810 CD
DOI: 10.1017/S1431927606066219

Microsc Microanal 12(Supp 2), 2006

TEM (HREM) and STEM (HAADF/EDS) Study of the Metallic Dispersion in Supported Ruthenium Catalysts

J.C. Hernández, D.M. Vidal, A.B. Hungría, S. Trasobares, M.P. Rodríguez-Luque, C. Mira, J.J Calvino and J.A. Perez-Omil

Departamento de Ciencia de los Materiales, Ingeniería Metalúrgica y Química Inorgánica. Universidad de Cádiz. Facultad de Ciencias, Puerto Real (Cádiz) 11510 Spain

Noble metals highly dispersed on cerium-zirconium mixed oxide supports are commonly employed as a component in three ways catalysts (TWC) and currently they are tested in catalytic processes for hydrogen production [1]. The dispersion of the metallic phase, defined as the fraction of metallic atoms exposed at the surface, is one of the key parameters determining the behaviour of these catalysts. It is well known that this parameter can be estimated from the analysis of Particle Size Distributions obtained using Electron Microscopy techniques [2].

In this contribution the results of the characterization of ruthenium nanoparticles supported on different oxides (Al_2O_3, $Ce_{0.5}Zr_{0.38}Tb_{0.12}O_2$,, $Ce_{0.62}Zr_{0.38}O_2$ and $Ce_{0.8}Tb_{0.2}O_2$), using high resolution electron microscopy (HREM), high angle annular dark field (HAADF) in scanning-transmission (STEM) mode and X-Ray spectroscopy (EDS), are presented. From these data, the dispersion of the metallic phase is determined. The nano-structural evolution of the catalysts has also been followed after reduction treatments in an atmosphere of H_2 (5%)/Ar at increasing temperatures in the range 623K - 1173K.

The analysis of the electron microscopy images of the samples shows the convenience of using HAADF technique in addition to HREM for the characterization of these catalysts. In the case of the Al_2O_3 supported Ru catalysts, HAADF imaging [3] improves the contrast between the metal particles and the support, as compared to HREM. This allows extending the range of measurable particles diameters (figures 1.a and 1.b). For the sample studied in this contribution, the dispersion values calculated from the particle sizes distribution curves obtained by HREM and HAADF are similar, but the use of HAADF increases the reliability of the dispersion values observed for these samples. In the case of the cerium-zirconium supported Ru catalysts, HAADF images, in combination with EDS spectroscopy, fig. 4, are necessary to avoid misidentification of Ru particles.

The comparative analysis of data summarized in table 1 shows the following results: a) The initial dispersions of the Ru for the whole set of catalysts studied in this work (with the exception of the $Ce_{0.8}Tb_{0.2}O_2$ supported catalyst) are similar; b) the dispersion of both the alumina and the Ce-Tb mixed oxide supported Ru catalysts decreases notably with increasing reduction temperature; c) the dispersion of Ru does not change significantly for the catalysts based on Ce-Zr or Ce-Zr-Tb mixed oxides in the range of temperature studied here. Thus, these results show clearly that the incorporation of Zr to the cerium oxide or cerium-terbium mixed oxide matrix allows a stabilization of the metallic dispersion. The origin of this effect is a matter of further study at this moment.

References

[1] S. Bernal et al., *Top. Catal*. 28 (2004) 31
[2] Special Issue: HRTEM for Catalysis, *Catal. Today* (3) (1995) 23
[3] S.J. Pennycook et al, *Nature*. Vol. 336 (1988) 565
[4] We acknowledge the financial support from Ministry of Education and Science of Spain (MAT2002-02782) and Junta de Andalucia (FQM334, FQM110). Electron microscopy imaging was carried out in the Central Service of Science and Technology from Universidad de Cadiz.

TABLE 1. Evaluation of the metallic dispersion with the thermal treatment.

Catalyst	Reduction 623K	Reduction 1173K
$Ru(3\%)/Al_2O_3$	58	34
$Ru(1\%)/ Ce_{0.62}Zr_{0.38}O_2$	55	48
$Ru(1\%)/ Ce_{0.5}Zr_{0.38}Tb_{0.12}O_2$	57	47
$Ru(1\%)/ Ce_{0.8}Tb_{0.2}O_2$	31	15

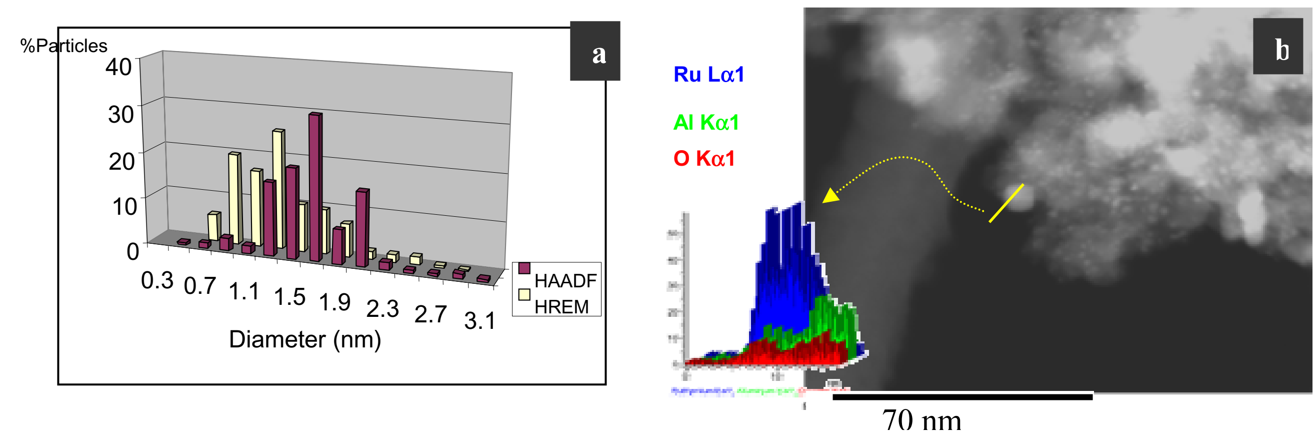

FIG. 1.a) Distribution of particles sizes for $Ru-Al_2O_3$ after reduction at 623K as established by HAADF and HREM. b) HAADF Image of $Ru-Al_2O_3$ after reduction at 1173K. An X-EDS composition profile of a particle is also shown.

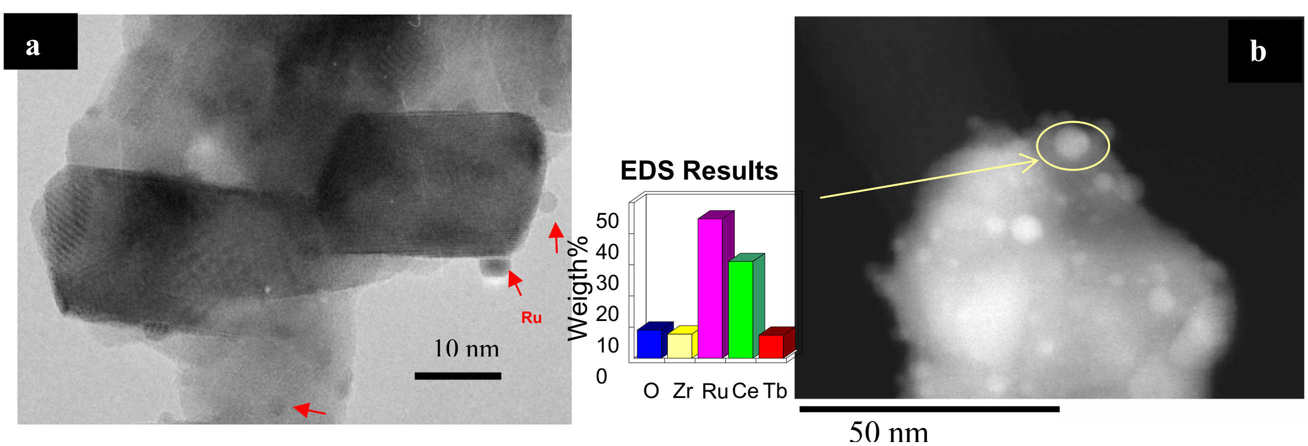

FIG. 2. HREM (a) and HAADF (b) images of $Ru - Ce_{0.5}Zr_{0.38}Tb_{0.12}O_2$ after reduction in H_2 (5%)/Ar at 1173K. The results of EDS analysis of a particle of a Ru particle are included.

https://doi.org/10.1017/S1431927606066219 Published online by Cambridge University Press