JOURNAL OF CATALYSIS **140**, 453–463 (1993)

XPS and Reaction Investigation of Alkali Promotion of Rh/La_2O_3

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Received November 6, 1991; revised October 28, 1992

In order to investigate the combined effect of a promoter and a detached support species on a supported metal catalyst, alkali promotion of Rh on the decorative support La_2O_3 was investigated by X-ray photoelectron spectroscopy, X-ray diffraction, H_2 and CO chemisorption, ethane hydrogenolysis, and cyclopropane hydrogenation. Previously, decorating lanthana moieties have been found to partially suppress ethane hydrogenolysis and cyclopropane hydrogenation on Rh/La_2O_3. The major effects of alkali promotion of Rh/La_2O_3 on these reactions were a decline in apparent activation energy for ethane hydrogenolysis and a moderate additional suppression of cyclopropane hydrogenation activity. Alkali promotion of the more active Rh/SiO_2 reference catalyst, which is not decorated by support entities, resulted in a much more significant suppression of these reactions. For Rh/La_2O_3, alkali promotion appeared to block sites and/or pathways for hydrogen spillover. In addition, Rb inhibited the Rh-catalyzed decomposition of carbonate species on the lanthana support. No additional effect of alkali promotion was indicated on the -1-eV shift of Rh $3d_{5/2}$ binding energy observed on Rh/La_2O_3 relative to Rh/SiO_2. This is consistent with the lack of a Rh $3d_{5/2}$ binding energy shift observed for Rb-promotion of Rh/SiO_2. The Rb $3p_{3/2}$ binding energy was shifted to the same extent as Rh in $Rb/Rh/La_2O_3$, suggesting that the chemical environment for Rb differs between SiO_2-supported and La_2O_3-supported systems or, more likely, that the binding energy shifts observed for this system are just due to differences in the binding energies for the reference carbon on SiO_2 vs on La_2O_3. © 1993 Academic Press, Inc.

INTRODUCTION

The impact that the support (*1–8*) and alkali promoters (*9–12*) can have on the catalytic properties of Rh for CO hydrogenation has been the subject of considerable research. Changes in the selectivity and/or activity of transition metals upon alkali promotion have been variously attributed to electronic effects involving charge transfer from the promoter to the metal resulting in an increase in electron density on the metal (*13, 14*), an electrostatic effect due to the strong field surrounding the highly polar alkali species (*15*), chemical interactions between adsorbates and alkali species (*16*), and geometric effects where decoration of the metal surface breaks up large ensembles of contiguous metal atoms with the subsequent suppression in rate for reactions requiring large ensembles (*11, 17, 18*). In the case of supports where decorative support–metal interactions appear to exist (e.g., SMSI supports such as TiO_2 or materials such as La_2O_3 where support species decoration is indicated) similar effects may be supposed (*7, 19–22*).

Differentiating between the various possible promoter roles and effects is further complicated when alkali promoters and interactive supports are simultaneously present. For example, Chuang has studied the effect of alkali promotion on CO hydrogenation over Rh/SiO_2, Rh/TiO_2, and Rh/La_2O_3 (*5, 10, 23*). In all cases, total activity was partially suppressed upon addition of alkali. Rh/TiO_2 was found to be very active toward hydrocarbon production, and alkali promotion resulted in an increase in oxygenate selectivity. Rh/SiO_2 was selective

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0021-9517/93 $5.00

for C_2 oxygenates and this selectivity was suppressed by promotion in favor of C_2 hydrocarbons. In the unpromoted form, Rh/La_2O_3 was selective for methanol production. C_2 oxygenate selectivity was enhanced for a Li-promoted catalyst, unchanged for a K-promoted catalyst, and suppressed for a Cs-promoted catalyst.

The objective of this study was to explore the nature of the interactions between metal and promoters in a system where alkali species and decorative support species both act as promoters. K- and Rb-promoted and unpromoted Rh/La_2O_3 were studied along with Rb-promoted and unpromoted Rh/SiO_2 for comparison purposes. These systems were probed using H_2 and CO chemisorption, XRD, XPS, and ethane hydrogenolysis and cyclopropane hydrogenation reactions. Because of the relatively large ensemble of surface atoms required to constitute a reaction site for the structure-sensitive ethane hydrogenolysis (*24–26*), this reaction has been found to be sensitive to decorative effects (*19, 27–30*). As a result of the smaller ensemble required for cyclopropane hydrogenation to propane (*29, 31–33*), it should be useful in probing surface details in highly decorated systems.

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. K- and Rb-promoted Rh/La_2O_3 and Rb-promoted Rh/SiO_2 were prepared by impregnating the dried samples to incipient wetness with aqueous solution of K_2CO_3 or $RbNO_3$ followed by redrying overnight at 90°C. A promoter level of 0.5 alkali atoms per Rh atom ratio was used. The catalysts were reduced after final impregnation and drying by heating in 100 cc/min of flowing H_2 (UHP grade, Linde) at 2°C/minute from 25 to 400°C, then holding at 400°C 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. 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 dissolving in nitric acid. The presence of La^{+3} from dissolution of the support did not interfere with 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 and desorbed for 1 h under vacuum at temperature. Total H_2 and CO isotherms were measured at room temperature after being exposed to 300 Torr of the respective gas for 16 h. Reversible isotherms were then determined after evacuating the samples for 30 min. 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 spectrometer using Cu K_α radiation.

XPS 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 sealed probe for reduction and XPS measurements. The sealable probe, which permitted the transfer of the reduced samples from an external reactor

TABLE 1

H_2 and CO Chemisorption Results

Catalyst	Alkali promotion ratio	H/Rh[a]		CO/Rh[a]		*CO/H* Irr.
		Total	Irr.	Total	Irr.	
3.0% Rh/SiO_2	None	0.78	0.63	0.67	0.63	1.0
2.9% Rh/SiO_2	Rb/Rh = 0.5	0.89	0.54	0.43	0.38	0.70
2.9% Rh/La_2O_3	None	0.55	0.52	0.08	0.08	0.15
2.8% Rh/La_2O_3	K/Rh = 0.5	0.27	0.22	0.07	0.07	0.32
2.4% Rh/La_2O_3	Rb/Rh = 0.5	0.12	0.10	0.03	0.03	0.28

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

to the spectrometer without exposure to air, has been described elsewhere (*34*). Rereduction of the samples prior to XPS measurements was carried out at 400°C under a 100 cc/min flow of H_2 for 2 h. Binding energy measurements were referenced to C 1s = 284.7 eV unless otherwise noted 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 1s line was resolved using the GAMMET curve fitting program which has been described previously (*35*).

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). The reactor feed and reaction products were analyzed with an on-line Varian 3700 gas chromatograph equipped with an 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. Activity measurements were made in order of increasing reaction temperature. Before ending a run, activity at a lower temperature was re-checked to ensure that no change occurred in the catalyst. 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 build up of carbonaceous species. With the system and techniques used in this study, reaction rates were reproducible to within ±6%.

RESULTS

Hydrogen and CO chemisorption results for the catalysts in this study are summarized in Table 1 on an absorbed atom per total Rh atom basis. The Rh/Si and Rh/La XPS signal intensity ratios are listed in Table 2, along with those for the promoter species. For Rh/SiO_2 the effect on H_2 chemisorption was mixed with total uptake increasing from 0.78 to 0.89, while the irreversible declined from 0.63 to 0.54. Alkali promotion resulted in a partial suppression of both total and irreversible CO chemisorption. The declines in irreversible adsorption were such that the irreversible CO/H ratio fell from 1.0 to 0.70 upon promotion.

For the lanthana-supported samples, the Rh/La XPS signal intensity ratio increased from 0.069 to 0.084 for the unpromoted vs the K-promoted sample, respectively. This

TABLE 2

XPS Signal Intensity Ratio Results

Catalyst	Rh/support ratio Rh $3d$/Si $2p$ or Rh $3d$/La $3d_{5/2}$	Promoter/support ratio Rb $3p_{3/2}$ or K $2p_{3/2}$ per Si $2p$ or La $3d_{5/2}$
Rh/SiO_2	0.097	—
$Rb/Rh/SiO_2$	0.089 ± 0.008	0.091 ± 0.033
Rh/La_2O_3	0.069	—
$K/Rh/La_2O_3$	0.084 ± 0.006	0.168 ± 0.022
$Rb/Rh/La_2O_3$	0.036	0.11

ratio fell to 0.036 for the Rb-promoted catalyst. Both total and irreversible H_2 uptake fell upon promotion with K. As discussed previously (*7, 8, 22, 36, 37*), CO chemisorption is suppressed with lanthana as the support. The addition of K had little effect on CO uptake. Both H_2 and CO uptake were significantly less for Rb/Rh/La_2O_3, although the $(CO/H)_{irr}$ remained fairly constant.

Changes in the support as a function of reduction temperature have been discussed elsewhere (*44*). XRD indicated that the as-received support and the support following impregnation were $La(OH)_3$. A mixture of $La(OH)_3$, LaOOH, and La_2O_3 were observed after 400°C reduction. In this study, XRD was performed on the reduced catalysts after exposure overnight to room air. As noted previously (*7, 22*), the diffraction lines for LaOOH, which is formed after treatment in H_2 at 400°C, interfere with those of Rh. The exposure of the catalyst to room air overnight, however, results in conversion of La_2O_3 and LaOOH to $La(OH)_3$ and $La_2(CO_3)_3$ (*38–40*) which do not overlap with the reflections from Rh. No signal was observed from these samples suggesting that the Rh particles were <4.0 nm.

XPS results for Rh $3d_{5/2}$ binding energies were obtained for the reduced catalysts. Binding energies were referenced to C 1s = 284.7 eV, which resulted in a binding energy for Si $2p$ = 103.8 for the SiO_2-supported catalysts. The only exception was the K/Rh/La_2O_3 where K $2p$ lines excited by $Al_{\alpha 3,4}$ interfere with C 1*s* lines. In this case binding energies were referenced to the lattice oxygen of La_2O_3 at 528.2 eV, which corresponds to the graphitic carbon reference at 284.7 eV for Rh/La_2O_3 and the La_2O_3 blank. The Rh $3d_{5/2}$ binding energy of the unpromoted Rh/SiO_2 was 307.0 eV, while that of the Rb-promoted Rh/SiO_2 was 306.8 eV. These are consistent with Rh^0. A −0.9-eV shift in the Rh $3d_{5/2}$ binding energy was observed in going from SiO_2 to La_2O_3 as the support. The Rh $3d_{5/2}$ binding energy for the unpromoted Rh/La_2O_3 was 306.1 eV. The Rh $3d_{5/2}$ binding energies for K- and Rb-promoted Rh/La_2O_3 were 305.9 and 305.8 eV, respectively, within experimental error of the unpromoted catalyst.

A Rb $3p_{3/2}$ binding energy value of 238.8 eV was observed for the passivated Rb/Rh/SiO_2, while a value of 238.9 eV was observed after reduction. For Rb/Rh/La_2O_3, the Rb $3p_{3/2}$ binding energy was 238.2 eV in the passivated state and 237.9 eV in the reduced form.

Binding energies for O 1*s*, C 1*s*, and La $3d_{5/2}$ for the La_2O_3-supported catalysts in air passivated and reduced forms are summarized in Table 3. The O 1*s* peak at approximately 530.9 eV is assigned to hydroxide (OH^-) and carbonate (CO_3^{-2}) oxygen (*21*), while that at about 528.3 eV is assigned to lattice (O^{-2}) oxygen (*21*). The C 1*s* peak at 289.5 eV is attributed to carbonate carbon (*21*), while the lower energy peak is taken as adventitious carbon and assigned the value of 284.7 eV as the reference. No information can be ascertained regarding C 1*s* in the K/Rh/La_2O_3 due to interference from the K $2p$ lines excited by Al $K_{\alpha 3,4}$. The La $3d_{5/2}$ binding energy is also listed along with the binding energy difference between La $3d_{5/2}$ and the upscale satellite peak characteristic for lanthanum $3d$ levels (*21*). Changes in the O/La and C/La XPS signal intensity ratios for the oxide and hydroxide/carbonate oxygen and the carbonate and graphitic carbon are summarized in Table 4.

From Tables 3 and 4 it can be seen that for all passivated samples, the predominant form of oxygen was that in the carbonate and hydroxide forms. The presence of lattice oxygen for Rh/La_2O_3 and Rb/Rh/La_2O_3 indicates incomplete conversion of La_2O_3 and LaOOH to $La(OH)_3$ during exposure to air. The presence of carbonate carbon was also indicated. Upon reduction, the O/La XPS signal intensity ratio for hydroxide and carbonate oxygen fell and that for oxide oxygen grew. These ratios were nearly the same for each catalyst. Following reduc-

TABLE 3

Elemental Binding Energies (eV) for La_2O_3 Support

Sample	Treatment	O 1*s*		C 1*s*		La $3d_{5/2}$ Split[a]	
		(OH and CO_3^{-2})	(O^{-2})	(CO_3^{-2})	(Adv. C)[b]		
La_2O_3 Blank	Passivated	530.9	—	289.5	284.7	834.6	3.6
	400°C Reduction	530.9	528.2	289.2	284.7	832.7	4.4
Rh/La_2O_3	Passivated	530.8	528.9	289.3	284.7	833.8	4.0
	400°C Reduction	530.5	528.3	—	284.7	832.8	4.5
$Rb/Rh/La_2O_3$	Passivated	530.4	528.5	289.2	284.7	833.6	4.0
	400°C Reduction	530.4	527.9	288.9	284.7	832.5	4.5
$K/Rh/La_2O_3$	400°C Reduction	530.5	528.2[b]	N/A[c]	N/A[c]	832.8	4.5

[a] Upscale shift of satellite peak from main peak.

[b] Reference peak.

[c] Not available, as discussed in text.

tion, the carbonate C/La XPS signal intensity ratio fell by a factor of two for the blank, was completely eliminated for the unpromoted catalyst but remained unchanged for the Rb-promoted case. These changes on reduction were accompanied by a shift of the La $3d_{5/2}$ binding energy to a lower level and an increase in the satellite split as has been observed and discussed elsewhere (*21*).

Ethane hydrogenolysis results are summarized in Arrhenius plots found in Figs. 1 and 2. The rates have been normalized per gram of catalyst for these plots due to the uncertainties in determining the metal surface area in the presence of decorating supports and alkali promoters. The effect of alkali promotion on Rh/SiO_2 can be seen in Fig. 1 and on Rh/La_2O_3 in Fig. 2. The Arrhenius data have been extrapolated to 300°C in order to compare rate/gram catalyst and TOFs for ethane hydrogenolysis and are presented in Table 5.

Alkali promotion of Rh/SiO_2 resulted in over an order of magnitude decline in the ethane hydrogenolysis rate and TOF based

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 (OH and CO_3^{-2})	528 eV (O^{-2})	289 eV (CO_3^{-2})	285 eV (Adv. C)
La_2O_3 Blank	Passivated	0.69	0	0.030	0.155
	400°C Reduction	0.12	0.21	0.015	0.053
Rh/La_2O_3	Passivated	0.26	0.09	0.029	0.095
	400°C Reduction	0.12	0.23	0	0.050
$Rb/Rh/La_2O_3$	Passivated	0.33	0.10	0.017	0.050
	400°C Reduction	0.10	0.26	0.016	0.034
$K/Rh/La_2O_3$	400°C Reduction	0.12	0.32	N/A[a]	N/A[a]

[a] Not available, as discussed in text.

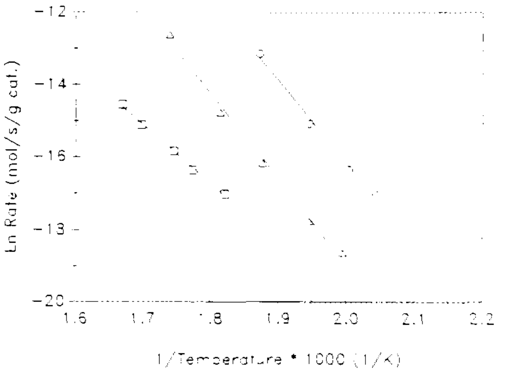

FIG. 1. Arrhenius plots for ethane hydrogenolysis over Rb-promoted and unpromoted Rh/SiO_2 and over Rh/La_2O_3: (○) Rh/SiO_2, (△) $Rb/Rh/SiO_2$, and (□) Rh/La_2O_3.

TABLE 5

Ethane Hydrogenolysis Activity at 300°C[a]

Catalyst	Specific rate $\times 10^7$ (mole/s-gm cat)	TOF_H $\times 10^3$ (H_{tot} basis) (s^{-1})	TOF_{CO} $\times 10^3$ (CO_{tot} basis) (s^{-1})
Rh/SiO_2	313	138	161
$Rb/Rh/SiO_2$	23	9.2	19
Rh/La_2O_3	1.3	0.8	6.0
$K/Rh/La_2O_3$	1.1	1.5	5.8
$Rb/Rh/La_2O_3$	2.0	6.8	30
La_2O_3 blank	0.0019	—	—

[a] From Arrhenius data.

on H_2 chemisorption. The TOF based on CO chemisorption fell by a factor of 8. In going from SiO_2 to La_2O_3 as the support, specific rate and TOF based on H_2 chemisorption fell by over two orders of magnitude, while the decline in TOF on a CO basis was by a factor of 27.

Essentially no effect of alkali promotion on rate was observed for the La_2O_3-supported catalysts. All La_2O_3-supported catalysts were nearly three orders of magnitude more active than the La_2O_3 blank. On a TOF basis, the only effect observed was for the Rb-promoted catalyst which exhibited a nearly five times greater activity than the unpromoted catalyst when normalized to either H_2 or CO uptake.

A large effect of alkali promotion was observed on the apparent activation energy which fell from 32 kcal/mol over Rh/La_2O_3 to 19 kcal/mol over $Rb/Rh/La_2O_3$ and to 14 kcal/mol over $K/Rh/La_2O_3$. Little effect on apparent activation energy was observed for the SiO_2-supported catalysts. Values of 45 and 46 kcal/mol were determined for Rh/SiO_2 and $Rb/Rh/SiO_2$, respectively.

Arrhenius plots summarizing the results for cyclopropane hydrogenation in this study can be found in Figs. 3 and 4. Again rate was normalized per gram of catalyst for these plots due to the uncertainties involved in determination of free metal sur-

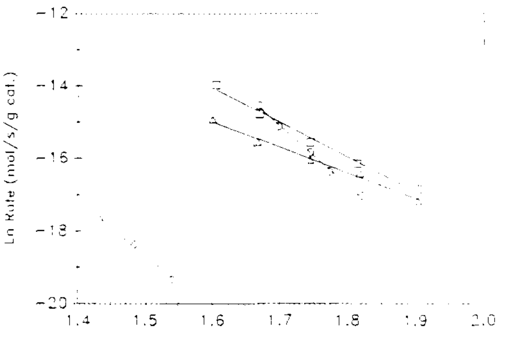

FIG. 2. Arrhenius plots for ethane hydrogenolysis over alkali-promoted and unpromoted Rh/La_2O_3: (○) Rh/La_2O_3, (△) $K/Rh/La_2O_3$, (□) $Rb/Rh/La_2O_3$, and (◇) La_2O_3 blank.

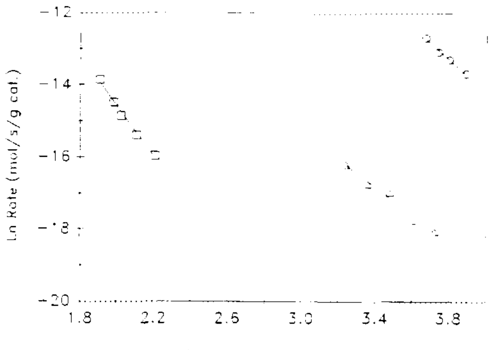

FIG. 3. Arrhenius plots for cyclopropane hydrogenation over Rb-promoted and unpromoted Rh/SiO_2 and over Rh/La_2O_3: (○) Rh/SiO_2, (△) $Rb/Rh/SiO_2$, and (□) Rh/La_2O_3.

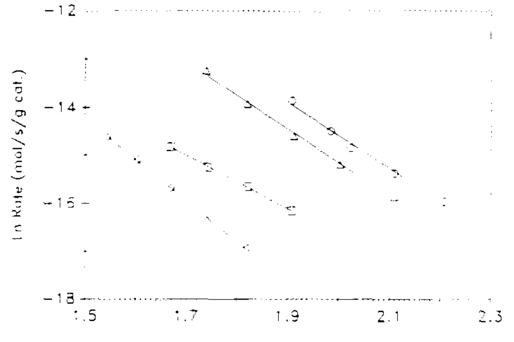

FIG. 4. Arrhenius plots for cyclopropane hydrogenation over alkali-promoted and unpromoted Rh/La$_2$O$_3$: (○) Rh/La$_2$O$_3$, (△) K/Rh/La$_2$O$_3$, (□) Rb/Rh/La$_2$O$_3$, and (◇) La$_2$O$_3$ blank.

face area. Alkali promotion resulted in over a 100-fold suppression of specific rate and TOF when comparing the unpromoted and Rb-promoted Rh/SiO$_2$ at 0°C based on an extrapolation of the Arrhenius data (see Table 6). The extrapolation of the data for Rh/La$_2$O$_3$ indicated five orders of magnitude suppression in specific rate and TOF based on H$_2$ uptake and over four orders of magnitude suppression in TOF based on CO uptake relative to Rh/SiO$_2$.

Based on extrapolation of Arrhenius data to 225°C (see Table 7), K-promotion of Rh/La$_2$O$_3$ resulted in a factor of 2 decline in specific cyclopropane hydrogenation rate while the specific rate over Rb/Rh/La$_2$O$_3$ fell by a factor of 7 vs the unpromoted catalyst. The Rb-promoted catalyst, however, was still nearly 10 times more active than the blank La$_2$O$_3$. Cyclopropane hydrogenation TOFs were approximately constant (within a factor of two) for all Rh/La$_2$O$_3$ catalysts.

TABLE 6

Cyclopropane Hydrogenation Activity at 0°C[a]

Catalyst	Specific rate × 10^8 (mole/s-gm cat)	TOF$_H$ × 10^5 (H$_{tot}$ basis) (s^{-1})	TOF$_{CO}$ × 10^5 (CO$_{tot}$ basis) (s^{-1})
Rh/SiO$_2$	319	1403	1633
Rb/Rh/SiO$_2$	1.8	7.1	15
Rh/La$_2$O$_3$	0.00067	0.0044	0.032

[a] From Arrhenius data.

TABLE 7

Cyclopropane Hydrogenation Activity at 225°C[a]

Catalyst	Specific rate × 10^7 (mole/s-gm cat)	TOF$_H$ × 10^3 (H$_{tot}$ basis) (s^{-1})	TOF$_{CO}$ × 10^3 (CO$_{tot}$ basis) (s^{-1})
Rh/La$_2$O$_3$	4.38	2.8	20
K/Rh/La$_2$O$_3$	2.48	3.4	13
Rb/Rh/La$_2$O$_3$	0.654	2.3	10
La$_2$O$_3$ blank	0.0875	—	—

[a] From Arrhenius data.

Apparent activation energies varied from 9 kcal/mol over Rh/SiO$_2$ to 8 kcal/mol over Rb/Rh/SiO$_2$. For the lanthana-supported samples the values ranged from 13 kcal/mol over Rh/La$_2$O$_3$ to 10 kcal/mol over Rb/Rh La$_2$O$_3$ to 14 kcal/mol over K/Rh/La$_2$O$_3$ to 17 kcal/mol over the blank.

Cyclopropane can react with H$_2$ to undergo ring opening to propane, simple hydrogenolysis to ethane and methane, or double hydrogenolysis to methane. Only ring opening was observed over Rh/SiO$_2$ and Rb/Rh/SiO$_2$ under differential conditions. Approximately 10% of the total cyclopropane converted over Rh/La$_2$O$_3$ was reacted by simple hydrogenolysis to ethane and methane in the 180–250°C temperature range where this catalyst exhibited differential activity. The same level of ethane and methane production was observed from Rh/SiO$_2$ when run at 200°C. It was a primary reaction since it occurred below the 250–325°C temperature range required for both propane and ethane hydrogenolysis over Rh/La$_2$O$_3$.

Both of the alkali-promoted Rh/La$_2$O$_3$ catalysts produced large amounts of ethane and methane by what might appear to be simple and double hydrogenolysis. For K/Rh/La$_2$O$_3$, selectivity to ring opening fell from 0.78 to 0, selectivity to simple hydrogenolysis rose from 0.22 to 0.24, and selectivity to double hydrogenolysis rose from 0 to 0.76 as the reaction temperature was raised from 250 to 300°C. For $Rb/Rh/La_2O_3$, selectivity to ring opening fell from 0.77 to 0.42, selectivity to simple hydrogenolysis rose from 0.16 to 0.19, and selectivity to double hydrogenolysis rose from 0.07 to 0.39 as reaction temperature was raised from 250 to 300°C. For both of these catalysts, this temperature range is the same as that where ethane hydrogenolysis activity was observed. Since propane hydrogenolysis is also expected in the same temperature range as ethane hydrogenolysis, the shifts in selectivity away from cyclopropane hydrogenation to simple and double hydrogenolysis are probably due to secondary reactions of propane and ethane.

DISCUSSION

The increase in total H_2 chemisorption with alkali promotion for Rh/SiO_2 (Table 1) runs contrary to the decline in irreversible H_2 and total and irreversible CO uptake. This may have been due to spillover of H_2 as was observed by Kesraoui *et al.* (*12*) for K-promoted Rh/SiO_2. The decline in the irreversible CO/H ratio suggests that CO adsorption is more greatly affected than H_2 by the presence of alkali. This decline in CO adsorption is probably indicative of decoration of the Rh surface by the promoter.

Determination of free metal surface area is a complex issue in systems where support moieties are thought to decorate the metal surface. For chemisorption, spillover of H_2 onto support species and reaction of CO to form surface carbonate species can result in an overestimation of metal surface area (*7, 22, 37*). For XPS, the presence of decorating moieties may attenuate the signal from the metal, resulting in an overestimation of particle size.

The much lower amount of CO adsorption relative to H_2 adsorption for Rh/La_2O_3 has been explained by spillover of H_2 onto the support and decorating moieties thought to give rise to the metal–support interaction in La_2O_3-supported noble metals (*7, 22, 37*). For K-promoted Rh/La_2O_3, the Rh/La XPS signal intensity ratio suggests an increase in Rh surface area, while the H_2 chemisorption results indicate a decline. An increase in metal dispersion with alkali promotion is well known. This has been postulated elsewhere for K-promotion of Rh (*12*). The suppression of H_2 uptake is consistent with the blockage of spillover pathways and/or poisoning of adsorption sites on the decorating moieties and support. This is in agreement with the observations of Marcelin *et al.* (*20*) for alkali-promoted Rh/TiO_2 in the SMSI state.

For $Rb/Rh/La_2O_3$, the Rh/La XPS signal intensity ratio, H_2 adsorption, and CO adsorption all declined, possibly suggesting an increase in Rh particle size. However, XPS also indicates the presence of carbonate species after reduction at temperatures sufficient to eliminate these species in the unpromoted case. Therefore, fewer sites would be available in the $Rb/Rh/La_2O_3$ case for carbonate formation during CO chemisorption resulting in the decline in CO uptake. The further decline in H_2 uptake suggests that either Rb is more effective in blocking H_2 spillover or that the carbonate species have a lower capacity for spillover H_2 than the unpromoted support, or both. The lower Rh/La signal intensity ratio may be due to large Rh particle size on the carbonated support. Alternatively, one might speculate that the Rh signal may be more highly attenuated by Rb species and/or by undecomposed support carbonate species decorating the metal.

The addition of alkali to Rh/SiO_2 had no significant impact on the Rh $3d_{5/2}$ binding energy indicating no electronic influence of promotion in contrast to previous observations for Ru/SiO_2 (*41*). The Rh $3d_{5/2}$ binding energy for all the La_2O_3-supported samples were shifted negatively relative to Rh/SiO_2, as was previously observed for Pd (*21*). Addition of alkali resulted in no additional Rh binding energy shift in either $K/Rh/La_2O_3$ or $Rb/Rh/La_2O_3$. Results for the Rb $3p_{3/2}$ binding energy in the reduced state in $Rb/Rh/La_2O_3$ vs $Rb/Rh/SiO_2$ indicate a -1.0 eV shift, similar in magnitude to that observed for Rh.

The difficulties of inferring electronic interactions arising from metal–support interactions from XPS experiments have recently been discussed (*42*). Possible changes in the binding energy, work function, and structure of the metal as well as changes in the work function of the reference material and the conductivity of the support may all combine to produce the observed shifts. The negative binding energy shift for noble metals when supported on La_2O_3 has been taken as evidence of decoration of the crystallite surface by lanthana moieties with transfer charge to the metal (*21*). In the present study, a similar binding energy shift for Rh supported on La_2O_3 was observed. However, the binding energy of Rb was shifted by the same amount. It seems highly coincidental that the binding energy, work function, and structure of these two species would be similarly affected by interaction with the support. Changes in the support or the binding energy of the adventitious carbon used as the reference appear more likely explanations for the binding energy shifts observed for La_2O_3-supported metals.

The changes in support composition are consistent with the previously discussed dehydration of $La(OH)_3$ to LaOOH and La_2O_3 and decomposition of $La_2(CO_3)_3$ (*21, 22, 38–40*). The addition of Rb appears to have had no impact on the dehydration process but did inhibit the Rh-catalyzed decomposition of the carbonate. This could be due to a direct impact on the Rh, a stabilization of the lanthanum carbonate, or perhaps to the formation of stable Rb_2CO_3.

For the structure-sensitive ethane hydrogenolysis, a 20-fold increase in rate per m^2 has been observed as dispersion increased from 0.4 to 94% (*24*). Decoration of the active Rh surface with small amounts of inert species resulted in a sharp drop-off in activity (*29*), attributable to a break up of the large ensembles required for this reaction (*25, 26*). Cyclopropane hydrogenation appears to be structure-insensitive over Rh (*29*), with high levels of inert decoration required to break up the small ensembles required for reaction and to cause a significant decline in activity.

A nearly one order of magnitude suppression in ethane hydrogenolysis activity was observed in going from the unpromoted to the Rb-promoted Rh/SiO_2. In the absence of an electronic effect of Rb promotion of Rh/SiO_2, as indicated by the Rh 3*d* XPS results, this suggests that the alkali promoter is decorating the Rh surface and breaking up reaction ensembles. The large suppression of the structure-insensitive cyclopropane hydrogenation reaction suggests that the decoration is extensive.

The effect of support in going from SiO_2 to La_2O_3 is even greater than the effect of alkali promotion on Rh/SiO_2 in suppression of both of these reactions, suggesting that a Rh surface is decorated to a greater extent by lanthana moieties in Rh/La_2O_3 than by alkali species in Rb/Rh/SiO_2 for the level of alkali promotion used here.

Little effect was observed on ethane hydrogenolysis specific rate upon alkali promotion of Rh/La_2O_3. This is attributed to the fact that decorating lanthana species already break up significant numbers of the surface atom ensembles required for reaction sites, severely suppressing the reaction. The observed activity is probably due to a relatively few unperturbed ensembles. Similar observations have been made for extensively decorated Rh/TiO_2 in the SMSI state (*43*). Activity comparisons on a TOF basis normalized by H_2 chemisorption are limited by the presence of H_2 spillover. Spillover H_2 would result in an overestimation of Rh surface area and therefore an underestimation of TOF. The impact would be relatively greater on the unpromoted catalyst, since alkali promotion appears to partially suppress H_2 spillover. TOF on a CO uptake basis is hampered somewhat by similar considerations, since CO can react to form carbonate and formate species with the support (*7, 37*). The XPS results suggest that alkali promotion inhibited the decomposition of carbonate species. As a result, more sites would be available to react with CO and the overestimation of TOF would be greater on the unpromoted catalyst.

The shift in apparent activation energy with alkali promotion was the major impact on ethane hydrogenolysis over Rh/La_2O_3. This shift does not appear to be due to an electronic influence of the alkali on Rh since none was observed by XPS. Mass transfer limitations as a result of alkali promotion also seem unlikely since no shift in apparent activation energy was observed for cyclopropane hydrogenation. The drop in activation energy may be due to an impact on the competitive adsorption of ethane and H_2, possibly as a result of the suppression of H_2 spillover upon alkali promotion.

The effect of alkali promotion can also be seen from the cyclopropane hydrogenation results. Although the lanthana decoration severely suppressed the specific rate (Table 6), an additional moderate decline was observed upon addition of alkali (Table 7) suggesting further decoration. Again, analysis on a TOF basis is complicated by H_2 spillover and CO interaction with the support to form carbonate and formate species which would tend to cause an overestimation of the reactive surface. The impact of each of these phenomena would be expected to be relatively greater on the unpromoted catalyst. When this is considered, a slight decline in activity on a TOF basis may be inferred. However, the effect of alkali promotion was still small relative to the effect of decoration from lanthana moieties from the support.

CONCLUSIONS

The effect of Rb- and K-promotion on Rh/La_2O_3 has been investigated in this study using H_2 and CO chemisorption, XPS, XRD, ethane hydrogenolysis, and cyclopropane hydrogenation. Unpromoted and Rb-promoted Rh/SiO_2 were also studied for comparison purposes.

In the case of Rh/SiO_2, Rb promotion resulted in a decoration of the crystallite surface leading to a partial suppression of ethane hydrogenolysis and cyclopropane hydrogenation and of CO chemisorption. No effect on the Rh $3d_{5/2}$ binding energy was observed due to this promotion.

For Rh/La_2O_3, K- and Rb-promotion appeared to block sites and/or pathways for the spillover of H_2 from Rh to the decorating lanthana moieties and/or the support. Ethane hydrogenolysis activity was unaffected by alkali due to the already extensive breakup of reaction site ensembles by the decorating lanthana moieties. Alkali promotion did result in a decrease in apparent activation energy for this reaction, possibly as a result of suppression of H_2 spillover. A moderate suppression of cyclopropane hydrogenation upon alkali addition suggested additional decoration. For both reactions, the impact of alkali promotion on the Rh properties was secondary to the large impact of La_2O_3 as the support. The presence of Rb inhibited the Rh-catalyzed decomposition of the carbonate species on the support.

Rh $3d_{5/2}$ binding energies were shifted by nearly −1 eV for Rh/La_2O_3 relative to Rh/SiO_2, but no further effect of alkali promotion on Rh binding energies was observed. The Rb $3p_{3/2}$ binding energy was similarly shifted for $Rb/Rh/La_2O_3$ vs $Rb/Rh/SiO_2$, suggesting that Rb was affected in a similar manner as Rh. This could be due to different chemical environments for Rh and Rb between SiO_2 and La_2O_3 supports. Alternatively, the binding energy of the carbon used as a binding energy reference may have differed between the two supports.

ACKNOWLEDGMENTS

The authors acknowledge financial support for this work by NSF (Grant CBT-8715541). Insightful discussions with Dr. Laszlo Guczi and Dr. Rachid Oukaci are also gratefully acknowledged.

REFERENCES

1. Ichikawa, M., *J. Chem. Soc. Chem. Commun.*, 566 (1978).

2. Ichikawa, M., *Bull. Chem. Soc. Jpn.* **51,** 2268 (1978).
3. Ichikawa, M., *Bull. Chem. Soc. Jpn.* **51,** 2273 (1978).
4. Katzer, J. R., Sleight, A. W., Gajardo, P., Michel, J. B., Gleason, E. F., and McMillan, S., *Faraday Discuss. Chem. Soc.* **72,** 121 (1981).
5. Chuang, S. C., Ph.D. dissertation, University of Pittsburgh, 1985.
6. Underwood, R. P., and Bell, A. T., *Appl. Catal.* **21,** 157 (1986).
7. Underwood, R. P., and Bell, A. T., *Appl. Catal.* **34,** 289 (1987).
8. Kieffer, R., Kiennemann, A., Rodriquez, M., Bernal, S., and Rodriguez-Izquierdo, J. M., *Appl. Catal.* **42,** 77 (1988).
9. Kagami, S., Naito, S., Kikuzono, Y., and Tamaru, K., *J. Chem. Soc. Chem. Commun.,* 226 (1983).
10. Chuang, S. C., Goodwin, Jr., J. G., and Wender, I., *J. Catal.* **95,** 435 (1985).
11. Blackmond, D. G., Williams, J. A., Kesraoui, S., and Blazewick, D. S., *J. Catal.* **101,** 496 (1986).
12. Kesraoui, S., Oukaci, R., and Blackmond, D. G., *J. Catal.* **105,** 432 (1987).
13. Ertl, G., Weiss, M., and Lee, S. B., *Chem. Phys. Lett.* **60,** 391 (1979).
14. Praliaud, H., Primet, M., and Martin, G., *Appl. Surf. Sci.* **17,** 107 (1983).
15. Lang, N. D., Holloway, S., and Norskov, J. K., *Surf. Sci.* **150,** 24 (1985).
16. Sachtler, W. H. M., Schriver, D. F. Hollenberg, W. B., and Lang, A. F., *J. Catal.* **92,** 429 (1985).
17. McClory, M. M., and Gonzalez, R. D., *J. Catal.* **89,** 392 (1984).
18. Reick, J. S., and Bell, A. T., *J. Catal.* **100,** 305 (1986).
19. Resasco, D. E., and Haller, G. L., *J. Catal.* **82,** 279 (1983).
20. Marcelin, G., Lester, J. E., and Mitchell, S. F., *J. Catal.* **102,** 240 (1986).
21. Fleisch, T. H., Hicks, R. F., and Bell, A. T., *J. Catal.* **87,** 398 (1984).
22. Gallaher, G. R., Goodwin, Jr., J. G., Huang, C.-S., and Houalla, M., *J. Catal.* **127,** 719 (1991).
23. Chuang, S. C., Goodwin, Jr., J. G., and Wender, I., *J. Catal.* **92,** 416 (1985).
24. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **8,** 348 (1967).
25. Sachtler, W. M. H., and Van Santen, R. A., *Adv. Catal.* **26,** 69 (1977).
26. Martin, G. A., *J. Catal.* **60,** 345 (1979).
27. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24,** 283 (1972).
28. Ko, E. I., and Garten, R. L., *J. Catal.* **68,** 233 (1981).
29. Wong, T. C., Brown, L. F., and Haller, G. L., *J. Chem. Soc. Faraday Trans 1* **71,** 519 (1981).
30. Ko, E. I., Hupp, J. M., and Wagner, N. J., *J. Catal.* **86,** 315 (1984).
31. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6,** 92 (1966).
32. Dalla Betta, R. A., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **19,** 343 (1970).
33. Cale, T. S., and Richardson, J. T., *J. Catal.* **94,** 289 (1985).
34. Patterson, T., Carver, J., Leyden, D., and Hercules, D. M., *J. Phys. Chem.* **80,** 1900 (1976).
35. Proctor, A., and Hercules, D. M., *Appl. Spectrosc.* **38,** 505 (1984).
36. Mitchell, M. D., and Vannice, M. A., *Ind. Eng. Chem. Fundam.* **23,** 88 (1984).
37. Hicks, R. F., Yen, Q. J., and Bell, A. T., *J. Catal.* **89,** 498 (1984).
38. Rosynek, M. P., and Magnuson, D. T., *J. Catal.* **46,** 402 (1977).
39. Bernal, S., Botana, F. J., Garcia, R., Ramirez, R., and Rodriguez-Izquierdo, J. M., *Appl. Catal.* **31,** 267 (1987).
40. Bernal, S., Botana, F. J., Garcia, R., Ramirez, R., and Rodriquez-Izquierdo, J. M., *J. Chem. Soc., Faraday Trans. 1* **83,** 2279 (1987).
41. Shyu, J. Z., Goodwin, Jr., J. G., and Hercules, D. M., *J. Phys. Chem.* **89,** 4983 (1985).
42. Hicks, R. F., *in* "Characterization and Catalyst Development: An Interactive Approach" (S. A. Bradley, M. J. Gattuso, and R. J. Bertolacini, Eds.), ACS Symposium Series, Vol. 441, p. 214. American Chemical Society, Washington, DC, 1989.
43. Braunschweig, E. J., Logan, A. D., Datye, A. K., and Smith, D. J., *J. Catal.* **118,** 227 (1989).
44. Gallaher, G. R., Goodwin, Jr., J. G., and Guczi, L., *Appl. Catal.* **73,** 1 (1991).