Operando Characterization of Au/FeO_x-CeO_2/Al_2O_3 Catalysts During Water Gas Shift Reaction

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Introduction and Objectives

In the past decade, research has demonstrated the high potential of fuel cells to replace the internal-combustion engine in vehicles and to provide power in stationary and portable power applications. The hydrogen and the fuel cells together, represent a radically different approach to energy conversion. Nowadays, hydrogen is mostly produced from fossil fuels by a multistep process that includes catalytic autothermal reforming, always followed by the water–gas shift reaction (WGSR). A crucial prerequisite for the techno-economic success of fuel cells, especially those that operate either at low temperatures or in mobile applications, is the discovery of improved reforming and WGS catalysts for the generation of hydrogen which are much more active than those used in chemical plants [1]. Gold catalysts are extensively used for the WGSR, however is still difficult to find in the literature well performing and economically viable catalyst. In this work the development of gold based catalyst, essentially based on Ce-Fe mixed oxides-modified γ-alumina as support for the WGSR is proposed and compared to a gold catalyst iron oxide-promoted supported on a commercial CeO_2-Al_2O_3. Figure 1 shows a schematic representation of the prepared systems:

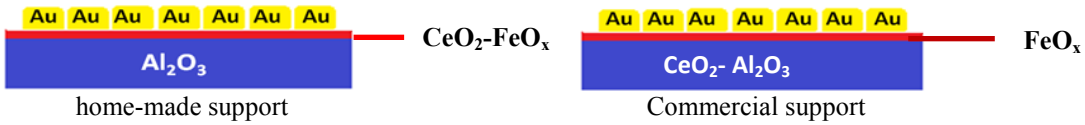

Figure 1: Schematic representation of the synthesized systems

The activity in the WGSR of the gold catalyst supported on the home-made support is remarkably higher than the Au catalyst supported on the iron-modified commercial support. In this scenario, the aim of this work is to understand the different behavior of these catalysts, under water gas shift reaction conditions, by employing several operando characterization techniques (XRD, EXAFS, DRIFTS, UV-Vis).

Results and Discussion

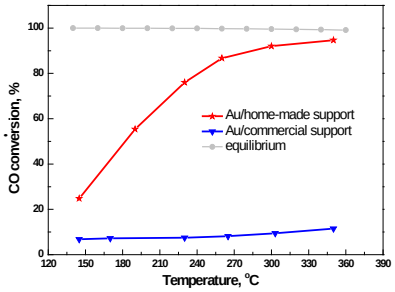

Figure 2. Catalytic activity in WGSR

The catalytic activity of the studied systems is compared in Figure 2. Although both catalysts have comparable gold and ceria loadings their catalytic activities are completely different. Gold dispersed on the home-made support almost reached equilibrium conversion at 330ºC while the catalyst prepared on the commercial support is hardly active in WGS. Operando XRD measurements (Figure 3) revealed two important differences between the catalysts that may explain the data shown in Figure 2. First, gold nanoparticles are smaller in the homemade catalyst. Assuming that CO oxidation occurs with the participation of Au-OH species formed at a peripheral gold atom by transfer of a support hydroxide ion and that these species further reacts with CO molecules adsorbed on a low-coordination gold atom, it can be concluded that the smaller the gold particle size the higher the catalyst activity. Therefore, the homemade system composed of very small and well-dispersed gold nanoparticles does show a higher catalytic activity in the WGSR. In the presence of oxides with redox properties, Ce-Fe mixed oxides, CO oxidation may also occur by oxide ions transferred from the support. Thus, iron oxide must play a role enhancing ceria redox properties favoring water dissociation that typically takes place on the support [2]. Our XRD data points to Ce-Fe solid solution in the homemade catalysts enhancing the reducibility of the ceria phase and favoring oxygen transfer reactions. On the contrary, the iron-promoted commercial support show diffraction lines associated to the presence of an iron spinel (Fe_3O_4) resulting in a less reducible support.

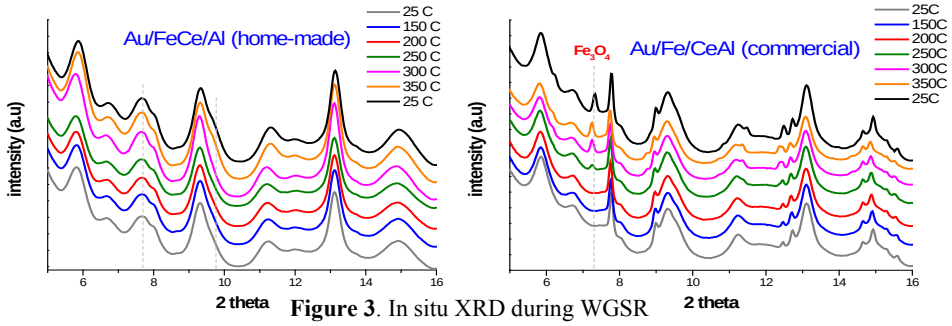

Figure 3. In situ XRD during WGSR

Conclusions

Operando experiments clarify that Au/FeO_x-CeO_2/Al_2O_3 catalysts can be a highly efficient for the WGSR if the formation of the iron spinel Fe_3O_4 (an inactive specie for WGSR) is avoided. Actually iron improves the ability of ceria to carry out the water dissociation only if it is able to maintain its maximum oxidation state facilitating ceria reduction.

References

[1] Ch. Ratnasamy and J.P.Wagner, *Catal. Rev*. 51 325-440 (2009).
[2] J.A. Rodriguez, S.A. Ma, P.Liu, J.Hrbek, J.Evans, M. Pérez, *Science* 318, 1757 (2007).