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PREPARATION OF SOME RARE EARTH OXIDE SUPPORTED RHODIUM CATALYSTS: STUDY OF THE SUPPORTS

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ABSTRACT

The present work deals with the preparation of some lanthana, samaria and ytterbia supported rhodium catalysts. The three oxides used as starting supports are actually hydrated and carbonated in bulk; the intensity of the processes, and even the nature of the resulting phases are quite different from each other. It has been found that the impregnation process induces further carbonation of lanthana, to such an extent that the carbonated phase becomes the major component of the support. No similar effects could be detected on samaria and ytterbia.

From the study of the reduction step, experimental conditions which allow the preparation of true rare earth oxide supported rhodium catalysts have been devised. In order to achieve this, reduction temperatures ranging from 723 K (La_2O_3) to 623 K (Yb_2O_3) were found to be necessary. In the case of lanthana the phases resulting from the use of lower reduction temperatures were also studied. It can be concluded from the present work that the behaviour as support of lanthanide oxides, particularly in the case of lanthana, is even more complex than had been presumed earlier.

INTRODUCTION

At present, it is generally acknowledged that the supports play an active role in determining the activity and selectivity of dispersed metal catalysts [1].

In spite of this, only a few of the papers dealing with metals supported on rare earth oxides have shown some concern about the actual nature of the phases acting as supports in this type of catalyst [2-5].

The absence of studies aimed at characterizing the supports is particularly noticeable in the case of the lanthanide oxide supported phases, because these oxides, even the heaviest members of the series, become hydrated and carbonated in bulk by simple exposure to atmospheric H_2O and and CO_2 [6-9].

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Since the most commonly used procedure to deposit the transition metal onto the 4f oxide support implies either the impregnation or the ion exchange from aqueous solutions of the precursor salts [10-16], chemical and structural alterations of the support should be expected to occur through the whole preparation process [17]. In other words, the actual nature of the support phases, and presumably the catalytic properties of the corresponding supported metals [18], can be strongly influenced by the preparation conditions.

As a consequence of the lack of detailed results about the evolution undergone by the rare earth sesquioxides throughout the impregnation and reduction processes, no criteria are at present avaible on the preparation conditions to be used in order to obtain metal crystallites dispersed on well known support phases. As will be deduced from the results reported here, the absence of such criteria has caused that many catalysts described in the literature as rare earth oxide supported metal phases are probably constituted by supports other than true lanthanide oxides.

The present work deals with the preparation of some lanthana, samaria and ytterbia supported rhodium catalysts. For all the reasons above, our attention will be focused on the study of the supports. This will allow to establish reduction conditions leading to the preparation of true 4f oxide supported metal catalysts. It can also be deduced from this work that the behaviour as support of the lanthanide oxides, specially in the case of lanthana, is much more complex than that found on the classical supports like silica or alumina. Even more, as we have already pointed out [19], and will confirm here, the occurrence of carbonation phenomena on the 4f oxides, an aspect to which very little attention has been paid up to the present, introduces further elements of complication in the study of the behaviour of the rare earth sesquioxides as supports of transition metals.

EXPERIMENTAL

In the present work three rare earth sesquioxides have been studied: La_2O_3, Sm_2O_3 and Yb_2O_3. The lanthanum oxide was from Ventron, 99.9 %. The samaria sample was from Fluka, 99.9 %. The ytterbium oxide was prepared in our laboratory following the procedure reported elsewhere [6]. The oxides were further exposed to air up to their complete stabilization. The BET surface areas of aged-in-air samples were found to be: 10 m^2g^{-1} for lanthana, 8 m^2g^{-1} for samaria, and 45 m^2g^{-1} for ytterbia. The values of the BET surface areas did not significantly change upon impregnation of the supports.

The rhodium nitrate used as precursor salt was from Ventron, $Rh(NO_3)_3xH_2O$, with 36 % metal content.

The rhodium nitrate, from an aqueous solution was deposited onto the supports by the incipient wetness impregnation technique. In order to achieve the final metal loading, 1 %, six impregnation cycles consisting of wetting at room temperature, followed by drying in air at 383 K for 10 h, were needed. A lanthana impregnated sample with 10 % metal loading has also been prepared. In this case, as much as nineteen impregnation cycles were needed in order to reach the desired metal loading.

The experiments of thermogravimetric analysis (TG), temperature programmed desorption (TPD) and temperature programmed reduction (TPR) were all carried out in flow of either He or H_2, rate flow 1 $cm^3 s^{-1}$; the heating rate was always 0.1 $K \cdot s^{-1}$. The analysis of the gases evolved from the TPD and TPR experiments was performed by Mass Spectrometry (MS), with a VG Spectralab SX 200, interfaced to a microcomputer Apple IIe. The experimental device of TPD(R)-MS has been described and characterized elsewhere [20,21].

The X-ray diffraction (XRD) studies were carried out with a Siemens D-500. The radiation used was CuKα with a nickel filter.

RESULTS AND DISCUSSION

Study of the starting support phases

The phases used as starting materials in the preparation of the supported rhodium catalysts consisted of lanthanum, samarium and ytterbium oxides, which had been previously exposed to atmospheric H_2O and CO_2 up to their stabilization. As is discussed at length in [22], the behaviours in air of these rare earth sesquioxides are quite different from each other. Though bulk hydration and carbonation processes do occur in the three cases, the intensity of these processes, as well as the nature and thermal stability of the resulting phases are not the same. These differences can be clearly seen on the TPD-MS spectra reported on Figure 1. Upon aging in air, lanthana actually consists of partially carbonated hydroxide [6,7]. In the case of samaria and ytterbia samples studied here, the transformation is only partial, leading, respectively, to hydroxycarbonate and hydrated carbonate phases [22].

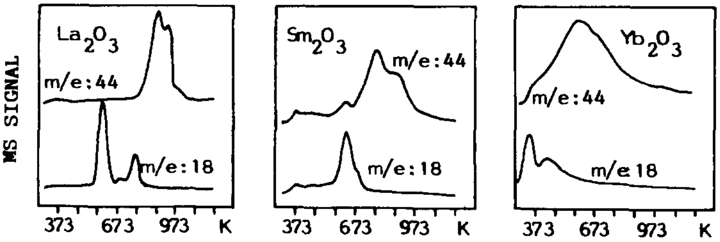

Fig. 1. TPD-MS spectra for m/e:18 (H_2O) and m/e:44 (CO_2) corresponding to aged-in-air lanthana, samaria and ytterbia.

Study of the impregnated phases

The phases resulting from the impregnation of the aged-in-air oxides with the aqueous solution of $Rh(NO_3)_3$ have been studied by TG, TPD-MS and X-ray diffraction.

The XRD diagrams for samaria and ytterbia supported $Rh(NO_3)_3$ samples, Fig. 2, essentially agree with those of the corresponding starting oxide samples. Then, no evidence can be obtained from the XRD study of the alterations occurred at the supports.

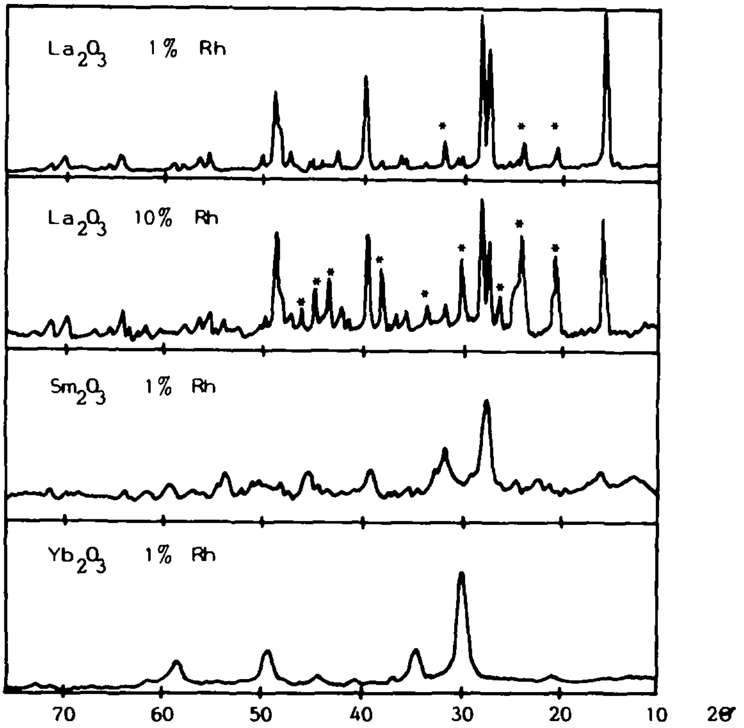

Fig. 2. XRD diagrams of the impregnated $Rh(NO_3)_3$ rare earth oxide samples, recently prepared. In the case of lanthana two samples with 1% and 10 % metal loading are included.

The diffraction patterns obtained for the two $Rh(NO_3)_3$/lanthana samples, with 1% and 10 % metal loading, also reported on Fig. 2, show the coexistence of lines that can be assigned to an ancylite-like hydroxycarbonate phase, $La(OH)CO_3$ [23], marked with asterisks on Fig. 2; as well as others corresponding to $La(OH)_3$. It is worthnoting that the lanthanum hydroxide is the only crystalline phase that can be observed on the XRD diagram of the aged-in-air lanthana sample [7].

It can also be deduced from Fig. 2 that the intensity of the lines adscribed to the hydroxycarbonate phase is much higher on the sample with

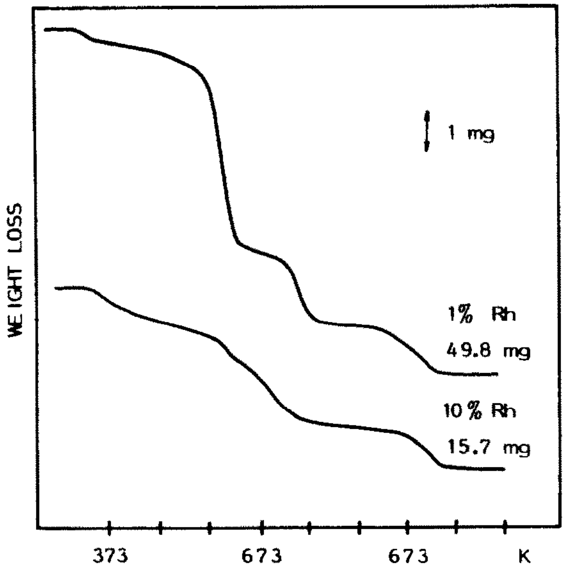

Fig. 3. Diagrams of recently prepared lanthana impregnated $Rh(NO_3)_3$ samples with 1 % and 10 % metal loadings.

10 % metal loading (19 impregnation cycles), which suggest that the larger the number of impregnation cycles the heavier the carbonation occurring on lanthana. This has also been confirmed by TG. In effect, from the last step of the TG traces reported in Fig. 3, an estimate of the amounts of CO_2 taken up by the support in the lanthana impregnated samples, with 1 % and 10 % metal loadings, can easily be made. These amounts were found to be, respectively, 2.6 mg and 7.8 mg per 100 mg of support, much higher than the 1.2 mg taken up by lanthana simply aged in air. As can be seen in Fig. 4, the interpretation of the TG diagrams is also supported by our TPD-MS studies on the impregnated lanthana.

If the impregnated lanthana samples are exposed to air, at ordinary temperature and presure, they slowly take up further amounts of CO_2. Thus, over a sample with 1 % metal loading exposed to air for a prolonged period of time, CO_2 uptakes as high as 9,8 % could be observed. This means that about the 80 % of the support is actually constituted by the hydroxycarbonate phase, $La(OH)CO_3$. Since this supercarbonation of the sample has never been found when the oxide is simply aged in air, even for years, it would be concluded that the nucleation of the hydroxycarbonate phase is specifically associated to the impregnation process.

Summarising, when the usual procedure of impregnation of the 4*f* oxides is followed [10-16], the lanthanum oxide takes up amounts of CO_2 much higher than those resulting from its simple stabilization in air. Likewise, the

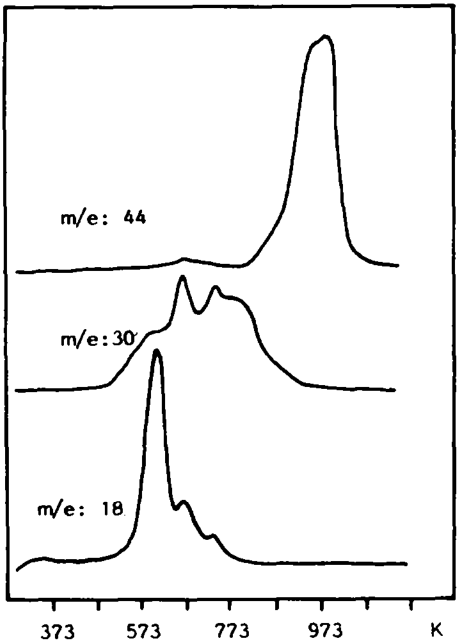

Fig. 4. TPD-MS spectra for m/e:18 (H_2O), m/e:30 (NO) and m/e:44 (CO_2) of $Rh(NO_3)_3$/lanthana, 1 % metal loading, recently prepared.

impregnation process induces the formation of a crystalline phase, identified as $La(OH)CO_3$, ancylite-like, not found in the aged-in-air lanthana. Then the carbonation of lanthana should be considered a major feature of its behaviour as transition metal support. On the other hand, it is obvious from the present study that the actual nature of the support in the lanthana impregnated rhodium nitrate samples remains rather undefined, depending on the impregnation treatment, but also on the further manipulations to which the impregnated sample can be submitted.

Study of the reduction process

Figure 5 shows the TPR-MS spectra obtained for the series of precursor/ support systems studied here.

The reduction to ammonia (m/e:17) of $Rh(NO_3)_3$, as deduced from the comparison of the signals at m/e:17 and m/e:18, takes place at temperatures ranging from 393 K to 453 K. The lowest reduction temperature is observed on the ytterbia supported sample, and the highest one on $Rh(NO_3)_3$/lanthana (10 % metal loading). No strong influence of the nature of the support on the reducibility of the rhodium nitrate can be deduced from our data. Furthermore, in [24] quite similar reduction temperatures have been found on alumina supported rhodium samples. On the contrary, the results reported

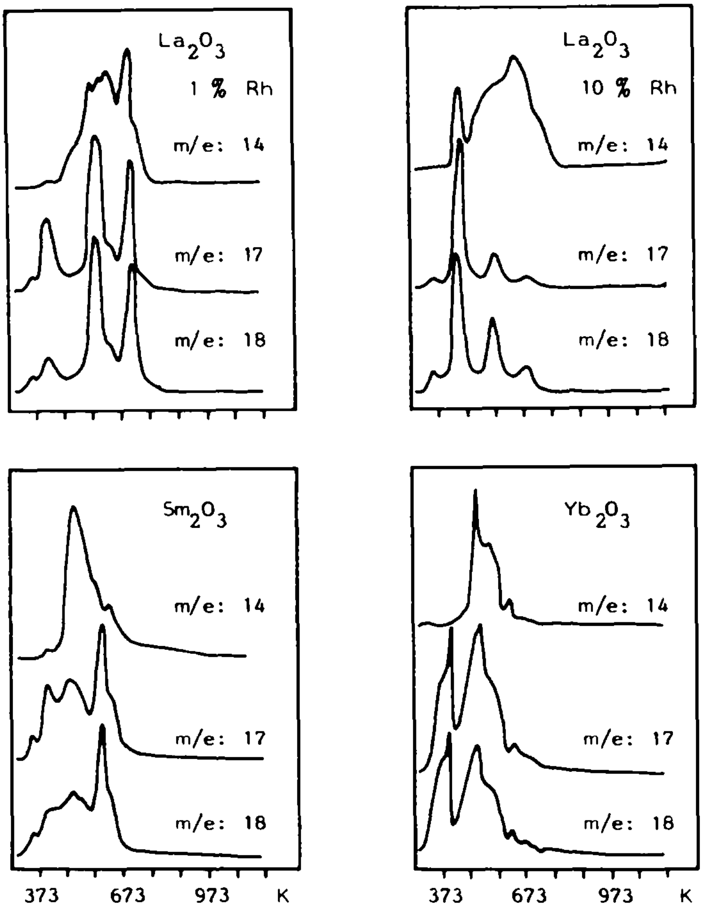

Fig. 5. TPR-MS spectra for m/e:14(CH_4), m/e:17 (NH_3,H_2O) and m/e:18 (H_2O) corresponding to the $Rh(NO_3)_3$ impregnated rare earth oxide samples, recently prepared.

on Fig. 5 seem to indicate that the higher dispersion of the precursor salt the lower the reduction temperature. In effect, the lowest reduction temperature has been found on the support with the highest surface area, Yb_2O_3, and on the other hand, on the two lanthana supported samples a shift to higher temperatures is observed as the metal loading is increased.

Regarding the evolution undergone by the supports through the process of reduction of the impregnated samples, the comparison of the traces for water (m/e:18) included in Fig. 1 and 5 suggests that the dehydration of the supports is not essentially modified by the presence of rhodium. Though the interpretation of the TPR spectra for H_2O depicted on Fig.5 is obviously complicated by the simultaneous evolution of water proceeding from the reduction of both the rhodium salt and the carbonated phase on the supports, the shape and position of the peaks due to the dehydration of the supports can be roughly recognized on the diagrams. In contrast with earlier reports for lanthana supported palladium catalysts [3], no evidence can be obtained from our study of the activating effects of the metal on the dehydration of the rare earth oxide supports.

Contrary to that found for the dehydration reaction, the rate of reduction of the carbonated phase on the supports is very notably enhanced by the presence of the transition metal. In effect, as can be deduced from the traces for m/e:14 (CH_4) the reduction of the carbonate species starts at about 473 K, whereas in the absence of rhodium, i.e. TPR-MS of aged-in-air lanthana, the evolution of CH_4 can only be observed above 773 K. It would also be noted that in the presence of rhodium the amounts of evolved CO_2 are very small, which would indicate that its transformation to methane is practically complete.

From TPR-MS diagrams reported on Fig. 5, reduction conditions allowing the preparation of true rare earth oxide supported metal catalysts can reasonably be established. In effect, according to Fig. 5, reduction temperatures as high as 723 K, 673 K and 623 K, would be needed in order to prepare, respectively, the lanthana, samaria and ytterbia supported rhodium phases. To our knowledge, this type of information cannot be obtained from the current literature.

If lower reduction temperatures than those indicated above are used, support phases other than the corresponding sesquioxides would constitute the actual catalysts. From our point of view, many catalysts described in the literature as M/4f oxide phases have been prepared under conditions which do not guarantee that the true 4f oxide supports can be obtained, in spite of which their catalytic properties have been discussed assuming that rare earth oxide constitute the actual supports. Very recently [18], however, it has been shown that the catalytic properties for the hydrogenation of CO of the so-called magnesia supported rhodium catalysts depend on whether the actual support phase is MgO or $Mg(OH)_2$, which in turn is determined by the selected reduction temperature.

In relation to Fig. 5, it can also be noted that the use of a single reduction temperature to prepare a series of rare earth oxide supported metal catalysts may lead to the preparation of quite different support phases, the actual nature of which would depend on the specific oxides. Only in the case of using sufficiently high reduction temperatures, the behaviour of the whole series of catalysts can reasonably be discussed on the assumption that the 4f oxides constitute the actual supports.

Study by X-ray diffraction of the reduced samples

In the case of the two impregnated samples of lanthana, the XRD allows to obtain further details about the actual nature of the support phase resulting from some specific reduction conditions. Figure 6 shows the XRD diagrams corresponding to the phases obtained upon reduction at 623 K and 723 K of both 1 % and 10 % metal loaded samples of impregnated lanthana. The reduction conditions were the same used in the TPR experiments. The samples were held in a flow of H_2 for 1 h at the reduction temperature.

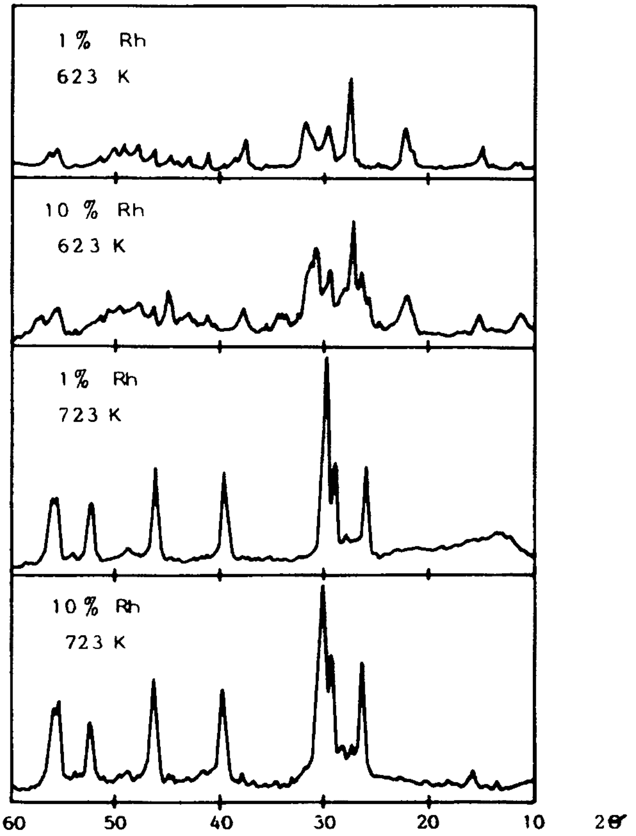

Fig. 6. XRD diagrams of the catalysts obtained upon reduction at both, 623 K and 723 K, the two $Rh(NO_3)_3$ impregnated lanthana samples (1 % and 10 % metal loadings).

The XRD diagrams of the samples reduced at 723 K correspond to those of the hexagonal phase of La_2O_3, which confirms our previous conclusions about the reduction temperature to be used in order to obtain true lanthana supported rhodium catalysts.

Upon reduction at 623 K, the XRD patterns obtained for the samples with 1 % and 10 % metal loading were found to correspond, respectively, to the lanthanum oxyhydroxide, LaOOH, and to a mixture of LaOOH and type II dioxymonocarbonate of lanthanum, $La_2O_2CO_3$-II. The differences observed bewteen the two samples above, which can be reasonably understood in terms of differences in the carbonation level reached by the support in either of the samples, suggest a notable complexity in the behaviour of lanthana as support. In effect, the results above indicate that the actual nature of the lanthana support depends not only on the reduction temperature, but also on the impregnation treatment, and presumably on the manipulations carried out with the impregnated sample before the reduction treatment. In any case, it is obvious from the present study that the reduction process induces very strong chemical and structural changes in the support, not sufficiently stressed in the current literature.

The study by XRD of the samaria and ytterbia supported rhodium catalysts did not show the presence of lines other than those of the corresponding oxides, even after reduction temperatures as high as 973 K. In this respect, it can be noted that no diffraction lines corresponding to either the metal or any phase containing rhodium could be observed, even in the case of the lanthana supported catalysts with 10 % metal loading. These results, which would suggest the existence of well dispersed metal particles, are not, however, consistent with the studies of adsorption of H_2 and CO carried out on Rh/La_2O_3 (10 % metal loading). In accordance with these studies the adsorption capacity of these catalysts, specially in the case of CO, is very low. This behaviour of Rh/La_2O_3 (10 %), which should be considered rather anomalous, suggest the existence metal-support interaction phenomena like those earlier reported by Hicks *et al.* on lanthana supported palladium catalysts [3]. Studies by HRTEM are currently underway in order to get some further insight into the nature of this interaction.

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