Impact of the support composition on the performance of Au/CeO_2-Fe_2O_3 catalysts in PROX and WGS reactions

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Introduction

The utilization of pure hydrogen as energy source in proton exchange membrane fuel cells has stimulated extensive research for development of active WGS and PROX catalysts. Au/ceria catalysts have been proven very efficient for both reactions [1,2]. The stability of catalysts under operating conditions is an important issue. A very recent study of Au/doped-ceria catalysts for PROX has revealed the beneficial role of ceria modification for activity enhancement and improved resistance towards deactivation caused by the presence of CO_2 and H_2O in the PROX feed [3]. Mixed CeO_2-Fe_2O_3 oxides with different ratio were prepared and used as supports of gold catalysts in order to optimize their performance. The selection of these oxides was based on previous experience and on the following considerations: i) Fe_2O_3 is the main component of high-temperature WGS catalysts. Investigations of Au/Fe_2O_3 catalysts have shown that it is also a very suitable support for active low-temperature WGS and PROX catalysts [4,5]; ii) ceria is interesting because of its unique redox properties, high oxygen storage capacity and ability to promote metal dispersion.

Experimental

CeO_2-Fe_2O_3 oxides with atomic ratio Ce/(Ce+Fe) 0.25, 0.50 and 0.75, (as well as pure CeO_2 and Fe_2O_3) were synthesized by coprecipitation using urea as precipitation agent. The gold catalysts (3.5 wt.% Au) were prepared by the deposition-precipitation method and characterized by N_2 physisorption, XRD, HRTEM, FTIR and H_2-TPR. The catalytic activity and selectivity measurements for PROX and WGS reactions were carried out `in conventional flow reactor systems [3,4].

Results and discussion

XRD diffraction peaks related to fluorite structure of CeO_2, hematite structure of α-Fe_2O_3 and metallic Au are easy detectable in the XRD patterns of the catalysts. The intensity of the peaks of CeO_2 continuously weakens, while those of hematite intensify with the increase of Fe_2O_3 content. The intensity of Au^0 main peak is minimized for $AuCe_{0.5}Fe_{0.5}$. The analysis of TPR profiles reveals a significant effect of gold on the reducibility of mixed oxides. The peaks, which are related to the surface reduction of ceria and of hematite-to-magnetite in TPR profiles of mixed oxide catalysts shift to lower temperatures. The surface ceria reduction in $Au/Ce_{0.5}Fe_{0.5}$ occurs at lower temperature (130 ^oC) than in $Au/Ce_{0.75}Fe_{0.25}$, which has a higher

CeO_2 content (150 °C). This result correlates with the observed catalytic activity-selectivity trends in the PROX reaction (Fig. 1). Moreover, $Au/Ce_{0.5}Fe_{0.5}$ exhibits the best tolerance to the presence of CO_2 and H_2O in the feed. FTIR spectra collected after $CO+O_2$ interaction at 90 K evidence better reactivity of $Au/Ce_{0.5}Fe_{0.5}$ compared to $Au/Ce_{0.75}Fe_{0.25}$, as confirmed by the strong intensity of the band at 2341 cm^{-1} due to CO_2 produced in the presence of a high concentration of metallic Au particles (band at 2102 cm^{-1}) on the surface of this catalyst. WGS activity tests demonstrate also better performance of $Au/Ce_{0.5}Fe_{0.5}$ in comparison with $Au/Ce_{0.75}Fe_{0.25}$.

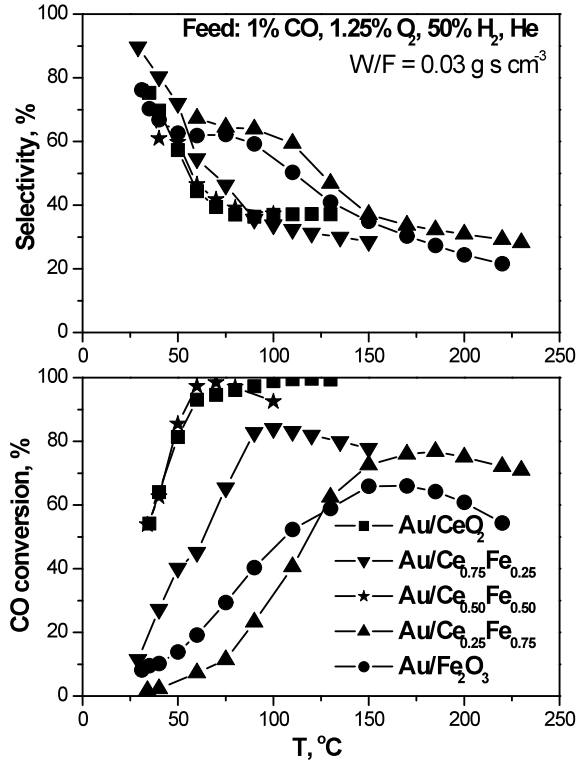

Figure 1. Catalytic behavior of Au/CeO_2-Fe_2O_3 catalysts in CO PROX reaction.

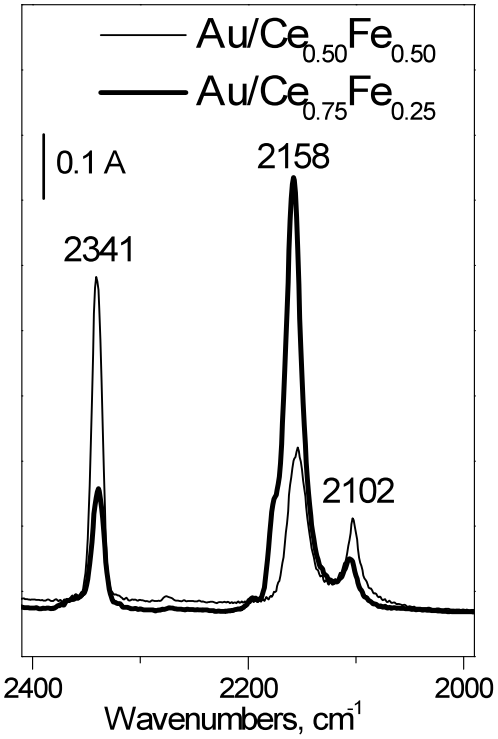

Figure 2. FTIR absorption spectra after interaction between CO and O_2 at 90 K.

Conclusions

Gold particle size, the nature and the amount of Au sites depend on the composition of mixed CeO_2-Fe_2O_3 oxides. These properties strongly influence the catalytic performance of the supported gold catalysts in PROX and WGS reactions. In order to obtain a better understanding of the behavior of the catalysts, detailed characterization by HRTEM and FTIR spectroscopy will be reported.

References

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