Contribution ID: **67** Type: **Oral presentations**

Unraveling the working architecture of real catalysts by near-ambient XPS

Thursday, 18 June 2015 13:00 (20 minutes)

The structure of heterogeneous catalysts is dynamic and both their surface structure and composition may be modified when the gaseous conditions change in order to adapt their electronic properties and geometry to the new atmosphere. Some structures and active phases only exist under reaction conditions and can differ from those identified under UHV conditions [1]. Thus, the study of catalytic systems under real conditions is essential to identify the active species at work, as the restructuring driven by the environment may induce strong changes in their properties and behavior. We have carried out an operando XPS study in the CIRCE beamline (NAPP endstation) at ALBA synchrotron of bimetallic rhodium-palladium nanoparticles supported over cerium dioxide (RhPd/CeO2) for producing hydrogen through the ethanol steam reforming reaction (ESR), which represents an attractive route for renewable hydrogen generation for energy applications. We have monitored both the surface restructuring and chemical state of two systems: (i) unsupported model Rh0.5Pd0.5 nanoparticles (4±1 nm) and (ii) model Rh0.5Pd0.5 nanoparticles supported on CeO2 powder (which constitutes a real catalyst). Both systems were exposed to reducing, oxidizing and ESR conditions (0.05 mbar) to produce hydrogen. Three photon energies were chosen (670, 875, and 1150 eV) in order to perform a depth-profile study of both systems to infer the environment-induced rearrangement and the development of a core-shell structure of oxidation states. We demonstrate that the reducible ceria support plays a crucial role in the catalytic process by providing new active sites strongly affecting both the physical and chemical properties of the metal nanoparticles which, in turn, have a strong effect on the catalytic performance (Figure 1). The interaction of the metal nanoparticles with the ceria support not only provides active oxygen atoms to the superficial metal atoms of the nanoparticles, but also limits the reorganization of the metals under reaction (quenching effect) with respect to the unsupported metal nanoparticles [2]. This work constitutes one of the few examples reported where the surface of a real catalyst has been characterized by XPS under controlled atmospheres closely reproducing working conditions.

References

[1] F. Tao, M. Salmeron, In situ studies of chemistry and structure of materials inreactive environments, Science 331, 171–174 (2011).
[2] N. J. Divins, I. Angurell, C. Escudero, V. Pérez-Dieste, J. Llorca, Influence of the support on surface rearrangements of bimetallic nanoparticles in real catalysts, Science 346, 620–623 (2014).

Caption (s) - Add figures as attached files (2 fig. max)

Figure 1. Scheme of the changes experienced by unsupported RhPd nanoparticles and RhPd supported on CeO2. In the absence of a support, the model nanoparticles decomposed ethanol and were more strongly reduced for all the environments tested and the reduction temperature affected the amount of metallic phase found in Rh and Pd. In contrast, the capability of CeO2 as a support to activate water and to donate oxygen atoms determined the oxidation states of the noble metals under the same reaction conditions and ESR was effective.

Primary author: Prof. LLORCA, Jordi (Universitat Politècnica de Catalunya)

Co-authors: Dr ESCUDERO, Carlos (ALBA-CELLS); Dr DIVINS, Núria J. (Universitat Politècnica de Catalunya); Dr PÉREZ-DIESTE, Virginia (ALBA-CELLS)

Presenter: Prof. LLORCA, Jordi (Universitat Politècnica de Catalunya)

Session Classification: Session 7 - II ALBA User's Meeting 2015

Track Classification: II ALBA User's Meeting