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PREPARATION OF LANTHANA SUPPORTED RHODIUM CATALYSTS. OCCURRENCE OF HEAVY CARBONATION PHENOMENA ON THE SUPPORT.

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ABSTRACT

The preparation of lanthana supported rhodium catalysts, with 1% and 10% metal loading, was investigated. The impregnation of lanthana induces nucleation on the support of a crystalline hydroxycarbonate phase, $La(OH)CO_3$, which can represent up to 80% of the original lanthanum oxide.

The study of the reduction process shows that the behaviour of lanthana support is very complex. Following the occurrence of carbonation phenomena on lanthana, the nature of the phase acting as support after the reduction treatment depends not only on the reduction conditions, but also on the previous treatment of the sample to be reduced. Reduction conditions allowing the preparation of true lanthanum oxide supported rhodium catalysts can be established.

INTRODUCTION

The most commonly used procedure to prepare lanthana supported metal catalysts involves either impregnation or ion exchange of the oxide with aqueous solutions of the transition metal precursor salt [1-7].

Since lanthanum oxide is considered to be a highly active phase against water [8,9], it has been suggested [10] that the preparation of M/La_2O_3 catalysts by the above methods would involve strong chemical and structural rearrangements on the support. It has been proposed [10] that the dehydration of the rare earth oxide support occur throughout the reduction process and might well induce the partial coverage of the metal particles by the support.

The simple manipulation of lanthana in air induces not only its hydration but also its carbonation in bulk [11,12]. Carbonation has received very little attention in the literature on rare earth oxide supported metal catalysts [13,14]. Carbonation of lanthana should not be disregarded in the design of new experimental methods for the preparation of M/La_2O_3 catalysts [15].

No studies investigating the nature of the phases used as starting materials in the preparation of rare earth oxide supported metal catalysts or their evolution through the whole preparation process have been published. This report covers the investigation of these aspects of the chemistry of metal/support systems constituted by 4f oxides involving the preparation of some lanthana supported rhodium catalysts, with 1% and 10% metal loading.

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EXPERIMENTAL

Lanthana, 99.9% pure oxide and rhodium nitrate, 36% of which had a metal content were obtained from Ventron.

The oxide (10 m^2 g^{-1} BET surface area) previously stabilized in air, was impregnated (incipient wetness technique) with an aqueous solution of $Rh(NO_3)_3$ and dried in air at 383 K for 10 h. This impregnation cycle was repeated 6 times to achieve 1% loading, and 18 times for 10% metal loading. The impregnating solution was four times more concentrated for the 10% loading than for the 1%.

Thermogravimetric Analysis (TG) and Temperature Programmed Reduction (TPR) were carried out in a flow of either He or H_2 at a flow rate of 1 cm^3 s^{-1} and a heating rate of 0.1 K s^{-1}. Analysis of the gases evolved from the TPR experiments was performed with a Mass Spectrometer (MS), Vacuum Generator, model Spectralab SX-200, interfaced to an Apple IIe microcomputer.

The X-ray Diffraction (XRD) diagrams were obtained on a Siemens, model D-500. Radiation CuK_α and a nickel filter were used.

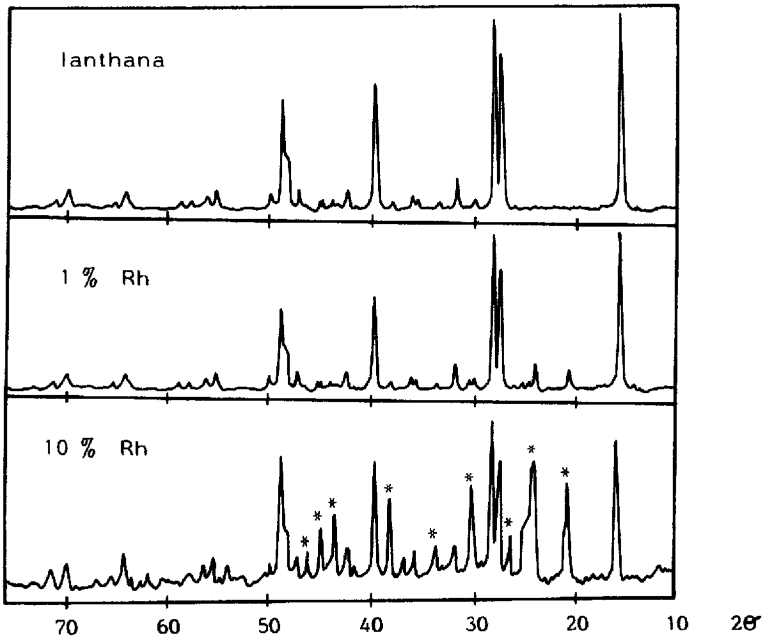

FIGURE 1 X-ray diffraction diagrams corresponding to lanthana and to the lanthana supported rhodium nitrate phases with 1% and 10% metal loadings.

RESULTS AND DISCUSSION

On exposure to atmospheric H_2O and CO_2, the lanthanum oxide completely transforms into carbonated hydroxide in less than 24 h [14]. The total amount of CO_2 taken up, as determined by TG, was 1.2% equivalent to 28 molec nm^{-2} of BET surface area. This amount does not change significantly even when exposure to air of the oxide is prolonged for years.

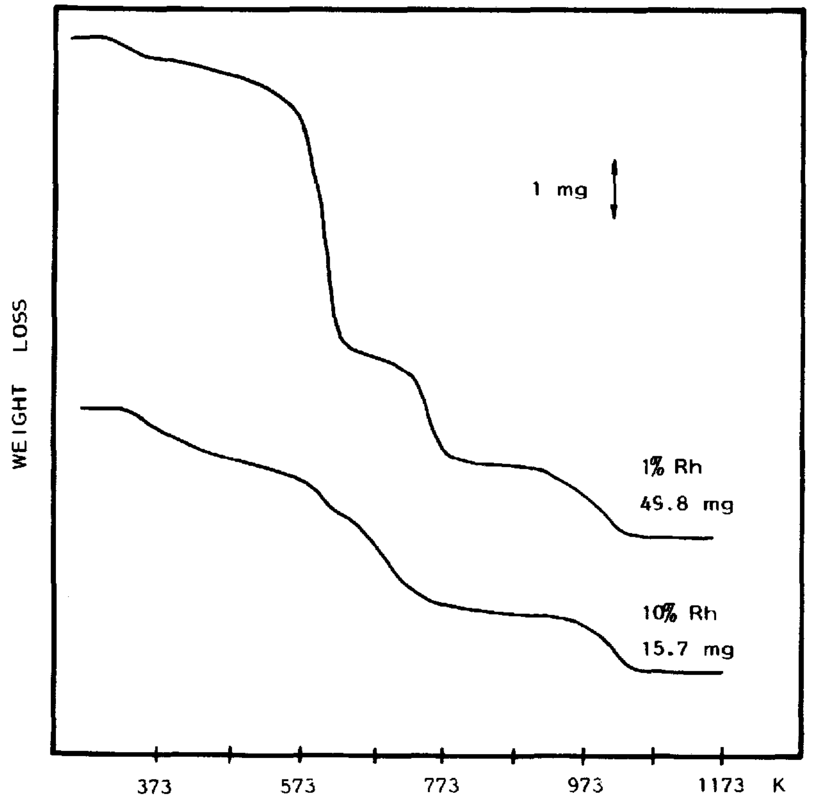

FIGURE 2 TG traces in flow of He for 1% and 10% rhodium loading samples of $Rh(NO_3)_3/La_2O_3$.

Figure 1 shows the XRD diagrams corresponding to the two freshly impregnated samples $Rh(NO_3)_3$/Lanthana, with 1% and 10% metal loading. The diagram of the oxide aged in air, in which the only diffraction lines that can be observed are those of $La(OH)_3$, has also been included in Figure 1 for comparison.

In Figure 1, the XRD lines which do not correspond to $La(OH)_3$ have been marked with an asterisk. These lines, which can only be observed on the impregnated samples, appear at 2θ: 20.5°, 23.8°, 26.1°, 29.9° and 37.9°; their intensity is much higher on the sample with 10% metal loading (18 impregnation cycles). According to the ASTM file, these lines might correspond to a lanthanum hydroxy-carbonate, $La(OH)CO_3$, ancylite-like phase, similar to that reported in ref. 16. These results suggest that the impregnation treatment induced further uptake of CO_2 with formation of a new carbonated phase, which did not exist on the oxide aged in air.

From the last step of the TG diagrams (Figure 2) the amount of CO_2 taken up by the two impregnated samples is estimated to be 2.6% and 7.8% for the samples with 1% and 10% metal loading, respectively. Thus, the larger the number of impregnation cycles, the heavier the carbonation process. However, when the im-

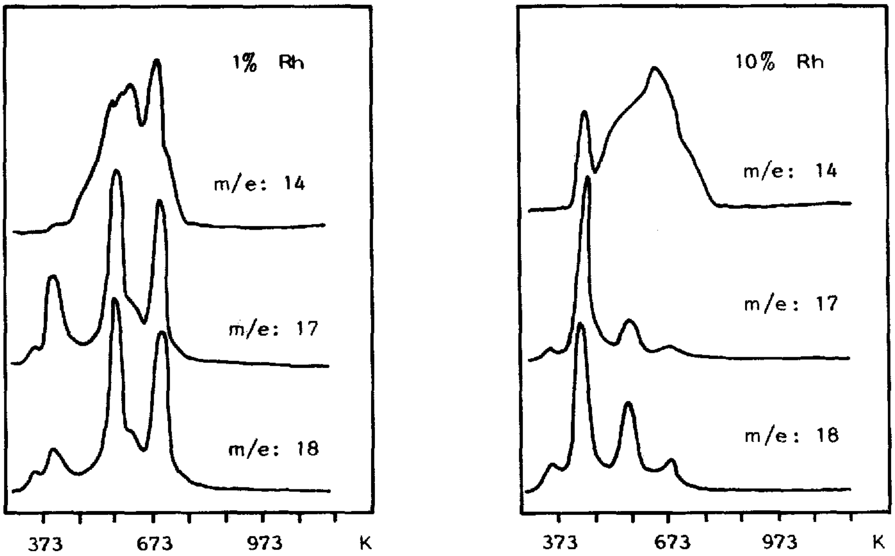

FIGURE 3 TPR traces for mass/charge: 14, 17 and 18, corresponding to the lanthana supported rhodium nitrate phases with 1% and 10% metal loadings.

pregnated samples are exposed to air the uptake of CO_2 continues. Thus, on prolonged exposure to air, amounts of CO_2 as high as 9.8% have been found on a sample with 1% metal loading. This means that approximately 80% of the original lanthanum oxide has transformed into hydroxycarbonate. It is obvious that such a heavy carbonation process, and those less intense reported above, cannot be disregarded in any analysis of the behaviour of lanthana support. The actual nature of the support phase resulting from the impregnation treatment is not well defined, and depends on how the impregnation was carried out and on how long the sample was stored and manipulated in air after the impregnation step.

Figure 3 shows the TPR-MS spectra of both 1% and 10% metal loading, impregnated samples. As deduced from the comparison of the traces corresponding to m/e: 17 and m/e:18, reduction to ammonia of the rhodium nitrate takes place at 393 and 453 K respectively. Since the starting support phase and the procedure to prepare the two impregnated samples were the same, but the corresponding metal loadings were very different, it can be concluded that dispersion of the metal precursor salt would be higher for the sample with lower metal loading. Thus, the above results suggest that the higher the dispersion of the precursor the lower the temperature at which its reduction occurs. This interpretation is consistent with our results for the reduction of rhodium nitrate supported on two ceria samples with different surface areas of 19 m^2 g^{-1} and 110 m^2 g^{-1}. The lowest reduction temperature was observed on the latter sample [17].

The evolution undergone by the support can be followed through the diagrams corresponding to m/e:18 (H_2O) and m/e:14 (CH_4). The traces for m/e:44 have not

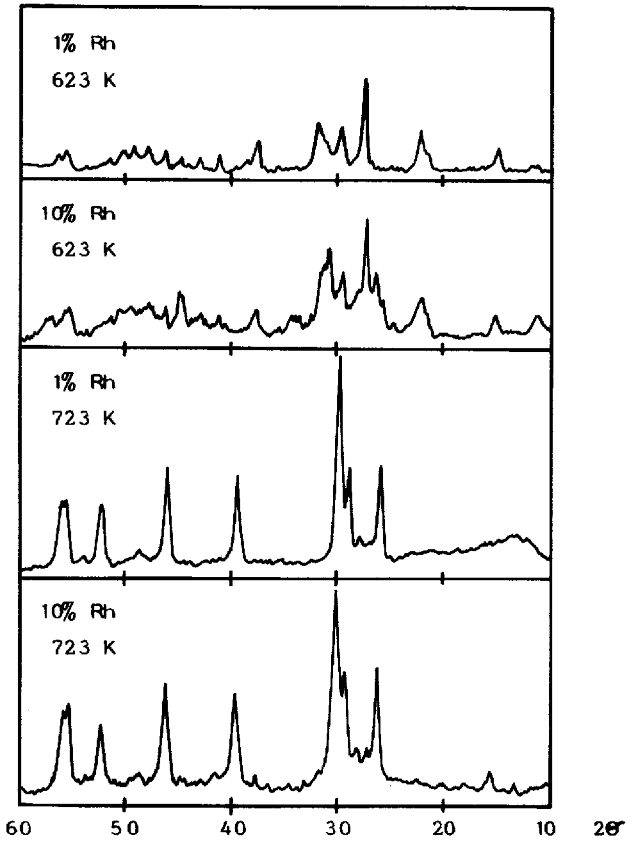

FIGURE 4 X-ray diffraction diagrams of the catalysts obtained upon reduction at 623 and 723 K both 1% and 10% rhodium loading samples of $Rh(NO_3)_3/La_2O_3$.

been plotted because, in both 1% and 10% samples, the amounts of evolved CO_2 were very small and took place at about 383 K. According to Figure 3, the evolution of methane starts at approximately 473 K, a much lower temperature than that found in the TPR-MS studies carried out on the support only, in which case the reduction of the carbonated phase occurs above 773 K. In brief, the reduction of the carbonate species is strongly activated by the presence of rhodium.

In contrast, the TPR-MS spectra for H_2O included in Figure 3 fail to confirm the activating effect of the dispersed metal on the dehydration of lanthana suggested in ref. 14. Though the interpretation of the traces for m/e:18 is to some extent complicated by the evolution of water proceeding from the reduction of both the rhodium nitrate and the carbonated phase on the support, the position and shape of the peaks due to the dehydration of the support can be recognized in Figure 3. Accordingly, the dehydration of the support in H_2 flow would take place through the same mechanism observed in inert gas flow [12]. In this mechanism, $La(OH)_3$ dehydrates to La_2O_3 through an intermediate LaOOH step. The occurrence of such a mechanism is confirmed by the XRD study reported in Figure 4.

It is obvious from the analysis of Figure 3 that, depending on the reduction conditions, phases other than the lanthanum oxide can constitute the actual support, and that, in order to obtain true lanthana supported rhodium catalysts, reduction temperatures of about 723 K would be necessary. To confirm this, two reduction temperatures, 623 and 723 K, were chosen. The H_2 flow and the heating rate in the reduction treatments were the same as used in the TPR-MS experiments. The samples were kept in a flow of H_2 for 1 h at the reduction temperature.

Figure 4 shows the XRD diagrams of the catalysts resulting from the reduction treatments mentioned above. The XRD patterns for 1% and 10% metal loading samples reduced at 723 K, agree well with that of the hexagonal phase of La_2O_3, which confirms the estimate made from the TPR-MS spectra reported in Figure 3. The results of the reduction treatment at 623 K show some differences between samples. The diffraction pattern of the sample with 1% metal loading corresponds to lanthanum oxyhydroxide, LaOOH, while that for the 10% rhodium loading sample indicates the existence of a mixture of phases that include in a type II dioxymonocarbonate, $La_2O_2CO_3$-II, in addition to LaOOH. These differences can be related to the heavier carbonation undergone by lanthana during the impregnation step for the sample with the highest metal loading.

Also worth noting in Figure 4 is the complete absence of diffraction lines due to either the metal or to any other phase containing rhodium, even for the catalyst with 10% rhodium loading. However, this result, which would suggest the existence of well dispersed metal particles, is not consistent with the H_2 and CO adsorption capacities observed on these catalysts. Thus, for a sample with 10% metal loading reduced at 723 K, the apparent H/Rh ratio was found to be 0.3, and the CO/Rh ratio approximately 10 times lower. This rather unusual behaviour, as well as the likely occurrence of a hydrogen spill over phenomena on the Rh/La_2O_3 catalyst (which is supported by both the current literature [7] and some preliminary results of H_2-TPD obtained by us), suggest that as well as structural rearrangements occurring at the support, partial coverage of the metal particles by lanthana might well take place. Similar metal-support interaction phenomena on lanthana supported metal catalsyts have been reported [14,18].

In summary, the present work has established reduction conditions that ensure the preparation of true lanthanum oxide supported rhodium catalysts. As a result of the intense carbonation phenomena induced on lanthana by the impregnation process, the actual nature of the support phases resulting from reduction treatments carried out in the temperature range usually reported in the literature would depend not only on the selected reduction temperature, but also on the impregnation treatment and the treatment of the impregnated sample before its reduction. Thus, taking into account the occurrence of carbonation phenomena on lanthana, an aspect of its chemistry almost completely ignored in the current literature on rare earth oxide dispersed metal catalysts, the behaviour of this 4f sesquioxide as a support becomes even more complex than earlier presumed [10].

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