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Metal–support interaction phenomena in rhodium/ceria and rhodium/titania catalysts: Comparative study by high-resolution transmission electron spectroscopy*

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Abstract

The high resolution transmission electron microscopy (HRTEM) study of Rh/CeO_2 and Rh/TiO_2 catalysts reduced at temperatures ranging from 473 K to 773 K suggests that the metal-support interaction phenomena they show are different. In contrast to that found for Rh/TiO_2, over Rh/CeO_2 no metal decoration effects could be observed. Likewise, the chemisorptive and catalytic behaviour of Rh/CeO_2 does not exhibit drastic changes with the reduction temperature. The HRTEM images, however, reveal the occurrence of quite singular rhodium-ceria interaction phenomena.

Keywords: high resolution electron microscopy; rhodium/ceria; rhodium/titania; SMSI effect

INTRODUCTION

According to some recent works [1–3], ceria supported metal catalysts would exhibit strong metal–support interaction effects similar to those well known to occur on titania supported metal catalysts [4,5]. It should be noted, however, that some other results dealing with Rh/CeO_2 [6,7] and Pt/CeO_2 [8] recently reported do not seem to support the occurrence of what might be called a classic SMSI effect; i.e. no strong inhibition of their chemisorptive properties could be observed in refs. 6–8 upon reducing the M/CeO_2 catalysts at temperatures as high as 773 K.

At present, there is a general agreement on the difficulties existing to arrive at a fine characterization of ceria supported metal catalysts [6,8–10]. As we

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have recently shown [11–13], the chemistry of the interaction between some classic probe molecules like hydrogen and Rh/CeO_2 catalysts should be considered rather complex; on the one hand, ceria can chemisorb large amounts of hydrogen [11,14]; on the other hand, the adsorption/desorption rates observed on H_2–CeO_2 are very sensitive to the presence of dispersed metal as well as to the pretreatment of the catalyst [11–13]. In brief, conventional chemisorption studies cannot be used in a straightforward way to characterize ceria supported metal catalysts. Likewise, microstructural information about these catalysts is almost completely lacking. In fact, transmission electron microscopy techniques have seldom been applied to investigate M/CeO_2 catalysts [7,15,16]. Moreover, it has been suggested that TEM cannot be fruitfully used to characterize M/CeO_2 catalysts [8].

To investigate further the nature of the interactions occurring at the rhodium/ceria interface, it seemed interesting to us to compare the chemical and microstructural properties of two Rh/CeO_2 and Rh/TiO_2 catalysts prepared at our laboratory. As will be shown below, high resolution transmission electron microscopy (HRTEM) has proved to be a very powerful tool to investigate the nature of the metal–support interaction phenomena observed on the Rh/CeO_2 catalysts.

EXPERIMENTAL

The catalysts, Rh/CeO_2 and Rh/TiO_2, were prepared by the incipient wetness impregnation technique from an aqueous solution of $Rh(NO_3)_3$. The ceria sample was a low-surface-area commercial sample from Alpha Ventron, 99.9% pure. Before the impregnation treatment, the titania sample, Degussa P-25, was reduced in flowing hydrogen at 773 K for 3 h, evacuated, and finally reoxidized at 673 K with flowing oxygen for 1 h. The titania sample resulting from this pretreatment was 80% rutile and exhibited good textural stability. The metal loading was 2.4% for the Rh/CeO_2 catalyst, and 5% for Rh/TiO_2. The reduction of the precursor/support systems was carried out in flowing hydrogen ($1\ cm^3\ s^{-1}$), at a heating rate of $10\ K\ min^{-1}$. The reduction time at 773 K was 1 h for Rh/CeO_2 and 3 h for Rh/TiO_2.

The HRTEM study was performed with a transmission electron microscope, JEOL-2000-EX, equipped with top entry specimen holder and ion pump. The structural resolution was 0.21 nm. The samples to be introduced in the microscope were prepared as reported elsewhere [7]. To prevent fast reoxidation in air of the Rh/CeO_2 catalysts they were flushed, after reduction, with inert gas for 1 h at the reduction temperature, cooled to 191 K, always in a flow of inert gas, then treated at 191 K with a mixture O_2(5%)/Ar for 30 min, further warmed up to 295 K in the oxidizing mixture, and finally exposed to air. The transfer to the microscope was carried out immediately.

The volumetric adsorption studies were all performed in a conventional high vacuum system equipped with a capacitance gauge, MKS Baratron, model 220 BHS. The catalysts were reduced "in situ" and further evacuated for 1 h at the reduction temperature before the adsorption run.

The catalytic activity measurements were carried out in a microreactor under differential conditions. Benzene hydrogenation was used as the test reaction. The experimental conditions were: reaction temperature: 303 K, benzene partial pressure: 30 Torr (1 Torr=133.3 Pa); hydrogen partial pressure: 730 Torr; hydrogen flow-rate: 1 cm^3 s^{-1}; weight of catalyst: 50 mg. Under these conditions, cyclohexane, C_6H_{12}, was the only reaction product.

RESULTS AND DISCUSSION

Table 1 accounts for the results of the hydrogen chemisorption studies carried out on both Rh/CeO_2 and Rh/TiO_2 catalysts. In accordance with the apparent H/Rh data reported in Table 1, our Rh/TiO_2 sample exhibits the typical behaviour of a catalyst presenting the classic SMSI effect [4,5]. Likewise, its catalytic behaviour for benzene hydrogenation is in good agreement with the chemisorption results. In effect, for the catalyst reduced at 473 K, the reaction rate was found to be: 0.76 mmol (C_6H_{12}) g^{-1}(Rh) s^{-1}, becoming negligeable after reduction at 773 K. As in the case of the chemisorption studies, if the Rh/TiO_2 catalyst reduced at 773 K is reoxidized and further reduced at 473 K, the activity is partly recovered reaching a value of 0.58 mmol (C_6H_{12}) g^{-1}(Rh) s^{-1}.

In contrast with the results above, the Rh/CeO_2 catalysts do not show dramatic differences of chemisorptive properties upon increasing the reduction temperature from 523 K to 773 K. As several different workers [6,7,10–12] have clearly shown, over ceria supported rhodium catalysts at 298 K, hydrogen

TABLE 1

Hydrogen chemisorption study of Rh/CeO_2 and Rh/TiO_2 catalysts

Catalyst	T_{red} (K)	S_{BET}[a]	H/Rh[b]
Rh/CeO_2	523	11	0.40
Rh/CeO_2	623	12	0.35 (0.31)
Rh/CeO_2	773	10	0.23 (0.27)
Rh/TiO_2	473	20	0.47
Rh/TiO_2	773	20	0.00
Rh/TiO_2[c]	473	20	0.20

[a] BET surface (m^2 g^{-1}).

[b] Apparent H/Rh values determined from volumetric adsorption isotherms recorded at 295 K and 191 K (data in parenthesis).

[c] Catalyst previously reduced and evacuated at 773 K for 1 h, later reoxidized and evacuated a 673 K for 1 h.

spillover can occur to a considerable extent. Accordingly, the apparent H/Rh values reported in Table 1 may include some contribution of the hydrogen adsorption on the support. It has been shown in refs. 13 and 16 that hydrogen adsorption studies at 191 K can fruitfully be used to estimate metal dispersions in Rh/CeO_2 catalysts, and, therefore, that the comparison of the results obtained from the isotherms recorded at 298 and 191 K would allow us to estimate the intensity of the spillover process occurring at 298 K. In the present case, the results reported in Table 1 indicate that the contribution of the hydrogen adsorption on ceria to the apparent H/Rh values is rather small. This observation, which is consistent with the low surface area of the support sample used here (Table 1) shows that the chemisorptive properties of the rhodium microcrystals are not drastically inhibited upon increasing the reduction temperature up to 773 K. This contrasts with some earlier results on Pd/CeO_2 [1], Rh/CeO_2 [2] and Ni/CeO_2 [3], in accordance with which reduction treatments at 673 K would induce a SMSI-like effect on the catalysts. The catalytic activity data for the benzene hydrogenation on our Rh/CeO_2 catalyst lead, however, to the same conclusion as the chemisorption studies commented on above. In effect, no dramatic inhibition of the activity could be observed, the reaction rate on the catalyst reduced at 773 K being 0.16 mmol (C_6H_{12}) g^{-1} (Rh) s^{-1}.

Figs. 1a and b show HRTEM images corresponding to the Rh/TiO_2 catalyst reduced at 473 K and 773 K, respectively. In good agreement with some earlier HRTEM studies on Rh/TiO_2 [18], the micrographs presented in Figs. 1a and b indicate that upon increasing the reduction temperature, strong microstructural modifications do occur on the catalyst. Low reduction temperature (Fig. 1a) leads to a quite narrow metal crystallite size distribution, its mean value being around 2.5 nm. Also worth noting, the metal presents very neat profiles corresponding to well faceted, clean microcrystals. In contrast with this, the HRTEM images for the Rh/TiO_2 catalyst reduced at 773 K (Fig. 1b) show rhodium crystallites with much more diffuse profiles, which clearly indicates the occurrence of metal decoration phenomena. According to Fig. 1b, this very thin amorphous layer of support does not completely cover the metal particles, in spite of which there is a total inhibition of the chemisorptive properties and activity of the catalyst. This observation, in good agreement with the very recent literature [19], suggests that both geometric and electronic factors would contribute to the SMSI effect in Rh/TiO_2 catalysts.

The HRTEM micrographs for Rh/CeO_2 catalysts reduced at 623 K and 773 K reported in Figs. 2a and b, respectively, do not show any evidence for the occurrence of metal decoration phenomena. In fact, no matter the reduction temperature, the rhodium exhibits very neat, well faceted microcrystals, their mean size being around 3 nm. Some earlier HRTEM microscopy studies dealing with Rh/CeO_2 [7,20,21] and Pt/CeO_2 [16] lead to the same conclusion. In brief, the absence of metal decoration phenomena, as the chemisorption and

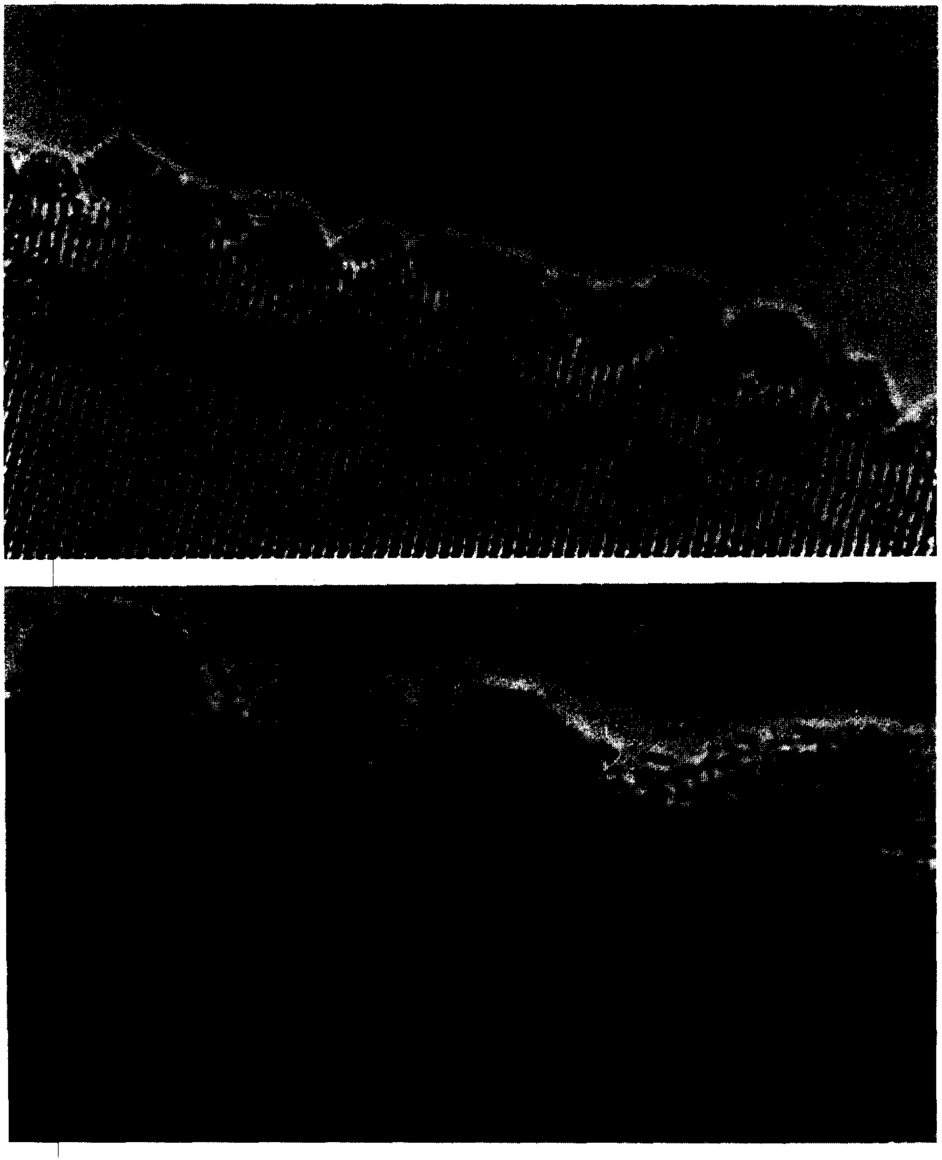

Fig. 1. HRTEM images corresponding to Rh/TiO_2 catalysts reduced at: (a) 473 K; (b) 773 K.

catalytic activity results commented on above, strongly suggest that, under the preparation conditions used here, the Rh/CeO_2 catalysts do not reach the classic SMSI state, well documented on Rh/TiO_2 [18], and confirmed by our own results in this work.

It should be noted, however, that the HRTEM images, as some earlier STEM

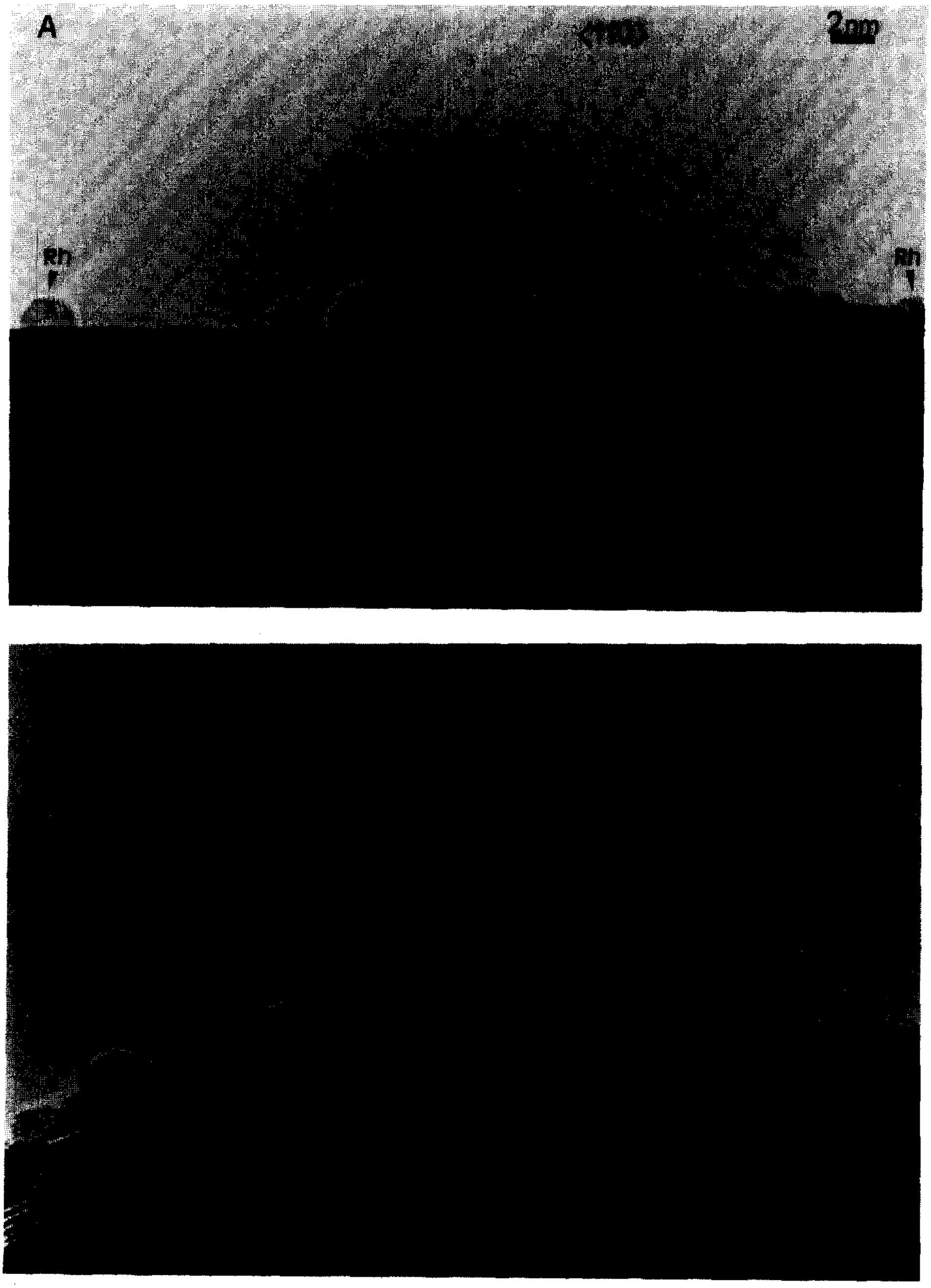

Fig. 2. HRTEM images corresponding to Rh/CeO_2 catalysts reduced at: (a) 623 K; (b) 773 K.

and microdiffraction studies [15,20] did, have shown some additional, very interesting features on the nature of the metal–support interactions occurring in ceria supported rhodium catalysts. First of all, within the range of reduction temperatures investigated here, no significant metal sintering effects can be deduced from the HRTEM images. Also worth of being outlined, twinning, in spite of being considered an usual mechanism of stabilization of small metal particles, is very seldom observed in the case of the Rh/CeO_2 catalysts [15]. Finally, nanodiffraction [15] and HRTEM [13,20,21] studies carried out on different Rh/CeO_2 catalysts prepared in our laboratory have clearly shown the occurrence of a quite singular epitaxial relationship between the metal and the support. It consists of the growing of (hkl) planes of rhodium parallel to the same (hkl) planes of ceria [15]. Figs. 2a and b confirm the occurrence of such a relationship. In fact, the images reported in Figs. 2a and b, corresponding to the [110] zone axis of both metal and support, show (111) planes of Rh ($d_{(111)}$: 0.220 nm) growing parallel to (111) planes of CeO_2 ($d_{(111)}$: 0.312 nm). As has been discussed earlier [20,13], this type of epitaxy leads to a quite singular rhodium/ceria interface in which four (111) metal planes fit three (111) planes of the support, this implying the regular appearance of metal dislocations at the interface.

The emsemble of the observations made from the analysis of the HRTEM images reported in Fig. 2 might well be interpreted as indications of the existence of some particular, may be strong, rhodium–ceria interaction. Nevertheless, the comparison of the chemical and the microstructural behaviour of the Rh/CeO_2 and Rh/TiO_2 catalysts deduced from this work strongly suggest that the nature of the metal–support interaction phenomena these two catalysts present, at least within the range of experimental conditions investigated here, is different. Some earlier studies from our laboratory [7,13], in which a number of different Rh/CeO_2 catalysts were investigated, are also in agreement with the conclusion above.

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