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Solid state chemistry of the preparation of lanthana-supported metal catalysts – study of the impregnation step

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The solid state reactions occurring at the support throughout the preparation process of lanthana-supported metal catalysts is reported. Specifically it is concerned with the impregnation step. When following the usual procedure, i.e. impregnation of lanthana with an aqueous solution of the precursor, heavy carbonation of the support with formation of a hydroxycarbonate phase, $La(OH)CO_3$, was found to occur. Simulated impregnation treatments with distilled water have shown that the nucleation of the hydroxycarbonate phase, not observed on lanthana simply exposed to air, is not specifically induced by the presence of the precursor salt. Likewise, it has been found that the nucleation of $La(OH)CO_3$ does not take place upon heating the oxide in air at 383 K, as in the drying treatment which follows the wetting step of the impregnation process. Accordingly, nucleation of the new carbonated phase must occur during the wetting step. Once the formation of $La(OH)CO_3$ has begun, the support can slowly take up further amounts of CO_2 by simple exposure to air. In this way, impregnated support phases actually consisting of as much as 80% $La(OH)CO_3$ could be observed. It can be concluded from the present work that the occurrence of carbonation phenomena on lanthana constitutes a major feature of its behaviour as a support of the transition metals. To date, however, this is an aspect which has received very little attention.

1. Introduction

Since the pioneering papers of Ichikawa [1, 2], the attention paid to the lanthanum oxide-supported transition metal phases has notably increased. At present, both the catalytic activity data [3–5] and the characterization studies [6, 7] suggest that the behaviour of this new type of supported metal catalyst ought to be considered rather unconventional.

As recently suggested [8], the high reactivity of the lanthanum oxide against H_2O [9–11] may be one clue to the interpretation of singularities of the lanthana-supported metal catalysts. In effect, it has been proposed [8] that the reduction treatment, in addition to allowing the preparation of the dispersed metal, induces the dehydration of the support from $La(OH)_3$ to La_2O_3. The latter reaction would be responsible for the partial coverage of the metal particles by the support. In other words, the preparation of lanthana-supported metals, at least when following the usual procedures [3–5, 8], implies the occurrence of solid state reactions at the support, which obviously can influence the microstructure of the resulting metal/support phases, and, in summary, the general properties of these phases. No similar phenomena are observed in the classic metal/support phases, as in the case of the silica- and alumina-supported metals.

According to results reported previously [12–14], the manipulation in air of lanthana not only causes its complete hydration, but also the carbonation of the sample to such an extent as to be considered a bulk process. However, in studies of the behaviour as a support of lanthanum oxide, the latter reaction has either been ignored or rather vague references to it have been made [6, 15].

In a very recent paper [16], we discussed some aspects of the preparation of lanthana-supported phases, where the likely occurrence of carbonation phenomena on the support should be taken into account. Likewise, some preliminary results obtained by us have shown that lanthana samples impregnated with the metal precursor salt exhibit higher carbonation levels than the oxide samples simply exposed to air, which suggests that the impregnation step can induce further carbonation of the support [17]. These results, as well as the complete absence of information about this topic in the current literature, prompted us to carry out the investigation reported here.

In the present work, in effect, the solid state reactions occurring at the support through the impregnation step of the preparation process of two lanthana-supported rhodium catalysts with quite different metal loadings were studied. In accordance with this study,

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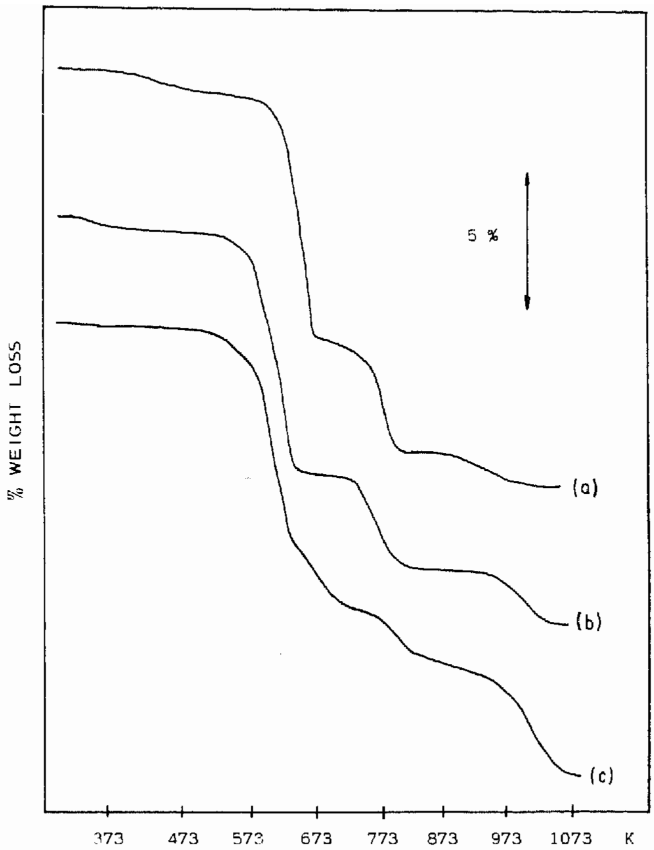

Figure 1 TG diagrams of lanthana, (a) stabilized in air, (b) submitted to six cycles of wetting–drying with distilled H_2O, (c) after 18 wetting–drying cycles with distilled H_2O.

with no precedents in the current literature, the carbonation of lanthana should be considered a major feature of its behaviour as support of the transition metals. This introduces additional elements in the discussion of such behaviour, and, in summary, can contribute to a better understanding of the actual nature of this complex metal/support system.

2. Experimental details

The lanthanum oxide used here was a commercial sample from Alfa-Ventron, 99.9% pure. Before its use as support, the lanthana sample was exposed to air for several weeks. This exposure time is much longer than that needed to achieve the complete stabilization of the oxide, ~24 h [13]. The BET surface area of the oxide aged in air, as determined by nitrogen adsorption at 77 K, was found to be 10 $m^2 g^{-1}$. This value did not significantly change upon treating the sample either with an aqueous solution of rhodium nitrate or with distilled water. The metal precursor salt was $Rh(NO_3)_3 \cdot 2H_2O$ from Ventron, and had a 36% metal content.

The lanthana impregnated rhodium nitrate samples with 1% and 10% metal loadings were prepared by the incipient wetness impregnation technique. In the first case (1% rhodium loading), the impregnating solution contained 1 g rhodium salt in 100 cm^3 H_2O. To prepare the 10% metal loading sample the concentration of the solution was four times greater. In either case, the corresponding aqueous solution of $Rh(NO_3)_3$ was added dropwise to a known weight of the support, which was stirred thoroughly after each drop. New drops of the solution were added until the pore volume was filled, at which point the next drop would produce a slurry in the beaker. The sample was then dried in air, at 383 K, for 10 h. In order to achieve the desired metal loading, the impregnation treatment was repeated six times (1% sample), or eighteen times (10% sample).

Thermogravimetric analysis (TG) and temperature programmed decomposition (TPD) experiments were all carried out in a helium flow at 1 $cm^3 sec^{-1}$, and a heating rate of 0.1 K sec^{-1}. The analysis of the evolved gases from the TPD experiments was carried out with a mass spectrometer (MS), Vacuum Generator, model Spectralab SX-200, interfaced to a microcomputer Apple IIe. The TPD-MS experimental device has been described and characterized elsewhere [18, 19].

The infrared spectra were recorded with an instrument Perkin Elmer, model 710B. The samples were studied in a matrix of KBr (2.5% of the sample) pressed under 5×10^8 Pa.

The X-ray diffraction (XRD) studies were carried out using a Siemens, model D-500 instrument. The radiation was Cu$K\alpha$, and a nickel filter was used.

3. Results

3.1. Starting support phase

As stated above, the starting support phase used in both the actual impregnation studies and those of simulated impregnation with distilled water, was a lanthanum oxide previously stabilized in air. In this way, problems inherent to work with a support phase not well-defined are precluded. This aged in air lanthana sample has been found to show a behaviour similar to that reported by us for several other lanthana samples [12–14]. Thus, the TG trace of the sample studied here, Fig. 1, is characterized by three

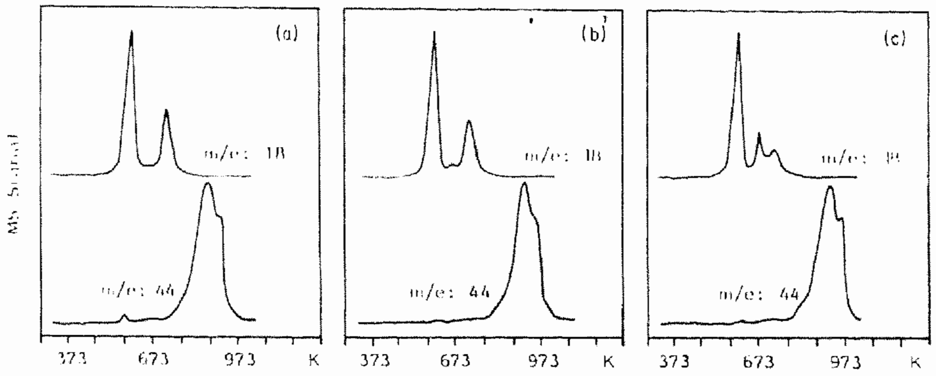

Figure 2 TPD-MS diagrams of lanthana, (a) stabilized in air, (b) after six cycles of wetting–drying with distilled H_2O, (c) submitted to 18 wetting–drying cycles with distilled H_2O.

well-defined steps. Rosynek and Magnuson [10, 11] have assigned the first two steps to the dehydration of $La(OH)_3$ to La_2O_3 through an intermediate oxyhydroxide phase, LaOOH. The third step is interpreted by them as due to decomposition of surface carbonate species. As discussed previously [13, 14], however, the carbonation undergone by lanthana, upon exposure to air, cannot be considered a simple surface process. In fact, from the TG reported in Fig. 1, the amount of CO_2 taken up by lanthana is estimated to be equivalent to 27 mol nm^{-2}, much higher than 8 mol nm^{-2} estimated for a surface process. Accordingly, we have proposed the formation of a hydroxycarbonate-like phase, which can be formulated as $La_2(OH)_4CO_3$ [13, 14]. It is worth noting that the formation of this phase cannot be detected by XRD, which has probably contributed to the occurrence of a bulk carbonated phase on the aged in air lanthanum samples being ignored.

In summary, earlier results obtained by us on various lanthana samples [13, 14], as well as those corresponding to the sample used here, support that, upon exposure to air, the oxide rapidly and completely transforms into partially carbonated hydroxide. Neither the nature nor the amount of the carbonated phase have been found to change after prolonged exposure to air, even for years.

3.2. Support treated as in the impregnation process with distilled water

In addition to the characterization of the starting support phase, our study of the impregnation process includes investigation of the evolution undergone by lanthana when submitted to a series of wetting–drying cycles with both distilled water and aqueous solutions of rhodium nitrate. The study of the alterations induced on the support by either of the above treatments, simulated or true impregnation processes, is aimed at obtaining information about the likely influence of the presence of the transition metal salt on the solid state reactions occurring at the support during the impregnation step.

Fig. 1 shows the TG traces of lanthana treated 6 and 18 times with distilled H_2O, as well as that of the starting support. According to the TPD-MS study reported in Fig. 2, the last step of the TG traces above corresponds to the evolution of CO_2. Then, this step can be used to estimate the amount of CO_2 taken up by the support. As deduced from Fig. 1, the larger the number of impregnation cycles, the higher the carbonation of lanthana. Furthermore, the TG diagram for the sample treated 18 times shows a fourth decomposition step, at 650 K, which could indicate the occurrence of alterations in the mechanism of decomposition of the treated samples with respect to that of the starting lanthana. The appearance of a new decomposition step can also be deduced from the TPD-MS spectra in Fig. 2, according to which the dehydration of the treated sample shows a peak between the two characteristic features observed on lanthana simply aged in air.

The diffraction pattern of the starting lanthana sample, included in Fig. 3, agrees well with that reported in the ASTM file for $La(OH)_3$. In the case of the samples treated 6 and 18 times, however, additional lines, those marked with asterisks in Fig. 3, can easily be observed. This series of lines, the intensity of which grows with the number of wetting–drying cycles, fits well with that reported previously [20, 21] for a lanthanum hydroxycarbonate phase, that can be formulated as $La(OH)CO_3$. This suggests that the simulated impregnation treatments carried out on the lanthana aged in air induces not only further uptake of CO_2 by the sample, but also the formation of a new crystalline hydroxycarbonate-like phase, not existing in the untreated sample. This interpretation is also consistent with the results of the infrared spectroscopic study reported in Fig. 4.

Three regions can be distinguished in the infrared spectra depicted in Fig. 4: the range of the OH stretching modes (3000 to 4000 cm^{-1}); the typical range containing the absorptions due to the carbonate modes described as ν_1, ν_2, and ν_4 in Gatehouse *et al.*'s notation [22] (1000 to 1700 cm^{-1}); and the range, below 1000 cm^{-1}, at which bands due to ν_3, ν_5, ν_6 modes of the carbonate species, as well as that at around 640 cm^{-1}, assignable to a deformation mode La–O–H of the hydroxide [23, 24], can be observed.

From analysis of Fig. 4, important morphological changes can be observed in the carbonate bands in the 1000 to 1700 cm^{-1} range. In effect, after three treatment cycles, sharper bands at 1440 and 1500 cm^{-1} develop over the broader ones at 1380 and 1480 cm^{-1} which exist in the lanthana sample aged in air. Like-

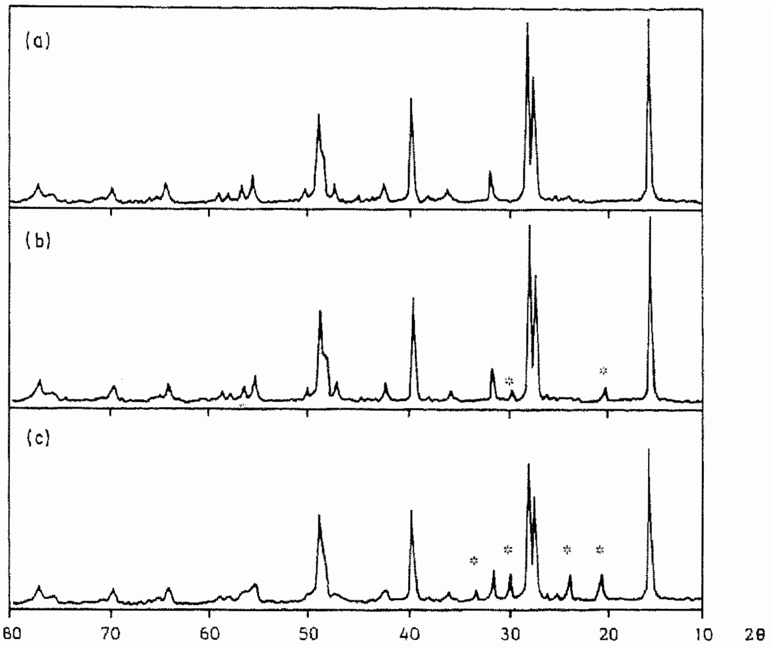

Figure 3 Study by XRD of lanthana. (a) stabilized in air, (b) after six wetting–drying cycles with distilled H_2O, (c) submitted to 18 wetting–drying cycles with distilled H_2O.

wise, upon increasing the number of wetting–drying cycles, the asymmetrical band at 1070 cm^{-1} found in the starting lanthana sample transforms into a clearly resolved doublet, in which the sharp absorption at 1090 cm^{-1} finally becomes stronger than that at 1070 cm^{-1}. These results can be rationalized, assuming that the wetting–drying treatments induce the formation of a new phase on lanthana. Furthermore, this new carbonated phase is not formed when a sample of lanthana aged in air is held at 383 K, in air, for sufficient time to complete the eighteen treatment cycles. In effect, the study by TG, XRD and infrared spectroscopy of the sample resulting from a prolonged treatment at 383 K (approximately 2 weeks) did not show any evidence of the alterations reported above. This suggests that the main process responsible for the occurrence of the new carbonated phase would be the wetting step rather than the drying treatment in air at 383 K.

In the stretching OH range of the spectra included in Fig. 4, the existence of two features can be noted. The sharp, strong band at 3600 cm^{-1} can be assigned to $La(OH)_3$ [11, 13, 23, 24]. The lower frequency band initially appears as a broad feature centred at about 3400 to 3410 cm^{-1}. Upon increasing the number of treatment cycles, the band becomes better defined, stronger, and moves slightly to higher frequencies, 3425 cm^{-1}. It can also be deduced from Fig. 4 that the intensity of this band increases in parallel with that of the carbonate bands, and, on the other hand, that the difference of intensity between the bands at 3600 and 3425 cm^{-1} diminishes as the number of treatment cycles increases. Very recently, Dexpert *et al.* [25] have discussed the infrared spectra of the lanthanide hydroxycarbonates, $Ln(OH)CO_3$. According to this study, the ancylite-like, A-type, 4*f* hydroxycarbonates are characterized in the ν_{OH} range by a doublet, hardly resolved for elements belonging to the first half of the

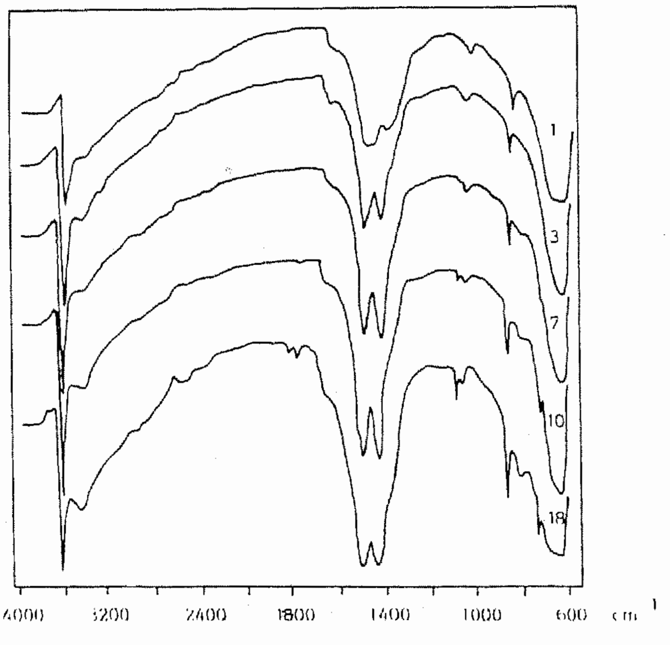

Figure 4 Study by infrared spectroscopy of lanthana submitted to successive cycles of wetting–drying with distilled H_2O. The number of cycles is indicated on the right-hand side.

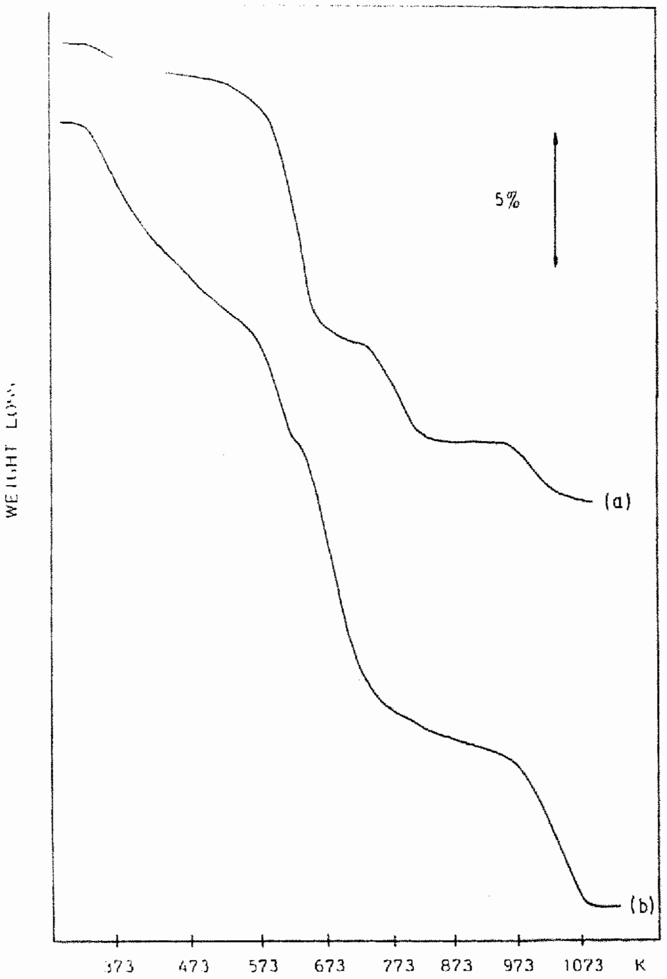

Figure 5 TG diagrams of recently prepared lanthana impregnated samples with (a) 1% and (b) 10% metal loading.

lanthanide series, the average frequency of which ranges from 3425 to 3515 cm^{-1} as the atomic weight of the rare earth element increases. In summary, the infrared spectra reported in Fig. 4 are also consistent with the occurrence, associated with the series of wetting drying treatments, of further uptake of CO_2 leading to the formation of a new crystalline phase, A-type $La(OH)CO_3$.

3.3. Impregnated samples

Two lanthana-impregnated rhodium nitrate samples, with 1% and 10% rhodium loadings, were prepared. Six and eighteeen impregnating cycles were necessary in order to achieve the desired metal loadings.

Fig. 5 shows the TG diagrams of the two impregnated samples recently prepared. From the last step of these diagrams, the total amount of CO_2 taken up by the support can be estimated. In the present case, 2.6% and 7.8% were found to be the CO_2 uptakes by the samples with 1% and 10% rhodium loadings, respectively. These results, like those obtained on lanthana treated with distilled water only, indicate that the larger the number of impregnation cycles the higher the level of carbonation reached on the support.

The impregnated samples have also been studied by XRD (Fig. 6). This study reveals the existence of diffraction lines other than those corresponding to $La(OH)_3$. These additional lines, which are especially intense in the case of the sample with 10% metal

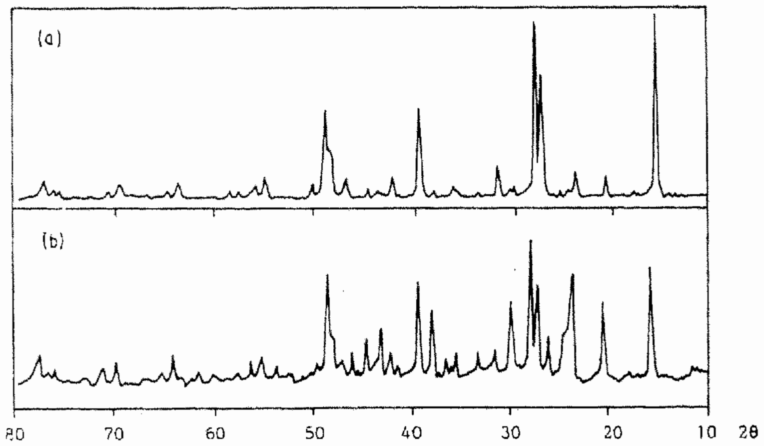

Figure 6 XRD study of recently prepared lanthana impregnated samples with (a) 1% and (b) 10% metal loading.

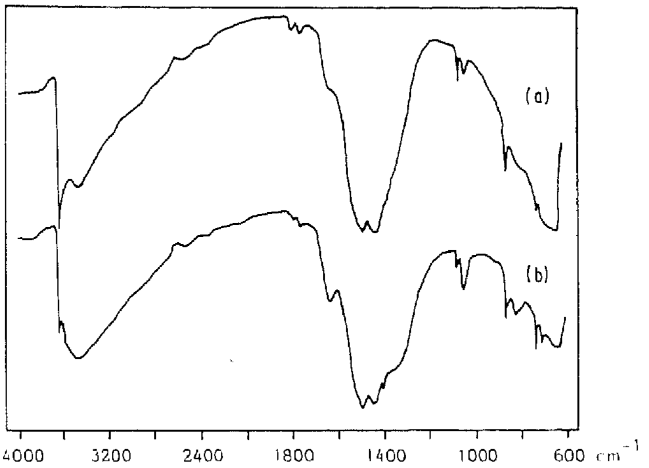

Figure 7 Infrared spectra of the recently prepared lanthana impregnated samples with (a) 1% and (b) 10% metal loading.

loading, agree well with those depicted in Fig. 3 and, therefore, should be ascribed to the presence of the hydroxycarbonate phase, La(OH)CO$_3$, previously reported [20, 21].

The infrared spectroscopic study of the impregnated samples is reported in Fig. 7. It can be deduced from analysis of this figure that the lanthanum hydroxide (band at 3600 cm^{-1}), coexists with a hydroxycarbonate phase peaking at 3425 cm^{-1}. In the 1000 to 1700 cm^{-1} region of the spectra, in addition to the bands due to carbonate species, the appearance of a broad shoulder centred around 1300 cm^{-1} can be noted, probably due to nitrate species incorporated in the support through the process of impregnation. In the case of the sample with 10% metal loading, a sharp feature at 1380 cm^{-1} can also be observed. This band can be assigned to nitrate vibration modes in the rhodium nitrate.

After its preparation, the impregnated sample with 1% rhodium loading was stored at room temperature with no special precautions. When this sample was studied some time later, it could be observed that the carbonation reaction had progressed very notably. Figs 8, 9 and 10 show, respectively, the TG, infrared spectroscopy and XRD diagrams of an impregnated sample prepared three years earlier. The diagrams are, from a qualitative point of view, similar to those obtained for the recently prepared impregnated sample. It is worth noting, however, that the last step of the TG trace on Fig. 8 indicates the occurrence of a very heavy carbonation. In fact, the amount of CO$_2$ taken up by the support, as estimated from the step mentioned above, was found to be 9.8%, the largest of the values observed here. It can also be noted in Fig. 8, that the weight loss associated with the decomposition step, centred around 650 K, appeared on the

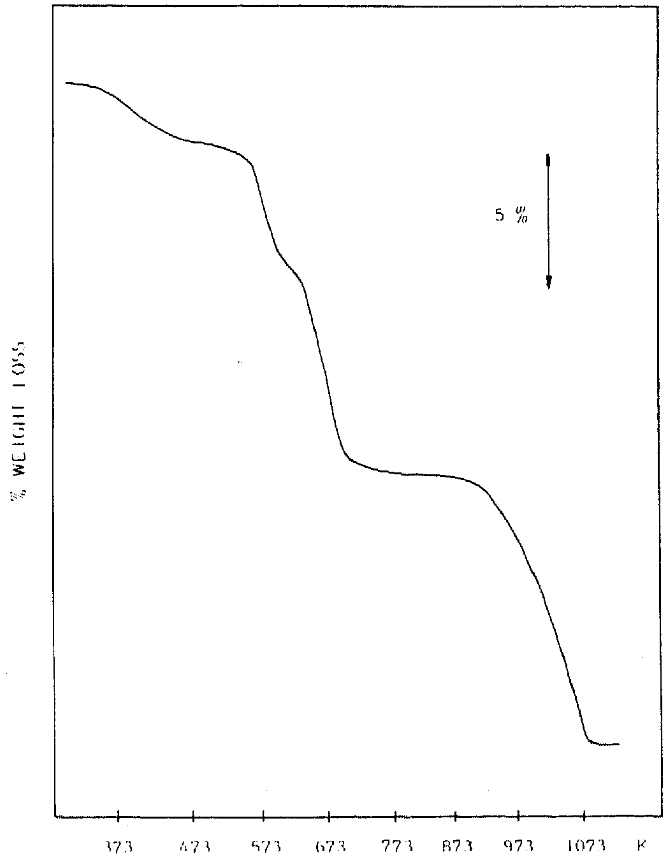

Figure 8 TG trace of a lanthana-impregnated rhodium nitrate sample (1% metal loading) exposed to air for a prolonged period of time.

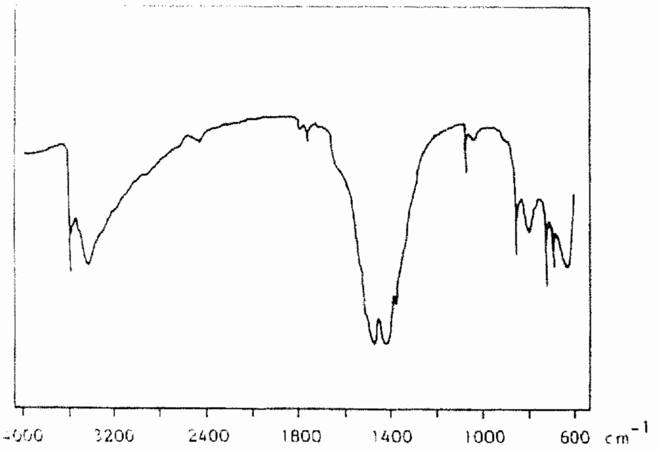

Figure 9 Infrared spectra of a lanthana impregnated $Rh(NO_3)_3$ sample (1% metal loading) exposed to air for a prolonged period of time.

impregnated and wetted with distilled H_2O samples, increases very notably. Because, in accordance with Fig. 2, this latter step essentially corresponds to the evolution of H_2O, the two steps mentioned above can be interpreted as the stages through which the crystalline hydroxycarbonate phase formed on the support transforms into the lanthanum oxide.

4. Discussion

In accordance with the results reported above, impregnation with an aqueous solution of a lanthana sample, previously stabilized in air, induces further uptake of CO_2 by the support. Amounts of carbonate as much as eight times larger than those found on the lanthana simply aged in air have been observed on the impregnated samples. Associated with this heavy carbonation of the support, modifications of the mechanism of its thermal decomposition, as well as the appearance of a crystalline, A-type, hydroxycarbonate phase, similar to that reported earlier [20, 21] have been found. This new phase could not be observed either on the lanthana aged in air samples, even in the case of very prolonged exposures to the air, or on heating at 383 K, in air, the support phase used as starting material in the present work. This suggests that the nucleation of the crystalline hydroxycarbonate phase should be induced by the wetting treatment, rather than by the drying treatment.

Our results also indicate that the presence of the rhodium salt in the aqueous solution is not the major reason for the occurrence of the nucleation process mentioned above. In fact, the formation of the same hydroxycarbonate phase could also be observed when the starting lanthana sample was treated with distilled water. In accordance with this, similar effects on the carbonation of lanthana ought to be expected from the impregnation treatments in which aqueous solutions are used, no matter what transition metal salt is used.

A further interesting finding of the present work is that, once the nucleation of the new hydroxycarbonate phase has occurred, the growth of this phase can continue by simple exposure of the sample to air, at room temperature. This means that in contrast to lanthana simply stabilized in air, which after approximately 24 h ageing reaches an apparent stabilization, unaltered by exposure to air for years [13, 14], the impregnated lanthana samples become labile against the uptake of further amounts of CO_2. In other words, the actual nature of the support remains rather undefined, so that the intensity of the carbonation process, which can reach very high levels, will depend very much on the number of impregnation cycles, and also on how the supported phase is manipulated and stored after its preparation.

It can be concluded from the results reported here that the behaviour of lanthana as a transition metal support is very complex. Thus, we have recently found [17] that the actual nature of the support phase resulting from the reduction, under the same conditions, of two recently prepared lanthana-impregnated rhodium nitrate samples, with 1% nd 10% metal loading, was not the same. In effect, upon reduction at 623 K, the catalysts obtained were, respectively, LaOOH-supported rhodium, and a mixture of lanthanum oxyhydroxide- and dioxymonocarbonate- ($La_2O_2CO_3$) supported rhodium. The differences in the carbonation level reached by the support in either of these cases responsible for the unobservation of the same support phase, can now be reasonably interpreted.

In summary, it is our point of view that when the ordinary procedure to deposit the transition metal salts on to the lanthana support phase is followed, i.e. using aqueous solutions of the precursor salts to carry out either the impregnation or the ion-exchange treatment [3–5, 8], occurrence of carbonation and further evolution of the carbonate phase formed, should be considered major features of the solid state processes

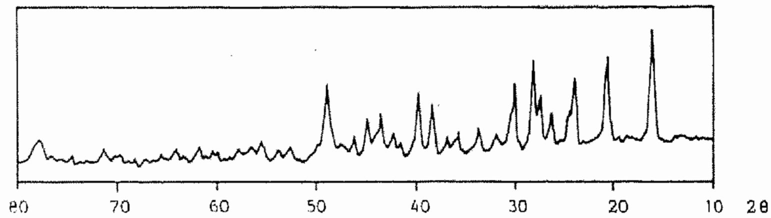

Figure 10 XRD diagram of a lanthana impregnated $Rh(NO_3)_3$ sample (1% metal loading) exposed to air for a prolonged period of time.

that take place on lanthana throughout the series of steps involved in the preparation of lanthanum oxide-supported metal phases.

Acknowledgement

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