

Carbon Nanotube Supported Pt-Co Catalysts for Low-temperature Preferential Oxidation of CO in a H₂-Rich Stream

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Introduction

Proton exchange membrane fuel cells (PEMFCs) with hydrogen rich gases as the fuel is known as a clean energy system with a high thermodynamic efficiency, but serious poisoning of Pt-anode by a trace of CO in H₂ is an awkward problem of it. Preferential oxidation (PROX) of CO with minimum loss of H₂ is considered as one of the promising methods and becomes one key step in the development of an economically feasible technology to produce hydrogen for PEMFCs. Previously, we reported that CNTs supported platinum catalysts with high loading of platinum of 15 wt% are very active for CO-PROX reaction at room temperature in reaction mixture of 2.5 vol% CO, 2.5 vol% O₂, 25 vol % H₂ and N₂ balance [1]. Further, we found that the promotional effects on the PROX reaction of CO in H₂ were evidenced with the Pt catalysts supported on CNTs, carbon nanofiber, graphite, and amorphous carbon with dopants of Ni-MgO or Fe-Al₂O₃ [2,3]. Herein, a kind of CNTs-supported Pt-Co (PtCo/CNTs) catalyst with high activity and excellent stability for the CO-PROX in H₂ stream is reported. Detailed structural and kinetic studies that address the effects of the cobalt are then shown.

Experimental

The bimetallic PtCo catalysts were prepared from H₂PtCl₆ and Co(NO₃)₂. The supports were dispersed in aqueous solutions of H₂PtCl₆ and Co(NO₃)₂. After evaporation, the solids were added into aqueous solution of formaldehyde and the suspension was refluxed at 363 K for 30 min. The final catalysts were obtained by filtration, drying and calcined at 623 K for 4 h in air. The metal loadings of Pt and Co was preset at 4 wt% and 0~2 wt%, respectively. They were determined by ICP-MS. The CO-PROX reaction was carried out using a fixed-bed reactor. The feed gas was typically composed of 1.0% CO, 1.0% O₂, 50% H₂ balanced with N₂, using GHSV=30,000 mL h⁻¹ g⁻¹. The outlet stream was analyzed by an on-line gas chromatograph.

Results/Discussion

TEM images in Figure 1 indicate that the metal nanoparticles are very uniform with size around 2-3 nm, independence of Co loading. The catalytic performance of PtCo/CNTs catalysts for

CO-PROX reaction as shown in Figure 1 demonstrates that CO can be totally removed over the catalyst 4%Pt-0.67%Co/CNTs at the temperatures ranging from 313 to 433 K, where the O₂ selectivity to CO₂ formation is kept at about 50%. The O₂ selectivity can be enhanced to about 70% while keeping CO conversion at 100% when the molar ratio of CO/O₂ is adjusted to 1/0.7 over the optimized catalyst 4%Pt-0.67%Co/CNTs (Figure 2). The catalyst 4%Pt-0.67%Co/CNTs can maintain 100% CO conversion and above 50% selectivity of O₂ for runs longer than 100 h at 353 K (Figure 2). The amount of CO-desorption on PtCo/CNTs decreases significantly as compared with Pt/CNTs, indicating an apparent weakening of CO-adsorption on the surfaces of PtCo/CNTs. The results of XPS imply that there are two kinds of Co species, one is interacted with Pt and likely to form Pt-Co alloy in reduction process and another, likely as CoO, is strongly interacted with CNTs and PtCo alloy. The high activity of the catalysts is essentially attributed to the interaction between Pt and Co with the formation of Pt-Co alloy.

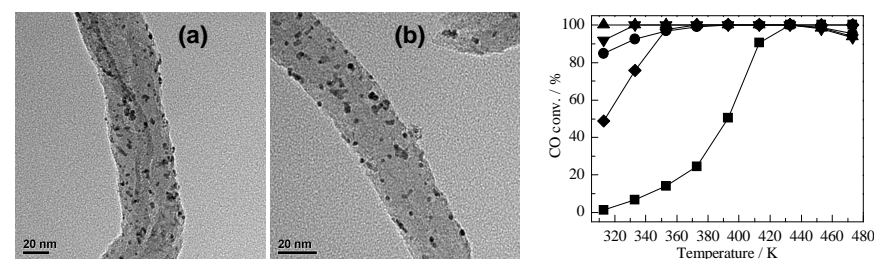


Figure 1. TEM images of (a) 4%Pt/CNTs and (b) 4%Pt-0.67%Co/CNTs; CO-PROX over (■) 4% Pt/CNTs, (●) 4%Pt-0.34%Co/CNTs, (▲) 4%Pt-0.67%Co/CNTs, (▼) 4%Pt-1.34%Co/CNTs, (□) 4%Pt-2.01%Co/CNTs.

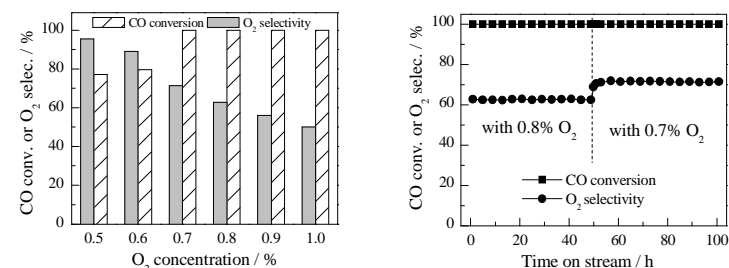


Figure 2. CO-PROX on 4%Pt-0.67%Co/CNTs under the conditions of 353 K, GHSV=40,000 mL g⁻¹ h⁻¹, feed gas=0.5-1.0% O₂, 1% CO, 50% H₂, 20% H₂O and 25% CO₂ balanced with N₂.

References

1. K. Tanaka, M. Shou, H. B. Zhang, Y. Z. Yuan, T. Hagiwara, A. Fukuoka, *Catal. Lett.* 126, 89 (2008).
2. H. W. Yang, G. Q. Yi, H. Q. Lin, K. Tanaka, Y. Z. Yuan, *Chin. J. Catal.* 30, 780 (2009).
3. K. Tanaka, M. Shou, Y. Z. Yuan, *J. Phys. Chem. C*, 114, 16917 (2010).