Highly sintering-resistant Au/TiO_2-HAP catalyst for CO oxidation at low temperatures

Hailian Tang[1,2], Kunfeng Zhao[1,2], Botao Qiao[1], Changzi Jin[1], Xin Liu[1], Junhu Wang[1*]
[1]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China*
[2]*Graduate University of Chinese Academy of Sciences, Beijing, 100049, China*
**corresponding author: wangjh@dicp.ac.cn*

Introduction

In the past decades, oxides supported Au nanoparticles (NPs) as catalysts have attracted extensive interest because of their extremely high activity and/or selectivity for numerous key chemical reactions [1,2]. However, the practical application of supported Au catalysts faces great challenge. A major issue is the low stability of gold NPs which tend to sintering easily under reaction, especially at higher temperatures, and loss their activity. Therefore, development of sintering-resistant supported Au catalyst is of great importance [3,4].

We recently found that a composite of FeO_x and hydroxyapatite (HAP) supported Au catalyst was not only highly active but also sintering-resistant [4]. A subsequent detailed study revealed that the HAP accounted for the high sintering-resistance [5]. Following this line, here we reported a new TiO_2-HAP supported Au catalyst which possessed even better sintering-resistance and CO catalytic oxidation performance.

Materials and Methods

The TiO_2-HAP composite (denoted as TH) were synthesized by chemical precipitation method. For comparison, a commercial TiO_2 (P25) (denoted as T) was selected and a pure HAP (denoted as H) support was also prepared. The Au NPs were loaded by a deposition-precipitation method targeting at a loading of 3 wt% [4]. The catalytic performance for CO oxidation was tested in a fix-bed reactor with 100 mg sample. The feed gas containing 1 vol% CO, 1 vol% O_2 and balance He was allowed to pass through the reactor at a flow rate of 33.3 ml min^{-1}, corresponding to a space velocity of 20,000 $ml g_{cat}^{-1} h^{-1}$. The effluent gas compositions were on line analyzed by a gas chromatograph (HP 6890) equipped with a TDX-01 column and a thermal conductivity detector using He as carrier gas.

Results and Discussion

The TEM images of Au/T and Au/TH catalysts calcined at different temperatures are presented in Fig. 1. It shows that the Au NPs on as-synthesized Au/T are about 3 nm, which is similar with the as-synthesized Au/TH but with a slightly wider size distribution. After being calcined at 400 °C, the Au NPs grew up to about 5 nm on Au/T while they keep almost unchanged on Au/TH catalyst, suggesting that the Au/TH catalyst is more sintering-resistant. Especially, when further increasing the calcination temperature to 600 °C, the Au NPs on Au/T significantly aggregated to form very large particles (~12 nm). Comparatively, although the Au NPs on Au/TH also grew up, the aggregation extent was much lower (from ~2 nm to ~4 nm). The Au/H catalyst showed a similar sintering-resistance with Au/TH (images not shown here for clarity), suggesting that the sintering-resistance originated from the HAP. The XRD analysis (data not shown here) was consistent with the TEM results. All these data provided unambiguous evidence that the Au/TH catalyst has excellent sintering-resistance.

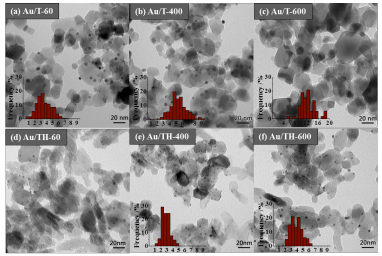

Fig. 1 TEM images of Au/T (a, b, c) and Au/TH (d, e, f) catalysts calcined at different temperatures.

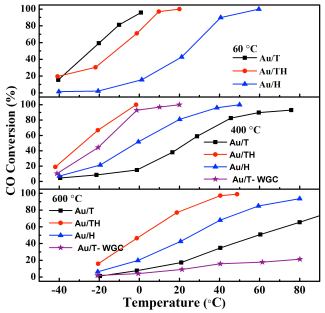

Fig. 2 Activity curves of CO oxidation on Au catalysts with different heat-treatments.

The activities of Au/T, Au/H and Au/TH catalysts with different heat-treatments for CO oxidation were tested. As shown in Fig. 2, without calcination, the Au/T catalyst exhibited the highest activity and could totally converted CO at temperature below 0 °C. The Au/TH exhibited a relatively lower activity (totally converting CO below room temperature) while Au/H had the lowest activity. However, after calcination at 400 °C, the activity of Au/TH and Au/H increased slightly, which might due to the increase of the interaction between Au and the supports or due to the reduction of Au (XPS data not shown here). However, the activity of the Au/T catalyst decreased seriously due to the aggregation of the Au NPs (Fig. 1a, b). After calciend at 600 °C, the activities of all these three samples decreased. However, the decrease extents are much different. As shown in Fig. 2, the Au/TH still gave 80% CO oxidation at room temperature and 100% CO oxidation at 50 °C after calcination at 600 °C, showing the excellent sintering-resistance and high activity.

Significance

A TiO_2-HAP composite supported Au catalyst was successfully developed. It is not only highly active for CO oxidation, but also strongly sintering-resistant against calcination at as high as 600 °C. The excellent sintering-resistant performance makes the supported Au catalysts are more practical applicable, even for the reaction occurred at high temperatures.

Acknowledgments

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