Hydrogen-alimented fuel cells (FC) have a strong potential to play a decisive role in the new energy system for the coming years. The production of H_2 pure enough to use it in fuel cells requires the development of very efficient catalysts for the WGS reaction. In our group several gold-ceria based catalysts have been developed presenting very promising results in this process [1,2]. The successful catalytic design makes mandatory an accurate knowledge about the reaction mechanism and the active species involved in the process. In order to address these issues a combination of several *in-situ/operando* characterization techniques is performed in this work using an optimized Au/CeO_2-FeO_x/Al_2O_3 catalyst. Synchrotron-based *in-situ* time-resolved X-ray absorption spectroscopy (TR-XAS) and *operando* DRIFTS during the WGS reaction are employed with the ultimate goal to establish structure-activity relations and to propose the most likely reaction pathways.

The obtained results may be summarized as follows:

1) Oxidation state from *in-situ* XANES: Au remains as metallic gold during the reaction. Ce evolves from Ce^{4+} to Ce^{3+} (actually complete reduction of ceria is not achieved). Fe is present as Fe^{3+} since the profile of the XANES matches to the hematite structure.

2) **Presence of oxygen vacancies on ceria**. Our Raman, XRD and UV-Vis data established the existence of oxygen vacancies in the ceria lattice, especially when iron is present.

3) Gold dynamics. *In- situ* EXAFS analysis indicates the competition between gold particles and water to nucleate in the oxygen vacancies of the support. This process is associated to the observed gold nanoparticles rupture and subsequent agglomeration depending on the reaction temperature.

4) Reaction intermediates. *Operando* DRIFTS data point out that the formation of either bicarbonate or carboxylic species play a key role during the WGS.

Considering these premises, an associative mechanism where the carboxyl intermediates domains the reaction can be proposed:

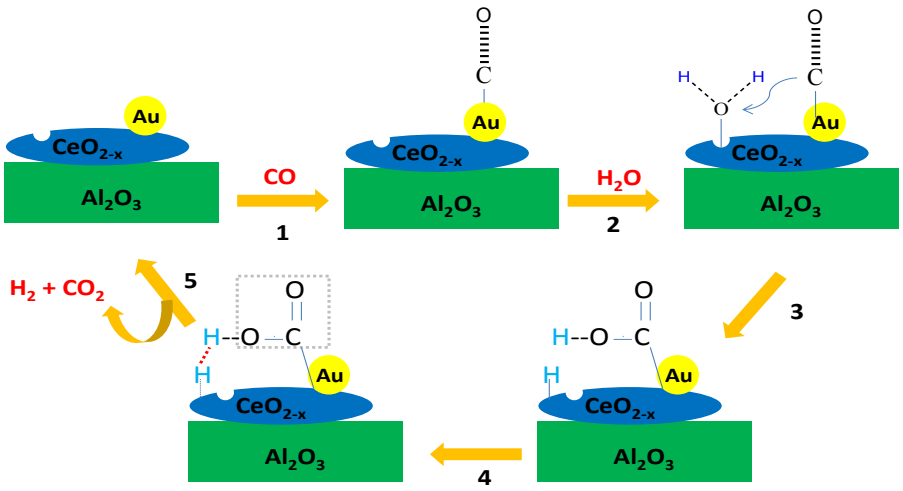


Figure 1*: Simplified WGS mechanism proposal for a Au/CeO_2-FeO_x/Al_2O_3 catalyst*

The main reactions pathways are:

1) Adsorption of CO on gold nanoparticles. 2) Activation of H_2O on the ceria oxygen vacancies. 3) The interaction between CO and activated H_2O on the metal-support interface. More specifically, this step represents the formation of the COOH intermediate due to the combination of CO and OH. This process may happen also in two steps. First the water rupture into OH and H and second the formation of the HO-CO bond. 4) Formation of the CO_2 and H_2. 5) Final release of the products.

Conclusions:

Our *in-situ/operando* study provides some relevant clues regarding the WGS mechanism and towards the catalyst design and future improvements. In particular, an associative route via carboxyl formation seems to control the process. The high catalytic performance is achieved when gold nanoparticles are in close contact with the structural defects of ceria and the oxygen mobility of the later is enhanced by the addition of promoters such as iron oxide.

References

[1] J. A. Odriozola, T. R. Reina, M. A. Centeno, S. Ivanova, V. Idakiev, T. Tabakova, Spanish Patent 201101163.

[2] M. González, T.R.Reina, S. Ivanova, M. A.Centeno, J.A. Odriozola J. Catal. 314 (2014) 1-9