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The terbium oxide as support of highly dispersed metals. Study of the Rh/TbO$_x$ catalytic system

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Abstract

A series of Rh/TbO$_x$ catalysts reduced at temperatures ranging from 623–973 K has been studied by means of X-ray diffraction, thermogravimetric analysis, volumetric adsorption temperature programmed desorption/reduction mass spectrometer (catharometer) techniques. All the catalysts consist of Rh/Tb$_2$O$_3$. No strong metal-support interaction effect could be observed. The decrease of the H/Rh ratio with the reduction temperature is interpreted as due to metal sintering. The amount of H$_2$ chemisorbed by the support is not larger than 2 H atom nm^2, thus suggesting a surface nature for this process.

Keywords: Supported rhodium catalyst; Terbia; Preparation; Hydrogen chemisorption; SMSI effect

1. Introduction

At present, large efforts are being devoted to investigating ceria-containing metal catalysts [1]. This contrasts with the scarce attention paid to other reducible 4f oxides, like praseodymia or terbia, closely related to ceria, from this point of view. In our opinion, however, M/4f oxide (TbO$_x$, PrO$_x$) catalysts can constitute useful model systems to investigate further some of the many very intriguing chemical and microstructural properties of the based-on-ceria catalysts [2,3].

This work reports on a series of Rh/Tb$_2$O$_3$ catalysts reduced at temperatures ranging from 623–973 K. From our study, two important aspects of their chemical behaviour: the likely occurrence of the so-called strong metal-support interaction (SMSI) effect [4,5], as well as the surface [6] or bulk [7] nature of the hydrogen chemisorption on the oxide support are discussed.

2. Experimental details

The metal was dispersed on TbO$_x$ by incipient wetness impregnation technique from a dry acetone solution of Rh(NO$_3$)$_3$. The terbium oxide was prepared in our laboratory by calcining at 873 K, for 4 h, the terbium containing phase obtained by precipitation with ammonia from an aqueous solution of Tb(NO$_3$)$_3$. The rhodium loading was 4 wt.%. The reduction treatments were performed in situ; the H$_2$ flow rate was 60 cm^3 min^{-1}, and the heating rate 10 K min^{-1}.

The thermogravimetric (TG) experiments were performed with a thermobalance, Perkin Elmer, model TG-A7. The temperature programmed desorption/reduction (TPD/TPR) studies were carried out in a flow of Ar(H$_2$): 60 cm^3 min^{-1}, at a heating rate of 10 K min^{-1}. In this latter case, either a catharometer (TPD-TC) or a mass spectrometer (TPD-MS) was used as analytical device. The H$_2$ and N$_2$ (77 K) volumetric adsorption studies were performed in a high vacuum system equipped with a capacitance gauge, MKS Baratron, model 220 BHS.

3. Results and discussion

Before proceeding with the reduction treatments, the precursor/support system (Rh(NO$_3$)$_3$/TbO$_x$) was heated in flowing O$_2$(5%)/He at 973 K for 1 h, and further cooled to 295 K, always in a flow of O$_2$. As deduced from the TPO and HRTEM studies reported in Ref. [8], the rhodium phase resulting from this pretreatment consists of Rh$_2$O$_3$. To investigate the nature of the support, the oxygen pretreated sample was studied by means of TG and TPD techniques. According to

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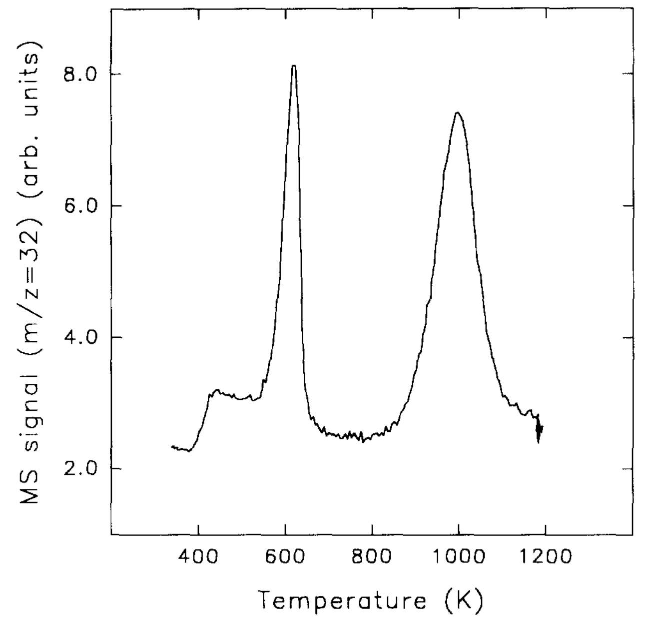

Fig. 1. TPD-MS Study of the rhodium precursor/support system resulting from heating $Rh(NO_3)_3/TbO_x$ in a flow of O_2(5%)/He, at 973 K, for 1 h, and its further cooling to 295 K under the oxidizing mixture. Trace for O_2 (m/c: 32).

Fig. 1, the TPD diagram shows three peaks at 450 K, 623 K and 1000 K. Earlier studies on a low surface area (2 m^2 g^{-1}) terbia sample [9] allow us to assign the latter two peaks to the reduction of terbia, whereas the feature at 450 K, which is absent in the TPD diagram reported in Ref. [9], would correspond to chemisorbed O_2. It is known that the reduction in flowing He of the supported Rh_2O_3 does not occur within the temperature range investigated here [8]. The whole experiment, i.e. heating of precursor/support system ($Rh(NO_3)_3/TbO_x$ in a flow O_2(5%)/He at 973 K for 1 h, further cooling to 295 K in O_2/He, and, finally, heating the resulting Rh_2O_3/Terbia system up to 1173 K in a flow of pure He, was reproduced by using TG analysis.

Assuming that the terbia phase resulting from the TPD and TG (He) experiments is Tb_2O_3 [9], the stoichiometry of the TbO_x phase present in the O_2 pretreated sample would be: $TbO_{1.83}$. The estimates made by using both TPD and TG techniques were in good agreement.

The $Rh_2O_3/TbO_{1.83}$ sample was further studied by TPR-MS. In accordance with Fig. 2, the trace for H_2O (m/c: 18) shows two peaks, the first one, at 373 K, corresponding to the rhodium reduction [10], that appearing at 523 K being assigned to the support reduction. Following the results obtained from the TPR-MS study, four reduction temperatures were selected: 623 K, 773 K, 873 K and 973 K. Since the fully reduced terbium sesquioxide is formed at 523 K, Fig. 2, all the catalysts investigated here would actually consist of Rh/Tb_2O_3. This is confirmed by the X-ray diffraction (XRD) study carried out on both the starting oxidized $Rh_2O_3/TbO_{1.83}$ sample, and the reduced catalyst, Fig. 3.

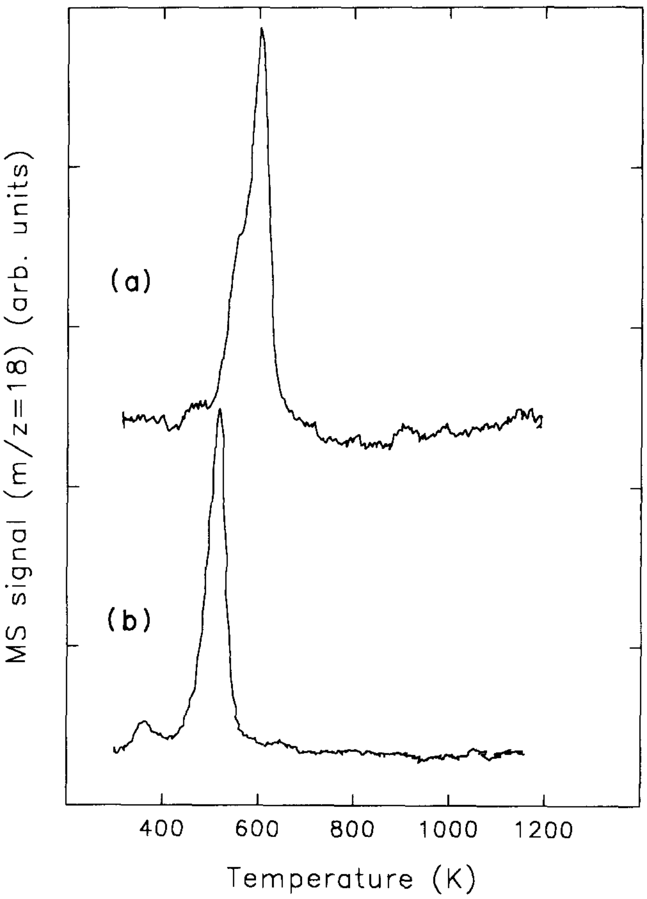

Fig. 2. (a) TPR-MS study of the rhodium precursor/support system resulting from heating $Rh(NO_3)_3/TbO_x$ in a flow of O_2(5%)/He, at 973 K, for 1 h, and its further cooling to 295 K under the oxidizing mixture (b). The trace for bare TbO_x pretreated in the same way is also included for comparison (a). Trace for H_2O (m/c: 18).

Table 1 accounts for the results of the hydrogen volumetric chemisorption study on the series of Rh/Tb_2O_3 catalysts. The experiments were performed on a sample successively treated as indicated in Table 1. To check the likely existence of hydrogen spill over, a phenomenon which is well known to occur on Rh/CeO_2 [2,3], the catalyst was heated under H_2 (P_{H_2}: 300 Torr), for 1 h, at several increasing temperatures: 373 K, 473 K and 623 K, and cooled again to 295 K under H_2 [11].

For the catalyst reduced/evacuated at 623 K, the apparent H/Rh ratio as determined from the first isotherm is 1.02. This value is close to that obtained for the catalyst reduced at 623 K and further evacuated at 773 K (H/Rh: 0.97). This contrasts with the observation made on Rh/CeO_2 [3,11], a catalyst for which the higher the evacuation temperature the lower the spill over rate at 295 K. In the present case, this rate seems to be very low even for the sample reduced/evacuated at 623 K. Under these circumstances, the

Table 1

Sample treatment	S_{BET} (m^2 g^{-1})	H/Rh			
		298 K	373 K	473 K	623 K
Standard O_2 pretreatment *					
evacuation 448 K	34.5				
Redn. 623 K (1 h)/evac. 623 K (1 h)		1.02			
Evacuation 295 K (0.5 h)		0.29			
Heating under H_2 ($P_{H2}=300$ Torr)			1.14	1.15	1.19
Evacuation 295 K (0.5 h)		0.23			
Evacuation 625 K	38.8				
Evacuation 773 K		0.97			
Evacuation 295 K (0.5 h)		0.27			
Heating under H_2 ($P_{H2}=300$ Torr)					1.16
Evacuation 295 K (0.5 h)		0.18			
Evacuation 773 K	39.9				
Standard O_2 Pretreatment *					
Redn. 773 K (1 h)/evac. 773 K (1 h)		0.82			
Heating under H_2 ($P_{H2}=300$ Torr)			0.98	1.12	1.12
Evacuation 295 K (0.5 h)		0.17			
Evacuation 773 K	35.7				
Standard O_2 pretreatment *					
Redn. 873 K (1 h)/evac. 873 K (1 h)		0.66			
Heating under H_2 ($P_{H2}=300$ Torr)			0.81	0.83	0.84
Evacuation 295 K (0.5 h)		0.15			
Evacuation 873 K	33.6				
Standard O_2 pretreatment *					
Redn. 623 K (1 h)/evac. 623 K (1 h)		0.76			
Heating under H_2 ($P_{H2}=300$ Torr)			0.98	1.01	1.01
Evacuation 295 K (0.5 h)		0.17			
Evacuation 623 K	29.0				
Standard O_2 pretreatment *					
Redn. 973 K (1 h)/evac. 973 K (1 h)		0.54			
Heating under H_2 ($P_{H2}=300$ Torr)			0.67	0.72	0.80
Evacuation 295 K (0.5 h)		0.13			
Evacuation 973 K	32.0				
Standard O_2 pretreatment *					
Redn. 623 K (1 h)/evac. 623 K (1 h)		0.60			
Heating under H_2 ($P_{H2}=300$ Torr)				0.80	0.86
Evacuation 295 K (0.5 h)		0.17			
Evacuation 623 K	25.7				

H/Rh values determined at 295 K would measure the amount of hydrogen chemisorbed on the metal, and therefore, we can conclude that, for Rh/Tb_2O_3–623 K, the metal is chemically active and highly dispersed.

The results reported in Table 1 for Rh/Tb_2O_3 reduced at 623 K also show that the H/Rh ratio increases upon heating the catalyst under H_2 up to 623 K. This suggests the activation of the spill over process [11]. If the increase of H/Rh, $\Delta(H/Rh)=0.17–0.19$, is referred to nm^2 of S_{BET}, we obtain: 2 H atom nm^{-2}, a value close to that determined for heavily reduced ceria [6]. By using as reference the surface concentration of oxygen in Tb_2O_3:6 O_2-nm^{-2}, the amount of chemisorbed H_2 is far lower than the monolayer. In good agreement with that suggested for H_2–CeO_2 [6], it seems reasonable to consider that the hydrogen chemisorption on terbia is a surface process.

The results discussed above for Rh/Tb_2O_3–623 K would also indicate that the terbia contribution to the total amount of chemisorbed H_2 is relatively small, which is also confirmed by the TPD-MS trace recorded for the catalyst reduced at 623 K and further cooled under flowing H_2 to 295 K, Fig. 4. In effect, the diagram in Fig. 4 consists of a single peak at 373 K, which can be assigned to H_2 desorbed from Rh [12], as well as a long tail almost 400 K wide, an important part of which would be due to H_2 desorption from the terbia support.

It can also be deduced from Table 1 that upon increasing the reduction temperature the amount of

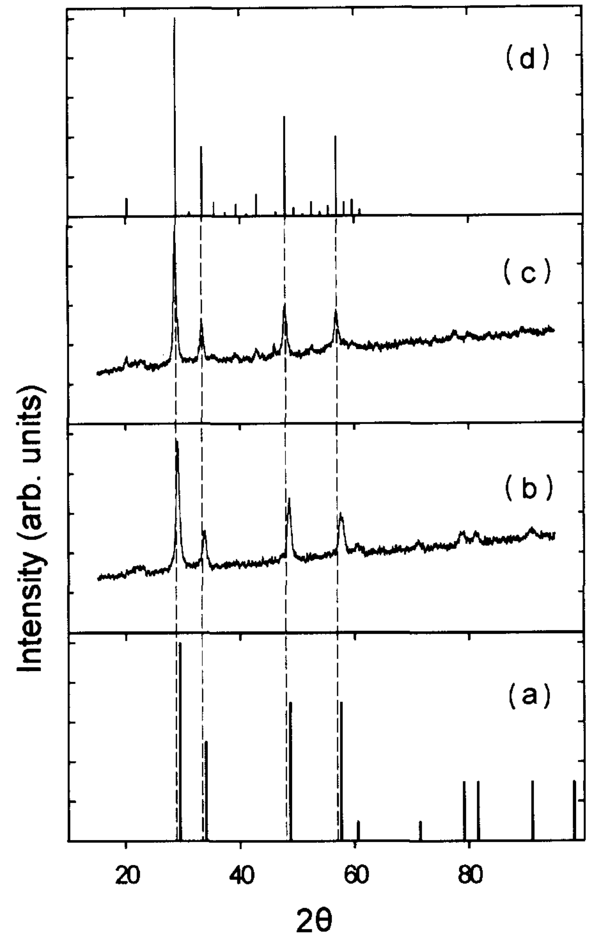

Fig. 3. X-ray powder diffraction diagrams corresponding to (b) the oxidized catalyst precursor ($Rh_2O_3/TbO_{1.83}$) and to (c) the Rh/Tb_2O_3 catalyst reduced at 773 K. The bar diagrams show the XRD patterns for (a) Tb_4O_7 and (d) Tb_2O_3 as reported in the ASTM file.

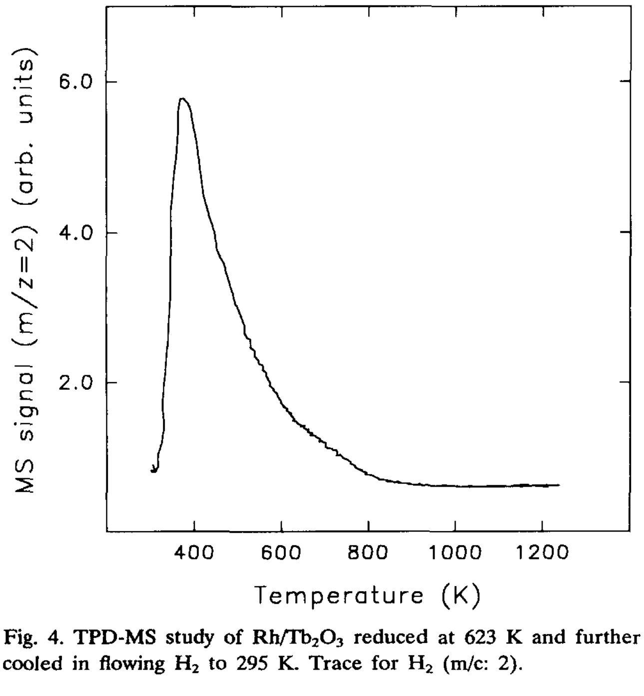

Fig. 4. TPD-MS study of Rh/Tb_2O_3 reduced at 623 K and further cooled in flowing H_2 to 295 K. Trace for H_2 (m/c: 2).

hydrogen chemisorbed on the catalysts, at 295 K, decreases. In spite of the high reduction temperatures reached here, no dramatic changes of the catalyst chemisorptive capability can be observed. On the contrary, there is a smooth decrease of the H/Rh ratio. Also worth of noting, the H/Rh ratio determined for Rh/Tb_2O_3-973 K is only slightly recovered upon reoxidation at 973 K with flowing O_2(5%)/He and further reduction at 623 K.

The ensemble of observations commented on in the previous paragraph suggests that the Rh/Tb_2O_3 catalysts investigated here do not exhibit the so-called SMSI effect, a phenomenon well known to occur on some reducible oxide supported noble metal catalysts like M/TiO_2 [4,13,14]. If it is taken into account that the variation of the BET surface area with the reduction temperature is rather slight, Table 1, we may conclude that metal sintering is the major responsible for the loss of the chemisorption capability observed on the series of Rh/Tb_2O_3 catalysts.

Finally, it would be noted that the Δ(H/Rh) value associated to the activation of the chemisorption process by increasing the adsorption temperature is similar for all the reduction temperatures. This observation reinforces our interpretation, because, as commented on above, neither the chemical nature of the support, Tb_2O_3 in every case, nor its textural properties significantly change within the whole range of reduction temperatures: 623–973 K.

To summarize, the results presented here show some interesting coincidences with those earlier reported for Rh/CeO_2 [3,6]. On the one hand, no evidence could be obtained for the occurrence of a SMSI-like effect [3]. On the other hand, also consistent with that reported for ceria [6], the hydrogen chemisorption on terbia seems to consist of a surface process.

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