdNi/CNTs and Pt/C (JM). Pt4f were 4f_{7/2} and 4f_{5/2} peak of zero valent Pt and Pt oxide; Ni 2p did not found Ni⁰ metal state, but contains low binding energy of NiO and Ni(OH)₂ and high binding energy of NiOOH. The content of Zero-valent Pt in Pt-PdNi / CNTs reached 75.3%, which was due to the formation of NiO_x prevent Pt oxidation reaction process, so as to protect the relative content Pt⁰ active center, thus greatly improving the catalytic oxidation capability of Pt. Therefore NiO_x catalyst can improve anti-poisoning capacity and catalytic performance of the catalyst.

3.4 Studies on Electrocatalytic Performance

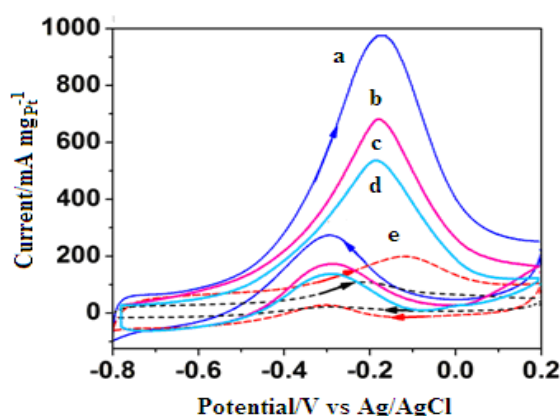


Fig. 4 The cyclic voltammetry of the catalysts in alkaline methanol solution

(a) Pt₁-Pd₃Ni₃ / CNTs (b) Pt₁-Pd₃Ni₆ / CNTs (c) Pt₁-Pd₃Ni₁ / CNTs (d) Pt / CNTs (e) Pt / C

Figure 4 showed the cyclic voltammetry results for the different ratio of catalyst, Pt / CNTs and Pt / C catalyst reference in 0.5 mol/L KOH. As can be seen from the results, the prepared Pt-PdNi / CNTs catalyst had a high ECSA. This was because Pt is grown on the surface of Pd alloy, and dispersion effect of NiO_x and CNTs on metal nanoparticles, thereby increasing the exposure rate of Pt atoms, thus contributing to the electrochemical surface area was increased, which Pt₁-Pd₃Ni₃ / CNTs catalyst had the highest current density. Obviously, forming a heterojunction structure and CNTs dispersed metal nanoparticles greatly enhanced the dispersion of Pt nanoparticles and improved the exposure of the active site, which was helpful to improve reaction activity.

Conclusions

(1) With carbon nanotubes (CNTs) as the carrier, NiO_x modified Pt-Pd heterogeneous particles were obtained by impregnation reduction method. By XRD and TEM analysis, the size of Pt-PdNi/CNTs catalyst particles was decreased with the increase of Ni content. The average particle diameter of Pt-PdNi / CNTs was 2.4 nm. The reason was the carrier surface amorphous form NiO_x as nucleation centers, so that the particle size is reduced.

(2) By XPS and electrochemical analysis, Pt-PdNiO_x/CNTs catalyst has excellent catalytic oxidation of methanol capacity, because of NiO_x enhanced the dispersion of Pt nanoparticles, and it hindered the exposure of the active site, which was conducive to the increase of electrochemical surface area, so that zero-valent Pt content in Pt-PdNi / CNTs reached 75.3%. This greatly improved the Pt-PdNiO_x / CNTs catalyst anti-poisoning ability and catalytic properties.

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