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Characterization of silica dispersed lanthana by CO_2 adsorption

G. Blanco, J.J. Calvino, M.A. Cauqui, G.A. Cifredo, J.A. Pérez Omil,
J.M. Rodríguez-Izquierdo* and H. Vidal

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Apartado 40, Puerto Real, 11510 (Spain)

Abstract

CO_2 adsorption on a series of La_2O_3/SiO_2 samples, with lanthana weight loadings ranging from 1.6% to 75%, have been studied. The results are interpreted on the grounds of a lantana–silica interaction model, also supported by data obtained from other physical characterization techniques (XRD, TEM, XPS). Such a model assumes that patches of an amorphous La–Si–O phase, embedded into the silica matrix, modify the support surface in a progressive way, leading to a full coverage for 37.5% La_2O_3. The nature of the mixed phase imposes a top limit of 2.8 molecules nm^{-2} to its CO_2 adsorption capacity.

1. Introduction

Rare earth oxides (REO) dispersed on conventional supports present interesting applications in catalysis. We have reported on the properties of binary La_2O_3/support systems for CO hydrogenation, CO oxidation and oxidative coupling of CH_4 [1]. The use of lanthana and other REO as promoters of Group VIII metals dispersed on SiO_2 [2–6] or Al_2O_3 [7–10] has improved their activities and selectivities for several reactions. To understand in depth the roles played by the REO, it is interesting to study their actual dispersion, as well as the mechanisms of interaction between the usual support materials and REO. A good deal of work has already been done on REO/Al_2O_3 systems, and CO_2 has been used in several cases as a probe molecule [10–15]. However, characterization studies on silica supported REO are much rarer [16].

In this paper, several complementary methods have been used to study the CO_2 adsorption on La_2O_3/SiO_2 systems. To our knowledge, no data are at present available on this particular topic. Based on these results and those obtained from other physical characterization techniques (XRD, TEM and XPS), a model to explain the lanthana–silica interaction has been proposed.

2. Experimental details

SiO_2 M5 Cabosil, kindly donated by Cabot, was used as the starting material. This support was impregnated with aqueous solutions prepared from $La(NO_3)_3 \cdot 6H_2O$ supplied by Fluka. The concentration of the solutions was adjusted to obtain the desired weight loadings, ranging from 1.6% to 75% lanthana. Following impregnation, the samples were dried in air at 363 K. The precursors prepared in this way were activated *in situ*, before each experiment, by heating them in a flow of air at 870 K for 4 h. The activated samples were further cooled in a flow of helium or under high vacuum before the CO_2 adsorption treatment. The gases used here, He and CO_2, supplied by SEO, with N50 specifications, were further purified by passing them through a zeolite trap and a cold trap at 230 K, respectively.

The specific surface areas of the calcined samples have been reported [1], ranging from 187 $m^2\ g^{-1}$ for pure silica to 157 $m^2\ g^{-1}$ of silica for the highest lanthana loading. An 8% La_2O_3/Al_2O_3 sample was prepared in a similar way starting from γ-Alumina Degussa with a specific surface of 105 $m^2\ g^{-1}$.

The temperature programmed desorption technique, using a VG SX200 mass spectrometer as analytical device (TPD-MS), was used as described elsewhere [17]. Prior to the TPD experiments, the samples were treated with flowing CO_2, at 60 $cm^3\ min^{-1}$, for 20 min. Then flowing gas was switched from CO_2 to helium for 60 min, and finally the temperature was raised at a heating rate of 10 K min^{-1}.

The volumetric adsorption experiments were performed at 295 K in a conventional high vacuum system, equipped with a MKS pressure transductor model BHS-1000. A conventional IR quartz cell was used to carry

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*Author to whom correspondence should be addressed.

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out the treatment of the self-supported sample wafers. The cell allowed pretreatment in a flow of air, the evacuation under high vacuum, and further treatments with CO_2 at 1 atm pressure. The spectra were recorded on a Mattson 5020 FTIR instrument.

X-Ray photoelectron spectroscopy data (XPS) discussed in the present work were obtained using a Leybold Heraeus LHS-10 electron spectrometer working with an Al anode (1486.6 eV), operated at 12 kV and 20 mA. Transmission electron microscopy images (TEM) were obtained in a JEM 2000 EX microscope, with a top entry specimen holder and an ion pump, with a structural resolution of 2.1 nm. X-Ray diffraction patterns of the calcined in air samples were recorded in a Siemens D-500 powder diffractometer operating with a Mo anode ($\lambda = 0.071$ nm).

3. Results

Figure 1 shows the TPD-MS diagrams recorded for the series of La_2O_3/SiO_2 samples treated with flowing CO_2, at 295 K. The CO_2 traces, *m/e* 44, are characterized by a strong peak, centered at 350 K, with a shoulder at slightly higher temperatures. The diagrams for water, *m/e* 18, show peaks at 390 K, broad shoulders up to 670 K, and a second maximum around 1070 K. As deduced from Fig. 1(f), the high temperature H_2O peak can be interpreted as due to silica dehydroxylation [18]. The samples untreated with CO_2 lanthana/silica only show the high temperature water peak. The thermal stability of the residual hydroxyl groups is not very sensitive to the presence of lanthana. This indicates that the lowering of the water desorption temperature is induced by CO_2 chemisorption.

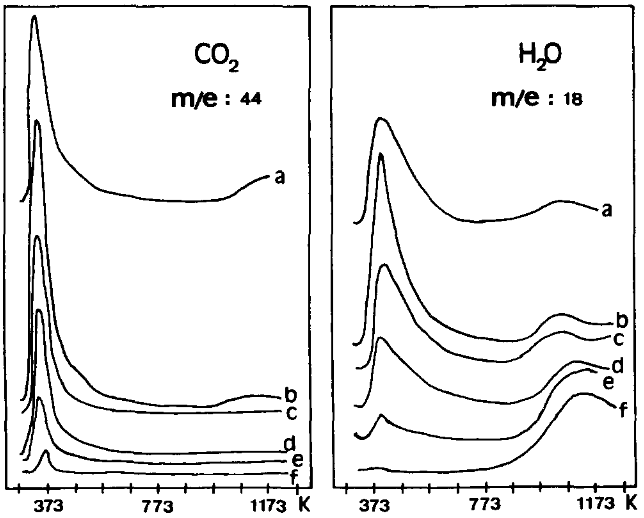

Fig. 1. CO_2 and H_2O traces corresponding to the TPD-MS experiments after treatment with CO_2 of La_2O_3/SiO_2 samples with (a) 75%, (b) 37.5%, (c) 18.75%, (d) 7.5%, and (e) 1.6% weight loadings. (f) Traces recorded for pure silica.

The CO_2 TPD-MS traces have been integrated from ambient temperature up to 673 K. The results are summarized in Table 1. It is obvious that the number of CO_2 molecules desorbing below 673 K grows with the La_2O_3 loading, reaching an apparent saturation for the sample with 37.5% lanthana. Compared to the theoretical full physical coverage of the surface (10–12 molecules nm^{-2}), the amount of desorbed CO_2 would be considered rather small. This suggests that the density of sites responsible for such a type of CO_2 adsorption is very low, the average distance between adjacent sites being about 3 nm.

CO_2 adsorption studies have also been carried out by volumetric methods, at 295 K. Following the first isotherm, the samples were outgassed for 1 h, at 295 K, and a second experiment was run. The new isotherm gave information about the CO_2 weakly retained by the La_2O_3/SiO_2 samples. The difference between the two isotherms above, allowed the amount of irreversibly chemisorbed CO_2 to be estimated. Table 1 also gives the results obtained from the volumetric adsorption studies.

Taking into account the accuracy of the quantitative TPD-MS estimates, the agreement between the amounts of chemisorbed CO_2 determined from volumetric measurements (irreversible adsorption) and TPD should be considered good. This indicates that peaks at 310–550 K in the TPD spectra (Fig. 1) correspond to irreversible chemisorbed CO_2, and therefore that the reversible forms would be eliminated by flowing inert gas at 295 K, before running the TPD experiments. In accordance with Table 1, the amount of reversible CO_2 adsorption is about ten times larger than that corresponding to the more strongly bound CO_2 and it increases with the La_2O_3 content up to a top limit of 2.5–2.8 molecules nm^{-2} for the 37.5% and 75% loadings. This saturation limit suggests that the number of sites available for the reversible adsorption of CO_2 remains far from that corresponding to the full physical coverage of the surface; however, it can reasonably be correlated

TABLE 1. Amounts of CO_2 determined by integration of the TPD-MS traces and from adsorption isotherms

La_2O_3 loading (wt.%)	Total[a] (mol nm^{-2})	Irreversible[a] (mol nm^{-2})	TPD-MS (mol nm^{-2})
75	2.8	0.26	0.27
37.5	2.5	0.26	0.26
18.7	1.4	0.09	0.11
7.5	0.8	0.05	0.07
1.6	0.34	0	0.023
0	0.22	0	0.03

[a] From volumetric adsorption measurements.

to the occurrence of definite atomic arrangements with a relatively high surface periodicity.

The OH stretching region of the IR spectrum of the 18% La_2O_3/SiO_2 sample pretreated at 870 K is shown in Fig. 2(a). The sharp absorption band at 3748 cm^{-1} can be associated with the existence of isolated silanol groups [18]. Such a band is always present in the spectra of silica samples calcined at the above-mentioned temperature (Fig. 2(b)). The shoulder of this band at a lower wavenumber can be interpreted as due to hydrogen bonded adjacent hydroxyls [18,19]. The treatment of this sample with CO_2 leads to a decrease in the absorption at 3748 cm^{-1}, and to the appearance of several bands at 3727, 3711, 2340, 1661, 1634 and 1518 cm^{-1} (Fig. 3). The bands appearing in the OH stretching region can be due to bicarbonate species, and the 1661, 1634 and 1518 cm^{-1} features indicate the formation of both bicarbonate and carbonate groups [11,17]. The strong absorption at 2340 cm^{-1}, slightly shifted from the gaseous CO_2 ν_3 band at 2349 cm^{-1}, and readily eliminated upon evacuation at ambient temperature, must be assigned to weakly adsorbed CO_2. In summary, the IR results are consistent with the conclusions drawn from the series of TPD and volumetric CO_2 chemisorption experiments. CO_2 chemisorption on La_2O_3/SiO_2 samples resembles the behaviour reported earlier for alumina dispersed lanthana in several qualitative aspects [11,13]. Figure 4 shows the IR spectra of CO_2 chemisorbed on La_2O_3 (8%)/Al_2O_3. Comparing Figs. 3 and 4, we may note that for La_2O_3/Al_2O_3, the band at 2347 cm^{-1} is much weaker than those appearing in the 1700–1200 cm^{-1} region. The reversible adsorption has been assigned to the interaction of carbon dioxide with low coordination surface La^{3+} ions [10–12], whereas the formation of bicarbonates is attributed to the interaction of CO_2 with basic surface OH groups. As observed in this work for La_2O_3/SiO_2 samples, both the formation of adsorbed CO_2 and HCO_3^- species is strongly enhanced when lanthana is dispersed on the support [11].

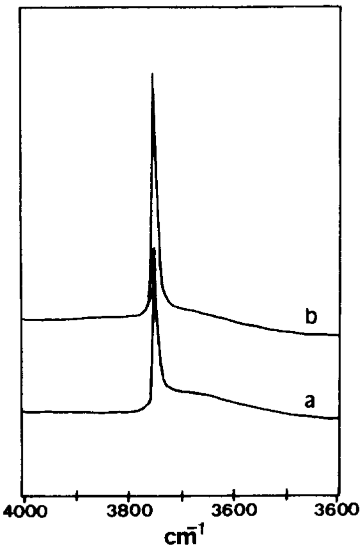

Fig. 2. FTIR spectra of (a) 18.75% La_2O_3/SiO_2, and (b) pure silica, following pretreatment in air at 870 K for 4 h. Absorbance in arbitrary units versus wavenumber.

TEM micrographs have been obtained for three La_2O_3/SiO_2 samples with 7.5%, 27% and 75% loadings. The first of these catalysts shows small dispersed particles, not larger than 2.5 nm. For the 27% loading, most of the silica surface appears covered by amorphous patches which should be attributed to a lanthanum containing phase. These patches, with an average size of 6 nm, appear to be embedded into the silica matrix and not just deposited onto the surface. For the 75% loading (Fig. 5), the surface of the sample appears fully

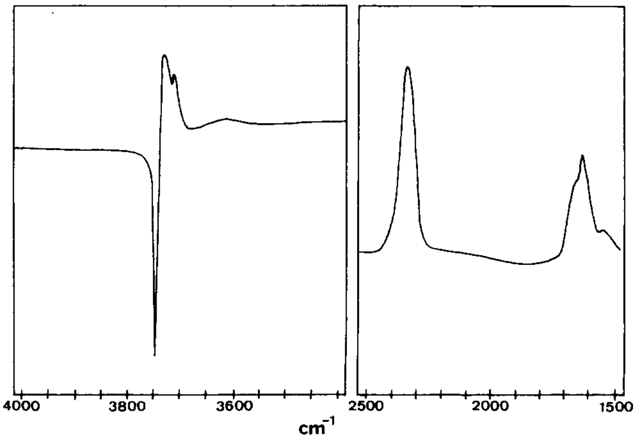

Fig. 3. Difference between the FTIR spectrum of 18.75% La_2O_3/SiO_2 treated with COD and the spectrum of the untreated sample. Absorbance in arbitrary units versus wavenumber.

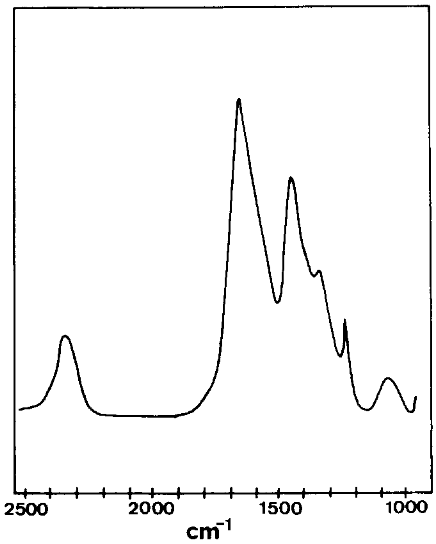

Fig. 4. Difference between the FTIR spectrum of 8% La_2O_3/Al_2O_3 treated with CO_2, and the spectrum of the untreated sample. Absorbance in arbitrary units versus wavenumber.

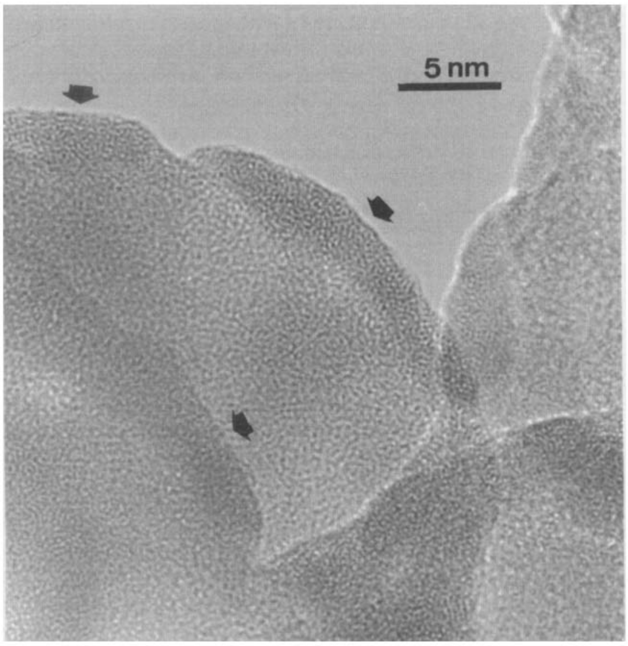

Fig. 5. TEM micrograph of a 75% La_2O_3/SiO_2 sample. The arrows indicate patches of an amorphous mixed phase covering the silica particles.

modified by the presence of an amorphous layer. The darkened areas, surrounding the borders of the silica particles, suggest that such an amorphous layer is around 2 nm thick.

4. Discussion

Several earlier works dealing with La modified aluminas have proposed that the lanthana overlayer can be envisioned as a single layer slab on the surface of the support [20]. Bettman *et al.* have studied a very broad range of La_2O_3 loadings on γ-alumina [13]. They concluded that for surface concentrations up to 6 La atoms nm^{-2}, lanthana is present as a bidimensional overlayer. As deduced from XRD, for higher concentrations, the excess of lanthana forms crystalline lanthanum oxide [13]. For calcination temperatures above 1070 K, $LaAlO_3$ can readily be observed. Ledford *et al.* [8,21] have also shown by XPS that lanthana is highly dispersed on γ-alumina.

The results obtained from the chemisorption studies reported here suggest that the saturation effect reached for the 37.5% La_2O_3/SiO_2 sample might well be associated with a lanthana monolayer on the silica surface. Assuming this, the theoretical number of La atoms nm^{-2} estimated from the lanthana loading mentioned above (37.5%) would correspond to the surface concentration for a single oxide layer [16].

However, other evidence from the present work indicates the formation of a three-dimensional lanthana/silica mixed phase. Thus, the TEM images suggest that the 75% La_2O_3/SiO_2 sample is coated by an amorphous layer about 2 nm thick. Such a thickness is not consistent with a tendency to the monolayer coverage model proposed for La_2O_3/Al_2O_3. A detailed analysis of the XRD patterns for the series of silica supported lanthana samples, indicate that the intensity of two broad bands, centered at 0.293 and 0.203 nm spacings, increasing with the lanthana loading. A model in which the lanthana interacts with the silica during the calcination step, leading to the formation of bulk amorphous La–Si–O patches, can alternatively be consistent with the experimental data reported here. The higher the La_2O_3 loading, the higher the surface coverage of silica. For the 37.5% loading, the silica surface appears almost completely covered by such patches. For higher loadings, lanthana contributes to increase the thickness of the coating phase.

Some XPS data at present available for a 27% La_2O_3/SiO_2 sample give additional support to this model. According to the method proposed in ref. 22, the estimated La3d/Si2p intensity ratio for a monolayer coverage is 5.72. In our case, the experimental intensity ratio varies with the calcination pretreatment from 0.85 up to 3.23, increasing but remaining far from 5.72, the value corresponding to the monolayer ratio. This also suggests the occurrence of a La_2O_3–SiO_2 interaction during calcination, but in a different way to that of La_2O_3–Al_2O_3 [13,20,21]. In this latter case, the experimental La/Al XPS signal intensity ratios are in excellent agreement with the theoretical estimate for the monolayer dispersion [21].

As already mentioned, the highest CO_2 adsorption capability has been observed for the 37.5% and 75% La_2O_3 loadings. Only one tenth of this amount corresponds to irreversible CO_2 adsorption, this fraction remaining almost constant for the lower loadings. In agreement with several other authors, it is reasonable to suggest that deficiently coordinated surface La^{3+} ions are the active sites for reversible CO_2 adsorption [11,12]. This assumption would allow a rough estimation of the La^{3+} surface concentration. The sites for CO_2 irreversible adsorption, which are present at very low surface concentration, should be correlated with the decrease in the intensity of the OH band at 3748 cm^{-1} and with the IR absorptions appearing at 3727 and 3711 cm^{-1} with CO_2 treatments. Since the bare silica does not chemisorb CO_2 in an irreversible way, we suggest that Si–OH groups with some particular environments, resulting from both the statistical dehydroxylation of the surface and the La distribution in the mixed phase, must be the active sites for this kind of adsorption.

In summary, assuming the proposed adsorption model, the total amount of adsorbed CO_2 can be considered as a good approximate estimate of the surface La^{3+} content. The saturation value of about 2.5 La atoms nm^{-2} is in agreement with the formation of patches of a mixed La–Si–O phase coating the silica particles, the full coverage of the particles of the support being reached in our case for a lanthana loading of 37.5%. The nature of the amorphous mixed phase would impose a top limit on the above-mentioned La surface concentration. This behavior is different from that of La_2O_3/Al_2O_3 systems in which the La is dispersed on the alumina surface at the atomic level forming a monolayer. The differences in the hydroxylation of the Al_2O_3 surface, and on the surface distribution and local environments of La, explain why in the latter case the irreversible chemisorption of CO_2 is more favored than the reversible chemisorption on deficiently coordinated La^{3+} ions.

Based on this work, CO_2 adsorption can be proposed as a method to determine the coverage of silica by an amorphous La–Si–O mixed phase. This information can be useful as a basis to discuss the catalytic behaviour of dispersed lanthana, as well as a necessary background for further understanding the promotion effect of lanthana in metal catalysts dispersed on modified silica supports.

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