

## Impact of the support composition on the performance of Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> and H<sub>2</sub>O in the PROX feed [3]. Mixed CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> is the main component of high-temperature WGS catalysts. Investigations of Au/Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> oxides with atomic ratio Ce/(Ce+Fe) 0.25, 0.50 and 0.75, (as well as pure CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>) 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<sub>2</sub> physisorption, XRD, HRTEM, FTIR and H<sub>2</sub>-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<sub>2</sub>, hematite structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and metallic Au are easily detectable in the XRD patterns of the catalysts. The intensity of the peaks of CeO<sub>2</sub> continuously weakens, while those of hematite intensify with the increase of Fe<sub>2</sub>O<sub>3</sub> content. The intensity of Au<sup>0</sup> main peak is minimized for AuCe<sub>0.5</sub>Fe<sub>0.5</sub>. 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<sub>0.5</sub>Fe<sub>0.5</sub> occurs at lower temperature (130 °C) than in Au/Ce<sub>0.75</sub>Fe<sub>0.25</sub>, which has a higher

CeO<sub>2</sub> content (150 °C). This result correlates with the observed catalytic activity-selectivity trends in the PROX reaction (Fig. 1). Moreover, Au/Ce<sub>0.5</sub>Fe<sub>0.5</sub> exhibits the best tolerance to the presence of CO<sub>2</sub> and H<sub>2</sub>O in the feed. FTIR spectra collected after CO+O<sub>2</sub> interaction at 90 K evidence better reactivity of Au/Ce<sub>0.5</sub>Fe<sub>0.5</sub> compared to Au/Ce<sub>0.75</sub>Fe<sub>0.25</sub>, as confirmed by the strong intensity of the band at 2341 cm<sup>-1</sup> due to CO<sub>2</sub> produced in the presence of a high concentration of metallic Au particles (band at 2102 cm<sup>-1</sup>) on the surface of this catalyst. WGS activity tests demonstrate also better performance of Au/Ce<sub>0.5</sub>Fe<sub>0.5</sub> in comparison with Au/Ce<sub>0.75</sub>Fe<sub>0.25</sub>.

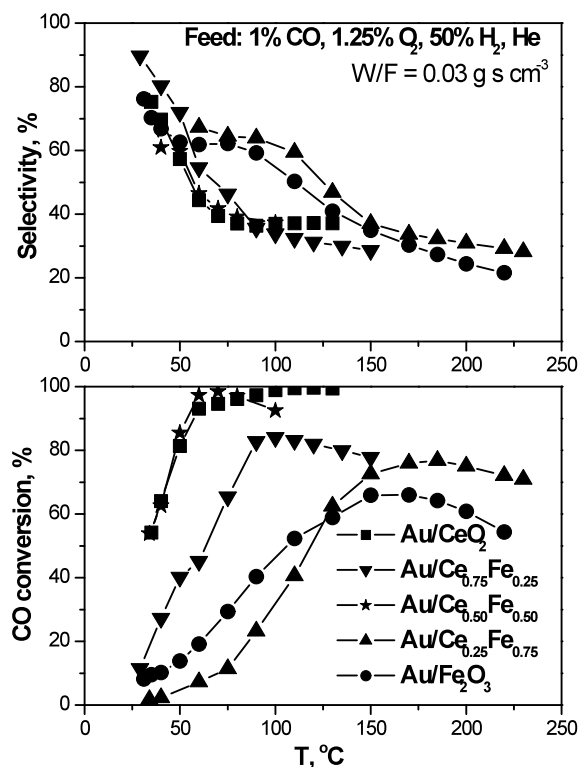


Figure 1. Catalytic behavior of Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> catalysts in CO PROX reaction.

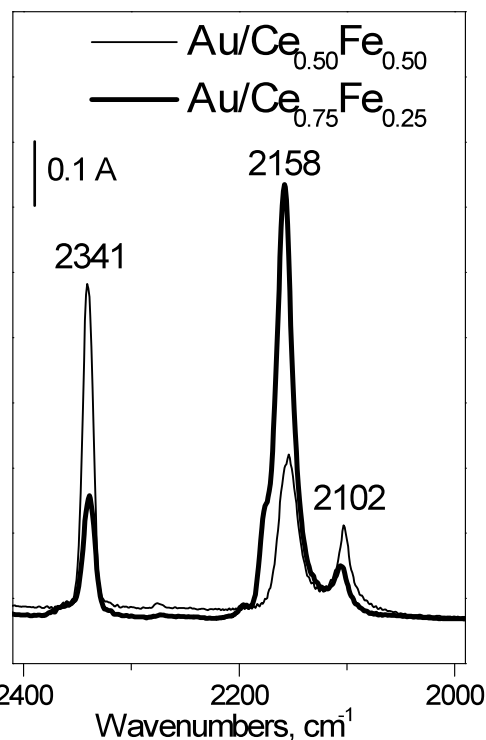


Figure 2. FTIR absorption spectra after interaction between CO and O<sub>2</sub> at 90 K.

## Conclusions

Gold particle size, the nature and the amount of Au sites depend on the composition of mixed CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> 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

- [1] Burch, R., Gold catalysts for pure H<sub>2</sub> production in the WGS: activity, structure and reaction mechanism, *Physical Chemistry Chemical Physics*, 8 (2006), 5483-5500 and references therein.
- [2] Schubert, M.M., Plzak, V., Garche, J., Behm, R.J., Activity, selectivity, and long-term stability of different metal oxide supported gold catalysts for the CO PROX in H<sub>2</sub>-rich gas, *Catalysis Letters*, 76 (2001), 143-150.
- [3] Avgouropoulos, G., Manzoli, M., Boccuzzi, F., Tabakova, T., Papavasiliou, J., Ioannides, T., Idakiev, V., Catalytic performance and characterization of Au/doped-CeO<sub>2</sub> catalysts for the CO PROX reaction, *Journal of Catalysis*, 256 (2008), 237-247.
- [4] Andreeva, D., Idakiev, V., Tabakova, T., Andreev, A., Low-temperature WGS over Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, *Journal of Catalysis*, 158 (1996), 354-355.
- [5] Avgouropoulos, G., Ioannides, T., Papadopoulou, Ch., Batista, J., Hocevar, S., Matralis, H., A comparative study of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and CuO-CeO<sub>2</sub> catalysts for the selective oxidation of CO in excess hydrogen, *Catalysis Today*, 75 (2002), 157-167.