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Study of the Support Evolution through the Process of Preparation of Rhodium/Lanthana Catalysts

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The evolution undergone by the support throughout the processes involved in the preparation of some lanthana-supported rhodium catalysts has been studied by thermal gravimetry, temperature-programmed decomposition – mass-spectrometry, temperature-programmed reduction – mass-spectrometry and X-ray diffraction. Following the impregnation process, the support consists of partially carbonated lanthanum hydroxide. A study of the reduction process shows that, at 623 K, a catalyst that can be described as Rh/LaO(OH) is obtained. Reduction temperatures as high as 723 K are necessary to prepare true Rh/La_2O_3 catalysts. In contrast to results observed for the dehydration of the support, the reduction of the carbonated phase on lanthana is strongly activated by the presence of the supported rhodium.

Recently the number of papers published dealing with lanthanide-oxide-supported metal catalysts has risen steeply for several reasons: on the one hand, when used for CO and CO_2 hydrogenation, these catalysts show a high selectivity towards oxygenated products;[1-9] on the other hand, quite singular metal–support interaction phenomena have been reported on some of these catalysts[10-12].

In contrast to classic supports such as silica or alumina, the rare-earth oxides, when exposed to atmospheric H_2O and CO_2 at normal temperature and pressure, undergo strong hydration and carbonation phenomena[13-17]. Accordingly, if 4*f* oxides are not very carefully manipulated, which is the case in most reports that have appeared up to now, the initial support phases used in the preparation of M/4*f* oxide catalysts are not in fact lanthanide oxides, but the phases resulting from their hydration and carbonation. The nature of these phases, on the other hand, depends on the 4*f* ion involved.[13-17]

Since the lanthanide sesquioxides, when used as starting phases in the preparation of supported-metal catalysts, are usually hydrated and carbonated in bulk, they may undergo notable structural and chemical transformations throughout the whole process of dispersal of the metal, *i.e.* impregnation, drying treatments and reduction. Likewise, depending on the particular conditions under which the reduction is carried out, phases other than true 4*f* oxides might well constitute the actual support.

Accordingly, in order to understand thoroughly the behaviour of this interesting group of catalysts, the singularities of the rare-earth oxides outlined above should be taken into account. In other words, the true nature of these supports and their evolution throughout the entire preparation process of the supported phases should be investigated in detail.

In the present work, based on our previous knowledge of the behaviour of lanthanum oxide exposed to the air,[16] the processes involved in the preparation of some lanthana-supported rhodium catalysts have been studied.

Since several authors[9,18] have prepared and stored various M/La_2O_3 catalysts before studying them, the behaviour of Rh/La_2O_3, when exposed to air, and the process of its re-reduction have also been investigated.

Experimental

The lanthanum oxide studied here was a 99.9% pure sample from Ventron. In order to work with a well known phase, the oxide was exposed to air for several weeks before its use as starting material in the preparation of the supported phases. The behaviour of this lanthana sample, when aged in air, was found to be similar to that reported by us for three other samples of this oxide.[16] The B.E.T. surface area of the Ventron sample stabilized in air, as deduced from its nitrogen adsorption isotherm at 77 K, was $10\ m^2\ g^{-1}$.

The rhodium salt used here was $Rh(NO_3)\cdot xH_2O$, 36% Rh, from Ventron. The rhodium nitrate, obtained from an aqueous solution, was deposited on to the support by the incipient-wetness impregnation technique. In order to achieve a final rhodium loading of 1%, six successive cycles of impregnation at 298 K, and drying in air at 383 K for 10 h, were necessary. The B.E.T. surface area of the impregnated sample was also $10\ m^2\ g^{-1}$. This value was not significantly modified after the reduction treatments at both 623 and 723 K.

The thermogravimetric analysis (t.g.) experiments were carried out in a Mettler microbalance, model ME-21. All these experiments were performed in a flow of gas, either He or H_2, the rate of flow always being $1 \times 10^{-6}\ m^3\ s^{-1}$ ($60\ cm^3\ min^{-1}$). The linear heating rate was $0.1\ K\ s^{-1}$.

The temperature-programmed decomposition (t.p.d.) and temperature-programmed reduction (t.p.r.) experiments were recorded under the following conditions: flow of gas (either He or H_2): $1 \times 10^{-6}\ m^3\ s^{-1}$; heating rate: $0.1\ K\ s^{-1}$. The analysis of evolved gases was carried out by means of Vacuum Generators Spectralab SX-200 mass spectrometer interfaced to an Apple IIe microcomputer. The experimental apparatus for t.p.d. (or t.p.r.) – mass-spectrometer used here has been described elsewhere.[19]

X-Ray diffraction studies were carried out with a Siemens instrument, model D-500, using Cu K_α radiation.

Results and discussion

Lanthanum oxide, when exposed to atmospheric CO_2 and H_2O for a few hours (*ca.* 24 h) at normal temperature and pressure is completely transformed into partially carbonated lanthanum hydroxide.[16] Therefore, in our case the starting support sample was not La_2O_3, but the phases resulting from its hydration and carbonation in air.

Taking into account the procedure followed to deposit the rhodium salt on to the support, we have also investigated the evolution undergone by the sample aged in air when submitted to six successive cycles of wetting in distilled water and drying in air at 383 K, as in the impregnation process. The sample resulting from the treatment above, which in order to be distinguished from the true lanthanum oxide will hereafter be referred to as La_2O_3*, has been investigated by X-ray diffraction, t.p.d.–m.s. and t.g. Fig. 1 summarizes the results of this characterization study.

From a comparison of the results in fig. 1 with those reported in ref. (16) for lanthana simply aged in air, no difference can be noted. As in ref. (16), the X-ray diffraction pattern, which does not allow the identification of carbonated phases, agrees well with that of $La(OH)_3$. However, it is obvious from the t.p.d.–m.s. diagrams in fig. 1(*b*) that carbonation of the sample has occurred. Furthermore, from analogies found between the so-called La_2O_3* sample and that simply aged in air, the same reaction scheme

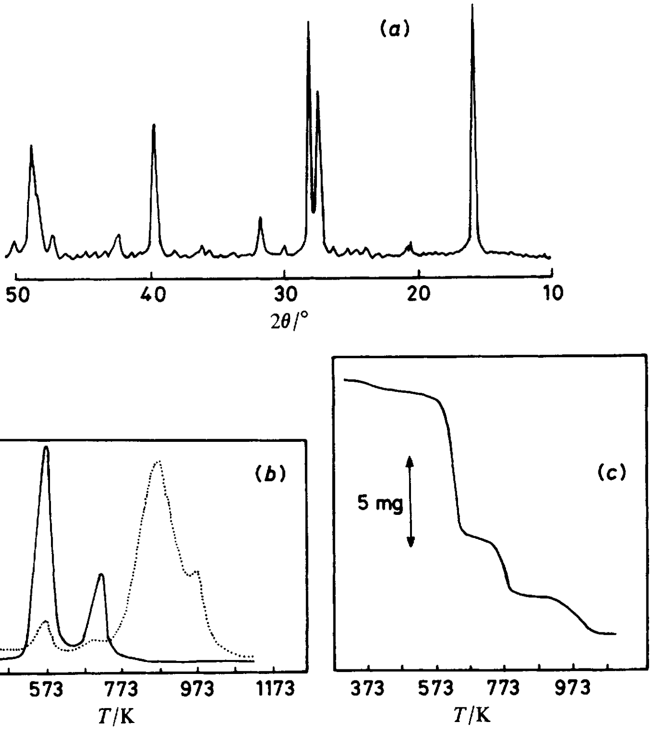
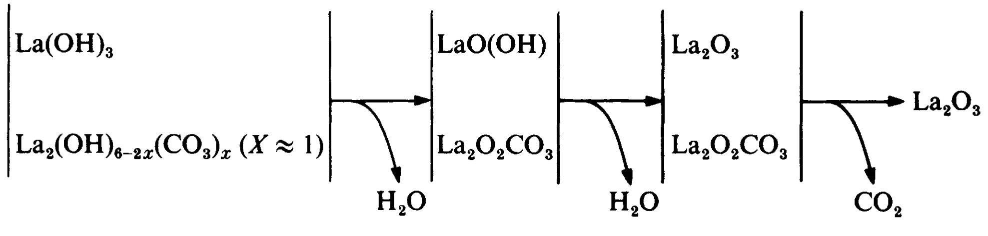


Fig. 1. Characterization studies on La_2O_3*. (*a*) X-ray, diffraction pattern. (*b*) T.p.d.–m.s. traces for water ($m/z = 18$, —), and carbon dioxide ($m/z = 44$, · · · ·). (*c*) T.g. diagram in flowing He (weight of sample, 91.8 mg).

proposed in ref. (16) can now be applied to interpret the thermal evolution of La_2O_3*:



In accordance with the scheme above, the amount of CO_2 taken up by La_2O_3* can be estimated from the last step of the t.g. diagram in fig. 1(*c*). When referred to 1 nm^2 of B.E.T. surface area, this amount is found to be 30 molecules per nm^2, much larger than 8 molecules per nm^2, the value proposed by Rosynek[20] for the surface carbonation of La_2O_3. In brief, La_2O_3* is carbonated in bulk.

The thermal evolution, in flowing helium, of $Rh(NO_3)_3/La_2O_3$* is reported in fig. 2(*a*). For comparative purposes, the t.g. trace for La_2O_3* shown in fig. 1, is also included in fig. 2(*b*). From a comparison of figs. 2(*a*) and (*b*) it can be deduced that the impregnation process does not induce significant alterations on the support. In fact, the only difference between traces (*a*) and (*b*) is the larger weight loss occurring up to 573 K on trace (*a*). This difference should be related to the decomposition of the rhodium nitrate.

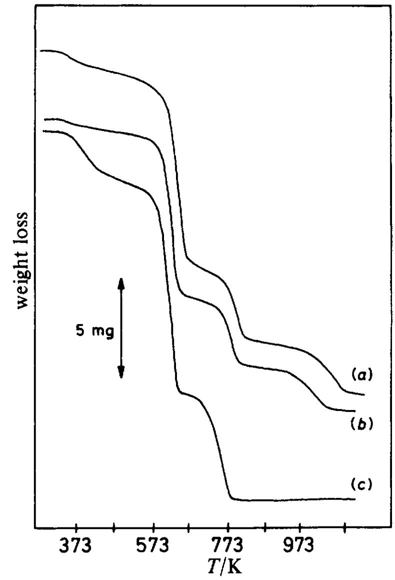


Fig. 2. T.g. diagrams corresponding to (*a*) decomposition in flowing He of 99.6 mg of $Rh(NO_3)_3/La_2O_3$*. (*b*) Decomposition in flowing He of 91.8 mg of La_2O_3*. (*c*) Reduction in flowing H_2 of 104.8 mg of $Rh(NO_3)_3/La_2O_3$*.

When $Rh(NO_3)_3/La_2O_3$* is decomposed in flowing H_2, the t.g. diagram [fig. 2(*c*)], is different from those reported in fig. 2(*a*) and (*b*). On the one hand, the weight loss taking place at 373–473 K is much better defined in fig. 2(*c*), which suggests that the reduction of $Rh(NO_3)_3$ occurs within a shorter range of temperature than its decomposition in flowing helium. On the other hand, the last decomposition step in fig. 2(*a*) and (*b*), that corresponding to the evolution of CO_2, completely disappears in fig. 2(*c*). Accordingly, in the presence of rhodium the reduction of the carbonated phase on the support is strongly activated.

In order to gain further insight into the process occurring throughout the preparation of the lanthana-supported rhodium catalysts, we have also investigated by t.p.r.–m.s. the thermal evolution of La_2O_3* (fig. 3) and $Rh(NO_3)_3/La_2O_3$* (fig. 4).

As can be seen in fig. 3, the decomposition in flowing H_2 of La_2O_3* takes place in three steps. The first two steps correspond to the evolution of H_2O and, as in the case of the decomposition in flowing He [fig. 1(*c*)], can be assigned to the dehydration of La_2O_3*. The third step, on the contrary, starts at a lower temperature (773 K) than that found in fig. 1(*c*) for the evolution of CO_2. Furthermore, this third step implies the evolution of CH_4 ($m/z = 16$ and 14), H_2O ($m/z = 18$) and CO ($m/z = 28$). Therefore, when only the support is heated, in flowing H_2, at temperatures above 773 K, the reduction of the carbonated phase occurs.

If, in a parallel experiment to that reported in fig. 3, the thermal evolution in flowing H_2 of $Rh(NO_3)_3/La_2O_3$* is studied (fig. 4), the reduction of the carbonated phase, as deduced from the observation of CH_4 and CO, starts at *ca.* 473 K and is completed below 773 K. These results, consistent with the t.g. study reported in fig. 2(*c*), confirm the activation by the metal of the reduction of the carbonated phase on the support. The results above, on the other hand, suggest that the reduction of the rhodium nitrate to the metal should occur below 473 K. In effect, as deduced from both the t.g. trace in fig. 2(*c*), mentioned above, and the evolution of NH_3, suggested by the t.p.r. diagrams corresponding to $m/z = 17$ and $m/z = 16$ in fig. 4, the reduction of $Rh(NO_3)_3$ takes place within the range 373–473 K.

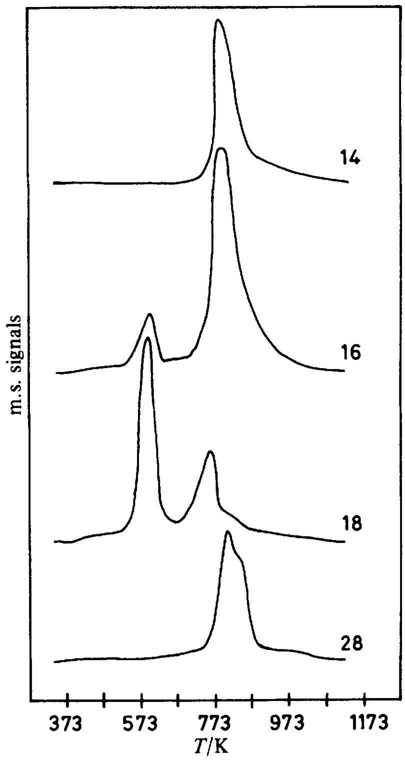


Fig. 3. T.p.r.–m.s. study of La_2O_3* (weight of sample, 50 mg).

Also, in contrast to what is observed in fig. 3, the reduction of the carbonated phase, in the presence of metal (fig. 4) takes place through a complex mechanism in which at least two steps can be distinguished. These two steps, centred at 573 and 723 K, agree approximately with the two stages through which the dehydration of the support occurs. Accordingly, the last two steps of the t.g. diagram in fig. 2(*c*) should include both the weight loss due to the dehydration of the support and that corresponding to the reduction of the carbonated phase.

Contrary to what is suggested in ref. (11), our results show that the dehydration of the support is not activated by the metal. The differences observed in ref. (11) between the X-ray photoelectron spectra obtained after heating in H_2 (*a*) the support only and (*b*) a lanthanum oxide-supported palladium phase should be reasonably interpreted as being due to the activation by the metal of the reduction of the carbonated phase on the support, rather than to its dehydration. The activation by the supported metal of the reduction of carbonate species on lanthana has also been reported in ref. (21).

In accordance with our results, in order to obtain true lanthanum oxide-supported metal catalysts, either special procedures, including the calcination of the starting support phase at temperatures as high as 1100–1200 K and its further manipulation in the absence of H_2O and CO_2, are followed, or reduction temperatures of *ca.* 723 K are used. Otherwise, phases other than lanthanum oxide would constitute the actual support. Since most of the papers dealing with M/La_2O_3 catalysts which have appeared up to the present have not taken into account the singularities of this support, particularly its likely carbonation in the bulk oxide when manipulated in air for a few hours, it is our opinion that in many cases catalysts improperly described as lanthana-supported metal phases have been investigated.

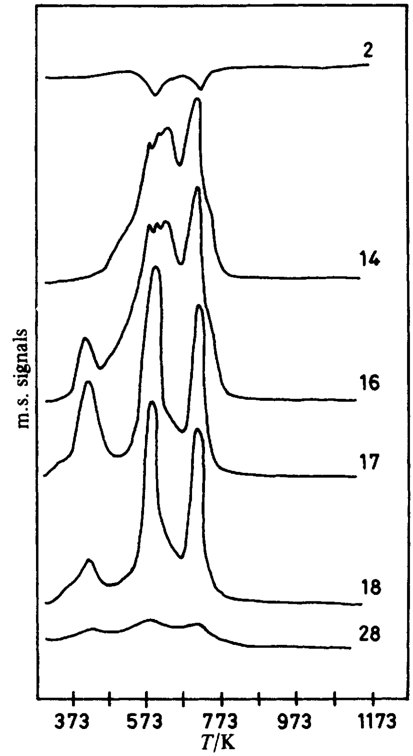


Fig. 4. T.p.r.–m.s. study of $Rh(NO_3)_3/La_2O_3$* (weight of sample, 50 mg) *m/z* values are as marked.

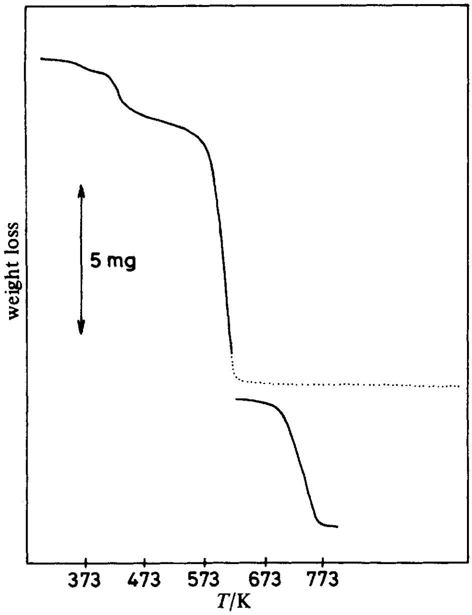


Fig. 5. Study of thermogravimetric analysis of the reduction by steps of 86 mg of $Rh(NO_3)_3/La_2O_3$*.

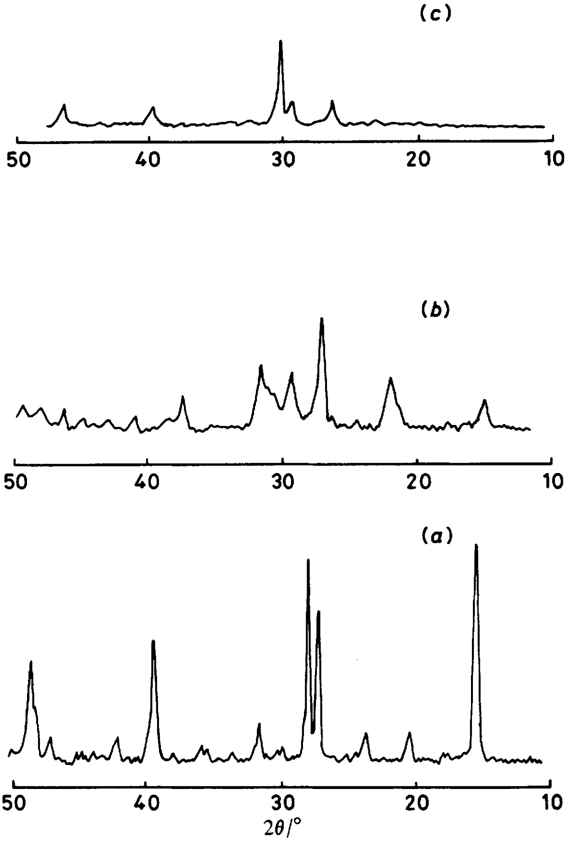


Fig. 6. X-Ray diffraction patterns corresponding to (*a*) $Rh(NO_3)_3/La_2O_3$*, (*b*) the catalyst resulting from the reduction of (*a*) at 623 K and (*c*) the catalyst resulting from the reduction of (*a*) at 723 K.

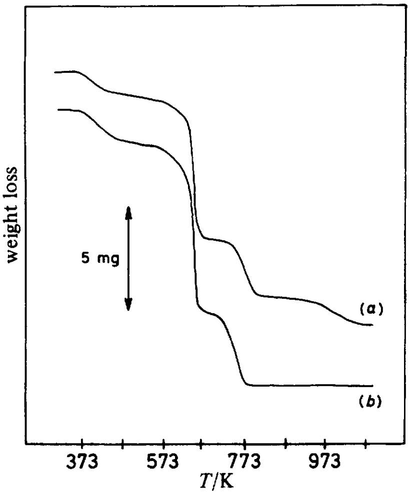


Fig. 7. Thermal evolution in (*a*) flowing He and (*b*) flowing H_2 of a Rh/La_2O_3 catalyst exposed to air for 24 h. [The catalyst was obtained from the reduction at 723 K of 79.6 mg of $Rh(NO_3)_3/La_2O_3$*.]

It can also be deduced from our results that, when the reduction of the precursor is carried out at 623 K, a relatively well defined support is obtained. In effect, fig. 5 depicts the t.g. diagram corresponding to the reduction by steps of $Rh(NO_3)_3/La_2O_3$*. The upper part of the figure accounts for the weight loss observed when the sample is heated to 623 K and held at this temperature for 1 h (dotted line) in flowing H_2. If, after this reduction treatment, the temperature is raised again, in a flow of H_2, the t.g. diagram shown in the bottom of fig. 5 is obtained. When the lower and upper parts of fig. 5 are brought together, the resulting t.g. diagram is similar to that reported in fig. 2(*c*). In accordance with the results included in fig. 2–4, discussed above, and the reaction scheme proposed in ref. (16) and reproduced here in order to interpret the thermal decomposition of La_2O_3*, it can be concluded that, when $Rh(NO_3)_3/La_2O_3$* is reduced, in a flow of H_2 for 1 h at 623 K, a catalyst consisting of Rh dispersed on partially carbonated lanthanum oxydroxide, LaO(OH), is obtained.

In order to confirm the statement above, the phases resulting from the reduction of $Rh(NO_3)_3/La_2O_3$* at both 623 and 723 K have been studied by X-ray diffraction. Fig. 6 shows the corresponding diffraction patterns and includes the diffraction pattern of $Rh(NO_3)_3/La_2O_3$*. The three diffraction patterns are quite different from each other. That of $Rh(NO_3)_3/La_2O_3$* is similar to the one depicted in fig. 1 for La_2O_3*, and can be assigned to $La(OH)_3$. With regard to the diagram for the catalyst reduced at 623 K, as suggested above only diffraction lines corresponding to LaO(OH) can be observed. Finally, the catalyst reduced at 723 K for 1 h shows the diffraction pattern of hexagonal La_2O_3, which confirms the conclusion drawn from t.g. and t.p.r.–m.s. in the sense that, at 723 K, a true Rh/La_2O_3. catalyst is obtained.

Since some of the authors working on lanthanum-oxide-supported metal catalysts store the prepared catalysts for some undefined time before studying them, we have also investigated the behaviour with regard to atmospheric H_2O and CO_2 of a sample of Rh/La_2O_3. For this purpose a catalyst reduced at 723 K as indicated above was cooled in a flow of H_2 to ambient temperature; then a flow of He was passed over the sample for 1 h, which was finally exposed to air at ambient temperature for 24 h.

Fig. 7(*a*) shows the t.g. diagram, in a flow of He, of the Rh/La_2O_3 catalyst stabilized in air. When this diagram is compared to that reported in fig. 1(*c*), it may be concluded that, in the present case, the presence of dispersed metal on lanthana does not modify the behaviour of the support when exposed to air.

The t.g. trace corresponding to the reduction, in flowing H_2, of the Rh/La_2O_3 catalyst aged in air is depicted in fig. 7(*b*). This trace is quite similar to that reported in fig. 2(*c*). Accordingly, as far as the evolution of the support throughout the reduction process is concerned, no significant difference should be observed between the catalyst prepared by reduction of $Rh(NO_3)_3/La_2O_3$* and that obtained by reducing Rh/La_2O_3 previously stabilized in air.

Conclusions

In summary, data concerning the evolution undergone by the support throughout the processes involved in the preparation of some lanthana-supported rhodium catalysts have been reported. Although the hydration of lanthanum oxide, when manipulated as is usual in order to prepare M/La_2O_3 catalysts, has been considered by some authors,[22-24] the carbonation in the bulk oxide, as well as the evolution of this carbonated phase throughout the reduction process, have not been sufficiently stressed. This omission, which is related to the smaller number of papers specifically devoted to the study of the behaviour of 4*f* oxides simply exposed to air, is however very important if one is to determine the nature of the support phase, and, ultimately, to understand thoroughly the behaviour of this novel type of supported-metal catalyst.

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