Active Gold Species during Preferential Oxidation of CO in H_2 over Au/CeO_2 Catalysts

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Introduction

Recently, considerable effort has been made in the design of suitable catalysts for the preferential oxidation of CO (PROX) required for producing high purity H_2 for the operation of low-temperature fuel cells. PROX catalysts should meet the requirements of high CO oxidation activity (to < 10 ppm) and high selectivity (> 50%) in the 80-110ºC temperature range in the presence of H_2 (50-75 vol%), CO_2 (20-24 vol%) and H_2O (2-10 vol%) [1,2]. In this case of WGS [2] and PROX [1,3] reactions, Au catalysts have shown to be very active, but there are still open questions regarding the nature of the active sites and of ways to stabilize them. The proposed active species include metallic Au nanoparticles, isolated Au cations, Au nanoparticles-support interface, and support structures with redox properties [4].

In this work we demonstrate that in the case of Au/CeO_2, both Au nanoparticles and cationic Au species are present on catalysts, their ratio depending on the Au content. All of our catalysts show high activity during the PROX reaction in the presence of 50-75% H_2 at 80-110ºC at GHSV = 12000 h^{-1}. However, the activity is a function of the Au content and of the concentration of O_2 and CO_2 in the feed, but there is no effect of H_2O. The reverse WGS reaction ($H_2 + CO_2 \rightarrow CO + H_2O$) starts at 252ºC

Materials and Methods

We prepared Au/CeO_2 catalysts having 0-1.3 Au wt. % by the deposition precipitation method. PROX was performed at 12000 h^{-1} using 0.8-1% CO, 0.4-1% O_2, 5-50% H_2, 0-10% H_2O, 0-24% CO_2, and N_2. Catalysts were characterized by XRD, diffuse reflectance in the UV-Vis region, CO-FTIR, Raman and XANES.

Results and Discussion

Our lowest gold content catalyst, i.e., 0.32%-Au/CeO_2, was highly active in the PROX reaction; X_{CO2} and S_{CO2} were 93% and 95% at 110ºC, respectively. On the other hand, catalysts having higher Au content, i.e., 1.32 Au wt. %, had X_{CO2} and S_{CO2} of 81% and 83% at 65ºC, respectively (Figure 1). This behavior was linked to the presence of cationic Au, with changes in CeO_2 lattice constant, and to the presence of gold nanoparticles as well. The ratio of cationic gold species to metallic gold nanoparticles on Au/CeO_2 catalysts strongly depends on gold content. This is discussed based on different characterization techniques as XRD, UV-vis, Raman, CO-FTIR and XANES spectroscopies.

The catalytic activity during PROX reaction on the Au content depends on the nature of gold species on catalysts. In general, the higher the gold content, the higher the amount of gold nanoparticles and the lower the light-off temperature of both CO and H_2 oxidations during PROX reaction, but also the lower the maximum CO conversion and the selectivity.

Significance

Results presented here show that both gold nanoparticles and gold cationic species are present on Au/CeO_2. The $Au_{np}/Au^{\delta+}$ ratio increases with Au content. Light-off temperatures, maximum conversions and selectivity for CO oxidation during PROX depend on the ratio of $Au_{np}/Au^{\delta+}$. We present a specific model that accounts for the contribution of each type of Au site.

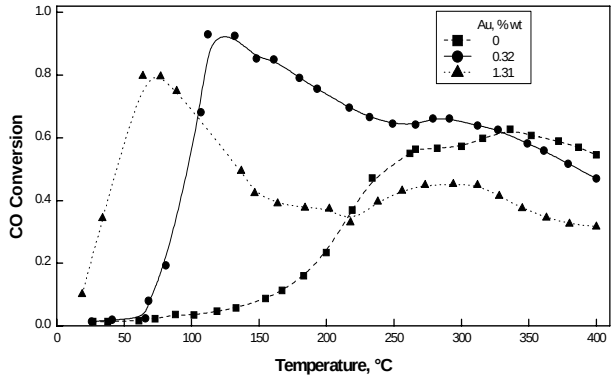

Figure 1. CO oxidation in H_2 as a function of Au content on Au/CeO_2 catalysts.

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References

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