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Thermal Evolution of the Support "Promoter" Effect in Rh/La_2O_3

GEORGE GALLAHER, JAMES G. GOODWIN, JR.,[1] CHEN-SHI HUANG,[2]
AND MARWAN HOUALLA[2]

*Department of Chemical and Petroleum Engineering, University of Pittsburgh,
Pittsburgh, Pennsylvania 15261*

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Suppression of CO chemisorption and the rates of ethane hydrogenolysis and cyclopropane hydrogenation along with a −1-eV shift in the Rh $3d_{5/2}$ binding energy were observed for a 200°C-reduced Rh/La_2O_3 catalyst compared to Rh/SiO_2. These results are consistent with the decoration model proposed for the metal–support interaction between La_2O_3 and noble metals, where the decorating species play the role of a promoter. The presence of these effects after such a mild pretreatment suggests that dissolution of the support by acidic precursor solutions during impregnation/drying and/or migration of support species during the early stages of reduction are probably the primary causes of the decoration. The extent of decoration appeared to be increased upon reduction of the La_2O_3-supported catalyst at 400°C as evidenced by a further suppression of CO chemisorption and cyclopropane hydrogenation rate. H_2 uptake, which greatly exceeded CO uptake after the 200°C reduction suggesting spillover of H_2 to decorating species and/or the support, increased further after a 400°C reduction indicating an increased capacity of the decorating species and support for spillover H_2. This thermal modification of the decorative overlayer occurs concurrent with the dehydration of $La(OH)_3$ to LaOOH and La_2O_3 and the Rh-catalyzed decomposition of $La_2(CO_3)_3$, those compounds which constitute the support after impregnation and/or exposure to air.

INTRODUCTION

Lanthanum oxide-supported noble metals have been the subject of several recent studies arising from the impact that this support has on activity and selectivity during CO hydrogenation on these metals (*1–8*). Enhanced methanol production has been observed for Pd/La_2O_3 (*2–5*), while Rh/La_2O_3 exhibits an increase in the production of C_2 oxygenates (*6–8*).

These effects have been attributed to a metal–support interaction involving the decoration of the metal crystallites with lanthana moieties (*4, 7, 9*). Details of the interaction have been inferred from chemisorption, IR, and XPS studies in the case of Pd and from primarily chemisorption and IR effects in the case of Rh. Explanations of the genesis of the phenomenon include an SMSI effect involving partial reduction of La_2O_3 to LaO_x (*9, 10*) (even though no stable partially reduced La species are known), structural and compositional changes in the support associated with thermal dehydration of $La(OH)_3$ to LaOOH and La_2O_3 (*4*), dissolution and redeposition of support material during impregnation and drying (*7, 8*), participation of the noble metals in the decomposition of lanthanum carbonates known to form during the impregnation process (*11*), and the formation of $LaRhO_3$ (*7, 12*). An understanding of the origins of the interaction is important in explaining its impact on CO hydrogenation.

This paper reports on the results of an

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[1] To whom correspondence should be addressed.

[2] Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15261.

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investigation undertaken to address the conditions giving rise to the proposed metal–support interaction. Since support material apparently decorates the metal surfaces, the metal–support effect can in large part be attributed to a "promoter" role by the decorating species.

Two Rh/La_2O_3 catalysts which had been initially reduced at 200 and 400°C were studied. A Rh/SiO_2 catalyst, reduced at 400°C and assumed to represent the noninteractive state, was also studied. The catalysts were characterized via H_2 and CO chemisorption, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Additional insight was gained from the use of ethane hydrogenolysis and cyclopropane hydrogenation reactions. Ethane hydrogenolysis is a structure-sensitive reaction requiring a relatively large ensemble of surface atoms to constitute a site (*13–15*). As such it has been previously found to be a useful probe for studying decoration effects as in SMSI catalysts (*16, 17*) as well as in Group VIII/Group IB bimetallic catalysts (*14, 18*). Cyclopropane hydrogenation is generally considered to be a structure-insensitive reaction (*19–21*), although there is evidence that on Ru this reaction may also be structure sensitive (*22*). Because of the small ensemble required to carry out this reaction, it should be more indicative of the extent of free Rh surface.

EXPERIMENTAL

Preparation

Nominal 3 wt% Rh catalysts were prepared by incipient wetness impregnation of La_2O_3 (Alfa Products) and SiO_2 (Aerosil 300, Degussa) oxide supports with aqueous solutions of $Rh(NO_3)_3$–$2H_2O$ (Alfa Products). The impregnated samples were dried overnight at 90°C in air. The Rh/SiO_2 and one Rh/La_2O_3 catalyst were reduced by heating in 100 cc/min of flowing H_2 (UHP grade, Linde) at 2°C/min from 25 to 400°C then holding at 400°C for 4 h. Another Rh/La_2O_3 sample was reduced by heating in 100 cc/min of flowing H_2 from 25 to 200°C at 2°C/min and holding there for 4 h. A La_2O_3 blank was prepared by impregnation with distilled water followed by drying overnight at 90°C and treating in H_2 at 400°C. Following this preparation procedure, the surface area of the La_2O_3-supported samples would be expected to be between 10 and 15 m^2/g (*25*). The nominal surface area of the SiO_2 support was 300 m^2/g. All samples were passivated in air at room temperature and stored for future use.

Characterization

Rh weight loadings were determined via atomic absorption spectrophotometry (AAS) using a Perkin–Elmer AA Model 300. Rh metal was extracted from the oxide supports by dissolution in nitric acid. The presence of La^{3+} from dissolution of the La_2O_3 support did not interfere in the determination of Rh content.

H_2 (UHP grade, Linde) and CO (CP grade, Linde) were used to perform chemisorption measurements in a glass high-vacuum static gas volumetry system in which an ultimate vacuum of 10^{-6} Torr was attained. Each sample was rereduced in 0.5 atm of H_2 at 400°C for 2 h except for the Rh/La_2O_3 sample originally reduced at 200°C which was rereduced at 200°C. Samples were then evacuated to 10^{-6} Torr for 1 h at temperature following reduction to remove chemisorbed hydrogen. After cooling to room temperature under dynamic vacuum, each catalyst was exposed to approximately 300 Torr of H_2 and allowed 16 h to equilibrate before the total adsorption isotherm was measured. When this was completed, the sample was evacuated under dynamic vacuum at room temperature for 0.5 h to remove all but the irreversibly chemisorbed hydrogen. A second isotherm was measured and taken to be weakly adsorbed hydrogen. The difference between the first and second isotherm when extrapolated to zero pressure was taken as the irreversibly chemisorbed hydrogen. The sample was then heated to and held at its original reduction temperature while being evacuated under dynamic vacuum to again remove the chemisorbed hydrogen. After cooling to room temperature under vacuum, the total, reversible, and irreversible CO chemisorption were determined in a manner similar to that of the H_2 chemisorption. Reproducibility of ±6% was observed using this method.

X-ray diffraction was carried out on air-passivated samples on a Rigaku X-ray diffractometer using a Mo K_α source. Additional XRD measurements were made on a General Electric XRD-5 diffractometer using Cu K_α radiation.

XPS

X-ray photoelectron spectroscopy spectra were obtained using an AEI 200A spectrometer equipped with an aluminum anode operated at 12 kV and 20 mA. The base pressure of the sample chamber was below 10^{-8} Torr. The spectrometer was interfaced with an Apple II-plus microcomputer for data collection and storage. The catalyst samples were pressed as pellets and mounted on a sealable probe for reduction and XPS measurements. The sealable probe, which permitted the transfer of the reduced samples from an external reactor to the spectrometer without exposure to air, has been described elsewhere (*23*). Rereduction of the samples prior to XPS measurements was carried out at 400°C (or 200°C) under a 100 cc/min flow of H_2 for 2 h. Binding energy measurements generally were referenced to C 1*s* = 284.7 eV and are accurate to ±0.2 eV. Intensity ratios were obtained by measuring the areas under the desired peaks normalized to unit time per channel. The O 1*s* line was resolved using the GAMMET curve-fitting program which has been described previously (*24*).

Activity Measurements

Ethane hydrogenolysis and cyclopropane hydrogenation studies were carried out in a quartz U-tube microreactor heated by a tube furnace controlled by an Omega temperature controller with a chromel–alumel thermocouple in the catalyst bed. A nominal 100 cc/min, 3 mol% hydrocarbon reaction mixture was prepared by diluting a flow of ethane (research grade, Linde) or cyclopropane (99.0%, Matheson) into a stream of H_2 (UHP grade, Linde). Hydrocarbon flows were controlled by a needle valve and H_2 flow was controlled by a Brooks flow controller. Total flow rate was calibrated with a soap bubble meter. The reactor feed and reaction products were analyzed with an on-line Varian 3700 gas chromatograph equipped with a FID detector and a 30 ft × 1/8 in, 23% SP-1700 80/100 Chromosorb column. The reactor was operated under differential conditions by keeping total hydrocarbon conversion below 10% and by using 100 mg of catalyst, except for the cyclopropane reaction over Rh/SiO_2, where 20 mg was used because of the high activity of the sample. Products were sampled after 10 min on stream with a 30-min H_2 bracket between runs at reaction temperature to prevent catalyst deactivation from a buildup of carbonaceous species.

RESULTS

Chemisorption

Chemisorption results for the catalysts in this study are summarized in Table 1. Total and irreversible H_2 and CO uptakes are listed on an adsorbed atom per total Rh atom basis. H_2 and CO adsorption for the Rh/SiO_2 sample were in close agreement. For the La_2O_3-supported samples several points should be made. First, the H_2 and CO uptakes were not in close agreement. The CO_{irr}/H_{irr} ratio was 0.46 for the 200°C sample, declining to 0.15 for the 400°C-reduced sample. Second, the H_2 uptake increased as the reduction temperature was increased from 200 to 400° while the CO uptake declined.

XRD

XRD was performed on the freshly reduced samples. A mixture of LaOOH and La_2O_3 was observed for the support, the 400°C-reduced catalyst, and the La_2O_3 blank. The only detected phase for the

TABLE 1

H_2 and CO Chemisorption Results

Catalyst	H/Rh[a]		CO/Rh[a]		CO/H
	Total	Irr.	Total	Irr.	Irr.
3.0% Rh/SiO_2(R400)[b]	0.78	0.63	0.67	0.63	1.0
2.9% Rh/La_2O_3(R200)[b]	0.39	0.28	0.14	0.13	0.46
2.9% Rh/La_2O_3(R400)[b]	0.55	0.52	0.08	0.08	0.15

[a] H atoms or CO molecules adsorbed per total Rh atoms present.

[b] Indicates original reduction temperature.

200°C-reduced sample was $La(OH)_3$. However, the presence of Rh cannot be ruled out on these freshly reduced catalysts since *d* spacings for the major reflections of Rh overlap those of LaOOH. However, both La_2O_3 and LaOOH react with moisture from room air reverting in time to $La(OH)_3$ (*25–27*) which does not interfere with Rh. No signal from Rh was observed from XRD performed on passivated samples indicating metal particles sizes <4.0 nm. TEM was also performed on these catalysts. The TEM micrographs for the SiO_2-supported catalyst confirm particles of the size (approximately 1.7 nm) indicated by the chemisorption results. Micrographs for the La_2O_3-supported samples were inconclusive due to the previously noted low contrast between Rh and La_2O_3 (*7*).

XPS

XPS results for these catalysts are summarized in Tables 2–4 and Figs. 1–3. The Rh/Si and Rh/La XPS signal intensity ratios are shown in Table 2. Increasing the reduction temperature from 200 to 400° resulted in a decline in the Rh/La XPS signal intensity ratio from 0.089 to 0.069, respectively. Rh $3d_{3/2}$ and Rh $3d_{5/2}$ spectra for the three catalysts in reduced form are shown in Fig. 1. Binding energies were referenced to C 1*s* = 284.7 eV. For the SiO_2-supported samples this resulted in a binding energy for Si 2*p* = 103.8 eV. In each case only metallic Rh was observed. Binding energies in the reduced and air-passivated forms are summarized in Table 2. The values of 307.4 and 307.0 eV for the passivated SiO_2-supported and La_2O_3-supported catalysts, respectively, are close to the 307.2-eV value expected for Rh^0 and this suggests that the passivated Rh particles were not heavily oxidized. Upon reduction, the Rh $3d_{5/2}$ binding energy for the La_2O_3-supported samples exhibited a negative shift relative to the SiO_2-supported sample. After a 400°C reduction, the $3d_{5/2}$ binding energy for Rh/SiO_2 was 307.0 eV while that for the La_2O_3-supported sample was 306.1 eV. The $3d_{5/2}$ binding energy for the 200°C-reduced Rh/La_2O_3 sample was 306.0 eV indicating no effect of reduction temperature on this phenomenon.

The sensitivity of La_2O_3 to its environment has been well documented (*9, 25, 26–28*), forming hydroxides and carbonates upon exposure to aqueous impregnating solutions or even room air. The changes undergone by the La_2O_3-support materials in this study can be seen in Figs. 2 and 3 and are summarized in Tables 3 and 4. The La 3*d* spectra exhibited the characteristic doublet splitting with satellite peaks upscale from the $3d_{5/2}$ and $3d_{3/2}$ peaks (*9*). The O 1*s* peak at approximately 530.9 eV can be assigned to hydroxide (OH^-) and carbonate (CO_3^{-2}) oxygen (*9*) while that at about 528.3 eV can be assigned to lattice oxygen (O^{-2}) (*9*). The C 1*s* peak at 289.5 eV is characteristic of carbonate carbon (*9*) while the lower energy peak is attributed to adventitious carbon and assigned a reference value of 284.7 eV.

The only O 1*s* peak observed in the pas-

TABLE 2

Binding Energy and XPS Signal Intensity Ratio Results for Rh

Catalyst	Treatment	Rh binding energies		Rh 3d/Si 2p or Rh 3d/La $3d_{5/2}$
		$3d_{5/2}$ (eV)	$3d_{3/2}$ (eV)	
Rh/SiO_2(R400)[a]	Passivated	307.4	312.0	0.142
	400°C rereduction	307.0	311.6	0.097
Rh/La_2O_3(R400)[a]	Passivated	307.0	311.7	0.060
	400°C rereduction	306.1	310.8	0.069
Rh/La_2O_3(R200)[a]	200°C rereduction	306.0	310.6	0.089
Rh metal		307.2	—	—
Rh_2O_3		309.1	—	—

[a] Indicates original reduction temperature.

sivated blank was that of the hydroxide at 530.9 eV. The presence of carbonate species was also indicated by the C 1s peak at 289.5 eV. This suggests that the passivated blank was primarily carbonated $La(OH)_3$. The hydroxide/carbonate oxygen peak diminished with treatment in H_2 at 400°C as evidenced by a decline in the hydroxide/carbonate XPS O/La ratio from 0.69 to 0.12 (see Table 4). Concurrently, a peak at 528.2 eV for lattice oxygen was observed and the XPS O/La ratio for it grew to 0.21. The carbonate carbon peak also diminished after a 400°C treatment with the carbonate C/La XPS signal intensity ratio dropping from 0.030 to 0.015. Accompanying these changes was a shift in the La $3d_{5/2}$ peak from 834.6 to 832.7 eV and an increase in the satellite split from 3.6 to 4.4 eV as has been observed and discussed elsewhere (9).

The passivated form of the Rh/La_2O_3 catalyst is that which was originally reduced at 400°C. In this case both hydroxide and oxide oxygen were present as indicated by peaks at 530.8 and 528.9 eV, respectively. In addition, the La $3d_{5/2}$ peak was at a lower value of 833.8 eV with a larger satellite split of 4.0 eV than the La_2O_3 blank. This indicates that this sample was not fully converted to the hydroxide form during passivation. However, the carbonate C/La XPS signal intensity ratio was 0.029 for the Rh/La_2O_3 sample vs 0.030 for the passivated blank indicating a similar level of carbonation. After reduction at 400°C, the hydroxide/carbonate oxygen O/La XPS signal intensity ratio dropped to 0.12 while the oxide O/La XPS ratio grew to 0.23. These levels are nearly identical to those of the blank La_2O_3 following similar treatment. In contrast to the blank La_2O_3, however, the peak at 289.3 due to carbonate carbon was completely eliminated.

The features of the 200°C-reduced Rh/La_2O_3 were very similar to the passivated blank La_2O_3. The hydroxide/carbonate O/La XPS signal intensity ratio was 0.63 with an oxide O/La XPS intensity ratio of 0.07 and the carbonate C/La ratio was 0.030. The La $3d_{5/2}$ peak was observed at 834.3 eV with a satellite split of 3.5 eV. These observations are consistent with a carbonated $La(OH)_3$ support. This sample was not studied in the passivated form but would be expected to be similar to the passivated blank La_2O_3.

Ethane Hydrogenolysis

Ethane hydrogenolysis results are summarized in the form of Arrhenius plots in Fig. 4. For comparison purposes, the rate per gram catalyst and TOF based on CO chemisorption, extrapolated via the Arrhen-

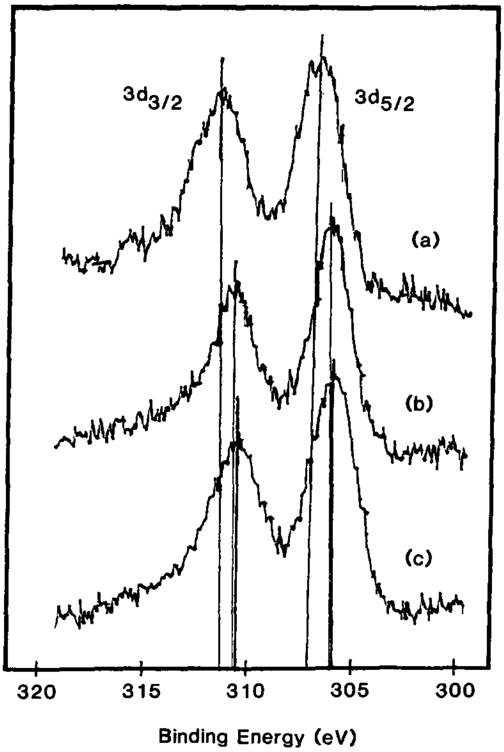

FIG. 1. Rh 3*d* XPS spectra of reduced Rh catalysts: (a) Rh/SiO_2; (b) Rh/La_2O_3—400°C reduced; (c) Rh/La_2O_3—200°C reduced.

ius data to 300°C, are listed in Table 5. Activity measurements were made for the Rh/SiO_2 catalyst between 225 and 260°C while those for both the 200°C- and the 400°C-reduced Rh/La_2O_3 samples were made between 275 and 325°C. Temperatures of 375 to 425°C were required to observe activity on the blank. Rate per gram catalyst dropped by over two orders of magnitude and TOF fell by a factor of 25 for the 400°C-reduced catalysts in going from SiO_2 to La_2O_3 as the support. In addition, the apparent activation energy was 45 kcal/mol for Rh/SiO_2 compared to 32 kcal/mol for the 400°C-reduced Rh/La_2O_3. The only observed effects of reduction temperature for the two La_2O_3-supported catalysts were a factor of 2 increase in TOF and a drop in apparent activation energy from 40 to 32 kcal/mol as the reduction temperature was increased from 200 to 400°C. It should be noted that the temperature range necessary for observable ethane hydrogenolysis activity (i.e., 275 to 325°C) for the 200°C-reduced catalyst was *significantly above* its reduction temperature. Activity over the La_2O_3 blank was nearly three orders of magnitude lower than that on the Rh/La_2O_3 catalysts and exhibited an apparent activation energy of 30 kcal/mol.

Cyclopropane Hydrogenation

The results for cyclopropane hydrogenation in Arrhenius form can be found in Fig. 5. Rh/SiO_2 exhibited activity for this reaction between −16 and 0°C but the amount of catalyst had to be reduced from 100 to 25 mg in order to maintain differential conditions. Activity measurements were made for the 200°C-reduced Rh/La_2O_3 between 85 and 125°C, while temperatures between 160 and 230°C were required for the 400°C-reduced sample. Activity over the blank was observed from 275 to 375°C. Rate per gram catalyst and TOF based on CO uptake were extrapolated using the Arrhenius data to 150°C for comparison purposes and are given in Table 5. A more than two orders of magnitude drop in rate per gram catalyst and a factor of 40 decline in TOF can be seen in going from the Rh/SiO_2 catalyst to the 200°C-reduced Rh/La_2O_3 catalyst. An additional two orders of magnitude decrease in rate per gram catalyst and TOF was observed as the reduction temperature was increased to 400°C. This sample, however, was two orders of magnitude more active than the blank La_2O_3. The apparent activation energy for Rh/SiO_2 was 9 kcal/mol. Values observed over the La_2O_3-supported samples were 15, 14, and 15 kcal/mol for the 200°C-reduced, 400°C-reduced, and La_2O_3 blank, respectively.

The reaction of cyclopropane with H_2 can proceed via three pathways: (1) ring opening to propane, (2) a simple hydrogenolysis to ethane and methane, and (3) a double hydro-

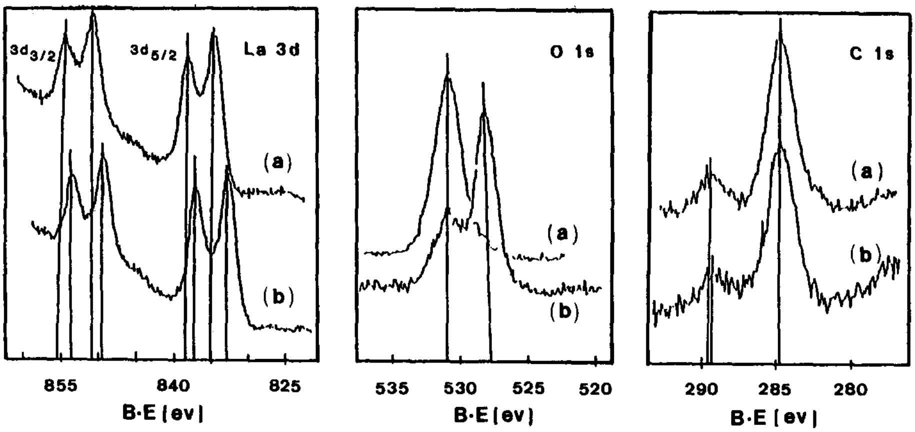

FIG. 2. XPS spectra of support elements for an air-passivated and reduced La_2O_3 blank: (a) passivated; (b) reduced.

genolysis to methane only. Under differential conditions only ring opening was observed over Rh/SiO_2 while some simple hydrogenolysis to ethane and methane was observed over both Rh/La_2O_3 samples. This simple hydrogenolysis accounted for approximately 5% of the cyclopropane converted over the 200°C-reduced Rh/La_2O_3 and nearly 10% of the cyclopropane reacted over the 400°C-reduced Rh/La_2O_3. This selectivity appeared to be a function of the reaction temperature rather than the catalyst, since the same product distributions were observed over Rh/SiO_2 when the reaction was run at the temperatures where the La_2O_3-supported catalysts exhibited activity. It was a primary reaction since propane hydrogenolysis activity in each case was only observed in the higher temperature range where ethane hydrogenolysis activity was also observed. The La_2O_3 blank exhibited nearly 50% selectivity for the isomerization product propene.

DISCUSSION

The results presented above clearly illustrate the significant impact that lanthana as a support can have on the properties of Rh. Previous studies with Pd/La_2O_3 and Rh/La_2O_3 have suggested a decoration of metal crystallite surfaces with some form of a lanthana moiety (*4*, *9*, *7*, *11*).

Comparing the 400°C-reduced catalysts, CO uptake was lower for Rh/La_2O_3 than Rh/SiO_2. This could be due to lower Rh dispersion on La_2O_3 vs SiO_2. However, a comparison with the XRD results suggests that the CO chemisorption underestimates Rh dispersion. This may be indicative of decoration of the Rh surface which blocks adsorption sites in agreement with previous observations (*7*, *8*, *12*, *28*). This is also consistent with the suppression of the ethane hydrogenolysis and cyclopropane hydrogenation reactions which indicate a breakup of reaction ensembles.

The lack of a severe impact of use of La_2O_3 as the support on H_2 adsorption has been taken as a sign of spillover from the metal to the decorating species and, perhaps, the support (*7*, *8*, *12*, *28*). In the present case an increase of reduction temperature was observed to cause an increase in hydrogen adsorption. The Rh/La XPS signal intensity ratio serves as an independent measure of dispersion and indicates decreasing dispersion with increasing reduction temperature. This would be expected if sintering of the metal particles occurred at the higher reduction temperature. Based on

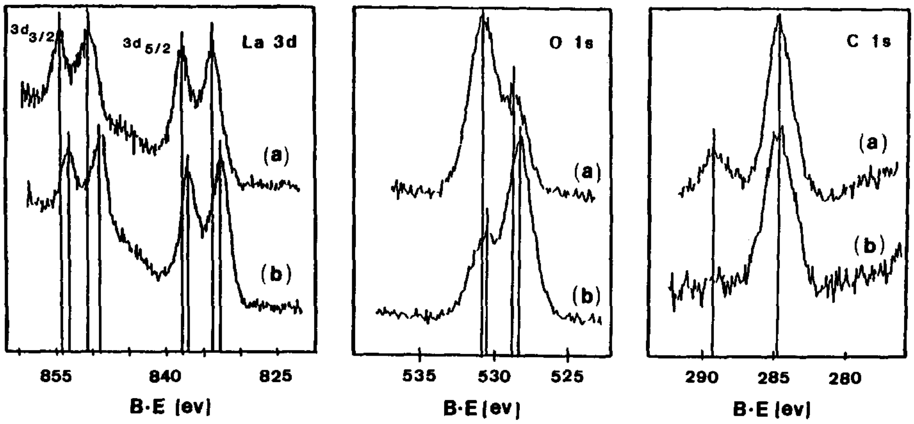

FIG. 3. XPS spectra of support elements for air-passivated and reduced Rh/La_2O_3 catalysts: (a) passivated; (b) reduced.

dispersion arguments alone, a decrease in CO and H_2 chemisorption would be expected. This would appear to be the case for CO uptake, although, possible differences in adsorption stoichiometry and the formation of carbonate and formate species (*7, 28*) from the reaction of CO with –OH groups in the $La(OH)_3$ and LaOOH phases known to be present after treatment at these temperatures could complicate this interpretation. Interaction of CO with the support would tend to overestimate the free Rh surface area. The trend for H_2 adsorption runs contrary to that expected based on dispersion. This result fits an hypothesis that the ability of the decorating species and/or the support to accept spillover hydrogen is increased by an increase in the dispersion of the decorating species or by a change in the composition of the decorating species and support after the higher reduction temperatures.

The nearly −1-eV shift in the Rh $3d_{5/2}$ binding energy for the La_2O_3-supported catalysts vs Rh/SiO_2 is similar to the observations of Fleisch *et al.* (*9*) for the Pd/La_2O_3

TABLE 3

Elemental Binding Energies (eV) for La_2O_3 Support

Sample	Treatment	O		C		La	
		1s (OH^- and CO_3^{-2})	(O^{-2})	1s (CO_3^{-2})	(Adv. C)[b]	$3d_{5/2}$	Split[a]
La_2O_3 blank	Passivated	530.9	—	289.5	284.7	834.6	3.6
	400°C rereduction	530.9	528.2	289.2	284.7	832.7	4.4
Rh/La_2O_3(R400)[c]	Passivated	530.8	528.9	289.3	284.7	833.8	4.0
	400°C rereduction	530.5	528.3	—	284.7	832.8	4.5
Rh/La_2O_3(R200)[c]	200°C rereduction	530.6	528.5	288.5	284.7	834.3	3.5

[a] Upscale shift of satellite peak from main peak.
[b] Reference peak.
[c] Indicates original reduction temperature.

TABLE 4

XPS Signal Intensity Ratios for La_2O_3 Support Elements

Sample	Treatment	(O 1*s*)/(La $3d_{5/2}$)		(C 1*s*)/(La $3d_{5/2}$)	
		531 eV	528 eV	289 eV	285 eV
La_2O_3 blank	Passivated	0.69	0	0.030	0.155
	400°C rereduction	0.12	0.21	0.015	0.053
Rh/La_2O_3(R400)[a]	Passivated	0.26	0.09	0.029	0.095
	400°C rereduction	0.12	0.23	0	0.050
Rh/La_2O_3(R200)[a]	200°C rereduction	0.63	0.07	0.030	0.044

[a] Indicates original reduction temperature.

system. In that study, a negative binding energy shift of up to −0.7 eV was attributed to coverage of the Pd crystallites by support material ($La(OH)_3$, LaOOH, La_2O_3) which was subsequently reduced to "LaO_x" resulting in charge transfer from the LaO_x to the Pd. In the present study, the binding energy shift was observed after a 200°C reduction. No additional shift was observed after reduction at 400°C. This suggests either that 200°C reduction is sufficient to partially reduce the overlayer (which is not observed for the bulk support; see discussion below) or that decoration by carbonated $La(OH)_3$ is sufficient to produce the phenomenon. The latter interpretation implies that no reduction of lanthana moieties is required to produce negative binding energy shifts. Supporting the concept that negative binding energy shifts can be observed without reduction of decorating species is a study of alkali-promoted Ru/SiO_2 by Shyu *et al.* (*29*). In this study, negative binding energy shifts were attributed to a modification of the extraatomic relaxation with possible charge transfer from highly polarized, alkali compounds.

Other possible explanations for the observed difference in Rh $3d_{5/2}$ binding energy for SiO_2- and La_2O_3-supported Rh must also be considered. First, it is possible that the binding energy was shifted positively in the case of the highly dispersed Rh/SiO_2 as a result of the small Rh particle size. To check this a Rh/SiO_2 catalyst, which H_2 chemisorption suggested had an average particle size of 6.9 nm, was run and the same 307.0 eV binding energy for Rh $3d_{5/2}$ was observed. Second, it is possible that binding energy of the adventitious C 1*s* peak used as a reference may differ when going from SiO_2 to La_2O_3 as the support. Fleisch *et al.* (*9*) justified the use of graphitic carbon as a reference in Pd/La_2O_3 based on the agreement between the Pd $3d_{5/2}$ binding energies of Pd foil and mixtures of Pd-black and La_2O_3, as well as the agreement between reported and observed values of the Pd $3d_{5/2}$

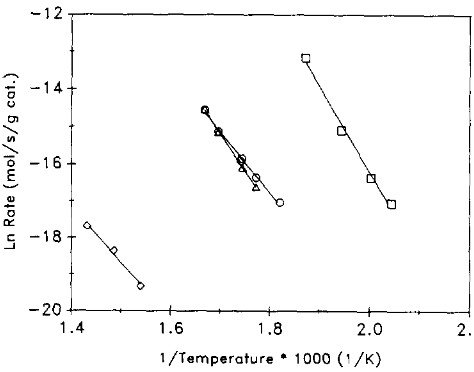

FIG. 4. Arrhenius plots for ethane hydrogenolysis over 3% Rh catalysts: (□) Rh/SiO_2; (△) Rh/La_2O_3—200°C reduced; (○) Rh/La_2O_3—400°C reduced; (◇) La_2O_3 blank.

TABLE 5

Cyclopropane Hydrogenation and Ethane Hydrogenolysis Activity Data[a]

Catalyst	Reduction temperature (°C)	Cyclopropane activity at 150°C		Ethane activity at 300°C	
		Rate (mol/s/g cat) × 10^6	TOF[b] (s^{-1}) × 10^3	Rate (mol/s/g cat) × 10^7	TOF[b] (s^{-1}) × 10^3
3.0% Rh/SiO_2	400	1230	6310	313	161
2.9% Rh/La_2O_3	200	6.33	154	1.05	2.55
2.9% Rh/La_2O_3	400	0.0404	1.89	1.29	6.04
La_2O_3 blank	400	0.0004	—	0.0018	—

[a] Extrapolated via Arrhenius data.

[b] Based on total CO uptake.

binding energies for both palladium chloride precursors and the PdO formed upon calcining their catalysts. The binding energies reported here for the support elements are in excellent agreement with those reported in that study. However, results from a study of alkali-promoted Rh/La_2O_3 (*30*) observed the binding energy of Rb $3p_{3/2}$ to be shifted negatively by the same 1 eV as Rh $3d_{5/2}$ for $Rb/Rh/La_2O_3$ when compared to $Rb/Rh/SiO_2$. While it is possible that the state of Rb is different between SiO_2-supported and La_2O_3-supported catalysts, the similarity in the binding energy shifts for Rh and Rb suggests that carbon referencing may be a problem.

The changes undergone by the La_2O_3 support after treatment in H_2 at 400°C were qualitatively consistent with the dehydration of $La(OH)_3$ and decomposition of $La_2(CO_3)_3$ reported elsewhere (*9, 25–27*). For the blank, the form after treatment ap-

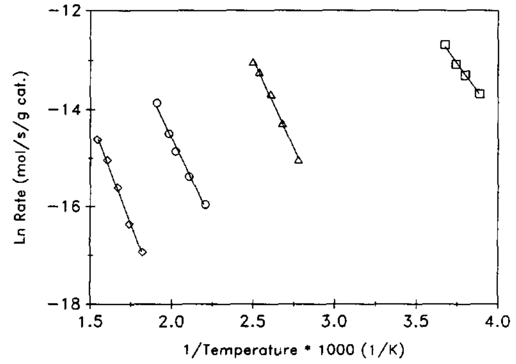

FIG. 5. Arrhenius plots for cyclopropane hydrogenation over 3% Rh catalysts: (□) Rh/SiO_2; (△) Rh/La_2O_3—200°C reduced; (○) Rh/La_2O_3—400°C reduced; (◇) La_2O_3 blank.

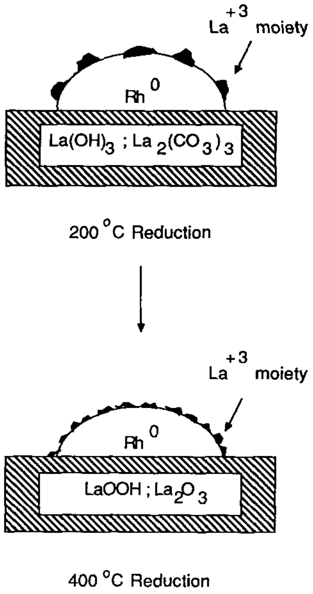

FIG. 6. Schematic depicting change in decorative overlayer with increasing reduction temperature for Rh/La_2O_3.

pears to have been a mixture of LaOOH and La_2O_3 along with some carbonate species. Contrary to the results reported for Pd (*9*), the presence of Rh did not appear to accelerate the dehydration process since both the Rh/La_2O_3 and the La_2O_3 blank samples had the same final hydroxide–carbonate and oxide O/La XPS signal intensity ratios. However, Rh did appear to catalyze the decomposition of the carbonate as evidenced by the lack of a C 1*s* peak attributable to CO_3^{-2} after reduction at 400°C in agreement with the results of Bernal *et al.* (*26, 27*). Reduction at 200°C resulted in a carbonated, hydroxide phase similar to the blank passivated in air.

For structure-sensitive reactions, changes in metal dispersion result in changes in rate. For ethane hydrogenolysis, an increase in rate with increasing dispersion has been observed (*13*). Over Rh, Yates and Sinfelt observed a 20-fold increase in rate per square meter of metal as dispersion increased from 0.42 to 94% (*13*). Specific rate, however, was significantly lower for higher metal dispersion. Higher hydrogenolysis activity has been attributed to large ensembles (*15*) and open surface morphology (*32*). As the particle size decreases, the site concentration of low index plane ensembles increase due to an increase in the relative amounts of low index planes resulting in an increase in specific activity. In the limit of decreasing particle size, however, the specific rate eventually must decline due to the lack of sufficiently large surface ensembles on the facets of the small metal crystallites. Cyclopropane hydrogenation over supported Pt is considered a classic example of structure insensitivity (*19*). However, increasing activity with increasing dispersion has been observed over supported Ru (*22*). Structure insensitivity has been suggested over supported Ni (*31*), while studies over single crystal Ni have indicated structure sensitivity (*32*). For Rh, an increase in conversion by a factor of 4 was observed by Wong *et al.* (*21*) as dispersion increased from 23 to 91%, suggesting that activity on a TOF basis was invariant and that if cyclopropane hydrogenation is structure sensitive over this metal, it is only moderately so.

Insight into the impact of decorative effects on structure-sensitive and structure-insensitive reactions has been gained from the study of bimetallic catalysts where one component is much less active than the other. In Ni–Cu catalysts, Cu is inactive for hydrogenation and hydrogenolysis reactions and preferentially segregates to the particle surface. The addition of small amounts of Cu, which is inactive for ethane hydrogenolysis, to Ni results in a dramatic suppression of activity which then declines more gradually with further Cu addition (*14*). For cyclohexane dehydrogenation (*14*) and cyclopropane hydrogenation (*31*), however, activity remains nearly constant until very high Cu contents before falling precipitiously. Similar observations have been made for ethane hydrogenolysis and cyclopropane hydrogenation over Rh–Ir catalysts (*21*), where Ir is much less active than Rh. This behavior is interpreted as a breakup of the large ensembles required for the structure-sensitive ethane hydrogenolysis upon even small addition of the inactive component. For the structure-insensitive reactions which require smaller ensembles, the TOF does not decline until the active component is almost entirely replaced.

The metal–support interaction between Rh and La_2O_3 can readily be seen from the impact on the ethane hydrogenolysis and cyclopropane hydrogenation reactions. The XRD measurements indicate that Rh dispersion is greater than ca. 30%. In going from the SiO_2-supported to the La_2O_3-supported catalyst reduced at 400°C, a drop of over two orders of magnitude was observed in ethane hydrogenolysis activity on a rate/gram catalyst basis while the decline was by a factor of 25 on a TOF basis at 300°C. A decline in cyclopropane hydrogenation rate on a per gram catalyst basis of over four orders of magnitude and a decline on a TOF basis of over three orders of magnitude were observed at 150°C. It should be noted that as a result of interaction between CO and the La_2O_3 support to form carbonate and formate species (*7, 28*), TOF on a CO uptake basis may be slightly underestimated. The magnitude of suppression for each reaction is much larger than can be accounted for by a change in metal dispersion alone, and is indicative of extensive decoration by La_2O_3 moieties which physically block the Rh surface thereby breaking up ensembles for both reactions.

For ethane hydrogenolysis, no difference in rate/gram catalyst and a small increase in TOF of factor of 2 were observed with increasing reduction temperature suggesting that the extent of decoration after the lower temperature treatment was sufficient to break up most of the ensembles active as reaction sites. Again it is noted that the 200°C-reduced catalyst had to be run at temperatures nearly 100°C above its reduction temperature in order to observe ethane hydrogenolysis activity. Therefore, these reaction results should be taken as indicative of the surface after the higher temperature treatment. A few sites remain which are unaffected even after the higher reduction temperature. Similar observations have been made for alkane hydrogenolysis reactions over extensively decorated Rh/TiO_2 systems (*33, 34*).

The apparent activation energy of 45 kcal/mol observed for ethane hydrogenolysis over Rh/SiO_2 compares well with the value of 42 kcal/mol reported by Yates and Sinfelt (*13*). The lowering of the apparent activation energy over Rh/La_2O_3 from 40 to 32 kcal/mol as reduction temperature was increased from 200 to 400°C may indicate a shift in the route for hydrogenolysis. Such a decrease has been previously attributed to an increase in the extent of dehydrogenation of the C_2H_x surface species which undergo C–C bond scission (*35, 36*).

For cyclopropane hydrogenation, a decline in rate/gram catalyst of two orders of magnitude and an 80-fold drop in the TOF were observed as the reduction temperature was increased from 200 to 400°C. Again, the magnitude of the decline when compared to changes in metal dispersion from XRD, XPS Rh/La ratios, and CO chemisorption suggests further decoration of the surface. This increase in extent of decoration is consistent with the decline in CO uptake with increasing reduction temperature previously noted. The apparent activation energies observed for cyclopropane hydrogenation over all samples studied compare favorably with the value of 11 kcal/mol reported by Dalla Betta *et al.* (*20*).

The large magnitude of suppression for both of these reactions suggests that decoration was extensive regardless of reduction temperature since island formation of the decorating species would leave large islands of active Rh surface (*18*). The fact that the La_2O_3-supported Rh exhibited much higher activity than the blank La_2O_3 suggests that the Rh particles were not completely encapsulated and had sites available consisting of more than single Rh atoms.

SUMMARY

The metal–support interaction between Rh and La_2O_3 in the reduced catalyst has been found to result in a suppression of CO chemisorption, a negative shift of nearly 1 eV in the Rh $3d_{5/2}$ binding energy, and a drastic suppression in the rates of ethane hydrogenolysis and cyclopropane hydrogenation in comparison to Rh/SiO_2. These effects are consistent with the proposed model of decoration of the Rh crystallites with support species. They were observed even after reduction at 200°C, a temperature insufficient to induce change in the $La(OH)_3$ and $La_2(CO_3)_3$ which constitute the support after impregnation or exposure to air. The presence of these effects after such a mild pretreatment suggests that dissolution of the support by acidic precursor solutions during impregnation/drying or migration of support species during the early stages of reduction is probably the primary cause of the decoration. The decorative overlayer is modified by reduction at 400°C resulting in a further suppression of CO chemisorption and cyclopropane hydrogenation rate and in an increase in H_2 chemisorption. This modification is probably due to an increase in the extent of decoration and occurs concurrently with dehydration of the $La(OH)_3$ in the support to LaOOH and La_2O_3 and a Rh-accelerated decomposition of the $La_2(CO_3)_3$ (see Figure 6).

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