COMPOSITION EFFECTS OF PtSb ALLOY ON BASE-FREE OXIDATION OF GLYCEROL

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Abstract

A series of PtSb alloy nanoparticles with different composition immobilized on carbon nanotubes were synthesized and applied for glycerol oxidation in a base-free condition. The phase composition of the PtSb alloy has been found to exert great influence on their catalytic performance. With similar particle sizes, the catalyst with a Pt_3Sb phase exhibits higher activity and selectivity to dihydroxyacetone (DHA) than the catalyst with a PtSb phase. Moreover, the exposure of Pt_3Sb (008) is beneficial to the enhancement of catalytic performance. These results suggest that the specific structure of PtSb nanoparticle could contribute to the improved performance for selective oxidation of glycerol to DHA.

Keywords

Glycerol oxidation, PtSb alloy, Phase composition.

Introduction

Glycerol, a major by-product of bio-diesel production, has been considered as a key platform chemical for producing high-value added chemicals (Huber et al., 2006). Conversion of glycerol via different reaction pathways, for example, hydrogenolysis, oxidation, and dehydration etc., has been investigated intensively over the last decade (Zhou et al., 2008). Oxidation of glycerol generates various valuable oxygenated derivatives such as glyceraldehyde, glyceric acid, dihydroxyacetone (DHA) and hydroxypyruvic acid, among which DHA is economically the most interesting product due to its potential applications in the cosmetics industry as a self-tanning agent and in fine chemical industry (Katryniok et al., 2011).

Among noble metals investigated so far, Pt is the most active catalyst for glycerol oxidation under base-free conditions. Interestingly, many groups have found that introducing a secondary metal component into Pt based catalyst, such as Bi or Sb species, is beneficial for the enhanced activity and selective oxidation of the secondary hydroxyl group of glycerol toward DHA under acidic conditions (Kimura et al., 1993, and Nie, et al., 2012). Recently, PtSb alloy nanoparticles supported on S-pretreated carbon nanotubes were tested for glycerol oxidation, which exhibited much higher activity and selectivity than PtBi/CNTs catalyst (Nie, et al., 2012). However, PtSb nanoparticle microstructure, which is a key factor to influence the catalytic performance in many cases, has received little attention. In this work, the intrinsic relation between PtSb nanoparticle microstructure and catalytic performance for glycerol oxidation is systematically studied to obtain fundamental insights into the effect of phase composition and to design highly efficient catalysts.

Experimental

Carbon nanotubes (CNTs) supported PtSb nanocatalysts were synthesized by incipient wetness co-impregnation, with different Pt:Sb atomic ratio based on almost the same total metal loading in order to obtain

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similar sized particles. The as-obtained catalysts were denoted as mPt-nSb, in which m and n denote the nominal metal loading (wt%). Glycerol oxidation was carried out in a batch reactor. The samples were drawn out intermittently from reactor for analysis using a high performance liquid chromatograph.

Results and discussion

Fig. 1 shows XRD patterns of PtSb/CNTs catalysts with different composition. Obvious diffraction peak at 25.6° and faint diffraction peak at 42.7° are assigned to the CNTs. Typical diffraction peaks of 41.4° and 43.7° are observed in 5.0Pt-5.0Sb/CNTs sample, which could be ascribed to PtSb (102) and PtSb (110) of PtSb nanoalloy. However, only Pt_3Sb was present in 6.5Pt-3.9Sb/CNTs and 9.5Pt-1.9Sb/CNTs samples, corresponding to Pt_3Sb(008) and Pt_3Sb(114). Another interesting phenomenon is that no metallic Sb diffraction peak can be observed in any of the spectra, suggesting that Sb was alloyed with platinum and highly dispersed on the external wall of CNTs.

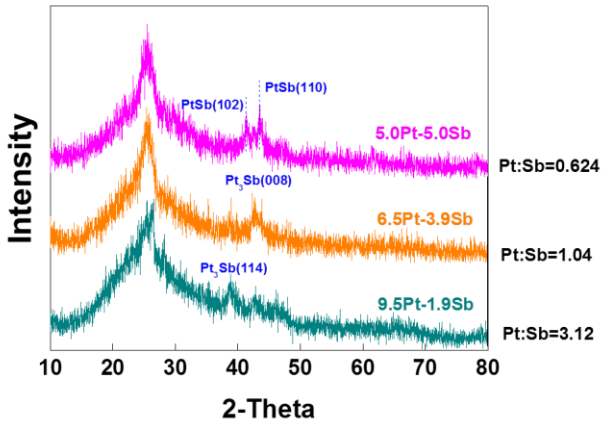

Figure 1. XRD patterns of PtSb/CNTs catalysts.

It should be noted that all samples had similar average particle size around 3.1 ± 0.1nm from TEM statistical analysis, as shown in Table 1. In addition, spherical shaped particles were mostly observed for bimetallic PtSb nanocatalysts from HR-TEM. Moreover, the outline and crystalline lattice of PtSb alloy can be clearly distinguished, which is in good agreement with the XRD results. While homogenously distributed PtSb particles were examined, no separated Sb lattices were detected. These results further indicated that Sb was incorporated into Pt in the form of PtSb alloy dispersed homogenously on the external wall of CNTs. HADDF-STEM-EDX analysis showed that the content of platinum and antimony were very close to the nominal values identified by consistent integrated spectrum of Pt and Sb from elemental linescans across single particle.

The catalytic activity, expressed as TOF, increased with the increase of Pt:Sb atomic ratio to a maximum (Pt:Sb=1), followed by a slight decline with a further increase of Pt:Sb. Excess of antimony in PtSb alloy, mainly forming PtSb, tended to be disadvantageous in terms of catalytic activity, while a small number of antimony introduced into Pt was beneficial to form Pt_3Sb, exhibiting enhanced catalytic performance for glycerol oxidation. Moreover, the exposure of Pt_3Sb (008) may also contribute to the high performance of 6.5Pt-3.9Sb/CNTs catalyst.

Table 1. Catalytic performance for selective oxidation of glycerol

Catalyst	d_{TEM} (nm)	TOF (h^{-1})[a]	Con (%)	S_{DHA} (%)
5.0Pt-5.0Sb	3.0	198.0	67.2	57.0
6.5Pt-3.9Sb	3.1	308.2	69.0	62.0
9.5Pt-1.9Sb	3.2	289.1	65.2	52.8

[a] defined as moles of glycerol converted per mole of total Pt loading per hour

Conclusions

The microstructure of PtSb nanoparticle has an important effect on base-free oxidation of glycerol to DHA. Pt_3Sb may exhibit much better performance than PtSb. In addition, the catalyst exposed to Pt_3Sb (008) showed enhanced catalytic activity and DHA selectivity than the catalyst exposed to Pt_3Sb (114). The insights reported here may aid to design high-efficient catalyst for base-free oxidation of glycerol.

Acknowledgments

This work is financially supported by the 111 Project of Ministry of Education of China (B08021).

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