

H₂ reduction reaction of Cu_xNi_{1-x}/CeO₂ (x = 0, 0.5, 1) nanoparticles

P. C. Kazmirczak¹, L. P. Matte¹, A. S. Kilian¹, L. Luza², M. C. M. Alves², J. Morais¹, J. Dupont², F. Bernardi^{1,*}

(1) Departamento de Física, Instituto de Física, Universidade Federal do Rio Grande do Sul, RS, Brazil

(2) Instituto de Química, Universidade Federal do Rio Grande do Sul, RS, Brazil

e-mail: bernardi@if.ufrgs.br

Ceria (CeO₂) is an advanced material used for catalytic applications mainly because oxygen vacancies at the surface can be rapidly formed and eliminated which gives to ceria the property of high capacity for oxygen storage [1]. Compared to different supports of metallic nanoparticles, ceria enhances the performance of catalysts in a variety of reactions such as the water gas-shift and the preferential oxidation of CO [1]. The reduction reaction is a key process employed in catalytic applications and it is very important to elucidate the atomic phenomena (core-shell structure formation, changes on the oxidation state, SMSI effect) existing in the nanoparticles in order to project the final desired properties of the catalysts. We have investigated *in situ* and *ex situ* the electronic and structural properties of Cu-Ni nanoparticles supported on CeO₂ and subjected to H₂ reduction. The metallic nanoparticles (~ 5 nm diameter) were synthesized by using the ionic liquid BMIBF₄ [2]. Thereafter, the nanoparticles were supported on CeO₂ and heated up to 500 °C in a H₂ atmosphere. The system was investigated by means of XPS (X-Ray Photoelectron Spectroscopy) and *in situ* XAS (X-Ray Absorption Spectroscopy) and DXAS (Dispersive XAS) techniques. All XAS measurements were performed in the transmission mode at the Ce L_{III} edge, Ni K edge and Cu K edge. The XPS and DXAS results show that Cu and Ni atoms were initially oxidized. Structural information was obtained by XAS technique and DXAS measurements reveal details about the kinetic of the H₂ reduction as a function of the reduction temperature and time. The reduction of the nanoparticle starts at ~285 °C for Cu/CeO₂, ~160 °C for Ni/CeO₂, ~190 °C (Cu) and ~435 °C (Ni) for Cu_{0.5}Ni_{0.5}/CeO₂ nanoparticles. After the beginning of the reduction it takes ~10 min for Cu/CeO₂, ~14 min for Ni/CeO₂, ~12 min (Cu) and ~14 min (Ni) for Cu_{0.5}Ni_{0.5}/CeO₂ to reduce completely the nanoparticles supported. The atomic arrangement at the surface of the nanoparticles is discussed based on the XPS results.

Acknowledgments: This work was supported by CNPq. The authors thank the LNLS staff.

[1] A. Trovarelli, *Cat. Rev.: Sci. and Eng.* **38**, 439-520 (1996).

[2] J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.* **102**, 3667-3691 (2002).