Highly active and stable supported palladium-gallium bimetallic catalysts for methane combustion

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Abstract: Catalytic combustion of methane is widely used in industrial and transportation activities. In this work, we adopted a novel strategy to prepare a GaO_x-doped Pd/Al_2O_3 catalyst. We observed a synergistic effect between palladium and gallium oxide via formation of a bi-functional active Pd–O–Ga component, which led to a highly active and exceptionally stable catalyst that could markedly suppress the sintering of noble metals under harsh conditions (hydrothermal treatment at 750 °C). It is believed that such a novel dual metal catalyst is promising in practical applications for methane combustion.

Keywords: methane combustion, nanocrystals, hydrothermal stability.

1. Introduction

Methane can induce a strong greenhouse effect of global warming potential 20 times higher than carbon dioxide[1]. Usually, methane combustion requires high temperatures, in which noxious emissions become a problem. Although noble metal-based (especially supported Pd) catalysts exhibit good performance under methane-lean conditions, high loadings and activity deterioration caused by sintering of nanoparticles remain the major drawbacks of the supported Pd catalysts[2]. At present, high loading and deterioration in activity caused by sintering of noble metals remain the major drawbacks of supported Pd catalysts[3]. Therefore, it is of significance to develop more efficient substitutes for industrial applications.

2. Experimental

Pd and Pd_5Ga_3 nanocrystals (NCs) were synthesized with $Pd(acac)_2$ or/and $GaCl_3$ being mixed with oleylamine (OAm) at 180 °C under an argon atmosphere. These NCs were loaded on γ-Al_2O_3 (Pd loading = 1.5 wt%) after calcination at 450 °C for 5 h. The obtained supported samples were denoted as Pd/Al_2O_3 and Pd-GaO_x/Al_2O_3, respectively. In order to investigate the hydrothermal stability, the samples were also calcined under 10 vol% H_2O/air atmosphere at 750 °C for 8 h, the obtained samples were denoted as Pd-GaO_x/Al_2O_3-HT and Pd/Al_2O_3-HT, in which the "HT" denote the "hydrothermal" treatments. Physicochemical properties of the samples were characterized by means of the XRD, TEM, HAADF-STEM, XPS, and H_2-TPR techniques, and their catalytic activities for the combustion of methane (2.5 vol% CH_4 + 20.0 vol% O_2 + 77.5 vol% N_2 (balance)) were evaluated in a fixed-bed microreactor at a SV of 80,000 mL/(g h). Reactants and products were analyzed online by gas chromatography.

3. Results and discussion

The XRD results reveal that the intermetallic Pd_5Ga_3 sample possessed an orthorhomibc crystal structure, and the Pd and PdO phases were present in the pure Pd NCs, whereas only PdO phase existed in the Pd-GaO_x NCs. The result suggests that GaO_x modification could promote the oxidation of the Pd NCs during the calcination process. The as-obtained Pd-based NCs were uniform in size (Figures 1). The Pd particles (40.3 nm in size) of the hydrothermally aged Pd/Al_2O_3-HT sample grew significantly, as compared to those (5.5 nm in size) of the fresh counterpart. This result clearly indicates the serious sintering of Pd NPs. However, an only slight growth of Pd-GaO_x NCs from 5.3 to 5.4 nm in mean size happened when the Pd-GaO_x/Al_2O_3 sample was hydrothermally treated.

It can be observed that catalytic activity of the supported Pd-GaO_x catalyst outperformed the supported Pd catalyst for methane combustion at a SV of 80 000 mL g^{-1} h^{-1} (Figures 2). To simulate the practical applications in methane combustion, we conducted the hydrothermal ageing experiment before methane combustion. It is found that the catalytic activity ($T_{90\%}$ = 432 °C) over Pd-GaO_x/Al_2O_3-HT was much better than that ($T_{90\%}$ = 522 °C) over Pd/Al_2O_3-HT. In other words, the Pd-GaO_x/Al_2O_3-HT sample was catalytically stable under the adopted conditions.

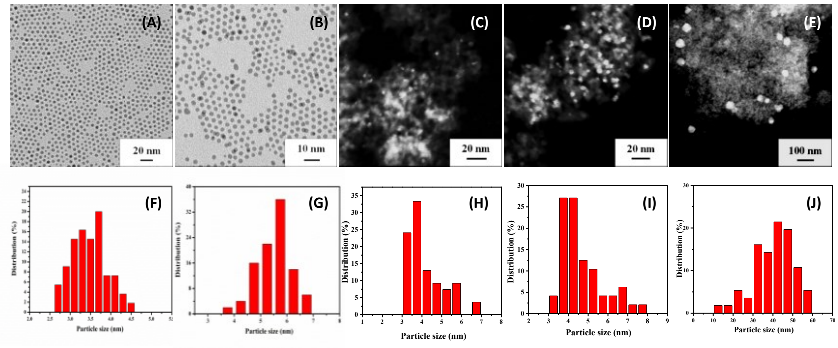

Figure 1. TEM images and particle-size distributions of (A, F) Pd_5Ga_3 NCs, (B, G) Pd NCs, HAADF–STEM images and particle-size distributions of (C, H) Pd-GaO_x/Al_2O_3, (D, I) Pd-GaO_x/Al_2O_3-HT, and (E, J) Pd/Al_2O_3-HT.

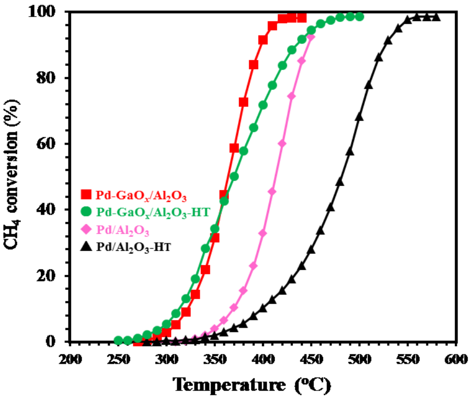

Figure 2. Methane conversion as a function of temperature over the samples at SV = 80,000 mL/(g h).

4. Conclusions

The Pd-GaO_x/Al_2O_3 catalyst was highly resistant to sintering, which showed a high catalytic activity for methane combustion and excellent hydrothermal stability. Pd-GaO_x/Al_2O_3 was a complex material with synergistic and bi-functional characters originating from formation of a Pd–O–Ga component that could enhance the Pd–O bond strength against sintering.

References

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