

## Atomic-scale structure of zirconia-supported on alumina

C. J. Dalmaschio<sup>(1)\*</sup>, E. R. Leite<sup>(1)</sup> and E. Longo<sup>(1)</sup>

(1) LIEC, Department of Chemistry, Federal University of São Carlos, P.O. Box 676, 13565-905 - São Carlos, SP, Brazil, e-mail: Cleocir@liec.ufscar.br

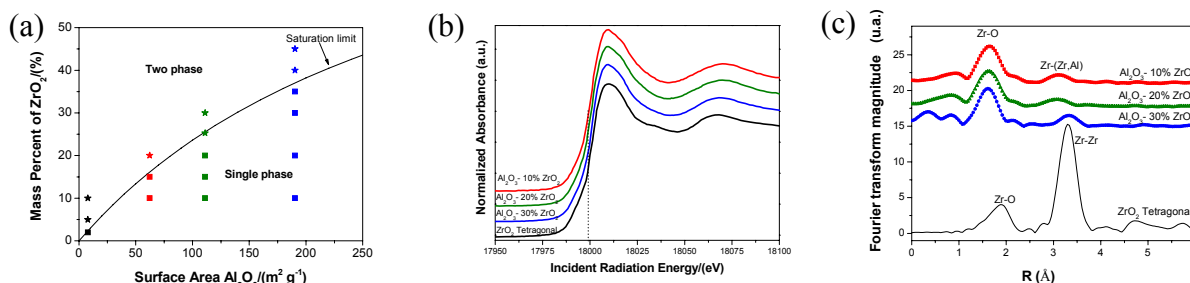
\* Corresponding author.

**Abstract** –Using a simple model that makes it possible to foresee the limit of surface oxide modifier that results in the complete coating of a support, four aluminas with different surface area were coating with zirconium oxide. The structure of materials was investigated using X-ray diffraction and X-ray absorption spectroscopy (XAS). The results showed that the zirconium oxide was dispersed on the support surface with excellent correlation of the experimental results with the diagram built from the model. XAS study comparing tetragonal ZrO<sub>2</sub> with the zirconium supported indicated a shorter Zr-Zr(Al) shell before phase separation.

Zirconium oxide and its mixed oxides present interesting catalytic properties which are generally attributed to the simultaneous presence of both acidic and basic sites on surface [1]. Aim to support zirconium oxide in alumina, a model that makes possible to foresee the limit of modifier oxide of surface that results in the complete support coating was used. From such limit, the crystalline lattice of the modifying material should be formed. In this way four alumina with surface areas between 7.8 and 190 m<sup>2</sup> g<sup>-1</sup>, upon which different zirconium oxide contents were deposited using a resin obtained through the polymeric precursors method for dispersion of modifier.

The characterization results for X-ray diffraction (XRD) presented excellent correlation with the diagram built from the model Fig. 1a, where the samples containing lower zirconium contents than those foreseen by the model presented only the crystalline phase of the support (alumina), represented by the squares in the graph. In the samples containing a percentage of zirconium exceeding the value limited by the solid line, crystalline phases corresponding to the support and the modifier material were identified, and are indicated in Fig. 1a as stars.

The short-range ordered structure of the material was evaluated by X-ray absorption spectroscopy of the Zr K-edge, which provided information about the local structure around zirconium atoms in the samples with a surface area of 111 m<sup>2</sup> g<sup>-1</sup> coated with 10, 20 and 30% (m/m) of modifier. X-ray absorption near edge structure (XANES) spectra indicated that the zirconium was in the IV oxidation state, as present in Fig 1b. To extended X-ray absorption fine structure (EXAFS) spectra applying the Fourier transform (FT) Fig 1c yielded a partial radial distribution function that allowed us to associate the distance of the neighbors in relation to Zr atoms. The FT results indicate that the first peak of the three coated samples, related to the first Zr-O coordination shell, was similar in intensity and position. Compared with tetragonal zirconia, the coated samples presented a smaller mean Zr-O distance. A similar effect was observed previously in a nanocomposite sample of aluminum and zirconium oxides and is likely associated with the formation of Zr-O-Al bonds [2]. The FT curves also indicated that the most significant differences between 2.5 and 4 Å. This region is related to the Zr-Zr distances in the tetragonal ZrO<sub>2</sub> sample and the Zr-(Zr,Al) distances in the alumina samples coated with zirconium oxide. In the sample coated with 30% (m/m) of zirconium, the position of the second peak coincided with the tetragonal zirconium, indicating the formation of the Zr-Zr shell, which was congruent with the XRD results and the model used to modifier the alumina.



**Figure 1:** Zirconia supported on alumina. a) XRD of samples with different surface area and saturation limit curve; b) Zr K-edge XANES spectra of sample with surface area of 111 m<sup>2</sup> g<sup>-1</sup>; c) FT of K-edge EXAFS spectra of sample with surface area 111 m<sup>2</sup> g<sup>-1</sup>.

### References

- [1] A. C. Faro Jr, K. R. Souza, V. L. D. L. Camorim, M. B. Cardoso, Phys. Chem. Chem. Phys. 5 (2003) 1932 - 1940.
- [2] X. Yang, M. Dubiel, H. Hofmeister, W. Riehemann, in: Proceeding XAFS13: 13th International Conference. Stanford (2007) 563 - 565.