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Lanthana-Promoted Rh/SiO$_2$

II. Studies of CO Hydrogenation

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A study of the influence of lanthana promotion on the hydrogenation of CO over Rh/SiO$_2$ has been conducted. Lanthana-promoted Rh/SiO$_2$ exhibits higher turnover frequencies for the synthesis of CH$_4$, C$_2$–C$_4$ hydrocarbons, CH$_3$OH, and C$_2$ oxygenates than unpromoted Rh/SiO$_2$. The turnover frequency for each product goes through a maximum with increasing lanthana addition. Lanthana promotion is also found to increase the selectivity for the formation of CH$_3$OH, C$_2$ oxygenates, and C$_2$–C$_4$ hydrocarbons and to decrease the selectivity for CH$_4$. The selectivity for C$_2$ oxygenates is optimized at low levels of lanthana addition. *In situ* infrared observations show that lanthana promotion blocks the chemisorption of CO onto surface Rh sites. Of particular interest is the observation of a band at 1725 cm^{-1}. This feature is assigned to CO adsorbed on a Rh site immediately adjacent to an LaO$_x$ island. The low frequency of this vibration is attributed to a weakening of the C–O bond caused by the interaction of lanthana cations with the oxygen end of the adsorbed CO. It is postulated that the interaction of the lanthana with the CO is responsible for the enhanced rates of CO dissociation and the formation CH$_4$ and C$_{2+}$ products. Infrared spectroscopy also provides evidence for acyl, formate, and acetate groups on the surface of lanthana-promoted Rh/SiO$_2$. The possible role of these species in the synthesis of products is discussed.

INTRODUCTION

The use of lanthana and other rare earth oxides as supports has been found to enhance the formation of oxygenated products during CO hydrogenation over Rh (*1–5*). Based on comparative studies of Rh/SiO$_2$ and Rh/La$_2$O$_3$ catalysts, Underwood and Bell (*6*) concluded that catalyst activity and selectivity depend on Rh particle size, and for Rh/La$_2$O$_3$, on the extent to which the Rh particles are decorated by LaO$_x$ ($x \leq 1.5$) moieties. To elucidate the effects of lanthana promotion, as distinct from those of Rh dispersion, the properties of a Rh/SiO$_2$ catalyst, having a fixed dispersion, promoted with increasing amounts of lanthana were investigated. The structure and composition of such catalysts and their behavior in the adsorption of H$_2$ and CO have been described in Part I of this study (*7*). Reported here is the influence of lanthana promotion on the activity and selectivity of Rh/SiO$_2$ for CO hydrogenation. Also discussed are the results of *in situ* infrared observations.

EXPERIMENTAL

The catalysts used were identical to those examined in the first part of this study and a description of their preparation and pretreatment may be found in Ref. (*7*). Briefly, lanthana was introduced by incipient wetness impregnation of a reduced and passivated 4% Rh/SiO$_2$ catalyst with an aqueous solution of La(NO$_3$)$_3$. The concentration of La(NO$_3$)$_3$ in the impregnating solution was adjusted to obtain the desired La content. Impregnation was followed by drying, calcination, and reduction. The average particle size of the dispersed Rh was 3.3 nm and was unaffected by promotion of the catalyst with lanthana.

Rate data were obtained using a stain-

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less-steel microreactor. Reactants were supplied to the reactor from a high-pressure gas manifold and products were analyzed on-line with a gas chromatograph. Additional details concerning this apparatus are given in Ref. (*5*). Experiments were initiated by reducing the sample (0.05–0.10 g) at 573 K for 15 h using 50 cm^3/min of pure H_2. After reduction, the sample was cooled to 530 K and pressurized with H_2 before the CO/H_2 flow was introduced. Reaction rates were recorded after a standard break-in period of 24 h on stream at $T = 530$ K, $P_{H_2} = 8$ atm, and $P_{CO} = 4$ atm. Reaction rates were determined from the mean value of product analyses obtained over a range of reactor residence times. The ethanol fraction of the C_2 oxygenates products increased and the acetaldehyde fraction decreased with increasing reactor residence time. The same effect of reactor residence time was observed for Rh/La_2O_3 (*5*) and was shown to be the result of the secondary reaction of acetaldehyde to ethanol. The sum of the acetaldehyde plus ethanol concentrations, as well as the concentrations of each of the other measured products, increased linearly with reactor residence time, indicating that other secondary reactions did not occur. In all cases the conversion of CO (CO_2-free basis) was kept below about 0.1%.

In situ infrared observations were carried out using specially designed infrared cells (*8*). The bodies of the cells are made of stainless steel CaF_2 windows are sealed to the body of each cell by Kalrez o-rings (Compound No. 4079, DuPont). The cells are heated externally by custom-made sheet heaters and are capable of operating at a temperature as high as 573 K and a pressure of at least 24 atm.

Two infrared cells were used connected in series, the first cell containing a self-supporting disk of SiO_2 (0.05 g) and the second cell, a disk of catalyst (0.05–0.10 g). The flow of gas was from the first to the second cell. Infrared experiments were initiated by reducing the catalyst and SiO_2 disks at 563 K and 1 atm for 2 h in pure H_2 flowing at 50 cm^3/min. Following reduction, the cells were cooled to 530 K and pressurized to the desired reaction pressure with H_2. Reference spectra were then recorded for both the SiO_2 disk and the catalyst sample disk. A flow of CO and H_2 ($P_{H_2} = 8$ atm; $P_{CO} = 4$ atm) was then passed through both cells. Product analyses and infrared spectra were recorded as a function of time on stream. The temperature of the samples in each infrared cell was measured by a thermocouple located at the edge of the sample disk. Because there is a temperature gradient across the catalyst sample disk caused by heat loss through the CaF_2 windows, the mean temperature of the sample was estimated to be lower than the measured temperature by about 10–15 K. Therefore, reaction rate measurements obtained using the infrared cell were lower than those obtained using the microreactor for the same recorded temperature.

Infrared spectra were recorded at 8 cm^{-1} resolution using a Digilab FTS 15/80 dual-beam FTIR spectrometer equipped with a narrow-band MCT detector. Elimination of the band for gas-phase CO in the spectra was performed by subtracting the absorbance spectrum for the SiO_2 disk from the catalyst absorbance spectrum. Typically 256 scans were coadded to obtain a satisfactory signal-to-noise ratio.

RESULTS

Table 1 provides a summary of sample characteristics (*7*). The quantity in the parentheses of the catalyst designations, and in the second column of Table 1, is the La content of the catalysts expressed as the molar ratio of La to the total surface Rh atoms, La/Rh_s. The concentration of surface Rh atoms was determined from the irreversible uptake of H_2 at 298 K on the unpromoted Rh/SiO_2. Since a large quantity of the added lanthana resides on the SiO_2 surface and is not in contact with the metal, La/Rh_s is not the atomic ratio that exists on the Rh crystallites (*7*). The last three

TABLE 1

Characterization of La-Promoted Rh/SiO$_2$ Catalysts by H_2 and CO Chemisorption

Catalyst	La/Rh$_s$	Weight percent La$_2$O$_3$	H_{irr}/Rh^a	H_{irr}/Rh^b	CO_{irr}/Rh^b
Rh/SiO$_2$	0	0	0.54	0.38	0.43
La(0.1)/Rh/SiO$_2$	0.1	0.25	0.49	0.33	0.44
La(0.5)/Rh/SiO$_2$	0.5	1.18	0.47	0.34	0.43
La(1.0)/Rh/SiO$_2$	1.0	2.46	0.32	0.24	0.32
La(2.5)/Rh/SiO$_2$	2.5	5.59	0.43	0.32	0.26
La(5.0)/Rh/SiO$_2$	5.0	10.6	0.39	0.31	0.16
La(10.0)/Rh/SiO$_2$	10.0	18.7	0.34	0.34	0.10

[a] T_{ads} = 195 K.
[b] T_{ads} = 298 K.

columns of Table 1 list the irreversible uptakes of H_2 at 195 and 298 K and CO at 298 K, all determined by volumetric chemisorption. The values of H_{irr}/Rh and CO_{irr}/Rh are the ratios of the quantities of irreversibly adsorbed H and CO, respectively, to the total Rh in the catalyst. As discussed previously (7), the CO uptake decreases much more rapidly with increasing La content than does the H uptake.

The evolution of reaction products with time on stream for Rh/SiO$_2$ and La(5)/Rh/SiO$_2$ was observed using the infrared cells. Time course curves are shown in Figs. 1 and 2 for CH_4, CH_3OH, and C_2 oxygenates. Similar data were obtained for C_2–C_4 hydrocarbons but are not illustrated. The turnover frequencies presented in Figs. 1 and 2 are all based on the total number of surface Rh sites in the sample, assuming all of these sites to be exposed to the reactants. Analysis of the catalyst samples by X-ray diffraction before and after reaction showed little evidence for sintering of Rh particles during reaction.

Steady-state activities and product distributions for both Rh/SiO$_2$ and La(5)/Rh/SiO$_2$ are achieved after 18–24 h on stream. As can be seen, the initial activities for all products are much higher than the steady-state activities and no measurable induction period was observed for the formation of any product. The influence of reaction time on the turnover frequency for C_2 oxygenates for La(5)/Rh/SiO$_2$ is slightly different

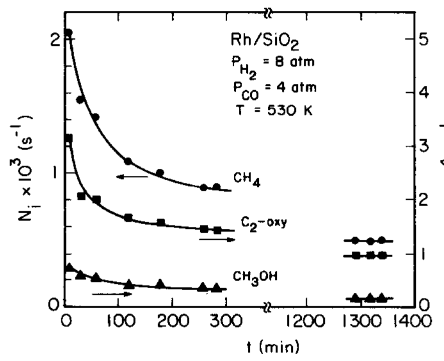

FIG. 1. Dependence of the turnover frequencies for CH_4, CH_3OH, and C_2 oxygenates on reaction time for Rh/SiO$_2$.

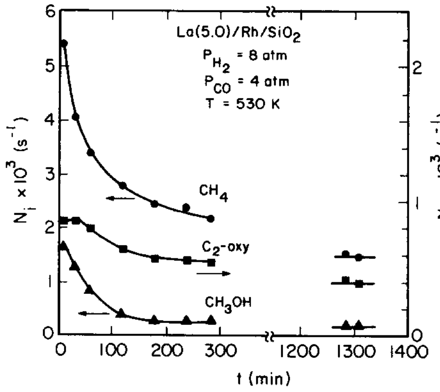

FIG. 2. Dependence of the turnover frequencies for CH_4, CH_3OH, and C_2 oxygenates on reaction time for La(5)/Rh/SiO$_2$.

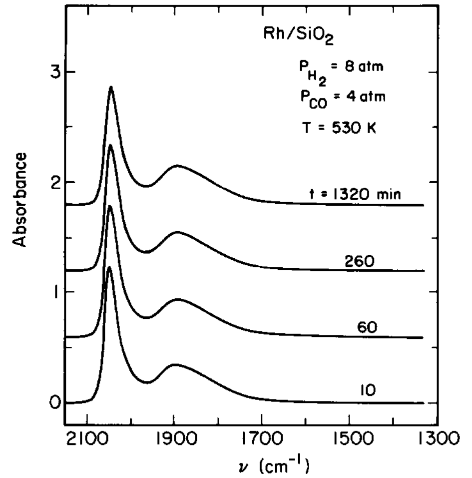

FIG. 3. Effect of reaction time on the infrared spectrum for Rh/SiO_2.

than that observed for Rh/SiO_2. The turnover frequency for C_2 oxygenates decreases monotonically with reaction time for Rh/SiO_2, while it initially increases slightly and then decreases to the steady-state value for $La(5)/Rh/SiO_2$. For both Rh/SiO_2 and $La(5)/Rh/SiO_2$, the turnover frequency for CH_3OH decreases monotonically with reaction time, but the decrease is much more extensive for $La(5)/Rh/SiO_2$ than for Rh/SiO_2. For $La(5)/Rh/SiO_2$, the activity for CH_3OH after 10 min is 10 times higher than the steady-state activity. By contrast, for Rh/SiO_2, the CH_3OH activity after 10 min is only 5 times higher than the steady-state value.

Comparison of the steady-state turnover frequencies for CH_4, CH_3OH, and C_2 oxygenates shows that the rates for all three products are much higher over $La(5)/Rh/SiO_2$ than over Rh/SiO_2. The turnover frequencies for CH_3OH and C_2 oxygenates over $La(5)/Rh/SiO_2$ are higher than those for Rh/SiO_2 by factors of 12.4 and 4.2, respectively. The CH_4 turnover frequency is a factor of 3 higher on $La(5)/Rh/SiO_2$ than on Rh/SiO_2. Thus, it is clear that the lanthana promoter increases the rate of synthesis of all products and increases the selectivity for oxygenates. This is consistent with our previous results (*5*, *6*) which show that Rh/La_2O_3 has a higher activity and higher selectivity for oxygenates than Rh/SiO_2.

The influence of reaction time on the infrared spectrum for Rh/SiO_2 is shown in Fig. 3. The band near 2045 cm^{-1} corresponds to linearly adsorbed CO on Rh and the broadband centered near 1890 cm^{-1} corresponds to bridge-bonded CO on Rh (*9*). No bands are observed below 1750 cm^{-1}. Reaction time has very little influence on the infrared spectrum except for a small (17%) decrease in the integrated intensity of the linear CO band. Comparison of these spectra with the spectrum obtained previously for CO chemisorption at 313 K (*7*) indicates that more than 90% of the Rh surface is covered by chemisorbed CO during reaction.

The influence of reaction time on the infrared spectrum for $La(5)/Rh/SiO_2$ shown in Fig. 4 is considerably different from that observed for Rh/SiO_2. It is clear that the band for linearly adsorbed CO near 2045 cm^{-1} decreases slightly with reaction time.

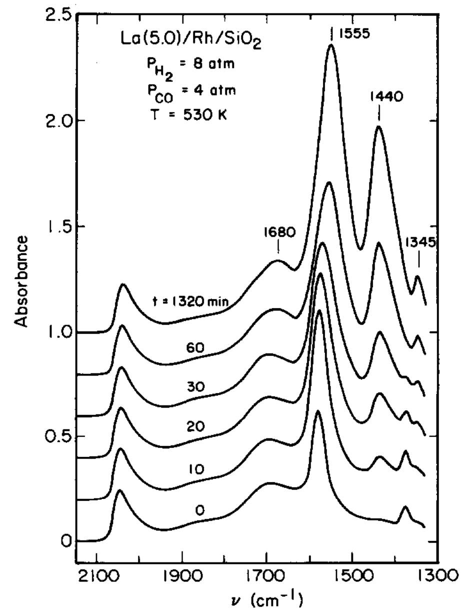

FIG. 4. Effect of reaction time on the infrared spectrum for $La(5)/Rh/SiO_2$.

The band for bridge-bonded CO (1800–1900 cm^{-1}) is not easily discernible, but appears to exhibit little change with reaction time. As can be seen, new bands appear in the spectrum below 1750 cm^{-1}.

The band near 1700 cm^{-1} for early reaction times is similar in size and shape to that observed previously at 1725 cm^{-1} for CO chemisorption at 313 K (*7*). This band was assigned to CO chemisorbed on Rh sites located near the perimeter of LaO$_x$ patches, where lanthanum cations interact directly with the oxygen end of the CO molecule and weaken the C–O bond. The frequency of this band in the present spectrum appears to be lower by about 25 cm^{-1} than that observed previously at 1725 cm^{-1}, but this is probably because of overlap with the band at 1680 cm^{-1}, which is discussed next.

The band at 1680 cm^{-1} increases in intensity with reaction time and reaches maximum intensity after 1320 min on stream. This band can be assigned to the C–O stretching vibration for adsorbed acyl species (CH_3CO–) (*10a,b,c, 11*). The bands appearing at 1580 and 1370 cm^{-1} after 2 min on stream are due to the asymmetric and symmetric stretching vibrations of bidentate formate groups (*12*). These two bands decrease in intensity with reaction time. Coinciding with the decrease in the formate bands is the appearance and subsequent increase in intensity of bands at 1555, 1440, and 1345 cm^{-1}. The bands at 1555 and 1440 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of adsorbed acetate ion. This assignment is based on the work of Fukushima *et al.* (*11*), who observed similar bands during CO hydrogenation over Mn-promoted Rh/SiO$_2$ and confirmed the assignment by experimental observation of the infrared spectrum of $Mn(CH_3CO_2)_2 \cdot 4H_2O$. The species giving rise to the band at 1345 cm^{-1} is unknown.

The reactivity of all of the surface species to H_2 was examined by switching the feed to the infrared cell from CO/H_2 to H_2 alone. A very rapid disappearance of all bands, except the acetate bands, was observed. The acetate bands were removed more slowly and disappeared after about 60 min in H_2.

Rate parameters for the synthesis of CH_4, CH_3OH, and C_2 oxygenates were determined for Rh/SiO$_2$ and La(5)/Rh/SiO$_2$, from rate data obtained using the microreactor, and are presented in Table 2. For the purposes of comparison, rate parameters determined previously for a La$_2$O$_3$-supported Rh catalyst (*6*) are also presented in Table 2. The activation energies were determined at $P_{H_2} = 8$ atm and $P_{CO} = 4$ atm for temperatures between 513 and 558 K. The H_2 partial pressure dependences were determined by varying P_{H_2} between 2 and 16 atm for a constant $P_{CO} = 4$ atm, and the CO partial pressure dependences were determined by varying P_{CO} between 2 and 16 atm for a constant $P_{H_2} = 8$ atm.

In agreement with previous observations (*5, 6*) there are large differences in the rate parameters for SiO$_2$- and La$_2$O$_3$-supported Rh. The parameters for La(5)/Rh/SiO$_2$ are

TABLE 2

Rate Parameters[a] for the Synthesis of CH_4, CH_3OH, and C_2 Oxygenates

Catalyst	CH_4				CH_3OH				C_2 oxygenates			
	A (s^{-1} atm^{-x-y})	E_a (kcal mol^{-1})	x	y	A (s^{-1} atm^{-x-y})	E_a (kcal mol^{-1})	x	y	A (s^{-1} atm^{-x-y})	E_a (kcal mol^{-1})	x	y
Rh/SiO$_2$	5.2×10^5	22.8	0.8	−0.1	1.2×10^0	13.5	1.3	−0.1	6.1×10^{-2}	8.5	0.5	0.6
La(5)/Rh/SiO$_2$	1.3×10^9	29.5	0.7	−0.3	3.8×10^2	17.1	1.3	−0.2	4.4×10^6	24.9	0.5	0.0
3.5% Rh/La$_2$O$_3$	1.0×10^{10}	32.0	0.7	−0.3	5.3×10^2	17.2	1.5	−0.1	2.2×10^{10}	34.4	0.5	−0.2

[a] Rate parameters were determined by fitting $N_i = Ae^{-E_a/RT}P_{H_2}^{x}P_{CO}^{y}$ to experimental data.

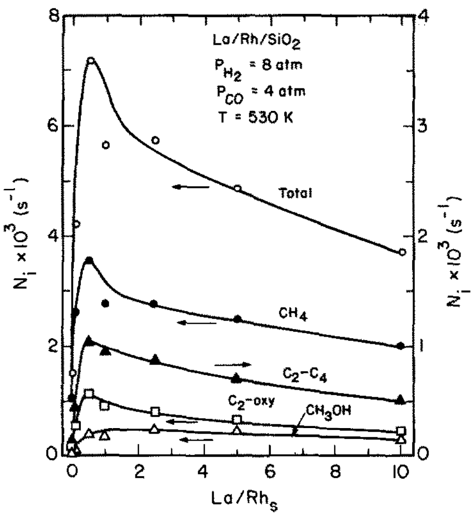

FIG. 5. Dependence of the turnover frequencies for the major products on La content.

intermediate between those for Rh/SiO$_2$ and Rh/La$_2$O$_3$, but are much closer to those for Rh/La$_2$O$_3$.

Table 2 shows that promotion of Rh/SiO$_2$ with lanthana causes an increase in the activation energies for the synthesis of CH$_4$, CH$_3$OH, and C$_2$ oxygenates. These increased activation energies are compensated for by large increases in the preexponential factors for the synthesis of each product. Lanthana promotion also decreases the value of y, the P_{CO} dependence, for all three products. The largest decrease is for C$_2$ oxygenates, for which y decreases from 0.6 for Rh/SiO$_2$ to 0.0 for La(5)/Rh/SiO$_2$. By contrast, the P_{H_2} dependences for all three products are comparable for Rh/SiO$_2$ and La(5)/Rh/SiO$_2$.

Shown in Fig. 5 is the influence of La content on the turnover frequencies for the synthesis of the major products under a fixed set of reaction conditions. All turnover frequencies are calculated based on the concentration of surface Rh atoms for the unpromoted Rh/SiO$_2$. With the exception of C$_2$ oxygenates, the turnover frequencies are calculated as carbon atoms in the product molecule per Rh surface site per second. For C$_2$ oxygenates, the turnover frequency is simply molecules of ethanol plus acetaldehyde per Rh surface site per second.

As can be seen in Fig. 5, the addition of lanthana to Rh/SiO$_2$ increases the turnover frequencies for the formation of all products, especially oxygenates. Maxima in the turnover frequencies are observed at La/Rh$_s$ = 0.5 for CH$_4$, C$_2$ oxygenates, and C$_2$–C$_4$ hydrocarbons. The activities for the synthesis of CH$_4$, C$_2$–C$_4$ hydrocarbons, and C$_2$ oxygenates over La(0.5)/Rh/SiO$_2$ are higher than those for Rh/SiO$_2$ by factors of 3.3, 8.4, and 8.8, respectively. The turnover frequency for CH$_3$OH synthesis is maximized at La/Rh$_s$ = 2.5 and is higher than that for Rh/SiO$_2$ by a factor of 11.

The turnover frequencies shown in Fig. 5 were used to calculate product selectivities and these results are shown in Fig. 6. The product selectivities were calculated on a CO$_2$-free basis assuming that C$_1$–C$_4$ hydrocarbons and C$_1$–C$_2$ oxygenates were the only products formed. It is apparent that the presence of La has a strong effect on the product distribution. Maxima in the selectivities for CH$_3$OH, C$_2$ oxygenates, and

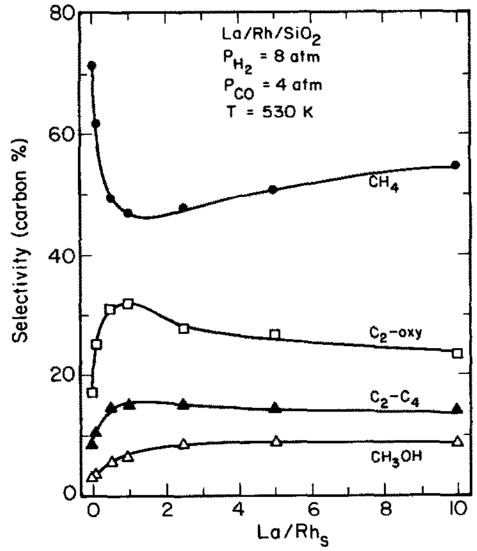

FIG. 6. Dependence of product selectivity on La content.

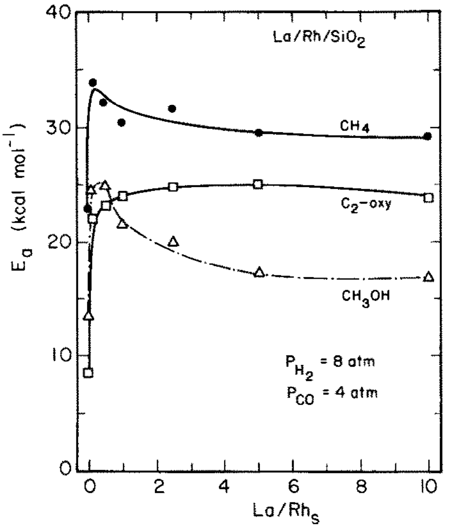

FIG. 7. Dependence of the activation energies for the synthesis of CH_4, CH_3OH, and C_2 oxygenates on La content.

C_2–C_4 hydrocarbons and a minimum in the selectivity to CH_4 are observed as La/Rh_s is increased. The highest selectivity for C_2 oxygenates is observed for La(1.0)/Rh/SiO_2 and is a factor of 1.9 higher than that for the unpromoted Rh/SiO_2. The selectivity for C_2–C_4 hydrocarbons is maximized at La/Rh_s = 2.5 and is a factor of 1.8 higher than that for Rh/SiO_2. The CH_3OH selectivity is highest at La/Rh_s = 5 and is a factor of 3.1 higher than that for Rh/SiO_2. By contrast, the selectivity to CH_4 is minimized at La/Rh_s = 1.0 and is lower than that for Rh/SiO_2 by 34%.

The influence of lanthana content on the activation energies for the synthesis of CH_4, CH_3OH, and C_2 oxygenates is presented in Fig. 7. The activation energy for a given catalyst was determined by fitting a minimum of six data points in the range 513 to 558 K to the Arrhenius expression. The estimated accuracy, based only on data scatter, is approximately ±2 kcal mol^{-1}. It is apparent from Fig. 7 that the addition of lanthana increases the activation energies for the synthesis of all three products and that the activation energy for each product is also a function of the lanthana content. The highest activation energies observed for CH_4 and CH_3OH are for the lanthana-promoted catalysts of very low lanthana content.

Shown in Fig. 8 is the influence of lanthana content on the infrared spectra obtained during steady-state CO hydrogenation. All spectra were recorded after 22 h on stream with $T = 530$ K, $P_{H_2} = 8$ atm, and $P_{CO} = 4$ atm. The absorbance is normalized to the quantity of surface Rh atoms in the unpromoted Rh/SiO_2 catalyst. The positions of the bands are approximately independent of lanthana loading and identical to those shown in Figs. 3 and 4.

A dramatic decrease is observed in the intensity of the band for linearly adsorbed CO with lanthana content. This decrease is similar to that which we have observed for CO chemisorption at 313 K (*7*). The integrated intensity of the band for linearly adsorbed CO for Rh/SiO_2 after 22 of reaction is slightly less than that observed for CO chemisorption at 313 K (*7*). By contrast, the intensity of the band for linearly adsorbed CO for La(5)/Rh/SiO_2 and La(10)/

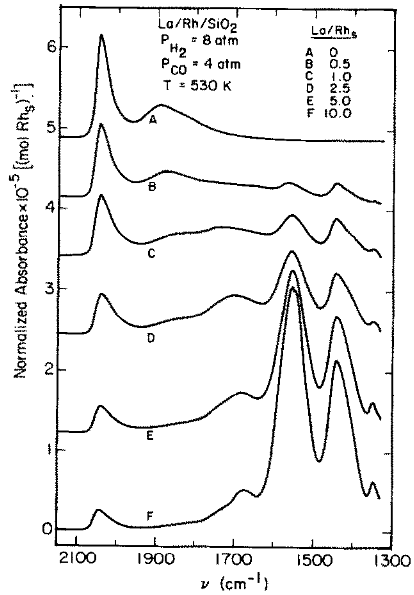

FIG. 8. Effect of La content on the infrared spectrum recorded during CO hydrogenation.

Rh/SiO_2 after 22 h of reaction is slightly greater than the corresponding integrated intensity for CO chemisorption at 313 K (*7*). A similar increase in the CO chemisorption capacity of the metal during reaction was observed for Rh/La_2O_3 (*6*) and a more extensive increase has been reported for Pd/La_2O_3 (*13*). These results indicate that a small portion of the surface Rh in the lanthana-promoted catalysts of high lanthana content becomes uncovered during reaction, due possibly to a change in the structure of the LaO_x overlayer.

It is also clear that the intensities of the acyl band at 1680 cm^{-1} and the acetate bands at 1555 and 1440 cm^{-1} increase with lanthana content. The intensities of the acetate bands are roughly proportional to lanthana content. Although it is difficult to separate the band at 1725 cm^{-1} from the band for acyl at 1680 cm^{-1}, it appears that the intensity of the band at 1725 cm^{-1} is maximized at $La/Rh_s \cong 2.5$–5.0. A maximum in the intensity of this band was also observed at $La/Rh_s \cong 2.5$–5.0 for CO chemisorption at 313 K in Part I of this study (*7*).

DISCUSSION

The characterization studies reported in Part I of this investigation (*7*) support the idea that lanthana promotion of Rh/SiO_2 results in the decoration of the Rh particles by LaO_x moieties but does not alter the average particle diameter. The patches of LaO_x inhibit the chemisorption of CO but have a negligible effect on the chemisorption of H_2, since H_2 chemisorbed on exposed Rh sites can spill over onto the surface of the thin LaO_x patches.

The results presented here clearly demonstrate that La promotion affects the CO hydrogenation activity and selectivity of Rh/SiO_2, as well as the rate parameters associated with the synthesis of specific products. The addition of lanthana results in higher turnover frequencies for the formation of all products (Fig. 5), much higher selectivities for CH_3OH, C_2 oxygenates, and C_2–C_4 hydrocarbons (Fig. 6), and higher activation energies for the formation of all products (Fig. 7). In addition, infrared spectra recorded under reaction conditions show evidence of oxygen-containing organic species on the surface of La-promoted Rh/SiO_2, which are not evident in the spectra recorded for unpromoted Rh/SiO_2.

$$
\begin{array}{rcl}
CO_G + S & \rightleftarrows & CO_S \\
CO_S + S & \rightarrow & C_S + O_S \\
C_S + xH_S & \rightleftarrows & CH_{x_S} (x=1\text{-}3) \\
CH_{3_S} + H_S & \rightarrow & CH_4 \\
CH_{3_S} + CH_2 & \rightarrow & CH_3CH_{2_S} \\
 & \vdots & \\
[CH_3(CH_2)_N]_S + S & \rightarrow & CH_3(CH_2)_{N-2}CH{=}CH_2 + H_S \\
[CH_3(CH_2)_N]_S + H_S & \rightarrow & CH_3(CH_2)_{N-1}CH_3 \\
[CH_3(CH_2)_N]_S + CO_S & \rightarrow & CH_3(CH_2)_NCO_S \\
CH_3(CH_2)_NCO_S + H_S & \rightarrow & CH_3(CH_2)_NCHO
\end{array}
$$

FIG. 9. Reaction mechanism for the synthesis of CH_4, C_{2+} hydrocarbons, and C_{2+} oxygenates.

The influence of LaO_x decoration on the catalytic properties of Rh can be interpreted in terms of the reaction mechanism shown in Fig. 9 (*14*). Nascent carbon produced by the dissociation of CO undergoes hydrogenation to form CH_{x_s} ($x = 1$–3) species. CH_{3_s} groups serve as precursors to CH_4 formation as well as chain growth centers for the formation of higher-molecular-weight products. The composition of the C_{2+} products is dictated by the nature of the chain growth termination step: β-hydrogen elimination produces α-olefins, α-hydrogen addition produces paraffins, and CO insertion followed by α-hydrogen addition produces aldehydes. Methanol is formed via the direct hydrogenation of molecular CO, and C_{2+} alcohols by hydrogenation of the corresponding aldehyde (*5*, *14*).

The mechanism presented in Fig. 9 suggests that the rate-limiting step in the formation of CH_4, C_{2+} hydrocarbons, and C_{2+}-oxygenated products is the dissociation of adsorbed CO. Studies by Winslow and Bell (*15*) have demonstrated that CO dissociation over Rh does not occur readily, even at elevated temperatures. This accounts for the lower activity of Rh relative to metals such as Ni and Ru which dissociate CO more readily. The rate of CO dissociation over Rh is enhanced by lanthana promotion, as was demonstrated in Part I of this work. We believe that this explains why the rates of CH_4 and C_{2+} products are significantly higher over lanthana-promoted Rh than over unpromoted Rh.

The mechanism by which lanthana promotion of Rh might enhance the dissociation of CO is considered next. It is envisioned that near the perimeter of LaO_x islands, CO can adsorb in such a fashion that the carbon end of the molecule is attached to the Rh and the oxygen end, to a La cation. The concurrent interaction of both ends of the molecule with the surface should weaken the C–O bond and thereby facilitate CO dissociation. This interpretation parallels that given by a number of authors recently (*16–22*) to explain the effects of metal oxide promoters on the dissociation of CO.

Evidence for the mode of CO bonding proposed above is derived from the observation of an infrared band at 1725 cm^{-1} when lanthana-promoted Rh/SiO_2 is exposed to CO at 313 K (*7*) or synthesis gas at 530 K (see Fig. 8). It is significant to note that Kiennemann *et al.* (*23*) have recently observed an identical band for ceria-promoted Rh/SiO_2, and Ichikawa and Fukushima (*24*) have observed a band between 1600 and 1800 cm^{-1} for titania-, and manganese oxide-, and iron oxide-promoted Rh/SiO_2. In each of the above studies, the low-frequency CO band is assigned to CO molecules interacting with both Rh and cations of the promoter.

As was illustrated in Fig. 7, the addition of even a small amount of lanthana to Rh/SiO_2 produces a very substantial increase in the activation energy for the synthesis of CH_4, CH_3OH, and C_2-oxygenated compounds. What is remarkable is that the highest activation energies roughly coincide with the highest catalyst activities seen in Fig. 5. Similar effects of lanthana have been observed in studies of CH_4 synthesis over Rh/La_2O_3 (*5*, *6*), Pd/La_2O_3 (*26*), and lanthana-promoted Pd/SiO_2 (*25*). While the effect of La on the activation energies for CO hydrogenation is well documented, an explanation is not yet at hand. All that can be said is that the measured activation energy is the net result of the contribution of the heats of adsorption of the reactants and the activation energies of the elementary steps in the reaction. Since details of the reaction mechanism are not well established, nor is it known whether the mechanism is the same or not for Rh/SiO_2 and lanthana-promoted Rh/SiO_2, it is impossible to speculate intelligently on the cause of the increases in activation energy.

In the discussion thus far, attention has focused on the influence of lanthana promotion on the synthesis of products derived via the dissociation of CO (i.e., CH_4, C_2–C_4 hydrocarbons, and C_2 oxygenates). Figure 5 reminds us that in addition to affecting the activity of Rh/SiO_2 for the formation of these products, lanthana also promotes the formation of CH_3OH. The means by which lanthana promotes CH_3OH synthesis is not clear. Inspection of Table 2 indicates that the activation energy for forming this product over $La(5)/Rh/SiO_2$ is only 3.6 kcal/mol larger than that for synthesis over Rh/SiO_2, and the H_2 and CO partial pressure dependences are virtually identical for both catalysts. The only parameter which changes significantly is the preexponential factor. This suggests that similar sites are involved in the CH_3OH synthesis over promoted and unpromoted Rh/SiO_2 but that the promoter in some fashion increases the number of active sites.

Finally some comments need to be made about the relationship of the acyl (ν_{CO} = 1680 cm^{-1}), formate (ν_{CO} = 1580, 1370 cm^{-1}), and acetate (ν_{CO} = 1555, 1440 cm^{-1}) groups present on the catalyst surface to synthesis of the observed reaction products. As may be seen in Fig. 8, the intensities of the infrared bands associated with these species increase monotonically with increasing La/Rh_s. None of these species are observed, though, in the absence of lanthana.

The concentration of acyl groups increases only slightly with reaction time for $La(5)/Rh/SiO_2$ (see Fig. 4), indicating that it is produced immediately upon onset of the synthesis reaction. Likewise, when the flow of CO to the infrared cell is terminated but the flow of H_2 is allowed to continue, the intensity of the acyl band at 1680 cm^{-1} declines very rapidly. Both observations suggest that acyl groups may be reaction intermediates (e.g., the precursor to acetaldehyde).

The bands at 1555 and 1440 cm^{-1}, associated with acetate groups, grow very slowly with time under reaction conditions (see Fig. 4), but once present are not readily removed even when the catalyst is exposed to pure H_2 at reaction temperatures. These trends suggest that the acetate groups are produced by the accumulation of reaction products (e.g., acetaldehyde and ethanol) on the deposited lanthana. The stability of the acetate groups to reduction makes it unlikely that these species are reaction intermediates.

The role of formate groups is more difficult to assess than those of the acyl and acetate groups. The bands for formate groups are observed for only a short period of time, immediately after the onset of reaction, but then disappear with longer reaction times. Consequently, insufficient information is available upon which to base a judgment as to whether formate groups are possible reaction intermediates.

SUMMARY AND CONCLUSIONS

The addition of lanthana to Rh/SiO_2 results in a higher activity for the formation of all products, a higher selectivity for oxygenates and C_{2+} hydrocarbons, and the stabilization of oxygenated surface species. The higher activity and higher selectivity for oxygenates when Rh/SiO_2 is promoted with lanthan are consistent with the previously observed higher activity and higher oxygenate selectivity for La_2O_3-supported Rh as compared to Rh/SiO_2 (*5, 6*).

The enhancement in the activity for the formation of CH_4 and C_{2+} oxygenates and hydrocarbons when Rh/SiO_2 is promoted with lanthana can be explained by the higher rate of CO dissociation observed for lanthana-promoted Rh/SiO_2 (*7*). The higher rate of CO dissociation is consistent with the observation by infrared spectroscopy of a form with a weakened C–O bond (ν_{CO} = 1725 cm^{-1}). This species is envisioned to be near LaO_x islands, where CO can adsorb in such a way that the carbon end of the molecule is attached to the Rh and the oxygen end, to a La cation. The concurrent influence of both ends of the molecule with the surface weakens the C–O bond and thereby facilitates CO dissociation.

Surface formate, acyl, and acetate groups were observed on lanthana-promoted Rh/SiO_2 by infrared spectroscopy during CO hydrogenation. The acyl group disappears very rapidly upon reduction with H_2, suggesting that it is a possible reaction intermediate. The stability of the acetate groups to reduction makes it unlikely that these species are reaction intermediates. Since insufficient information is available, it is impossible to judge whether formate groups are intermediates.

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