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Promoting Effect of Lanthana in the Hydrogenation of Carbon Monoxide over Supported Rhodium Catalysts

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ABSTRACT

The catalytic activity in the $CO+H_2$ reaction is reported for a number of supported rhodium catalysts including Rh/La_2O_3, Rh/SiO_2, Rh/Al_2O_3, as well as ternary phases $Rh/La_2O_3/SiO_2$ with lanthana loadings ranging from 0.1% to 8.5%. The highest conversions to C_2-oxygenates were found to occur over the lanthana containing catalysts. In the particular case of ternary catalysts a clear promoting effect of lanthana was observed, the highest activity and selectivity to oxygenates being found at quite low lanthana loading: 0.25%. Our studies of both characterization and catalytic activity suggest that the metal particles were coated by lanthana. According to the lanthanum and rhodium contents determined in the solutions resulting from the impregnation treatment, redissolution of lanthana during this step of the preparation of the catalysts was found to occur. An interpretation of the mechanism of coating of the metal crystallites by lanthana is presented.

INTRODUCTION

Rhodium-based catalysts have proved to be interesting phases for the synthesis of C_2-oxygenates from syngas [1–5].

According to some recent publications [6, 7], high activity towards C_2-oxygenates is associated with the occurrence of partial coverage of the rhodium crystallites by either the support, the promoter or even oxidized forms of the metal.

In the particular case of catalytic phases containing reducible supports or promoters, like vanadia, overcoating of the metal particles might well take place during the reduction step, by virtue of the mechanism responsible for the

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occurrence of the classic strong metal–support interaction (SMSI) effect [8, 9].

A second group of rhodium catalysts showing good properties for the synthesis of C_2-oxygenates are those constituted of basic supports or promoters, as is the case in rare earth oxide containing systems [1, 5, 10]. According to some earlier studies on lanthana supported palladium catalysts [11], upon reduction at temperatures around 623 K, coating of the metal particles by moieties of some reduced forms of lanthana, LaO_x, does occur. In other words, a SMSI-like effect would also be responsible for the behaviour of this type of catalyst. The stability of the lanthanum(III) ion, however, poses the question whether some mechanism other than that implying the reduction of lanthana, under relatively mild conditions, might explain the singularities of the behaviour as support and promoter of this oxide.

To gain some further insight into the nature of the processes involved in the coating phenomena occurring in lanthana supported metal phases, we have prpeared and characterized a Rh/La_2O_3 catalyst. The behaviour of this phase in the carbon monoxide hydrogenation reaction was also investigated. The studies of catalytic activity were extended to alumina and silica supported rhodium catalysts, as well as to a number of lanthana promoted silica supported rhodium catalysts with variable lanthana loading. The results of this study, as well as those obtained from some additional assays dealing with the process of preparation of the catalysts, also reported in the present work, have allowed us to shed some light on the mechanism of the process of covering the rhodium particles by lanthana.

EXPERIMENTAL

Catalysts

The lanthanum phase used here as starting support was prepared by precipitation of lanthanum nitrate in water using concentrated aqueous ammonia. Subsequently, the precipitate was filtered, washed with distilled water, dried in air overnight at 423 K and finally calcined in air at 823 K for 6 h. The phase thus obtained contained significant amounts of both nitrate and carbonate species [12].

The silica and alumina used here were commercial samples 0201 from Roth and 1095 from Merck, respectively.

The lanthana promoted samples were obtained by impregnating the silica sample with a convenient volume of an aqueous solution of lanthanum nitrate, followed by drying in air at 423 K overnight and calcination in air at 823 K for 3 h. Seven different catalysts, with lanthana loadings ranging from 0.1% to 8.5% by weight, were prepared.

The supported rhodium phases were all prepared in a similar way. the supports were impregnated with the required volume of an aqueous solution of $RhCl_3$ (21 mg cm^{-3}). The suspensions resulting from the impregnation treatment were dried overnight at 423 K and then calcinated at 623 K for 3 h. The precursor/support phases thus obtained were subsequently stored with no special precautions until they were reduced in situ in the catalytic reactor. The rhodium loading was always the same: 2.5% by weight.

Characterization studies

The thermogravimetric analysis (TG), temperature-programmed decomposition (TPD) and temperature-programmed reduction (TPR) studies were all carried out in a flow of either helium or hydrogen, at a flow-rate of 1 cm^3 s^{-1}, and at a heating rate of 0.1 K s^{-1}. The analysis of the gases evolved from TPD and TPR experiments was performed by mass spectrometry (MS) with a VG Spectralab SX-200 instrument, interfaced to an Apple IIe microcomputer. The experimental device was described and characterized elsewhere [13, 14].

The hydrogen and carbon monoxide volumetric adsorption studies were carried out in a conventional high-vacuum system at room temperature. A capacitance pressure gauge, MKS Baratron Model 220 BHS was used. Unless stated otherwise, the isotherms were obtained assuming equilibrium times of 30 min.

Catalytic activity studies

The catalytic activity measurements were carried out in a stainless steel high-pressure reactor. The gas flow through the reactor was controlled by a mechanical pressure regulator as well as a microvalve, the flow-rate being determined with a high-pressure flowmeter.

The catalysts were reduced in situ in flowing hydrogen, under a pressure of 2 MPa, while the temperature was raised stepwise from 293 K: 373 K (1 h), 473 K (1 h), 673 K (1 h) and finally 773 K (2 h).

The studies of catalytic activity were performed at 593 K at a total pressure of 7 MPa, carbon monoxide:hydrogen ratio: 1 and feed rate: 3 cm^3 g^{-1} s^{-1}. The condensable reaction products were collected in a high-pressure trap and further analysed by gas chromatography (GC). The gaseous products were analysed at the outlet, also by GC. The chromatographic conditions used were the same as these reported in ref. 15. The analytical determinations were carried out after running the reaction for 24 h.

The total conversion and selectivity parameters used in the present work were defined as follows:

$$\text{Total conversion} = \frac{\text{Moles of CO converted}}{\text{Moles of CO in the feed}}$$

$$\text{Selectivity} = \frac{\text{Moles of CO converted to X}}{\text{Moles of CO converted}}$$

RESULTS AND DISCUSSION

Preparation of the Rh/La$_2$O$_3$ catalyst

Figs. 1 and 2 illustrate the results of the study by TG and TPD-MS respectively of the lanthana impregnated rhodium chloride phase, which was calcinated at 623 K, and subsequently stored in air at normal temperature and pressure.

According to Fig. 1, the total weight loss of the sample on calcination was as high as 18.6%. It should also be noted from Fig. 1 that the decomposition process occurred through at least four steps. According to the TPD-MS study reported in Fig. 2, the first two weight losses on the TG diagram corresponded to the evolution of water. In fact, the TPD trace for *m/e*: 18 (water) presented in Fig. 2 showed two peaks. The first one, centred at around 373 K, could be assigned to weakly retained molecular water, whereas the second, that appearing at 593 K, should be interpreted as due to massive dehydration of the support phase.

From the TPD traces for *m/e*: 14 (NO$_x$), *m/e*: 16 (water, NO$_x$, carbon diox-

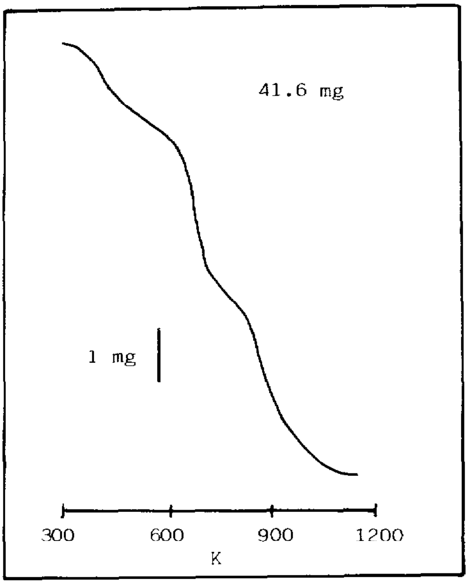

Fig. 1. TG study, in a flow of helium, of the lanthana impregnated rhodium chloride sample. The starting weight of the sample is indicated in the figure.

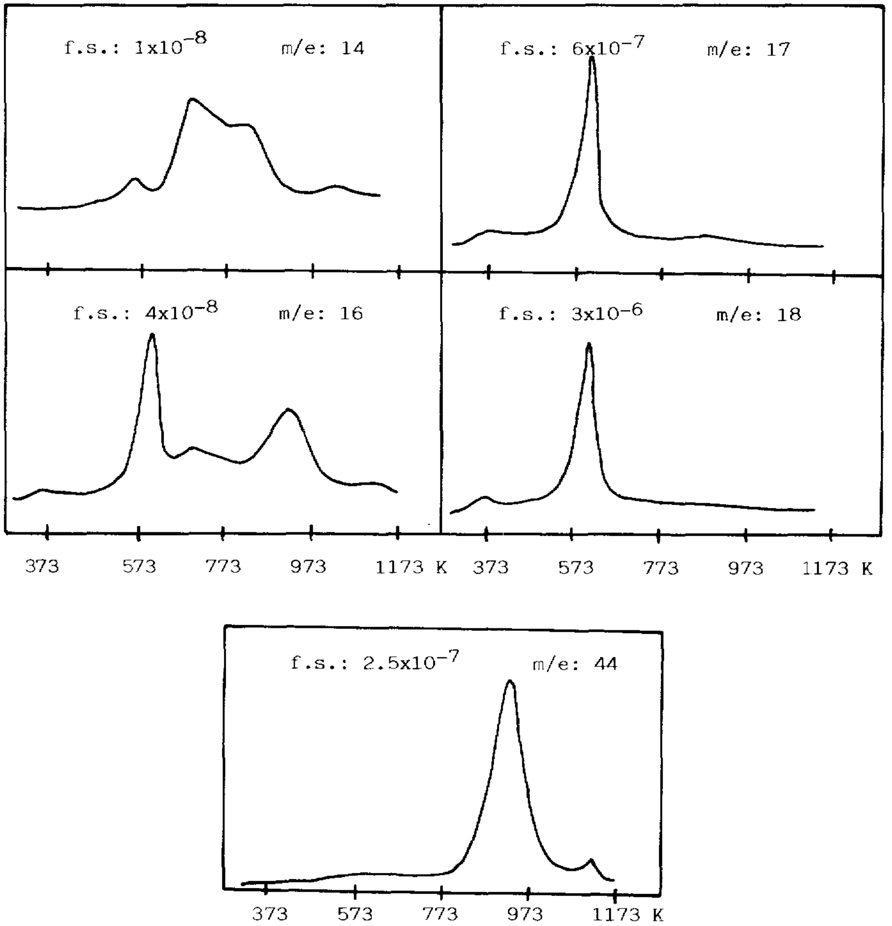

Fig. 2. Study by TPD-MS, in a flow of helium, of the lanthana impregnated rhodium chloride sample. The full scale (f.s.) of the ordinate (partial pressure) signal is indicated in the figure.

ide), and *m/e*: 44 (carbon dioxide) also reported in Fig. 2, the next two stages of the thermal process could be assigned to the decomposition of nitrate (third stage) and carbonate (fourth stage) species. The existence of such anions in the support phase could also be deduced from the broad unresolved IR band spreading over 200 cm^{-1} in the range 1300–1500 cm^{-1}.

The TG and TPD diagrams commented on above did not agree with those recently reported by some of us in a previous study on the preparation of some lanthana supported rhodium phases [16, 17]. It should be noted, however, that both the precursor rhodium salt and the starting support phase in refs. 16 and 17 were different from those used here. In any case, it could be reasonably deduced from Figs. 1 and 2 that the support actually consisted of a lanthanum hydroxynitrate–carbonate, the nature of which was very dependent on the preparation method.

Fig. 3 summarizes the TPR-MS study of the reduction in flow of hydrogen of the precursor–support system described above. The traces obtained for *m/e*: 44 (carbon dioxide), *m/e*: 18 (water), *m/e*: 17 (water, ammonia), *m/e*: 16 (water, ammonia, methane) and *m/e*: 14 (ammonia, methane) are depicted in Fig. 3. If the diagram corresponding to the latter four signals are analysed comparatively, the evolution of water, ammonia and methane can be deduced. In accordance with this analysis, the reduction of the nitrate and carbonate species belonging to the support took place at much lower temperatures than those at which they decomposed in a flow of inert gas. As was proposed earlier [16–18], this lowering of the temperature needed to eliminate the nitrate and

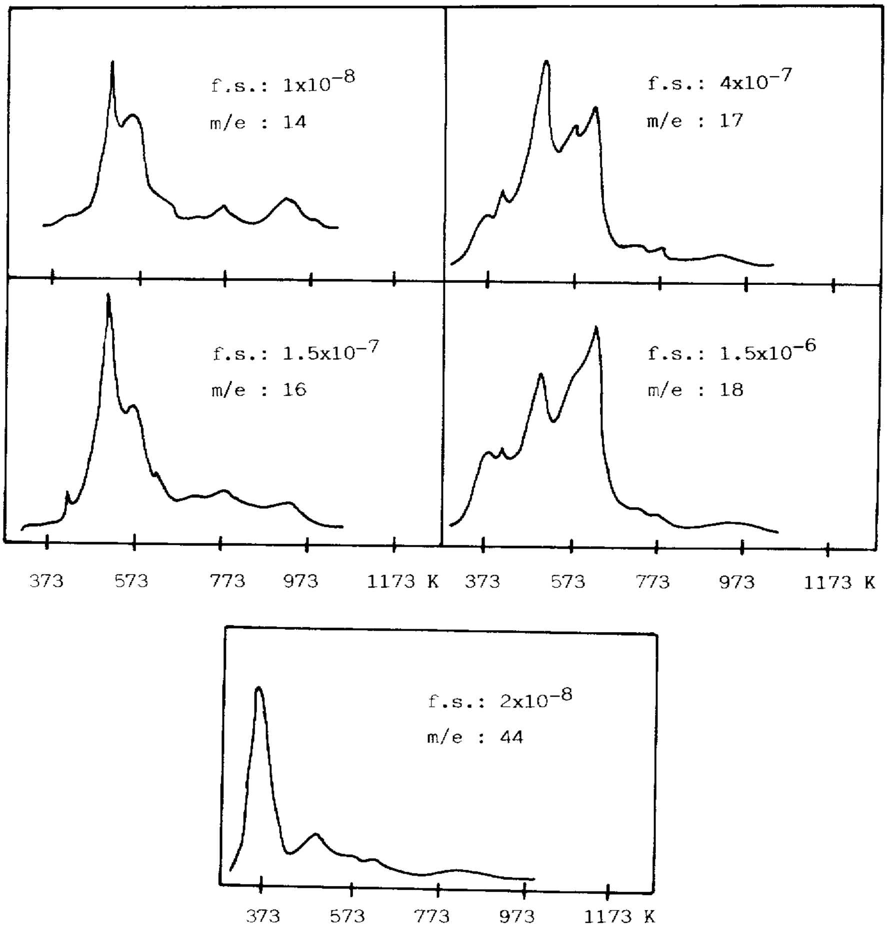

Fig. 3. Study of TPR-MS of the lanthana impregnated rhodium chloride sample. The full scale (f.s.) of the ordinate (partial pressure) signal is indicated in the figure.

carbonate species from the support might be related to the activation of the flowing hydrogen by rhodium.

From the results reported in Fig. 3, it can be concluded that in the present case the reduction of the precursor–support system at 723 K or higher temperatures would lead to the preparation of true lanthana supported rhodium catalysts. It was also obvious from our study that the process of preparation of the catalytic phase induced very strong chemical and structural modifications on the support. As was suggested in refs. 6 and 19, these alterations, which occurred on the support, could profoundly affect the behaviour of the resulting catalyst.

Characterization of the catalyst by hydrogen and carbon monoxide adsorption

The volumetric adsorption of hydrogen and carbon monoxide was investigated over two catalytic phases. Sample A was reduced at 623 K, in flowing hydrogen, at normal pressure, for 1 h, and then evacuated by pumping at the reduction temperature for approximately 30 min. The hydrogen:rhodium ratio, as determined by extrapolating the linear part of the isotherm to zero pressure was found to be 0.3. If the catalyst was kept in contact with hydrogen, at a pressure of approximately 300 Torr (40 kPa), a further slow uptake was observed. After 24 h the apparent hydrogen:rhodium ratio reached a value almost four times larger: 1.1. As was suggested earlier for some rare earth oxide supported rhodium catalysts [16, 20], this phenomenon could be interpreted as due to the occurrence of spill over.

The carbon monoxide adsorption by catalyst A was much smaller, almost zero.

Sample B was prepared by a method similar to that used in the catalytic activity studies. Since this sample was reduced in flowing hydrogen, under a pressure of 2 MPa, its preparation could not be reproduced in a conventional high-vacuum glass device. Accordingly, catalyst B ought to be reduced in the catalytic reactor, and then transferred to the adsorption chamber in the high vacuum system. Before carrying out the adsorption study, the catalyst was re-reduced and evacuated under the same conditions used to prepare sample A. The hydrogen:rhodium ratio thus estimated was 0.2. As in the case of sample A, the carbon monoxide uptake was negligible.

This unexpected difference between the amounts of hydrogen and carbon monoxide adsorbed by the catalysts was also observed on several lanthana supported metal catalysts [16, 21], and very recently, on some vanadia containing supported rhodium catalysts [22]. In all these cases, it was suggested that partial overcoating of the metal particles by either the support or the promoter occurred.

Catalytic activity measurements

Table 1 summarizes the results of the catalytic activity assays carried out on the so-called sample B of Rh/La_2O_3. The test reaction used here was the carbon monoxide hydrogenation process. For comparative purposes, results corresponding to silica and alumina supported rhodium catalysts, prepared in a manner similar to the preparation of the lanthana supported rhodium phase, are also included in Table 1.

The silica supported catalyst produced principally methane. In the case of $Rh?La_2O_3$, the conversions, especially to hydrocarbons, were quite low. With regard to the lanthana supported rhodium catalyst, it was noted that the conversion to C_2-oxygenates was much higher than that observed for the other two catalysts mentioned above; the conversion was approximately double that shown by Rh/SiO_2 and five times that found for $Rh?La_2O_3$.

According to refs. 7 and 23 the activity towards C_2-oxygenates of dispersed rhodium catalysts required that the metal crystallites were covered by non-metallic particles. This phenomenon could reasonably be assumed to occur in the case of our Rh/La_2O_3. In fact, the formation of patches of partially reduced lanthana, LaO_x, over the palladium metal particles was suggested by Hicks et al. [11], who found, as we did, a relative inhibition of carbon monoxide with respect to that of hydrogen [21]. In ref. 11 it was suggested that the classic mechanism proposed to interpret the SMSI effect [24] operates in lanthana supported metal catalysts. Taking into account the fact that the reduction of lanthana was not an easy process, at least under the conditions used in ref. 11 to prepare these catalysts, it seemed to us that alternative mechanisms for the occurrence of the metal particle covering in lanthana supported phases should be considered.

TABLE 1

Catalytic behaviour of several supported rhodium catalysts in the carbon monoxide hydrogenation reaction

Reaction conditions: temperature, 593 K; total pressure; 7 MPa; carbon monoxide:hydrogen ratio: 1.

Catalyst	Conversion			Selectivity			
	RH	ROH	CO_2	CH_4	MeOH	C_2-oxygenates	Total oxygenates
Rh/La_2O_3	14.7	4.6	3.7	61	2.4	16.4	23.6
Rh/SiO_2	9.2	1.6	0.2	78	0.1	12.2	14.1
Rh/Al_2O_3	1.9	0.9	0.2	50	3.3	21.5	26.8
Rh/La_2O_3*$/SiO_2$	7.8	7.5	1.8	45	4.5	34.5	44.6

* Lanthana loading: 0.25%.

As several recent results show [11, 16–18, 25] and those reported here confirm, when the usual exchange or impregnation method with aqueous solutions for the preparation of the catalysts was followed, the lanthana support underwent heavy hydration and carbonation reactions. Accordingly, the reduction of the precursor–support system implied parallel dehydration and decarbonation processes at the support, which might well be thought to be responsible for the coating of the metal crystallites. Against this interpretation for the appearance of support patches on the metal particles, however, it could be argued that the reduction treatment did not cause significant modification of the surface area of the catalyst.

The coating phenomenon could also be induced by the partial dissolution of the support during the impregnation step, followed by co-deposition of both support and metal precursor upon elimination of the excess aqueous solvent [8].

To further investigate the origin of the high activity towards C_2-oxygenates of the Rh/La_2O_3 catalysts, and its likely relationship to the partial coverage of the rhodium particles, we also studied the catalytic behaviour of several lanthana promoted silica supported rhodium phases. Seven different catalysts resulting from the variation of the lanthana loading were tested. Fig. 4 shows the total and oxygenate conversions observed over the whole series of catalysts. As can been seen from this figure a nice promoting effect was observed. This ef-

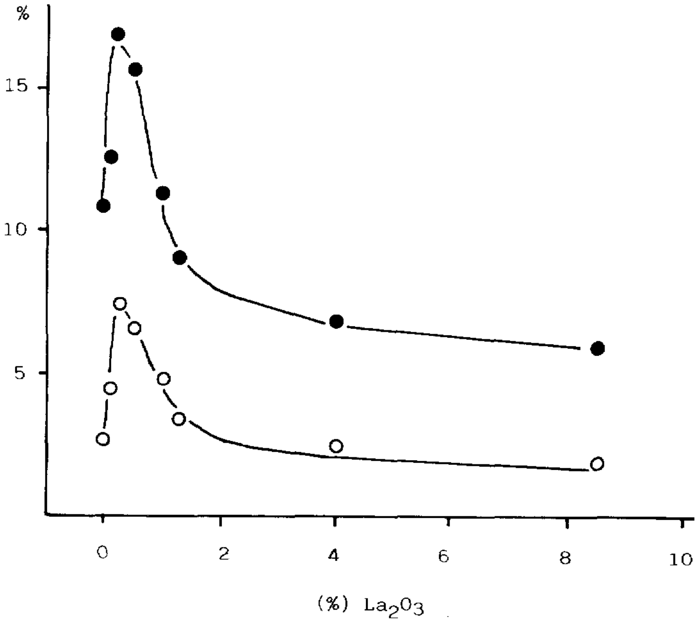

Fig. 4. Catalytic behaviour of $Rh/La_2O_3/SiO_2$ phases in the $CO+H_2$ reaction. Plots of the total (●) and oxygenate (○) conversion vs. lanthana loading.

fect, which was very sensitive to the lanthana loading, reached a maximum at quite low loading: 0.25%. The conversion and selectivity data corresponding to this particular catalyst are also reported in Table 1.

Assuming that lanthana was spread over the silica as a monolayer, the surface density of lanthanum ions in the catalyst with a lanthana loading of 0.25% would be around 1 lanthanum(III) per 10 nm^2. Since the promoting effect was considered to require a close contact between metal and promoter [4, 7, 23], it was concluded that both metal and promoter were not dispersed in a random way. In other words, to understand the observed promoting effect, some mechanism favouring the occurrence in close vicinity of each other of rhodium and lanthana should be devised. If it is recalled that the procedure followed here to prepare the ternary phases $Rh/La_2O_3/SiO_2$, essentially consisted of the impregnation of the La_2O_3/SiO_2 phase previously obtained with the rhodium salt, it is suggested that what occurred was redissolution of the promoter through the impregnation step and its further coprecipitation with the metal precursor. As the additional studies reported below will confirm, this seems to be the mechanism responsible for the coating of the metal crystallites by lanthana.

Redissolution of lanthana

To investigate the feasibility of the redissolution of lanthana throughout the impregnation step, the following experiment was carried out: 1 g of three different supports consisting of: (A) La_2O_3(0.25%)/SiO_2, (B) La_2O_3(2.5%)/SiO_2 and (C) La_2O_3 were treated with 2 cm^3 of an aqueous solution of rhodium chloride, pH 0.37, containing 18.5 mg of rhodium per cm^3. After the impregnation treatment, the suspension was centrifuged and the excess liquid about 0.2 cm^3, separated. The impregnated solid phase was washed twice with distilled water, and the resulting solution separated by centrifugation and added to the liquid portion recovered from the impregnation treatment. These solutions were then made up to 25 cm^3 with distilled water, the pH of the resulting solution measured, and the La^{3+} and Rh^{3+} content determined. Table 2 reports the results obtained from this study.

In Table 2 there are a number of aspects worthy of comment. Firstly, the amounts of La^{3+} recovered from the supports in cases A and B suggested that lanthana was completely redissolved during the impregnating treatment. It will be recalled that the excess volume of impregnating solution, 0.2 cm^3, represented 10% of the initial volume. In accordance with Table 2, the amount of lanthanum recovered from the impregnation treatment of supports A and B was approximately one tenth of the total amount of lanthanum contained in the solution. The correlation observed between the lanthana loading and the amount of extracted La^{3+}, about ten times larger in the case of support B, was also consistent with the above proposal. For support C, the amount of dissolved

TABLE 2

Study of the redissolution of lanthana during the impregnation step

Support	Analysis of the solution resulting from the impregnation treatment			Percentage of the total lanthanum and rhodium recovered from the impregnating solution	
	pH	La^{3+} ($mg\,l^{-1}$)	Rh^{3+} ($mg\,l^{-1}$)	La^{3+}	Rh^{3+}
La_2O_3(0.25%)/SiO_2	1.8	7.4	1100	9.5	73
La_2O_3(2.5%)/SiO_2	2.1	96.4	1060	12.0	70
La_2O_3	6.0	129.0	1	0.4	0

lanthanum seemed to be limited by the final pH of the solution, which was much higher in this case.

Regarding the extraction of rhodium, the result obtained for support C is particularly noteworthy. As can be deduced from Table 2, the amount of rhodium recovered from the impregnation of lanthana was negligible, whereas about 70% of the total rhodium present in the impregnating solution could be extracted in cases A and B. These data show a considerable difference between the two types of support and indicate the occurrence of a strong interaction between the precursor and the support in case C.

To us, the results included in Table 2 strongly suggest that the overcoating of the rhodium particles by lanthana, responsible for the high activity towards C_2-oxygenates observed on La_2O_3 containing catalysts, was due to the coprecipitation of the metal precursor and the redissolved lanthana phase. In this sense, the maximum observed in the promoting effect for 0.25% lanthana loading might be explained assuming that for this promoter loading an optimum is achieved in the coating of the metal particles by lanthana. Since the amount of dispersed rhodium remained constant, and the total amount of lanthana present in the support was redissolved during the impregnation treatment, the amount of promoter deposited onto the metal would increase as the promoter loading increased. This might well induce a relative deactivation of the catalyst diminishing both the total conversion and the activity towards C_2-oxygenates. In this case, blocking of active sites overrules the creation of new, highly active sites [26].

Concluding remarks

To summarize, the present work and the results reported earlier by several authors [11, 16, 17, 25], clearly demonstrated the singularities of the behaviour of lanthana as a support and promoter. Regarding the microstructural nature of lanthana containing, supported rhodium catalysts, their capacity to orientate the carbon monoxide hydrogenation reaction towards C_2-oxygenates, the characterization results, in particular the inhibition of the carbon monoxide uptake on Rh/La_2O_3, as well as some previous results in the literature [21], indicate that the formation of lanthana moieties which coat the metal crystallites is likely to occur. By contrast with some models suggested earlier [11], our results can be interpreted by assuming that the covering of the rhodium particles is caused by the redissolution of lanthana which occurred during the impregnation process.

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