**Structural design and optimization of $CeO_x$/ZnO porous nanorods decorated with Au nanoparticles for catalyzing the water-gas shift reaction**

Oliveira, C.[1], Rangel, M.[2], Teixeira Neto, E.[3] and Mazali, I.[1]

[1] University of Campinas - UNICAMP, Institute of Chemistry, Laboratory of Functional Materials, 13083-970, Campinas, SP, Brazil, [2] Federal University of Rio Grande do Sul (UFRGS), Institute of Chemistry, 90650-001, Porto Alegre, RS, Brazil, [3] Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, SP, Brazil

The water-gas shift reaction (WGSR) $CO + H_2O \rightleftharpoons CO_2 + H_2$, is an exothermic and reversible reaction, which is thermodynamically favorable below 220°C and kinetically favorable at higher temperatures. It is used to decrease the amount of CO from steam reforming streams, resulting in high-purity $H_2$. WGSR can be applied for purifying $H_2$ for fuel cells working with several feeds, such as biomass or biogas. Since the catalysts for WGSR were developed for industrial conditions, extensive research has been done to adapt the catalysts to work in fuel cells. Several metals and oxides have been studied, especially bimetallic catalysts, such as Pt-Re/$TiO_2$ [1]. Also, it was noted that the combination of different metal and oxides, such as Pt/$CeO_x$/$TiO_2$ or Cu/ZnO/$CeO_x$, affects the catalyst performance [2]. The combination of bulk/nanosized $CeO_x$ and Au nanoparticles has shown improved catalytic performance when compared to these catalysts, but some properties need to be improved: Au nanoparticles undergo sintering during the catalytic cycles, losing activity over several cycles. Also, the $Ce^{3+} \rightleftharpoons Ce^{4+}$ equilibrium is closely related to the catalyst performance, making the control of its balance mandatory during reaction [3]. ZnO is used at low temperatures control this equilibrium. In this work, a new catalyst for the WGSR comprised of $CeO_x$ porous nanorods, whose pores were accessed/enlarged by means of acid leaching with ZnO and anchor Au nanoparticles was prepared.

The design and preparation of Au NPs nanoporous $CeO_x$/ZnO catalyst is based on the combination of the hydrothermal synthesis of $CeO_x$ nanorods [4], followed by impregnation-decomposition cycles (IDC) [5], allowing the produce porous $CeO_x$ nanorods covered by a thin layer of ZnO. Following the synthesis of this double oxide material, Au NPs were supported on the porous nanorods, resulting in Au NPs strongly anchored inside the pores on the surface of the $CeO_x$/ZnO nanorods. This innovative strategy was developed in our group to prevent the sintering of Au NPs during the catalytic cycle(s).

High resolution scanning transmission electron microscopy (STEM) associated with energy dispersive X-ray spectrum imaging (EDS-SI) acquired using a FEI Titan Themis 60-300 microscope (Figure 1) allowed us to track the fabrication of the catalyst material by the observation of (1) the crystalline porous $CeO_x$ nanorods, helping determine the optimal acid leaching condition to maintain nanorod integrity while also exposing and enlarging its pores, (2) the uniform distribution of Zn on the nanorods surface and (3) the distribution of Au NPs (~1.8 nm) filling the pores.

[1] Galhenage, R. P., *et al.*, J. Phys. Chem. C, 120, 10866-10878 (2016).
[2] Luo, S., *et al.*, J. Phys. Chem. C, 121, 6635-6642 (2017).

[3] Puigdollers, A. R., *et al.*, ACS Catal., 7, 6493-6513 (2017).
[4] Silva, I. C., Sigoli, F. A., Mazali, I. O., J. Phys. Chem. C, 121, 12928 - 12935 (2017).
[5] Oliveira, C. S., *et al.*, Cryst. Growth Des., 17, 5398-5405 (2017).

We acknowledge the funding provided by CAPES and the INOMAT project (Fapesp 2014/50906-9 and CNPq 465452/2014-0). We thank LNNano-CNPEM (Campinas, Brazil) for the use of the FEI Titan Themis 60-300 microscope.

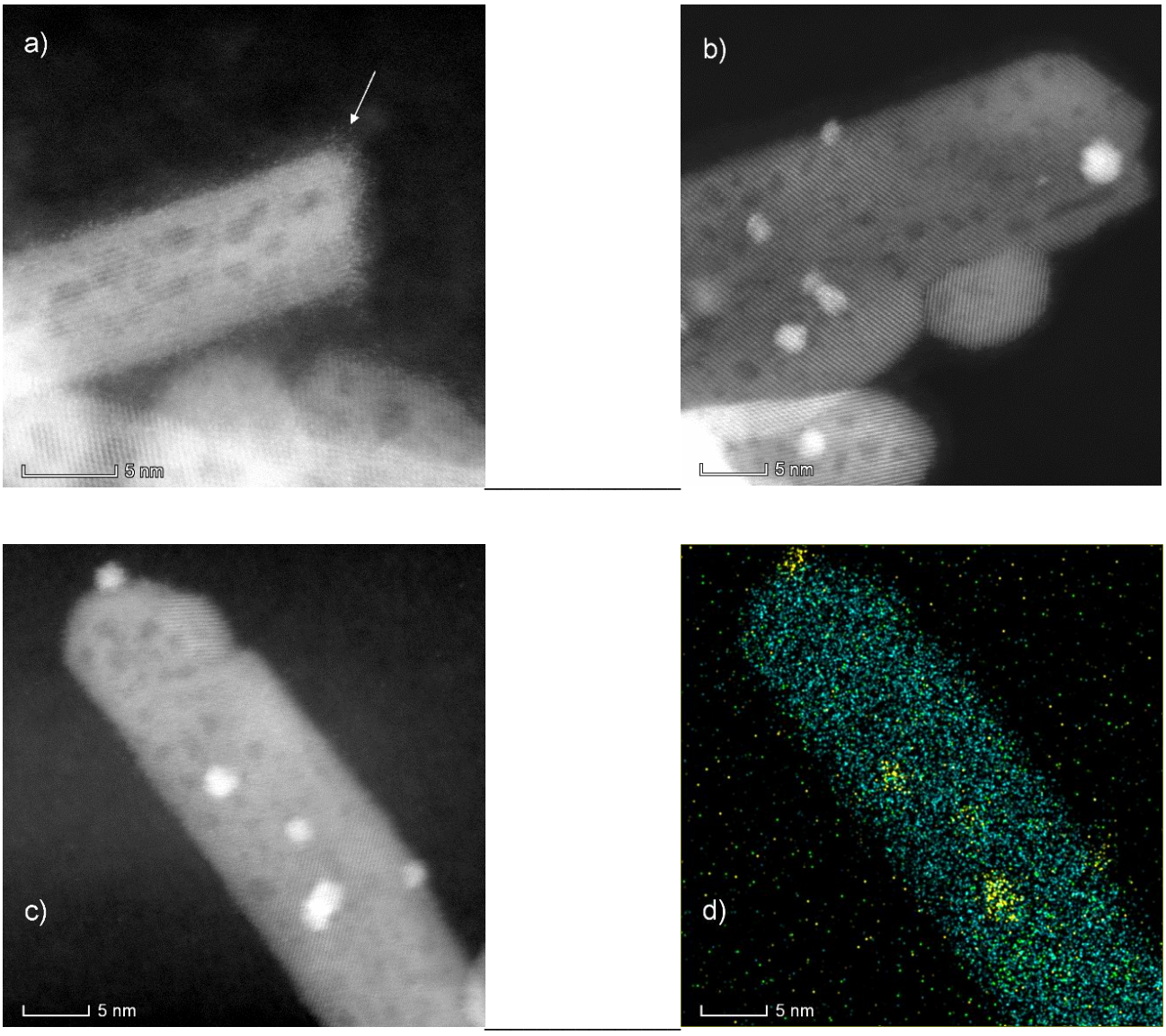


Figure 1 - $CeO_x$ porous nanorods appear highly crystalline in the HAADF-STEM image (a), before the deposition of Au NPs, with a thin layer of disordered ZnO (indicated by the arrow) coverig the nanorods. Very small Au NPs (b) anchored on the porous $CeO_x$/ZnO nanorods. HAADF-STEM image (c) and corresponding EDS-SI map (d) of the resulting catalyst material showing the distribution of Au (yellow), Ce (blue) and Zn (green).