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Influence of the preparation procedure on the chemical and microstructural properties of lanthana promoted Rh/SiO$_2$ catalysts

A FTIR spectroscopic study of chemisorbed CO

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Abstract

In this work, the influence of the preparation procedure on the chemical and microstructural properties of a series of Rh/La$_2$O$_3$/SiO$_2$ catalysts has been investigated. The catalysts were characterized by using HREM, H$_2$ and CO volumetric adsorption and FTIR spectroscopy of chemisorbed CO. From our study, significant effects were observed for the following preparative variables: (a) the lanthana loading; (b) the way of introducing the metal and promoter, either consecutive (lanthana first and then the rhodium salt) or by co-impregnation; and (c) the calcination temperature (873 K or 1173 K) applied for preparing the La$_2$O$_3$/SiO$_2$ intermediate phase onto which the noble metal was deposited.

Keywords: Supported metal; Rhodium; Lanthana; Silica; FTIR spectroscopy; CO chemisorption; Preparation

1. Introduction

The lanthanide oxides exhibit very interesting properties as promoters of highly dispersed metal catalysts. In particular, it has been shown that lanthana can substantially modify the chemical behavior of M/SiO$_2$ binary systems [1–3]. To the present, however, the precise origin of this promoting effect remains unclear. Moreover, the modifications induced by lanthana are found to vary from one laboratory to the other [4,5]. This suggests that the preparation method plays a key role in determining the final properties of the lanthana promoted catalysts.

In the present work we have focused our attention on the Rh/La$_2$O$_3$/SiO$_2$ system. Our major concern is the investigation of the influence of a number of preparative variables on the chemical and microstructural properties of the corresponding ternary catalysts. High resolution electron microscopy (HREM), as well as H$_2$ and CO volumetric adsorption were the main characterization tools applied in this study.

Upon reviewing the catalytic properties of the lanthana promoted noble metal catalysts, we may note that some of their most interesting applications consist of processes where CO is involved [6,7]. Accordingly, it seemed to us particularly relevant the investigation of the CO interaction with catalysts. The technique used for this purpose was FTIR spectroscopy. In addition to its intrinsic usefulness, this spectroscopic study provided us some additional information about the influence of the preparation procedure on the chemical behavior of our catalyst samples.

Our results are discussed with reference to those reported earlier for Rh/La$_2$O$_3$ [8,9]. From this comparative analysis some conclusions about the actual nature of both the promoting phase and the rhodium/lanthana interaction could be drawn. Regarding the latter of the two aspects mentioned above, it would be recalled that several authors have suggested the likely occurrence on M/La$_2$O$_3$ catalysts of strong metal/support interaction phenomena [10], SMSI-like effects, similar to those well known to occur on Rh/TiO$_2$ [11].

2. Experimental

The silica sample studied here was SiO$_2$ Cabosil M-5 (99% pure). Prior its use as support, this sample was calcined at 1173 K for 2 h. The BET surface area of this pretreated silica was 190 m^2 g^{-1}. We have prepared four Rh/La$_2$O$_3$/SiO$_2$ catalysts (Samples B–E) as well as one Rh/SiO$_2$ catalyst (A), which was used as a non-promoted reference. The noble metal loading was always 3% by

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weight. Two different lanthana loadings have been studied: 7.5% (Catalyst B) and 37.5% (Catalysts C, D and E) by weight. Both lanthana and rhodium precursor salts were deposited by using the so-called incipient wetness impregnation technique. A single impregnation cycle from aqueous solutions either of $La(NO_3)_3.6H_2O$ or $Rh(NO_3)_3.2H_2O$ with the convenient concentration were respectively used. The reduction treatment leading to the final catalysts were performed in a flow of H_2 of 60 cm^3 min^{-1}, at 773 K, for 1 h. The heating rate from 298 K to 773 K was 10 K min^{-1}.

Except sample E, which was prepared by coimpregnation of the rhodium and lanthanum salts and further reduced as indicated above, the remaining promoted catalysts were obtained by a consecutive impregnation procedure. After depositing the lanthanum salt, the samples were calcined at either 873 K (B and C) or 1173 K (D), thus obtaining the corresponding La_2O_3/SiO_2 samples. These binary samples were further impregnated with rhodium nitrate, and finally reduced.

The high resolution electron microscopy (HREM) images were obtained on a JEOL 2000 EX instrument. The microscope, which is equipped with a top entry specimen holder and an ion pump, has a structural resolution of 0.21 nm.

The volumetric adsorption experiments were performed at room temperature in a high vacuum manifold. The reduced catalysts were evacuated at the reduction temperature (773 K) for 30 min, further cooled to 298 K under vacuum, and finally put in contact with an increasing H_2 (CO) pressure up to a maximum value of 300 Torr.

The infrared spectra were recorded on a Mattson Spectrometer, model 5020. The spectra were obtained by averaging 100 scans with a resolution of 4 cm^{-1}. The samples consisted of selfsupported disks with a density of 10 mg cm^{-2}. The thermal and chemical treatments of the samples were performed in a quartz cell equipped with NaCl windows.

3. Results and discussion

Table 1 summarizes the results obtained from the volumetric chemisorption studies. The H/Rh and CO/Rh ratios were determined by extrapolation to zero pressure of the linear part of the corresponding isotherms. Except for sample E, the H/Rh and CO/Rh values determined for each of the catalysts are very close to each other. This observation is in good agreement with results reported by Borer and Prins in a recent study on the $Rh/La_2O_3/SiO_2$ system [12].

Table 1
Volumetric adsorption of H_2 and CO at 298 K

Catalyst	H/Rh	CO/Rh
A	0.43	0.44
B	0.65	0.63
C	1.08	1.18
D	0.64	0.55
E	0.90	0.30

The coincidence of the H/Rh and CO/Rh values determined for our catalysts, the absence of significant hydrogen spillover at 298 K, which is suggested by parallel H_2 temperature programmed desorption experiments reported elsewhere [13], as well as the small contribution of the CO chemisorbed on the support, which could be deduced from our FTIR study, allow us to conclude that the major contribution to the volumetric adsorption of both H_2 and CO comes from their chemisorption on the metal. Therefore, either H/Rh or CO/Rh ratios can in general be used to estimate the metal dispersion. Following the criteria suggested by Bell and coworkers [4,10] the CO/Rh values will be used here for this purpose. Accordingly, from the results reported in Table 1 it can be concluded that the rhodium dispersion decreases as follows: C>B>D>A.

The comparison of the CO/Rh values determined for catalysts A, B and C suggests that the presence of the promoter improves the metal dispersion. Moreover, the values obtained for catalysts B (0.63) and C (1.18) indicate that the rhodium dispersion increases as the lanthana loading does. The metal dispersion determined for sample D, CO/Rh: 0.55, deserves some further comments. In effect, the promoter loading was in this case 37.5%, the same as that of catalyst C. If it is taken into account that the only difference between samples C and D is the calcination temperature applied for obtaining the La_2O_3/SiO_2 intermediate phase, 873 K in case C, and 1173 K in case D; we conclude that this preparative variable modifies the lanthana promoting effect.

Earlier studies from our laboratory [2] have demonstrated that the impregnation of the La_2O_3/SiO_2 system, previously calcined at 873 K, with an aqueous solution of $Rh(NO_3)_3$ induces the leaching of the lanthanum containing phase. It has also been shown in Ref. [2], that the dissolved lanthanum phase coprecipitates with the rhodium salt during the subsequent drying step, thus contributing to a better dispersion of the noble metal. The differences between samples C and D commented on above can thus be interpreted as due to the stabilization of the lanthanum containing phase inherent to the increase of the calcination temperature from 873 K to 1173 K. This would prevent the leaching of this phase, and therefore, the positive effect of this phenomenon on the rhodium dispersion. Some previous studies on the La_2O_3/SiO_2 system [13,14] are also relevant to interpret our results. In effect, the X-ray diffraction (XRD) study of these binary samples calcined at either 873 K or 1173 K [13] does not provide any evidence of the presence of free lanthana or any other phase resulting from its aging in air, particularly $La(OH)_3$ [15]. This is also confirmed by the HREM images and CO_2 chemisorption results reported in Ref. [14]. In the case of the La_2O_3/SiO_2 sample calcined at 1173 K, however, the XRD diagram [13] shows some diffraction peaks, which can reasonably be interpreted as due to a silicate phase: $La_2Si_2O_7$ [16]. From these additional observations we conclude that, upon calcination, the lanthana is incorporated to the silica support as an amorphous silicate first, when calcined at 873 K, this phase evolving to a crystalline inactive-against-leaching silicate when treated at 1173 K.

Among the catalysts investigated here, sample E is the only one showing a strong disagreement between the apparent H/Rh and CO/Rh values, the latter being much smaller than the former. A rather similar behavior has already been reported for several M/La_2O_3 binary catalysts [8–10]. To interpret this anomalous chemisorptive behavior, a microstructural model has been proposed in [9]. This model, which was developed for M/La_2O_3 catalysts, assumes that during the impregnation step strong redissolution of the lanthana support does occur. The reduction treatment following the impregnation/drying step thus leading to a metallic phase which, though highly dispersed, is actually embedded in the support. As a result, an important fraction of the metal particles would be decorated/encapsulated, and therefore not accessible to the CO probe molecule. Under these circumstances, the amount of chemisorbed CO would measure the accessible metal surface rather than the actual dispersion. Also important, the large metal support interface created in this way would strongly favor the hydrogen transfer from the metal to the support. This side effect would justify the difference observed between the CO/M and H/M ratios. This model [9] would be in better agreement with the acknowledged stability of the La(III) oxidation state than that suggested by Hicks et al. [10]. In effect, in [10], by analogy with the so-called SMSI effect described for M/TiO_2 catalysts [11], it is proposed that the metal covering would be associated to the reduction treatment. After Ref. [10], this treatment, consisting of the heating of the sample, in a flow of H_2, at temperatures well below 773 K, would lead to a reduced lanthanum oxide, LaO_x ($x<1.5$), the actual phase decorating the metal.

In our opinion, the behavior of the sample E can also be interpreted on basis of the model suggested in Ref. [9]. It would be recalled that this sample was prepared by co-impregnation of the lanthanum and rhodium salt. Also worth of being outlined, the impregnation/drying treatment was directly followed by the reduction treatment with no previous calcination step. We propose that the co-deposition of the lanthanum and rhodium nitrates leads to a situation that is chemically close to that resulting from the dissolution/coprecipitation of lanthana occurred during the preparation of the Rh/La_2O_3 catalysts. If it is so, the further reduction treatment would generate a silica supported system actually consisting of highly dispersed rhodium embedded in a lanthana matrix. Our interpretation would be in agreement with two additional observations. First, no metal particles could be detected in the HREM micrographs recorded for sample E, Fig. 1. This contrasts with the HREM images obtained for samples A to D, Fig. 1, in which the rhodium particles can always be observed.

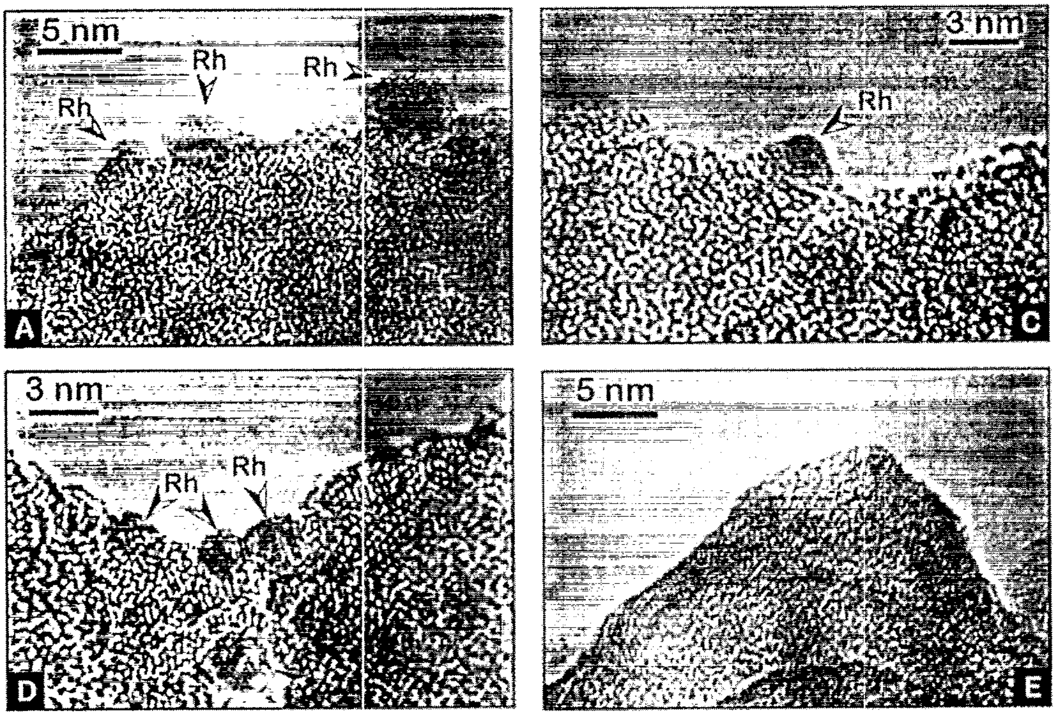

Fig. 1. HREM micrographs corresponding to Rh/SiO_2 (A) as well as to the $Rh/La_2O_3/SiO_2$ catalysts referred to as C, D and E. The arrows identify the observed metal particles.

Second, the CO/Rh ratio determined for sample E reduced at 573 K was found to be much smaller, 0.08, thus indicating an even poor accessibility of the metal crystallites. Since the TPR and TG data suggest that rhodium is fully reduced at 573 K, we conclude that the increase of the reduction temperature up to 773 K would favor the partial segregation of the metal microcrystals towards the lanthana surface. In this way, the fraction of exposed rhodium in catalyst E would be larger after reduction at 773 K.

To summarize, depending on the preparation procedure, the microstructural nature of the lanthana promoted silica supported catalysts can be very different. For catalyst B and C, the promoter would actually consist of an amorphous silicate leached during the rhodium nitrate impregnation step and further co-deposited with the rhodium salt upon drying. This promoting phase would lead to an accessible highly dispersed metal phase. In case D, consequently to its strong fixation to the silica support, the promoter would have little influence on the rhodium dispersion. Finally, we suggest that for catalyst E, the promoter actually consists of lanthanum sesquioxide embedded in which the highly dispersed metal phase would be present.

We have also investigated the interaction of our catalysts with CO. The FTIR spectroscopy was used as experimental technique. As is known [17,18], the FTIR spectrum of CO–Rh is characterized by three main kind of species: (a) gem-dicarbonyls associated with which a doublet at 2080–2100 cm^{-1} and 2020–2030 cm^{-1} is typically observed; (b) linearly bonded CO characterized by a single band peaking around 2060 cm^{-1}, and (c) bridge bonded CO, the characteristic features of which appears in the region 1850–1925 cm^{-1}.

Fig. 2 accounts for the IR spectra recorded for the lanthana containing catalysts reduced and evacuated at 773 K and further put in contact with 300 Torr of CO, at 298 K. As can be deduced from Fig. 2, there are significant differences from one sample to the other. This confirms the microstructural observations commented on above. In particular, if we focus our attention on the gem-dicarbonyl bands shown by the promoted samples, we may note that sample C shows the highest intensity, whereas the lowest intensity is observed on sample E.

It is generally considered that the dicarbonyl species are formed from highly dispersed metallic rhodium by the virtue of an oxidation process involving surface OH groups of the support [19–21]. The spectra corresponding to samples B, C and D would be in agreement with this model, because, as commented on above, the rhodium dispersion is much higher in case C, being closer to each other in cases B and D. The FTIR spectrum for sample E again is different from those of the remaining promoted catalysts. It consists of a single band which can be interpreted as due to linear chemisorbed CO. This suggests that metal oxidation mechanism leading to the formation of the dicarbonyl species hardly operates, at 298 K, in sample E. Yates and Kolasinski [19] have suggested that the mechanism above requires the existence of mobile CO–Rh^0 intermediate species. The very peculiar microstructure of catalyst E might well strongly disturb such a mobility thus preventing the operation of the mechanism at room temperature. Also worth of noting, after [19] the oxidation of rhodium requires isolated acidic hydroxyl groups; presumably the OH species surrounding the metal microcrystals in sample E would be coordinated to the lanthana surface, and therefore an increased basicity should be expected for them.

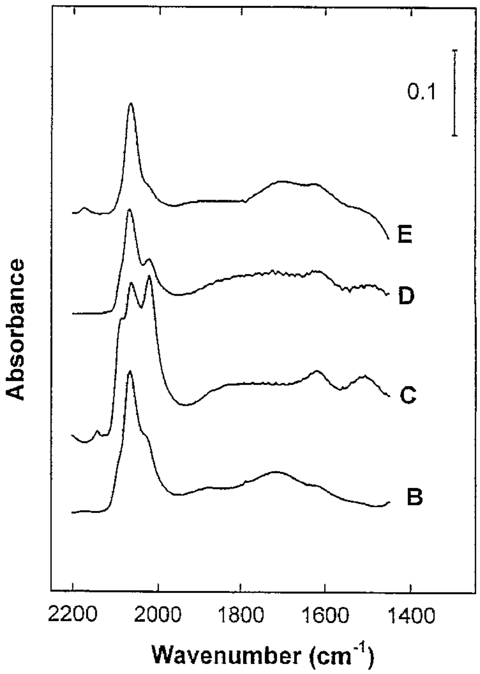

Fig. 2. FTIR study of the CO interaction with the whole series of lanthana promoted catalysts (B–E). Reaction temperature: 298 K; P_{CO}=300 torr.

We have also studied the influence of the temperature on the CO interaction with our catalysts. Fig. 3 shows the spectra recorded after heating the catalysts at 373 K under P_{CO}: 300 Torr. As expected, the intensity of the dicarbonyl bands increases for all the catalysts. Nevertheless, the differences already noted in Fig. 2 for the promoted samples continue to be observed, catalyst C showing the highest relative concentration of dicarbonyl species. Regarding Fig. 3, there is a second observation worth comment: in spite of the lower metal dispersion exhibited by catalysts A (Rh/SiO_2) compared to that of sample C, the FTIR spectrum recorded for the unpromoted catalyst indicates that all the metal present in it is in the form of gem-dicarbonyls with rather negligible contributions of both linear and bridged species. Two main reasons can be adduced to interpret these results. First, the relative intensity of the OH stretching band, Fig. 4, seems to decrease from samples A to C, thus suggesting that the incorporation of the promoter to the silica support induces a parallel

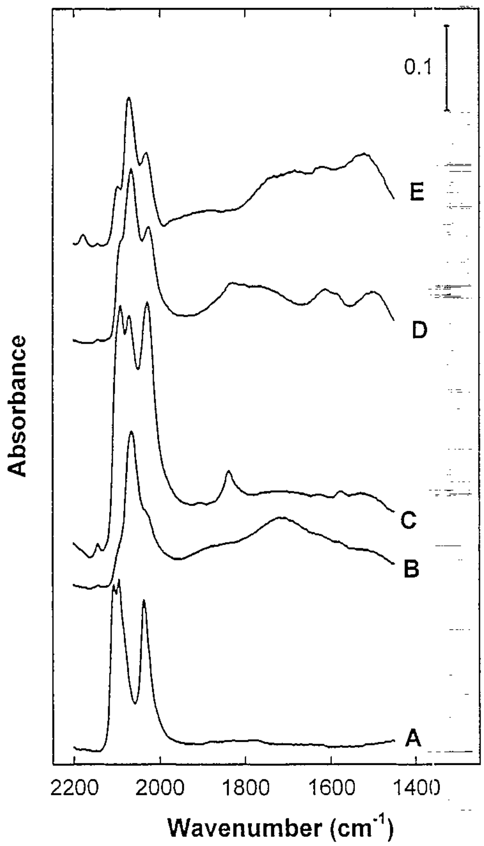

Fig. 3. FTIR study of the CO interaction with Rh/SiO_2 (A) and $Rh/La_2O_3/SiO_2$ catalysts (Samples B through E). Reaction temperature: 373 K; P_{CO}=300 torr.

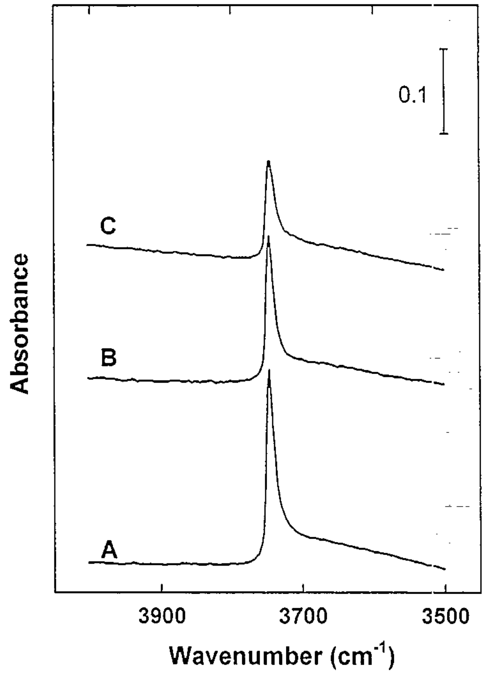

Fig. 4. FTIR spectroscopy of the O–H stretching region. Normalized spectra corresponding to catalysts A, B and C reduced and further evacuated at 773 K (not treated with CO).

decrease in the concentration of OH species, and therefore of the species to be involved in the rhodium oxidation process commented on above. Second, in accordance with the HREM images reported in Fig. 1, the rhodium particles dispersed on bare silica look in many cases like amorphous. This contrasts with the micrographs recorded for catalysts C and D, where metal fringes can often be identified. This would suggest that the promoter favors the presence of more crystalline, may be less reactive against the OH groups, metal particles, a factor also contributing to explain the differences of behavior we have noted between the promoted and unpromoted silica supported catalysts.

In conclusion, the results reported and discussed in this work clearly show that the preparation procedure has a very strong influence on the microstructural properties of the lanthana promoted Rh/SiO_2 catalysts. Critically important parameters characterizing the catalytic system like the metal dispersion, the crystallinity of the dispersed metal or the actual nature of the promoting phase can be substantially modified by controlling the preparation variables investigated here. In parallel with these microstructural effects, significant modifications of the chemical properties could be observed in this family of catalysts.

Acknowledgments

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