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HREM characterization of metal catalysts supported on rare-earth oxides: samarium oxide as support

S. Bernal, F.J. Botana, J.J. Calvino, G.A. Cifredo, R. García
and J.M. Rodríguez-Izquierdo
Department of Inorganic Chemistry, University of Cádiz, E-11510 Puerto Real, Spain

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High-resolution transmission electron microscopy has been applied to the characterization of the Rh/Sm_2O_3 system. The comparison between Rh/CeO_2 and Rh/Sm_2O_3 catalysts suggests a model of behavior that would be operative for metals supported on rare-earth sesquioxides. The model assumes that a significant dissolution of the support takes place during the impregnation step. As a consequence, the metal would be present in a highly dispersed state after the drying process, forming a mixed phase with the support material, which explains why metal crystallites are only observed after reduction followed by heat treatment at high temperature.

1. Introduction

It is well established that rhodium catalysts supported on rare-earth oxides are very effective for the selective synthesis of C_2-oxygenates from syngas [1,2]. The characterization of these catalysts by means of conventional H_2 or CO chemisorption methods is not an easy task; the support itself can adsorb significant amounts of the probe molecules, and it is difficult to determine the fraction of H_2 or CO adsorbed onto the metal phase [3,4]. The possibility of inhibition of the chemisorptive properties of the dispersed metal, due to metal–support interactions, makes the interpretation of the adsorption results even more complex, in turn making it more difficult to get reliable information concerning the state of dispersion of the metallic phase.

In the lanthanide series, it is convenient to distinguish the cerium dioxide, CeO_2, from the group of sesquioxides, Ln_2O_3. Our own results demonstrate the occurrence of distinctly different behavior when the oxides are exposed to air [5]. While the sesquioxides experience severe hydration and carbonation in the bulk, cerium dioxide is only modified at the surface. Other significant differences are the higher solubility of the sesquioxides in acid media, and the higher reducibility of CeO_2.

Some characterization results for Rh/CeO_2 catalysts have recently been published [6–8]. Average rhodium particle sizes were determined by means of high-resolution transmission electron microscopy (HREM), and the occurrence of an epitaxial metal–support relationship was established. The purpose of the present paper is the study of Rh/Sm_2O_3 catalysts by HREM. In accordance with our previous results, this system should be considered as a representative example of the group of Rh/Ln_2O_3 systems [5]. With the aim of emphasizing the differences between Rh/CeO_2 and Rh/Ln_2O_3 catalysts, new results corresponding to the ceria-supported metal samples are included and discussed.

2. Experiment

The ceria and samaria oxides used as support materials were commercial samples, 99.9% pure, supplied by Alfa Ventron (CeO_2) and Fluka (Sm_2O_3). The rhodium precursor was prepared by

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incipient wetness impregnation of the supports with aqueous solutions of rhodium nitrate in order to obtain 2.4% Rh weight loading on ceria and 5.4% on samaria. After wetting, these samples were dried in an oven at 373 K overnight. The surface areas after impregnation, determined by means of the B.E.T. method, were 18 and 27 m^2 g^{-1}, respectively.

In order to acquire general information and conventional characterization results for Rh/Sm_2O_3 catalysts, a broad variety of experimental techniques were applied. These included thermogravimetric analysis (TG), temperature-programmed decomposition (TPD) in flow of helium, temperature-programmed reduction (TPR) in flow of hydrogen, X-ray diffraction (XRD), hydrogen chemisorption, thermal desorption of hydrogen (H_2-TPD), and catalytic activity measurements for the benzene hydrogenation reaction at room temperature.

The electron microscope used for this study was a JEM 2000EX, equipped with a top-entry specimen holder and ion pump. Samples for HRTEM were prepared as reported elsewhere [6].

3. Results

Our previous HREM studies of the Rh/CeO_2 catalysts reduced in hydrogen at 523 and 773 K revealed the formation of small metallic rhodium particles, in the size range of 1–3 nm. Those rhodium particles often exhibited a definite orientation relationship with respect to the support [6–8] such as the parallel alignment of crystal lattices observed in ref. [8].

Fig. 1 shows a micrograph of a rhodium nitrate/ceria sample, that had not been reduced before introduction into the electron microscope. This micrograph provides identification of well dispersed metallic rhodium on the clean CeO_2 support. Thus, the rhodium nitrate present in this catalytic precursor can easily be reduced inside the electron microscope under the influence of the electron beam. The concentration of metal particles visible in fig. 1 is quite similar to that observed for the catalysts reduced in a flow of hydrogen [6–8].

Fig. 2 shows a micrograph of the rhodium nitrate/samaria unreduced sample following impregnation. In spite of the higher metal-loading/support-area ratio for this sample compared with the catalyst shown in fig. 1, particles corresponding to rhodium-containing phases (nitrate, oxide or metal) could not be observed. Moreover, the study of the supported particles in fig. 2 does not allow identification of the samarium sesquioxide phase. This result is in good agreement with other characterization data obtained by XRD, TG and TPD techniques, which demonstrate that, after impregnation, the support appeared in a highly hydrated and carbonated form, and no residual oxide phase remained [5,9]. Fig. 3 presents HREM images characteristic of Rh/Sm_2O_3 catalysts reduced in hydrogen flow at 473 and 773 K. Even in these samples, rhodium particles were rarely observed. Some isolated metallic particles could be identified for samples reduced at 773 K, but their concentration is far less than that of the Rh/CeO_2 catalysts. For these Rh/Sm_2O_3 samples, the crystallinity of the support increases with increasing reduction temperature. At temperatures above 773 K, lattice spacing characteristics of samarium sesquioxide are easily identified.

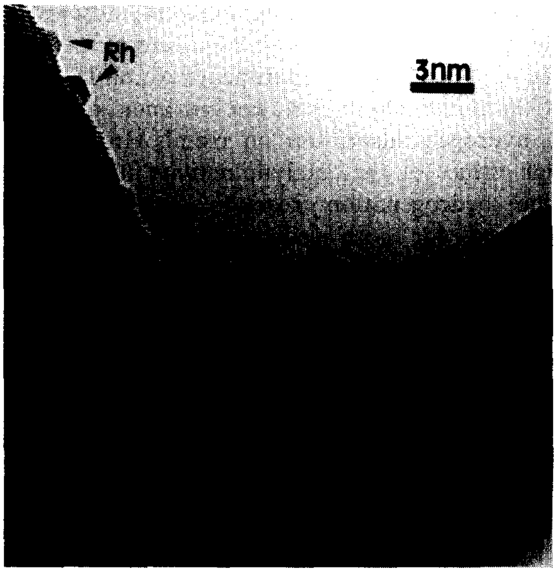

Fig. 1. HREM image of 2.4% Rh/CeO_2 precursor. The sample was not reduced prior to introduction into the microscope.

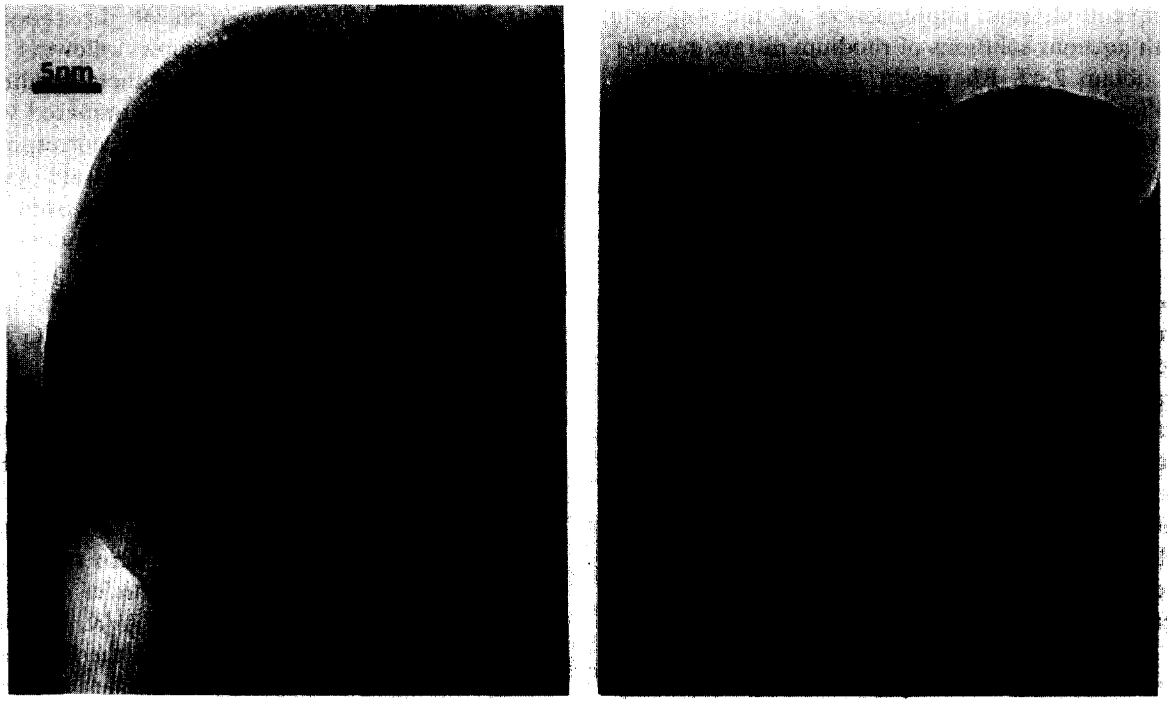

Fig. 2. HREM image of unreduced 5.4% Rh/Sm_2O_3.

Nevertheless, other experimental evidence strongly suggests the formation of metallic rhodium for reduced Rh/Sm_2O_3 catalysts. For example, by means of volumetric H_2 adsorption, the apparent H/Rh atomic ratios are of the order of 0.45. The H_2-TPD experiments exhibit H_2 peaks in the range 300–573 K, conventionally ascribed to hydrogen adsorption on metals. In addition, high values of the catalytic activity for the benzene hydrogenation reaction have been determined for both reduction temperatures. In summary, these results are indicative of the formation of metal following reduction at 473 K [10], although the identification of rhodium particles in the HREM images or by means of XRD is difficult.

The images shown in fig. 4 refer to Rh/Sm_2O_3 catalysts reduced in hydrogen at 773 K and further calcined in flowing helium up to 1173 K. The XRD study of this sample showed peaks characteristic of samarium sesquioxide and metallic rhodium. Metal particles with sizes ranging from 3.0 to 10.0 nm are easy to identify in the micrographs, and the lattice spacings of the support material match with those expected for Sm_2O_3. It is also significant that rhodium particles appearing on the edges of the support crystallites never have clean profiles. Metal particles appear overcoated or decorated by amorphous layers of material, which presumably come from the support.

4. Discussion

The results presented in this paper indicate dramatic differences between CeO_2 and Sm_2O_3 as catalytic supports.

In our opinion, the properties of samaria as a metal support are closely related to those of other RE sesquioxides. Some preliminary results on Rh/La_2O_3 [11] are, in fact, indicative of a behavior pattern similar to that of Rh/Sm_2O_3. Even after reduction, the concentration of metal particles that could be identified on lanthana by HREM was surprisingly low. This result also agrees with the comments of other authors con-

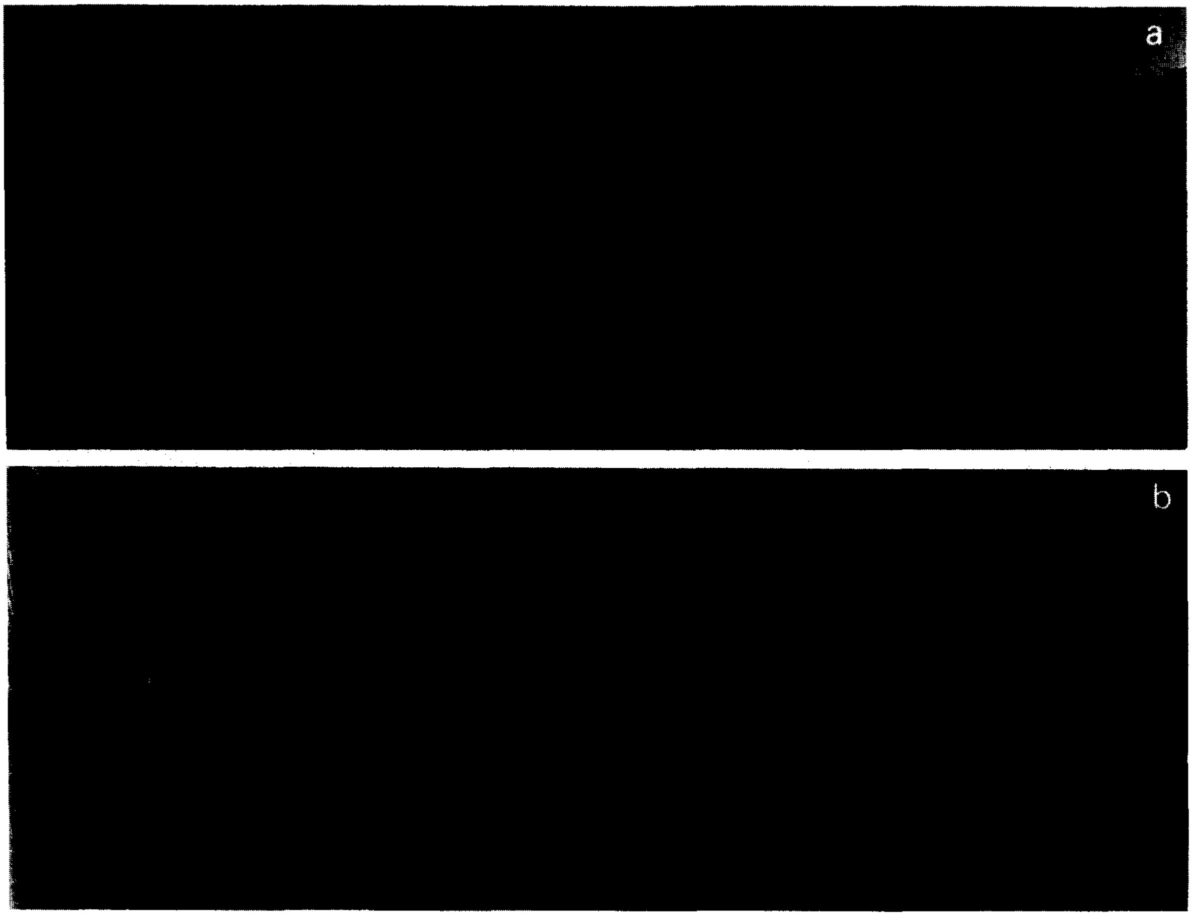

Fig. 3. HREM images of 5.4% Rh/Sm_2O_3 reduced at (a) 473 K, and (b) 773 K.

cerning difficulties in HREM studies for metals supported on RE oxides [4,12].

Since the differences between rhodium supported on CeO_2 and Sm_2O_3 are observed for unreduced samples, these differences should be ascribed to dissimilarities in the processes taking place during impregnation. Possibilities include the solubility of both supports in acid media, or the transformations that the oxides can experience in the presence of water and carbon dioxide. It is important to emphasize the high levels of acidity of the solutions used for impregnation (pH values lower than 1), suggesting that dissolution of significant amounts of Sm_2O_3 occurs during the wetting process; this would not be the case for CeO_2.

The idea of dissolution of the RE sesquioxides during the impregnation stage with rhodium nitrate solutions has been formerly suggested on the basis of wet chemical experiments [13,14]. During drying in an oven at 373 K the co-precipitation of Sm-and-Rh-containing species, with subsequent formation of some kind of mixed phases, would take place. The mixed phases, and the support itself, can experience further hydration and carbonation processes. This series of phenomena, which would not affect catalysts dispersed on CeO_2, can explain the differences between figs. 1 and 2, and the difficulty in identifying particles in fig. 2.

In agreement with conventional characterization data, evidence presented in the results indicates that, after reduction in flow of hydrogen, the

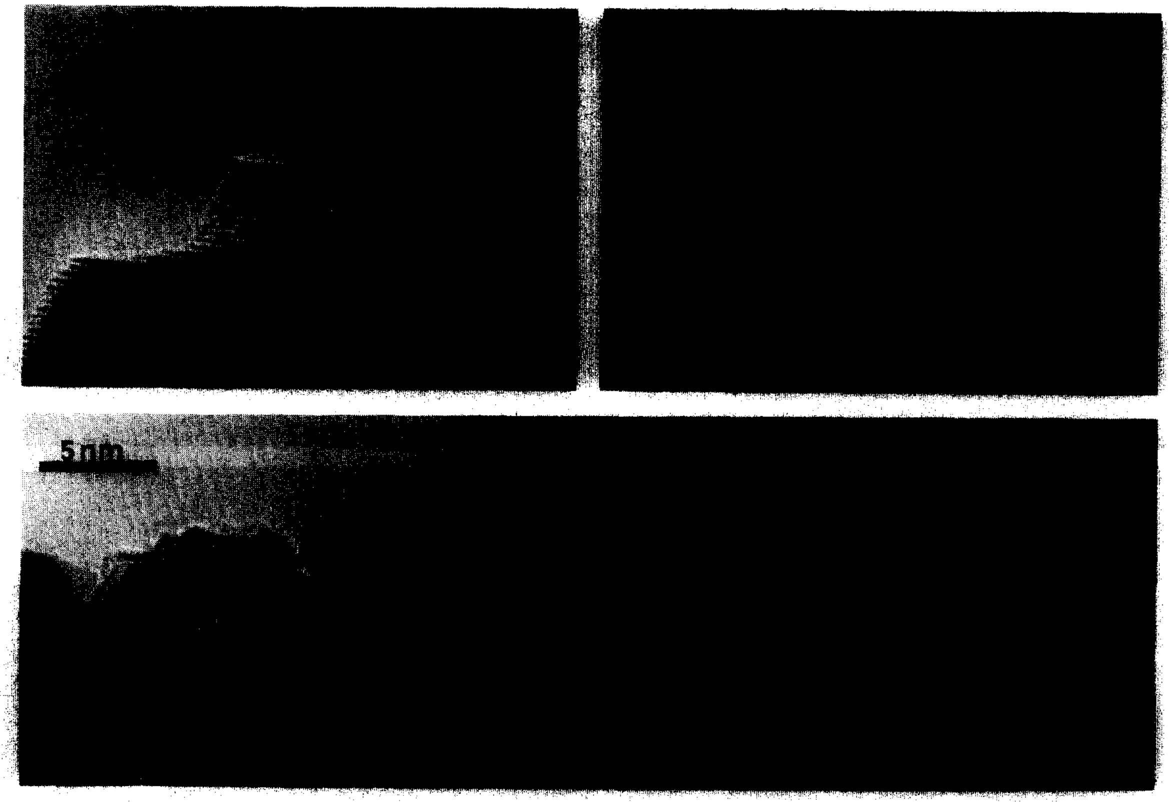

Fig. 4. HREM images of 5.4% Rh/Sm_2O_3 reduced at 773 K and further calcined in helium flow at 1173 K.

rhodium is present in its metallic state. However, it was still difficult to observe metal particles by HREM, suggesting that the metal could be dispersed at the atomic level, not only on the surface of the catalyst support but also in the bulk material.

A thermal treatment at high temperature (1173 K), for a sample previously reduced at 773 K, results in sintering of the support. In addition, the subsequent segregation of well defined rhodium particles, with sizes ranging from 3 to 10 nm, takes place. These Rh particles are easily observed in fig. 4. The characteristic overcoating or decoration of these particles is in agreement with our suggestions regarding the origin of the metal. If large metal particles are grown in the bulk and drawn out on the surface, small amounts of support material would also be extracted, remaining as regions of amorphous material on the crystalline metal particles. This possibility agrees with the model of behavior here proposed for M/Ln_2O_3 catalysts.

On the basis of XPS, IR spectroscopy and chemisorption results [3,15] the idea of decoration of metal crystallites by the support has been previously proposed for lanthana-supported palladium catalysts. It was suggested that partially reduced lanthana moieties, LaO_x, are involved in the decoration of palladium [3,15]. This idea closely resembles the mechanism proposed to interpret the behaviour of M/TiO_2 catalysts in the SMSI state [16]; however, this contradicts the low reducibility of lanthana.

The model of metal–support interaction suggested for M/Ln_2O_3 catalysts in this paper is based on well established chemical properties of the RE oxides, focusing attention on phenomena that the samples would experience during the impregnation.

5. Conclusions

The results presented in this paper demonstrate the capabilities of HREM for shedding light on the nature of metal–support interaction phenomena for metal catalysts supported on RE oxides, in contrast with problems previously reported by other authors for these series of catalysts [4,12].

Cerium dioxide and the RE sesquioxides present dramatic differences in their behavior as catalytic supports. Our results strongly suggest that, during the impregnation step, extensive dissolution of the RE sesquioxides would take place. As a consequence, the metal would probably be dispersed at the atomic level within the support. Thus, direct observation of the metal is difficult even after reduction of the catalysts at 773 K. Conversely, metal particles are easily identified by means of HREM for Rh/CeO_2 catalysts.

Acknowledgments

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