Applied Catalysis A: General 208 (2001) 111–123

APPLIED CATALYSIS
A: GENERAL

www.elsevier.com/locate/apcata

Catalytic behavior of lanthana promoted Rh/SiO_2 catalysts: influence of the preparation procedure

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Received 17 March 2000; received in revised form 16 June 2000; accepted 19 June 2000

Abstract

Benzene hydrogenation and *n*-butane hydrogenolysis reactions have been tested on a series of Rh/La_2O_3/SiO_2 catalysts, their catalytic properties being compared with those of a Rh/SiO_2 sample studied as reference. This investigation has revealed that both activity and selectivity can be controlled by the procedure followed to prepare the catalysts. In particular, the influence of preparative conditions such as the lanthana loading, method of introduction of the metal and promoter (either consecutive or by co-impregnation) and temperature of calcination (873 or 1173 K) of the intermediate La_2O_3/SiO_2 phase onto which the noble metal is later deposited, have been analyzed. The differences in the catalytic behavior have been correlated with the La_2O_3/SiO_2 interactions, leading to a different degree of surface hydroxylation and different Rh particle crystallinity.

Keywords: Rh/La_2O_3/SiO_2 catalysts; Benzene hydrogenation; *n*-Butane hydrogenolysis; Preparation procedure

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 metal/SiO_2 binary systems [1–3]. At present, however, the precise origin of this promoting effect remains unclear. Moreover, the modifications induced by lanthana are found to vary between laboratories [4,5]. This suggests that the preparation method plays a key role in determining the final properties of the lanthana-promoted catalysts. In fact, in a recent paper [6] we published some results obtained in the chemical and structural characterization of a series of lanthana-promoted Rh/SiO_2 catalysts that clearly showed how the preparation procedure has a very strong influence on the microstructure. We found that critically important parameters characterizing the catalytic system like the metal dispersion, the crystallinity of the dispersed metal or the nature of the promoting phase can be substantially modified by controlling the preparation variables. In particular, the influence of lanthana loading, the method of introducing the promoter (either before the metal or simultaneously with it) and the temperature at which the La_2O_3/SiO_2 system is precalcined before the Rh impregnation were investigated. In parallel with the microstructural effects, significant differences in the interaction with

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PII: S0926-860X(00)00692-X

CO as a consequence of the modification of the cited preparative variables were observed by FTIR spectroscopy.

We further [7] reported specifically on the characterization of La_2O_3/SiO_2 performed using HREM, XPS, XRD, EDS and CO_2 adsorption techniques. This work helped in the understanding of the structure of the binary system. In particular, it was found that lanthana particles are not formed in the La_2O_3/SiO_2 system, contrary to what had been previously reported in several studies on La_2O_3/Al_2O_3. Instead, amorphous and embedded particles of a mixed silicate phase were observed, even for low La_2O_3 loadings. The coverage of this mixed silicate was found to increase with the lanthana loading. In addition, this amorphous silicate phase was found to be soluble in acid media, which has significance for the preparation of metal/La_2O_3/SiO_2 samples as seen in [6]. As a matter of fact, this study was an indispensable step before using it as the support of a noble metal and further interpreting the catalytic behavior of the ternary system.

In the present work, on the basis of the previously accumulated information, we have focused our attention again on the Rh/La_2O_3/SiO_2 system. In this case, our major concern is the investigation of the influence of the above mentioned preparation variables on the catalytic properties of the corresponding ternary catalysts. Benzene hydrogenation and *n*-butane hydrogenolysis have been chosen as complementary test reactions to study the catalytic behavior due to their being structure-sensitive and structure-insensitive reactions, respectively. In addition, we present some results obtained by temperature-programmed reduction, high resolution electron microscopy and the study of the chemisorption of H_2 and CO that help in the discussion of the catalytic reaction data.

2. Experimental details

The silica sample studied here was SiO_2 Cabosil M-5 (99% pure). Prior to its use as a support, this sample was calcined at 1173 K for 4 h. The BET surface area of this pretreated silica was 190 m^2/g. We prepared four Rh/La_2O_3/SiO_2 catalysts (samples B–E) as well as one Rh/SiO_2 catalyst (sample A), which was used as a non-promoted reference. The noble metal loading was always 3 wt.%. Two different lanthana loadings were studied, the latter leading to a full coverage of SiO_2: 7.5 wt.% (catalyst B) and 37.5 wt.% (catalysts C–E) (expressed per gram of SiO_2). Both lanthana and rhodium precursor salts were deposited by using the incipient wetness impregnation technique. A single impregnation cycle from aqueous solutions either of $La(NO_3)_3\cdot 6H_2O$ or $Rh(NO_3)_3\cdot 2H_2O$ of a suitable concentration were used. The reduction treatment leading to the final catalysts was performed in a flow of H_2 of 60 cm^3/min for 1 h at three different temperatures: 573, 773 and 973 K. These were chosen after verifying by temperature-programmed reduction (TPR) (see below) and thermogravimetric analysis (TG) that the rhodium was in its fully reduced state at 573 K. The heating rates for reduction treatments and the TPR and TG experiments were all 10 K/min.

Except for sample E, which was prepared by co-impregnation of the rhodium and lanthanum salts and further reduced as indicated above without any prior calcination, the remaining promoted catalysts were obtained by a consecutive impregnation procedure. After depositing the lanthanum salt, the samples were calcined at either 873 K (samples B and C) or 1173 K (sample D), thus obtaining the corresponding La_2O_3/SiO_2 samples. These binary samples were further impregnated with rhodium nitrate, and finally reduced.

TPR experiments were carried out using a Spectralab SX200 mass spectrometer (MS) controlled through the Spectralab PC 200D 5.3 software which was also used for data acquisition and processing. The sample (around 100 mg) was heated in a flow of 60 cm^3/min of H_2 from 298 to 1273 K.

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

The high resolution electron microscopy (HREM) images were obtained on a JEOL 2000 EX instrument with a structural resolution of 2.1 Å. It allows the identification of phases by observing interplanar spacings above this value.

Prior to the catalytic assays of benzene hydrogenation, the samples (between 10 and 15 mg diluted in 100 mg of Al_2O_3) were reduced in a flow of H_2 (100 cm^3/min) at the selected temperature for 1 h and were cooled down in hydrogen to 305 K, at which temperature the reaction was carried out. The reaction feed consisted of 670 Torr of hydrogen and 100 Torr of benzene. A saturator containing benzene was placed in a bath whose temperature was maintained at 298 K to obtain the desired partial pressure. Analysis of the products (cyclohexane and benzene) was performed using a Hewlett-Packard 5710 gas chromatograph, equipped with a thermal conductivity detector. Product separation was performed by a GRAPHPAC CG (AW) column operating at 438 K. A 15 cm^3/min flow of helium was used as carrier. Chromatograms were registered using a HP 3380 integrator.

Pretreatment of the samples (30–50 mg) used in *n*-butane hydrogenolysis was the same as before, but the reaction temperature was 448 K. In this case, analysis was also performed at other temperatures (433–463 K) to estimate the activation energy of the reaction. The temperature range was chosen to avoid non-differential reaction conditions. The feed consisted of a 1:9 mixture of *n*-butane and hydrogen to give a total pressure of 760 Torr. Product analysis (methane, ethane, propane and isobutane) was performed in a Philips PU4410 gas chromatograph equipped with a flame ionization detector. For the product separation, a 20% BMEAS/CHROMP 20/100 column operating at 323 K was used. In this case, both system control and data acquisition were performed from an interfaced computer using the Philips Chromate Data System software.

For both reactions studied here, the influence of space velocity on the conversion was investigated and an inverse ratio between the parameters was found. This is indicative of the absence of diffusion control. In all cases, conversion was adjusted to values below 10% in order to guarantee differential operating conditions, so that the influence of the reactants partial presssure on the catalyst activity could be neglected. Also, for both reactions each experiment was monitored for at least 3 h to study the possible deactivation effects. As a reference, additional assays were also performed on bare La_2O_3/SiO_2 samples under the same experimental conditions. No conversion was observed in this case suggesting that the presence of Rh must be the main cause of activity in the $Rh/La_2O_3/SiO_2$ catalysts.

3. Results

3.1. TPR experiments

Fig. 1 shows the m/e=15 and m/e=18 signals registered in the TPR-MS experiment for each catalyst. In particular, these signals along with those corresponding to m/e=16 and m/e=17 (not represented here but similar in form) are the most significant as they include contributions from products like ammonia, methane and water whose evolution allows us to follow the course of the sample's reduction. It can be seen that sample A (Rh/SiO_2) is reduced at the lowest temperature. The shift of the reduction peaks towards higher temperatures suggests that ease of reduction diminishes as lanthana loading increases. The co-impregnated sample E has a different behavior, regarding both the shape of the peaks and the temperatures at which they appear, which are higher than for

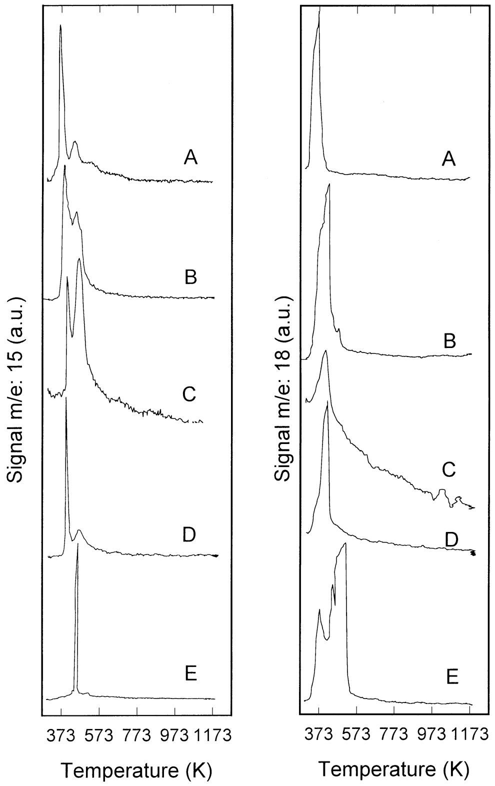

Fig. 1. Study by TPR-MS of the reduction process of the $Rh(NO_3)_3/La_2O_3/SiO_2$ system in the different catalysts.

the other samples. This can be interpreted by recalling that sample E did not undergo calcination, and so not only the Rh but also La is still present as hydrated nitrate (this gives rise to the desorption of more H_2O from $La(NO_3)_3{\cdot}6H_2O$). Also, the Rh and La phases are likely to be intimately mixed (as discussed later) since they were co-impregnated. These two phenomena might cause reduction of rhodium to the metallic phase to be slower. Catalysts C and D exhibit a different behavior, especially concerning the form of their $m/e=15$ signals. Note that the second peak centered around 450 K, which is only weak in samples A and D, is larger in sample B and becomes the most intense in sample C. This difference might be related to the reduction of species generated in the lanthana redissolution process which takes place in the case of samples B and C, but not in D, in which La_2O_3/SiO_2 had been precalcined at higher temperature and resistance against leaching had been found previously [6,7]. Finally, at 573 K all catalysts seem to be fully reduced as no species desorb above this temperature.

3.2. Volumetric adsorption

Results obtained from the volumetric chemisorption studies are summarized in Table 1. The H/Rh and CO/Rh ratios were obtained 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, in general, similar. This observation is in good agreement with results reported by Borer and Prins in a previous study on the $Rh/La_2O_3/SiO_2$ system [8].

The similarity of the H/Rh and CO/Rh values determined for catalysts A–D, the absence of significant hydrogen spillover at 298 K, which is suggested by parallel H_2 temperature programmed desorption studies [6], as well as the small contribution of the CO chemisorbed on the support, which could be deduced from a previous FTIR study [6], 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 [9,10] 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.

Table 1
Volumetric adsorption of H_2 and CO at 298 K

Catalyst	Reduction temperature (K)					
	573		773		973	
	H/Rh	CO/Rh	H/Rh	CO/Rh	H/Rh	CO/Rh
A	0.43	0.43	0.43	0.44	0.35	0.37
B	0.87	0.80	0.65	0.63	0.45	0.15
C	0.54	1.12	1.08	1.18	0.64	0.62
D	0.75	0.53	0.64	0.55	0.33	0.34
E	0.09	0.08	0.90	0.30	0.33	0.18

3.3. HREM study

Representative HREM micrographs of the catalysts reduced at 773 K are included in Fig. 2. Some observations can be made. First, no metal particles can be detected in the HREM images recorded for sample E. This contrasts with the HREM images obtained for samples A–D in which rhodium particles can always be observed. Second, there is no evidence for the presence of free lanthana or any other phase resulting from its aging in air, particularly $La(OH)_3$, in good agreement with previous XRD studies [6]. However, the more ordered appearance of some regions of the support, particularly in the vicinity of the metal particles, in the case of catalyst D, is consistent with the higher calcination temperature at which the La_2O_3/SiO_2 has been treated before the rhodium impregnation. Finally, it should be noticed that, as in the HREM images in Fig. 2, the rhodium particles dispersed on bare silica appear to be amorphous in many cases. This contrasts with the micrographs recorded for catalysts C and D, where fringes characteristic of Rh metal lattice spacings can often be identified. This would suggest that the promoter favors the presence of more crystalline metal particles. In addition, the particle sizes determined by HREM are in good agreement with the dispersion measured by volumetric adsorption of H_2 and CO.

3.4. Catalytic tests

Table 2 summarizes the catalytic activity values obtained in the study of the benzene hydrogenation

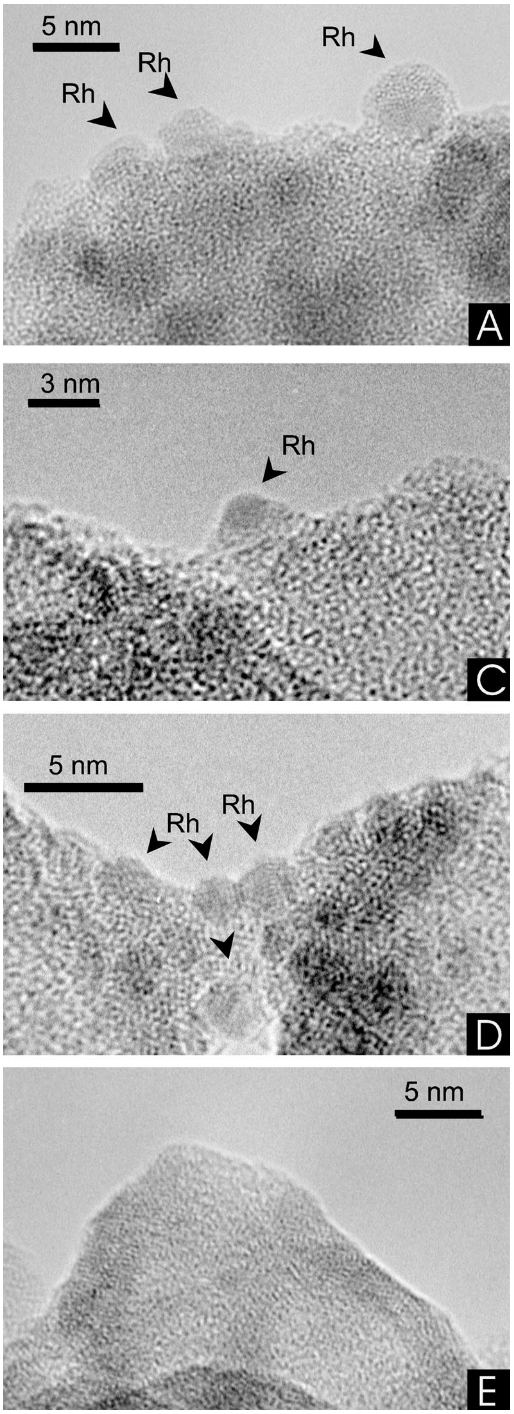

Fig. 2. HREM micrographs corresponding to Rh/SiO_2 (A) as well as to the Rh/La_2O_3/SiO_2 catalysts, referred to as C, D and E, reduced at 773 K. The arrows identify the observed metal particles.

Table 2
Catalytic activity and turnover frequency (TOF) in the benzene hydrogenation reaction at 305 K[a]

Catalyst	Reduction temperature (K)	Activity (cm^3 cyclohexane/g_{Rh} s)	TOF (molecules of cyclohexane per $atom_{Rh}$ s)
A	573	22.5	0.22
	773	26.1	0.25
	973	20.1	0.23
B	573	18.8	0.10
	773	20.5	0.14
	973	13.3	0.37
C	573	10.8	0.04
	773	11.9	0.04
	973	10.5	0.07
D	573	10.9	0.09
	773	17.3	0.13
	973	8.4	0.10
E	573	6.3	0.33
	773	12.8	0.18
	973	9.0	0.21

[a] Data obtained after 15 min from the start of the reaction. Catalyst amount: 10–15 mg diluted in 100 mg of γ-Al_2O_3 (120 m^2/g), total flow: 100 cm^3/min, P_{H_2}: 670 Torr and $P_{C_6H_6}$: 100 Torr.

reaction, referred to per gram of rhodium and measured for each sample and reduction temperature. Turnover frequency, calculated from activity and volumetric adsorption data, is also included. As can be seen, differences between the samples are relatively small. Nevertheless, especially for the catalysts reduced at 773 K, a trend in the activity values can be observed according to the sequence A>B>D>E>C. Therefore, the most active sample is that which does not contain lanthana. Also, comparison between samples B and C shows that activity decreases with lanthana loading. This would mean that the presence of lanthana does not have a positive promoting effect on the activity for benzene hydrogenation. However, if attention is paid to Fig. 3, in which evolution of the activity with time for the samples reduced at 773 K has been plotted, it can be clearly seen that it is sample A, Rh/SiO_2, which suffers the fastest deactivation. By contrast, for all the lanthana promoted samples this effect is so much slower that in some cases, such as for sample B, after 2 h of reaction the activity of the promoted sample is higher than that of Rh/SiO_2 (sample A). Similar results were obtained for the samples reduced at 573 and 973 K (results not shown).

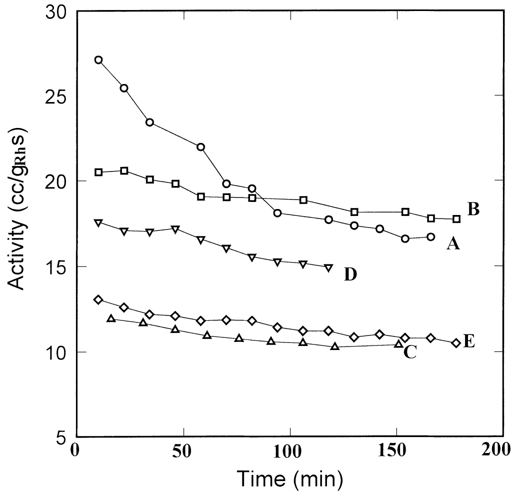

Fig. 3. Study of deactivation in the benzene hydrogenation reaction over the catalysts reduced at 773 K for 1 h (reaction temperature: 303 K).

Table 3 relates to the catalytic behavior in n-butane hydrogenolysis at 448 K, including both activity and selectivity values. In this table, activity is expressed as millimoles of n-butane converted per minute per gram of metal, while selectivity is expressed following criteria reported by Bond et al. [11]. In particular, if C_j is the number of moles of product formed during the reaction containing j atoms of carbon, the number of n-butane moles which react, A, would be $A=(C_1+2C_2+3C_3)/4$, while the selectivity, S_j, for each product could be expressed as $S_j=C_j/A$. Therefore, equation $S_1+2S_2+3S_3=4$ must be fulfilled. Table 4 shows the variation of the turnover frequency and activation energy with the reduction temperature for each sample. Tables 3 and 4 allow us to obtain similar conclusions to those derived from the study of the benzene hydrogenation reaction: the catalyst which in principle exhibits the highest activity is the one which does not contain lanthana, although its activity decays rapidly upon increasing the reduction temperature. In spite of this, the percentage of lanthana does seem to influence the selectivity as shown by results included in Table 3. According to them, preference towards formation of ethane as a reaction product, for example, varies in the order C>E>B>D>A. Activation energy values, however, are seen to change little either between samples or on changing reduction temperature.

Finally, as in the case of the hydrogenation of benzene, deactivation phenomena with reaction time

Table 3
Catalytic results in the n-butane hydrogenolysis reaction at 448 K[a]

Catalyst	Reduction temperature (K)	Activity (mmol/min g$_{Rh}$)					Selectivity			
		Methane	Ethane	Propane	Isobutane	Total	Methane	Ethane	Propane	Isobutane
A	573	21.8	27.2	21.8	0.1	70.9	0.6	0.8	0.6	0.0
	773	11.8	14.9	12.0	0.2	38.9	0.6	0.8	0.6	0.0
	973	0.9	2.6	1.0	0.1	4.6	0.4	1.1	0.4	0.1
B	573	0.8	4.1	1.0	0.2	6.1	0.3	1.3	0.3	0.1
	773	1.5	6.4	1.3	0.2	9.4	0.3	1.3	0.3	0.0
	973	2.0	4.1	2.2	0.2	8.5	0.5	0.9	0.5	0.0
C	573	1.8	11.2	1.8	0.2	15.0	0.2	1.5	0.2	0.0
	773	1.7	11.0	1.8	0.2	14.7	0.2	1.5	0.2	0.0
	973	0.9	3.1	0.9	0.2	5.1	0.3	1.2	0.3	0.1
D	573	1.1	3.5	1.2	0.2	6.0	0.3	1.1	0.4	0.1
	773	2.0	5.1	2.1	0.2	9.4	0.4	1.1	0.4	0.0
	973	2.0	2.4	2.0	0.2	6.6	0.6	0.7	0.6	0.1
E	573	0.9	3.9	0.8	0.1	5.7	0.3	1.4	0.3	0.0
	773	1.1	5.6	1.2	0.2	8.1	0.3	1.4	0.3	0.1
	973	0.3	1.2	0.4	0.2	2.1	0.3	1.0	0.4	0.2

[a] Data obtained after 10 min from the start of the reaction. Catalyst amount: 30–50 mg, total flow: 60 cm^3/min, P_{H_2}: 0.9 atm and $P_{C_4H_{10}}$: 0.1 atm.

Table 4
Activation energy (E_a) and turnover frequency (TOF) in the *n*-butane hydrogenolysis reaction at 448 K[a]

Catalyst	Reduction temperature (K)	E_a (kJ/mol)	TOF (molecules per atom$_{Rh}$ s)
A	573	184	0.28
	773	176	0.15
	973	171	0.02
B	573	196	0.01
	773	196	0.03
	973	159	0.10
C	573	188	0.02
	773	171	0.02
	973	184	0.01
D	573	184	0.02
	773	188	0.03
	973	188	0.03
E	573	–	0.12
	773	167	0.05
	973	–	0.02

[a] Data obtained after 15 min from the start of the reaction. Catalyst amount: 30–50 mg, total flow: 100 cm^3/min, P_{H_2}: 0.9 atm and $P_{C_6H_{10}}$: 0.1 atm.

have also been investigated for the hydrogenolysis of *n*-butane. This study is represented in Fig. 4, which shows results obtained for the samples reduced at 773 K. Notice how the presence of lanthana inhibits deactivation if compared to the reference, Rh/SiO$_2$. In the case of the non-promoted sample, although initially much higher, activity suffers a fast decay during the analysis period which is not observed in any of the promoted catalysts. An analogous behavior was found for the samples reduced at the other two reduction temperatures studied.

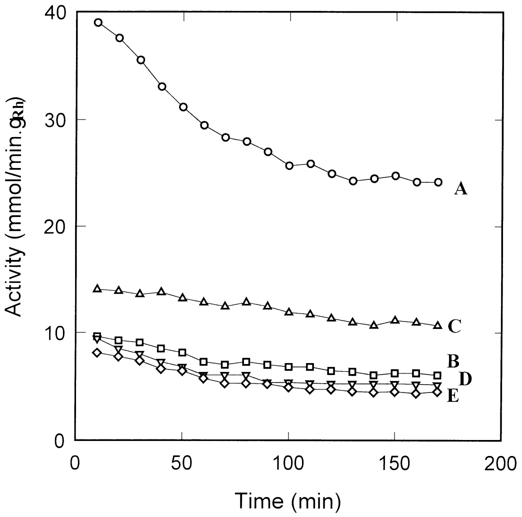

Fig. 4. Study of deactivation in the *n*-butane hydrogenolysis reaction over the catalysts reduced at 773 K for 1 h (reaction temperature: 448 K).

4. Discussion

As mentioned before, in this work the catalytic behavior of a series of Rh/La$_2$O$_3$/SiO$_2$ catalysts has been studied and special attention has been paid to the influence of the method used to prepare them. For this purpose, two reactions have been chosen as catalytic test reactions: benzene hydrogenation and *n*-butane hydrogenolysis.

4.1. Benzene hydrogenation

Benzene hydrogenation in particular, and hydrogenation of aromatic compounds in general, have been extensively employed to study catalysts based on supported noble metals [12–18]. A recent review by Stanislaus and Cooper [12] has shown the complexity of the fundamental aspects of this reaction. In our study, the results obtained suggest that catalyst A, Rh/SiO$_2$, is the one which presents the highest activity in the experimental conditions used here. A first idea that might be considered to interpret this result is a possible correlation between activity and metal particle size. According to chemisorption data shown in Table 1, the Rh/SiO$_2$ sample is the one of the series studied having the lowest Rh dispersion. Therefore, one could propose that activity increases with the particle size. However, several references in the literature point to the opposite relationship between these parameters [14,16], while others report ambiguous results in this regard [15]. In addition, it should be remembered that traditionally benzene hydrogenation is considered to be insensitive to catalyst structure. Considering our own results (Table 2), it should be noted that the activity of sample B reduced at 773 K and that of C reduced at 973 K, which appear to have similar metal dispersions (Table 1), are quite different. In conclusion, it does not seem that metal dispersion by itself is a critical parameter in the control of the activity of our catalysts.

Several recent papers suggest that the support may play a very active role in the C_6H_6 hydrogenation reaction [13–17]. For instance, Ioannides and Verykios [17], in the study of the interaction of benzene with SiO_2–, Al_2O_3– and TiO_2–supported Rh catalysts, of proposed that the benzene hydrogenation rate upon supported Rh crystallites can be significantly influenced, and even controlled, by the nature of the support surface. In such a case, estimation of turnover frequency (as done in Table 2) on the basis of experimental reaction rates and metal dispersion would be meaningless.

On the other hand, Vannice and co-workers [14–16], studying catalysts based on Pd and Pt dispersed on different supports, have outlined the role played by active centers for benzene adsorption existing on the support. Similarly, a correlation between the amount of benzene adsorbed on the support and activity of $Ni/TiO_2/ZrO_2$ catalysts for the benzene hydrogenation reaction has been reported by Wang et al. [19]. According to Peri [20], the benzene molecule is susceptible to adsorption at OH sites present on the surface of an oxide. Consequently, and in agreement with Chou and Vannice [14], if these OH sites were adjacent to a metal particle (metal-support interface), a benzene molecule initially adsorbed on the support might react rapidly with hydrogen previously activated by the metal.

The above observations might be applied in our case. Unfortunately, not enough characterization data of these OH centers of the support (La_2O_3/SiO_2) are available yet [21]. Additionally, submission of the support to metal impregnation, drying and further reduction in H_2 may alter drastically the nature and concentration of surface OH sites with respect to those presented by the bare support because of the possible associated phenomena of rehydroxylation, rehydration, H_2O desorption and further H_2 spillover. In spite of all the limitations of the study performed, considering previous information obtained by FTIR Spectroscopy [6] and the above mentioned literature references [13–20], it is very likely that addition of lanthana to Rh/SiO_2 catalysts induces a progressive loss of isolated OH groups (see Fig. 5), so reducing the concentration of sites on the support surface with the capacity to adsorb benzene [14]. This proposal could justify the differences observed between the promoted catalysts. In particular, why according to Table 2, sample B, i.e. that with the lowest La_2O_3 loading, is, after Rh/SiO_2, the most active among the catalysts studied here. In line with this, differences of behavior are smaller, although they do exist, between samples C, D and E, which have the same lanthana loading. In this case, and in spite of the apparent non-sensitivity of the reaction to metal dispersion, we attribute the slight differences observed to differences in the microstructure of the samples, in turn associated with differences in the preparation procedure. In this sense, HREM and H_2 and CO chemisorptive results, shown in Fig. 2 and Table 1, respectively, help to give some interpretation. As already anticipated in [6], we propose that while for catalyst B and C the promoter would actually consist of an amorphous lanthanum silicate leached during the rhodium nitrate impregnation step and then co-deposited with the rhodium salt upon drying [7], in the case of sample D, the more severe calcination treatment of La_2O_3/SiO_2 before the metal impregnation induces a strong bonding of the promoter to the silica support, making it less susceptible to leaching during the Rh impregnation step. These differences in the nature of the promoter phase could reasonably affect its interaction with the metal and therefore also the final catalytic behavior of the sample. Finally, in the case of sample E, prepared by co-impregnation and with no precalcination before reduction, we believe that the promoter consists of embedded lanthanum sesquioxide in which the highly dispersed metal phase would be present. In this peculiar microstructure the metal is initially less accessible, although the fraction of exposed rhodium would be larger after reduction at 773 K due to a partial segregation of the metal microcrystals towards the lanthana surface. This would explain the increase of H/Rh and CO/Rh ratios upon increasing reduction temperature as found in Table 1. 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 explain the difference observed between the CO/Rh and H/Rh ratios in catalyst E reduced at 773 K. This proposed structure might also help us to understand why this sample exhibits the lowest activity after reduction at 573 K, if compared with the rest of the samples, and why the activity increases and becomes more similar to that of catalyst C as reduction temperature increases (see Table 2).

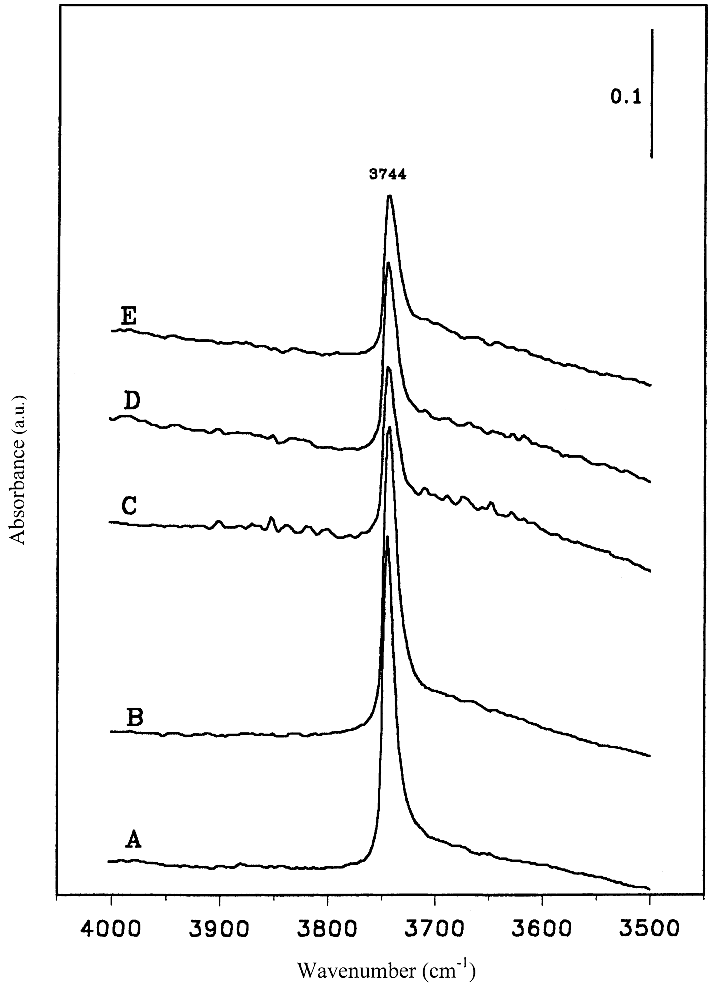

Fig. 5. FTIR spectroscopy of the O–H stretching region. Normalized spectra corresponding to the catalysts reduced and further evacuated at 773 K.

Participation of the promoter/support system in the benzene hydrogenation reaction over the Rh/La_2O_3/SiO_2 samples is also suggested by the general effect of reduction temperature on the activity. According to results included in Table 2, evolution of the activity with the reduction temperature follows a similar trend for all the catalysts: it increases when passing from 573 to 773 K, then diminishes at 973 K. This behavior might also be correlated with the surface concentration of OH groups that are active to chemisorb benzene. Note that, as shown by TPR-MS (Fig. 1), the study of the reduction process allowed us to conclude that at 573 K the rhodium present in the samples must be fully reduced. At this temperature, the high degree of hydroxylation of the support might lead to hydrogen bond interactions which would decrease the capacity of the OH groups to adsorb benzene. Peaks for the stretching vibration of hydrogen bonded OH groups have been observed in IR spectra (see Fig. 6) for these samples reduced at low temperature. Although spectra in Fig. 6 look in principle very similar to those shown in Fig. 5, the band corresponding to isolated OH groups seems to be slightly less intense, contrary to the shoulder at lower wavenumber which increases slightly in intensity and appears better resolved, specially for

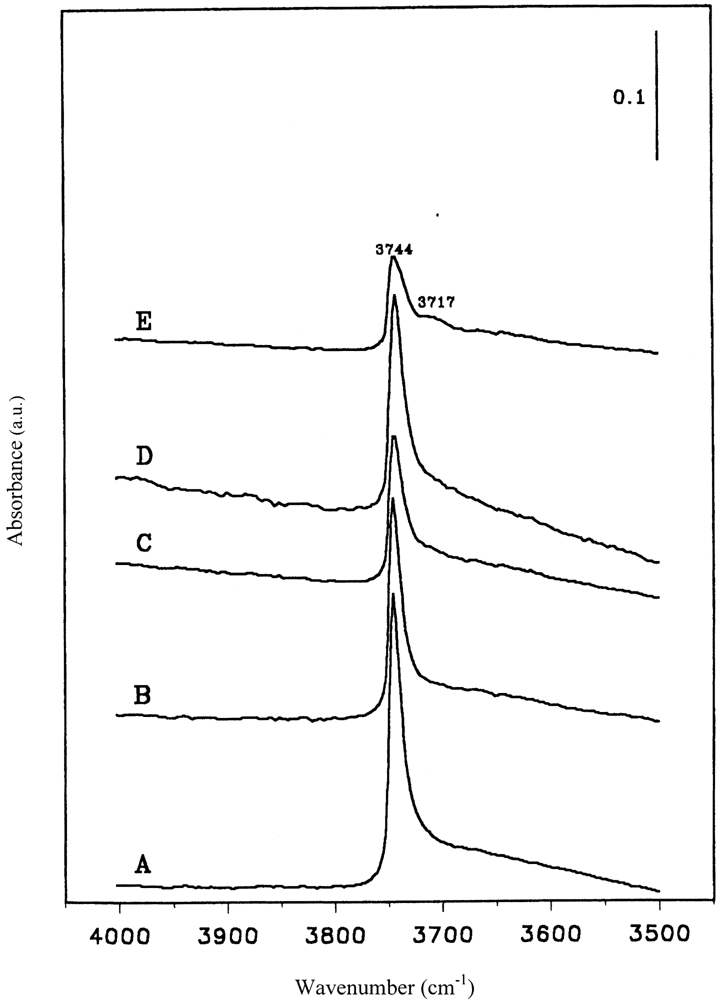

Fig. 6. FTIR spectroscopy of the O–H stretching region. Normalized spectra corresponding to the catalysts reduced and further evacuated at 573 K.

sample E. This finding might indicate that when raising the temperature from 573 to 773 K, evacuation removes the hydrogen bonded OH groups rather than the isolated ones, whose amount increases for this reason. These observations are consistent with studies on silica dehydroxylation previously reported in the literature [22,23]. Optimal OH group concentration would be reached after reduction at 773 K, whereas above this temperature (973 K), dehydroxylation of the support along with some sintering of the metal phase (Table 1) would cause the decrease of activity observed.

A last aspect of the benzene hydrogenation reaction worth noting is the deactivation observed with time. As can be seen in Fig. 3, the most active sample, Rh/SiO_2, is also the one which undergoes the most significant deactivation. We have found that the higher the temperature of reduction the more important this effect seems to be. In this way, for sample A (Rh/SiO_2) reduced at 973 K, activity decreased to 50% of the initial value 2.5 h after the start of the reaction. This phenomenon is much less significant in the case of the promoted samples, which indicates that lanthana, although it leads to catalysts with initially lower activity, clearly helps to stabilize catalytic performance. Notice in Fig. 3 how, after 2 h of operation, activity of sample A is similar to or even lower (in the case of sample B) than that of the promoted catalysts. Here it should be remembered that characterization by HREM (Fig. 3) gave indications of a poorer crystallinity of the rhodium metal particles in sample A, compared to the promoted catalysts. This might make them more sensitive to the poisoning effects due to impurities in the benzene stream or carbonaceous deposits.

4.2. *n*-Butane hydrogenolysis

The second reaction investigated in this work was hydrogenolysis of *n*-butane. As in the case of benzene hydrogenation, this is a reaction commonly studied as a characterization test of metal catalysts [24–29]. By contrast with the first reaction, it is considered to be sensitive to catalyst structure [29], therefore it might offer complementary information to that obtained from the study of benzene hydrogenation.

Another difference between these two reactions is that study of *n*-butane hydrogenolysis implies the investigation not only of activity but also of selectivity, i.e. of which C–C bond in the *n*-butane molecule is broken during the course of reaction: either the terminal one, with formation of $CH_4+C_3H_8$ or the central one, with formation of ethane.

4.2.1. Activity

As in the case of the benzene hydrogenation reaction, it is the Rh/SiO_2 (sample A) which is the most active of all the samples studied under the experimental conditions used here (Table 3). However, it is also the most sensitive to reduction temperature, so that, as shown in Table 3, as this parameter increases from 573–773 to 973 K, the sample suffers a strong deactivation. These large changes in activity can hardly be explained in terms of the relatively small variation of metal dispersion. Chemisorption studies (Table 1) indicate that the H/Rh ratio changes only from 0.43, after reduction at 573 K, to 0.35, in the sample reduced at 973 K. This is in good agreement with observations made by Kalakkad et al. [26,27].

Recently, Miller et al. [25] have studied propane hydrogenolysis on a series of catalysts based on Pt supported on different aluminosilicates. In that work, the authors find significant differences of activity between the catalysts investigated which they correlated with the chemical properties of the support used in each case. In particular, support OH concentration is outlined as an important preparative variable. Two main proposals are made to justify the role played by the OH sites on the modification of the catalytic behavior of platinum: (a) interaction with dispersed metal phase, which would make the platinum particles become electron deficient and (b) appearance of hydrogen spillover phenomena caused by stabilization of the hydrogen transferred from the metal to the support, due to the presence of OH groups with the appropriate characteristics.

An analogous explanation might be applied to the present work where, as already mentioned, a significant difference is observed between catalyst A and the lanthana promoted samples B–E. The important role attributed by Miller et al. to the surface OH sites [25] moves us to propose that differences observed in activity between sample A and the rest of the catalysts studied here might be correlated to the support properties in each case, in particular the concentration of OH groups on the surface. In fact this is illustrated by previous characterization by FTIR spectroscopy [6] which revealed differences between the samples in the intensity of the bands appearing in the O–H stretching region of the spectrum, as seen in Figs. 5 and 6. Notice also that, unlike for their intensities, the position of these OH bands apparently does not change from one sample to another suggesting that the nature of these surface sites must be almost the same for all catalysts. This result is in good agreement with two additional observations: (1) activation energy values (Table 4) seem to be practically independent both of sample identity and of the reduction temperature and (2) Miller et al. [25] also found that the amount of spillover hydrogen and the specific hydrogenolysis activity are influenced by the number of hydroxyl groups rather than their acid strength. In our opinion, both observations give more weight to the proposal made regarding participation of OH groups of the support in the reaction mechanism.

In [25] data corresponding to the influence of the reduction temperature on the catalyst activity were also reported. In general, it was found that activity decreases in a significant way as reduction temperature increases from 723 to 873 K. In our case a similar effect is observed. Catalyst A, particularly, shows great sensitivity to reduction temperature, its activity falling by a factor of 8 when reduction temperature passes from 773 to 973 K (Table 3). According to Miller et al. [25], the origin of this effect would be in the modifications induced by the thermal treatment on the concentration of the OH groups present on the support. A similar explanation might be applicable in the case of sample A. Notice that this proposal is also consistent with above considerations made in the discussion of the benzene hydrogenation results.

4.2.2. Selectivity

As mentioned before, analysis of selectivity results, also included in Table 3, is a second relevant aspect in the study of the *n*-butane hydrogenolysis reaction. Kalakkad et al. [26,27] have focused also on this aspect, trying to correlate the behavior of Rh/SiO_2 and Rh/Al_2O_3 catalysts with that exhibited by monocrystalline rhodium planes.

Regarding the selectivity results obtained in this work, a difference is observed between the non-promoted sample A (Rh/SiO_2) and the promoted catalysts. For sample A, selectivity to ethane remains stable for the lowest reduction temperatures (0.8), approaching the value of 1.0 found by Kalakkad et al. for Rh (1 1 1) or a Rh/SiO_2 sample reduced at 773 K (HRT) [26,27] when reduction temperature increases to 973 K. Contrary to what has been observed for sample A, the rest of the catalysts B–E show selectivity to ethane between 1.1 and 1.5 after reduction at 573 or 773 K, the values tending to diminish upon increasing reduction temperature to 973 K. In other words, the non-promoted catalyst and those containing lanthana exhibit, at the low reduction temperatures, ethane selectivity values below and above, respectively, those of monocrystalline Rh (1 1 1) or the catalyst with larger Rh particle size (Rh/SiO_2-HRT), evolving, after reduction at 973 K, towards a behavior more similar both to each other and to the samples of Kalakkad et al. [26,27].

Although information available about the mechanism of the reaction and, in particular, the parameters which determine selectivity, is so far limited, the catalysis results presented here along with those derived from previous structural and chemical characterization [6] allow us to make the following observations to explain the differences of behavior observed between promoted and non-promoted Rh/SiO_2 samples. First of all, influence of the crystallinity of the metal particles on the selectivity is likely to take place considering the structural sensitivity of the reaction. In this sense, it should be recalled that HREM observations (Fig. 2) suggested that crystallinity of the rhodium particles in the Rh/SiO_2 catalyst seems to be poorer than that observed in the promoted samples. Reasonably, reduction at high temperatures would help to improve crystallinity making the behavior of both types of catalysts more similar to each other as indeed is observed. Secondly, the fact that the above difference of behavior between La_2O_3-promoted and non-promoted samples almost disappears after reduction at 973 K, in terms of both activity and selectivity to ethane, suggests that the loss of activity of sample A as reduction temperature increases is caused by a much greater fall in the rate of scission of the terminal C–C bond than of the central one.

Kalakkad et al. [27] showed that the *n*-butane hydrogenolysis selectivity is sensitive to the nature of the Rh single crystal surface exposed. The authors also proposed that a high dispersion of the metal increases selectivity to ethane to values of about 1.6. They presented evidence to show that ethane selectivity increases with particle roughness. They suggested that small particles have rougher surfaces than larger ones. As the samples were reduced at increasing temperatures, the particles increased in size and were more able to form regular cubo–octahedral particles. These expose mainly (1 1 1) planes and so should tend to give rise to ethane selectivity values of 1.0. A similar correlation between these parameters is observed in our case. Comparison of results included in Tables 1 and 3, show that, with the exception of sample E, whose particular microstructure makes it difficult to estimate the metal dispersion through H_2 and CO chemisorption, a similar evolution is found for both metal dispersion and ethane selectivity according to the trend C>B>D>A. Further, for the lanthana-promoted samples, selectivity to ethane diminishes to values between 1.2 and 0.7 as reduction temperature increases, in good agreement with a logical growth of the metal particle size. This suggests that, in these samples, the Rh particles evolve towards a morphology in which the (1 1 1) planes are more exposed. By contrast, the non-promoted sample exhibits higher selectivity to ethane as reduction temperature increases to 973 K.

A possible explanation might be that, in this case, at low reduction temperatures the metal consists of larger, more amorphous particles (see Fig. 2) in which a mixture of the (1 1 1), (1 1 0) and (1 0 0), and possibly other, planes is exposed giving a selectivity of 0.8, whereas a more severe reduction improves crystallinity and induces formation of crystalline Rh particles that expose mainly (1 1 1) faces, thus explaining the increase of ethane selectivity to a value of 1.1.

5. Conclusions

1. The present work has been focused on the behavior of a series of $Rh/La_2O_3/SiO_2$ samples in two catalytic test reactions: benzene hydrogenation and *n*-butane hydrogenolysis. Special attention has been paid to the comparison with a non-promoted lanthana catalyst, Rh/SiO_2, studied as a reference, as well as to the influence of the preparation procedure. In particular, the effect of variables such as lanthana loading, the pretreatment of the promoter/support system, and the method used to incorporate the promoter and the metal (either sequential or by co-impregnation) has been investigated.
2. The results obtained have revealed that, depending on the preparative variables selected, both activity and selectivity may change significantly. The present investigation, in combination with previous characterization [6,7], demonstrates that preparation procedure and composition strongly influences the microstructure of the promoter phase, and consequently the catalytic behavior.
3. Two parameters in particular have been suggested to be at the root of the correlation between the preparation procedure and catalytic behavior: the concentration of OH sites on the support surface and the structural properties of the metal particles.
4. For both test reactions, evidence was found for the existence of a correlation between activity and concentration of OH sites on the support surface.
5. It is proposed that selectivity in the hydrogenolysis of *n*-butane is at least partly dependant on the roughness of the Rh particles following discussion in [27].

Acknowledgements

This work has received financial support from DGICYT under contracts PB94-1305 and PB95-1257, as well as from CICYT, contract MAT95-960931.

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