JOURNAL OF CATALYSIS **161,** 274–281 (1996)
ARTICLE NO. 0185

Effect of La^{3+} Promotion of Co/SiO_2 on CO Hydrogenation

George J. Haddad, Bin Chen, and James G. Goodwin, Jr.[1]

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

Received March 6, 1995; revised January 8, 1996; accepted February 9, 1996

A study of CO hydrogenation on La^{3+}-promoted Co/SiO_2 catalysts (La/Co atomic ratios of 0–0.75) has been performed using both global rate measurements and steady-state isotopic transient kinetic analysis (SSITKA). Aqueous impregnation (the means of adding La^{3+}) of Co/SiO_2 led to a significant decrease in the number of intermediates leading to methane during CO hydrogenation, but it did not alter the nature of the active sites. In a previous characterization paper (19) La^{3+} promotion of Co/SiO_2 was shown to moderate the strong Co–support interactions brought about by aqueous impregnation of the Co/SiO_2 and to enhance the reducibility of the Co oxide. La^{3+} addition to the Co/SiO_2 catalyst was found to lead to a significant increase in the activity for Fischer–Tropsch synthesis (on a per gram Co basis). The SSITKA results showed that the concentration of active intermediates leading to methane increased with increase in La/Co ratio. However, the TOF, the pseudo-first-order rate constant, the reactivity distribution function, and the activation energy were not affected by La^{3+} addition. Thus, it can be concluded that La^{3+} did not change the nature of the active sites, just their concentration. This increase in the concentration of active sites follows exactly the increase in surface Co^0. La^{3+} promotion ($La/Co \geq 0.1$) also caused the chain growth probability and the olefin/paraffin ratio to increase significantly at 220°C and for $H_2/CO = 2$.

INTRODUCTION

Natural gas offers an important source for fuel and chemical feedstocks using partial oxidation to generate a mixture of CO and hydrogen. Fischer–Tropsch synthesis (FTS) has been identified to be the most promising route for conversion of this synthesis gas to higher hydrocarbons.

Recent developments in FTS have centered on the production of high-molecular-weight paraffins which in turn can be hydrocracked to products in the middle distillate range. Co-based catalysts (1–13) are the preferred catalysts for natural gas conversion because of their high activity, high stability, relatively low cost, low selectivity for making CO_2, and high selectivity for making long chain paraffins. Currently, potential commercial Co catalysts consist typically of four components: Co metal, a small amount of a second metal (usually noble), oxide promoters (alkali, rare earth, and/or transition metal oxide such as ZrO_2), and a support (silica, alumina, or titania) (5).

It is mentioned in the patent literature that rare earth promotion of Co is beneficial for Fischer–Tropsch synthesis (6–11). Several studies (12–14, 16) have found improved selectivity for longer chain hydrocarbons upon rare earth promotion of Co catalysts. Halvorsen *et al.* (15) found Co on La_2O_3/SiO_2 to be highly dispersed and to have a lower CO-hydrogenation activity than Co on SiO_2. These results (15) were interpreted to indicate decoration of Co by lanthana moieties resulting in reduction of active metal surface area and leading to a decrease in activity. Barrault *et al.* (14, 17) observed that rare earth promotion gave rise to a 100-fold increase in specific activity and turnover frequency for Co–La/C catalysts for CO hydrogenation. They interpreted this as a strong indication of the formation of new sites. Ledford *et al.* (16) studied two methods of preparing La^{3+}-promoted Co/Al_2O_3 catalysts. They noted promotional effects only when La^{3+} was impregnated and calcined first followed by Co impregnation. No effects were observed when La^{3+} was impregnated second onto a calcined Co/Al_2O_3 catalyst. Low levels of La^{3+} promotion led to little effect on the structure. Vada *et al.* (12, 13) studied a $La^{3+}/Co/Al_2O_3$ system for CO hydrogenation using steady-state isotopic transient kinetic analysis (SSITKA) and found La^{3+} to increase the overall catalyst activity, chain growth probability, average site/intermediate activity, and the concentration of active surface intermediates leading to methane for a low loading of La^{3+} ($La/Co = 0.05$). However, at higher La^{3+} loadings ($La/Co = 0.10$), all of these parameters decreased with the exception (within experimental error) of chain growth probability and methane-producing site activities.

The effect of La on the properties of other F–T metals, such as precipitated Fe-based catalysts (17), has also been addressed. It was found (17) that rare earth oxides increased the dispersion of the iron particles, inhibiting their growth and further reduction. Also, for the same system, it was postulated that rare earth oxides encouraged the adsorption and dissociation of carbon monoxide and decreased the reactivity of the surface carbon species toward hydrogen due

---

[1] To whom correspondence should be addressed.

0021-9517/96 $18.00

to the electronic donation properties brought about by their basicities.

Previously, the impact of aqueous impregnation on the properties of prereduced Co/SiO$_2$ was studied (18). The process of promotion itself (aqueous impregnation) was shown to have a severe effect on the structure of the reduced Co catalysts. Co oxide decreased in favor of a Co silicate phase which reduced completely only above 800°C.

In a recent characterization study of La^{3+} promotion of Co/SiO$_2$ (19), La^{3+} was found to be well dispersed over the Co/SiO$_2$ catalyst. However, it did not seem to be well dispersed over the Co metal surface. It was suggested that La^{3+} forms island-like structures which block part of the surface Co sites but may also be located at the Co–SiO$_2$ interface. The results showed La^{3+} to regulate the strong Co–support interactions emerging from aqueous impregnation of Co/SiO$_2$, to enhance the reducibility of the Co oxide, and to result in a greater number of exposed Co atoms.

The literature results point out that the promotional effect of La on Group VIII metals can be variable, probably depending heavily on such parameters as how and when La is added to the catalyst precursor, the nature of the support, and the state of the catalytic metal. It would be useful to our evaluation of the effect of such promotion on a reaction to be able to count the number of active sites and determine their approximate activity rather than rely on measurements of global reaction rates alone.

SSITKA permits the study of catalyst surfaces under steady-state reaction conditions (12, 13, 19–22). Accurate measurements of the concentration of intermediates and their activities under reaction conditions are possible by using isotopic switching and keeping the reaction environment constant during the isotopic transient. The steady-state rate for methane formation for hydrogenation of surface intermediates as the rate determining step can be written as

$$R = (k_M)_{\text{true}} \cdot N_H \cdot N_M,$$

where $(k_M)_{\text{true}}$ is the true rate constant for methane formation, N_H represents the surface concentration of hydrogen, and N_M is the surface concentration of carbon-containing intermediates which lead to CH_4. N_H is unable to be determined because of the isotopic effect in switching from H_2 to D_2; however, N_M can be determined using isotopic switching of ^{12}CO to ^{13}CO. Assuming pseudo-first order kinetics, the rate can be determined as: $R = k_M \cdot N_M$ where $k_M = (k_M)_{\text{true}} \cdot N_H$. k_M is determined from $1/\tau_M$, where τ_M is the average surface residence time of the carbon in the reaction intermediates. From the steady-state isotopic transients, τ_M is easily determined.

This paper reports on a study dealing with the effect of La^{3+} promotion of Co/SiO$_2$ catalysts on CO hydrogenation. Although, La promotion of Fischer–Tropsch catalysts has been found to be advantageous under certain circumstances, the exact mechanisms of action of the rare earth promoters are still not very well understood, especially where those mechanisms may be affected by support effects.

EXPERIMENTATION

Catalyst Preparation

Catalyst nomenclature. Catalysts in this paper are identified by B-LaR, where "B" refers to the calcined, reduced, and passivated 20% Co/SiO$_2$ *base* catalyst; "La" to La^{3+} species; and "R" to La/Co atomic percent. La most likely exists mainly in the form of La_2O_3 after calcination. In the presence of H_2O or CO_2, it can form LaO(OH) and $La(OH)_3$ or $La_2(CO_3)_3$, respectively. Heating these compounds in the absence of H_2O or CO_2 cause them to revert back to La_2O_3 (23). In this paper La species will be referred to only as "La^{3+}".

Preparation of the base Co catalyst. The support used (Cab-O-Sil silica, amorphous fumed silica powder from Cabot Corp.) had impurities Na, Al, and K present in the amounts of 63, 46, and 26 ppm, respectively, as measured by inductively coupled plasma (ICP). The 20% Co/SiO$_2$ base catalyst (B) was prepared by impregnating the silica to incipient wetness using an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (J. T. Baker Inc.). Incipient wetness occurred at about 1.8 ml/g of silica. This step was followed by drying at 90°C overnight, calcining at 300°C for 6 h, and reducing in H_2 at 350°C for 22 h. During calcination and reduction, temperature ramp rates were 1°C/min. After reduction, the catalyst was passivated at 25°C by allowing air to leak slowly into the reduction chamber.

Preparation of La^{3+}-promoted Co catalysts. The prereduced and passivated base catalyst B was impregnated to incipient wetness with the appropriate amount of an aqueous solution of $La(NO_3)_3 \cdot 5H_2O$ (Aldrich Chemical Company, Inc.) to obtain catalysts with La/Co atomic ratios of 0.0, 0.05, 0.1, 0.2, 0.3, 0.5, and 0.75. After impregnation, the catalyst was allowed to dry in an oven overnight at 90°C. Finally, it was re-reduced in H_2 at 350°C for 22 h and passivated at 25°C.

Elemental Analysis

To check the final Co loadings, elemental analysis using ICP spectroscopy (Galbraith Laboratories) was carried out.

Hydrogen Chemisorption

The method used for gas volumetric chemisorption was comparable to that used by Reuel and Bartholomew (24). Re-reduction was done by flowing 100 cc/min of H_2 at 320°C for 12 h. The adsorption isotherms were measured at 25°C after initially equilibrating at 100°C by the decreasing pressure method. The high temperature for initial adsorption was used since the chemisorption process is known to be highly activated on cobalt (25). One hour was allowed for equilibration at each H_2 pressure at 25°C. The total amount of chemisorbed H atoms was used to determine the number of vacant Co^0 atoms at the surface using the relationship $H/Co_s = 1$ (24). The results from TPD experiments on the base catalysts (B and B-La0) and on selected La^{3+}-promoted catalysts (B-La10 and B-La75) agreed well with the respective irreversible amounts of chemisorbed H atoms obtained from static hydrogen chemisorption.

CO Hydrogenation

Fischer–Tropsch synthesis over the temperature range 200–230°C at atmospheric pressure was performed in a downflow differential fixed-bed stainless steel reactor (diameter = 6 mm). A space velocity (WHSV) between 5.5 and 13 h^{-1} and a H_2/CO ratio of 2 were used. The catalysts weights (100–260 mg) were held in the middle of the reactor using quartz wool. Flow rates were controlled by Brooks mass flow controllers. The feed composition was $H_2/CO = 33.3/16.7$ (cc/min). Ultrapure CO (Linde) was passed through activated carbon trap to reduce any possible moisture, hydrocarbon, Fe carbonyl contaminants. Ultrapure H_2 (Liquid Carbonic) was passed through a deoxo unit followed by a molecular sieve trap before being fed into the reactor. Using a ramp rate of 1°C/min, the catalysts were first heated in 60 cc/min H_2 flow to 320°C and then re-reduced *in situ* at this temperature for 12 h prior to reaction. The reduced catalysts were then cooled down in flowing H_2 to the initial reaction temperature of 220°C. The startup procedure for CO hydrogenation on Co catalysts can be of critical importance due to their activity and to rapid deactivation by carbon deposition at higher temperatures if exotherms occur during startup. Usually, such exotherms during startup result in greatly reduced catalyst activity. Due to the use of SiO_2 as the support, the low weight of catalyst used, the relatively high flow rate used, and the low conversion of CO, the startup procedure used in this research in order to determine accurate initial reaction rates appeared to be very effective. The catalyst activities observed were similar to those of other Co/SiO_2 catalysts where reaction was initiated slowly by increasing reactant concentrations over several hours.

The catalyst bed temperature was controlled by Omega temperature controllers using a thermocouple at the bottom of the bed. The inlet temperature at the top of the bed was controlled using heat traced lines. This provided approximately equal temperatures at both ends of the bed. The reaction conditions were chosen so that differential reaction conversion levels were obtained. The flow to the reactor was switched from H_2 to the H_2 and CO mixture to start reaction. Samples of the products were taken after 5 min of reaction to study the initial activity of the catalysts. Hydrogen bracketing was performed after each reaction evaluation for 1 h in order to restore the activity of the catalysts. The temperature was then changed to 210, 200, and in some cases to 230°C and reaction sampled as before at each reaction temperature. Reaction was then measured again at 220°C to confirm that the catalyst had not deactivated during the measurements. Reaction was continued at 220°C for about 17 h in order to determine time-on-stream behavior to steady-state reaction.

The postreactor zone was heated at 220°C to avoid condensation of heavy products. Analysis of the high-molecular-weight hydrocarbons was performed by passing product samples to a Perkin Elmer 8000 gas chromatograph. This GC was equipped with a 30-m DB-5 capillary column (J&W Scientific) and FID. The GC oven temperature was maintained at 35°C for 5 min. It was then heated at 5°C/min to 200°C and held there until the completion of the analysis. Ultrapure He (Liquid Carbonic) was passed through a molecular sieve trap before being used as a carrier gas for the FID at a flow rate of 2 cc/min. A second GC (Varian 3700) was used for the analysis of the light hydrocarbons (mainly C1 to C6). This was done by manual injection of samples. This GC was equipped with a 6′ Porapack 80/100 column (Alltech) and an FID detector. The C_5 results were used to link the two GC analyses. Calibration of the GC's was performed by using a calibrated hydrocarbon gaseous mixture to determine retention times, amounts, and types of the products.

SSITKA was performed using a differential fixed-bed glass microreactor (diameter, 6 mm). The reaction was performed at 220°C and 1.8 atm using a reaction feed composition $H_2/CO/He = 20/2/78$ (cc/min). The high H_2/CO ratio of 10 was used to keep the catalyst deactivation at a minimum. The isotopic switch $^{12}CO/^{13}CO$ was done after 5 min of reaction. A trace amount of argon was fed with the ^{12}CO flow to allow for the determination of gas phase holdup. A Leybold-Inficon Auditor 2 mass spectrometer equipped with a high speed data acquisition system and controlled by a 386 PC was used to monitor the concentrations of Ar, ^{12}CO, ^{13}CO, $^{12}CH_4$, and $^{13}CH_4$ in the exit stream. A Varian 3700 GC was used to calibrate the mass spectrometer signal. The residence time of the gas phase in the system was shortened to less than 6 s by minimizing the dead volume in the tubing lines.

RESULTS

ICP done on the water phase of a (20% Co/SiO_2 + water) slurry heated at 90°C for 12 h to investigate any leaching of contaminants from the silica to the solution during the impregnation steps of the catalyst preparations revealed no such occurrence.

Table 1 presents the static hydrogen chemisorption results for this series of catalysts taken from a previous study

TABLE 1

Characteristics of Unpromoted and La-Promoted 20% Co/SiO$_2$ Catalysts (19)

Catalyst	H_2 Chemisorption[a] (μmol H_2/g Co) Total	Irrev.	% Co reduced during standard reduction[b] at 320°C	d_p[a,c] (nm)
B	380	295	80	18
B-La0	225	180	30	11
B-La05	318	231	50	13
B-La10	361	292	47	12
B-La30	450	369	50	9.5
B-La75	482	404	48	9.0

[a] Static H_2 chemisorption at 100°C. Error estimated at ±10%.

[b] Obtained from TPR 100–900°C after *in situ* reduction at 320°C for 12 h.

[c] Est. assuming $H_{tot}/Co_s = 1$, 5.46×10^{-20} m^2/Co$_s$, $d_p = 5/S_{Co}/\rho_{Co}$, and based on percentage Co reduced during standard reduction at 320°C.

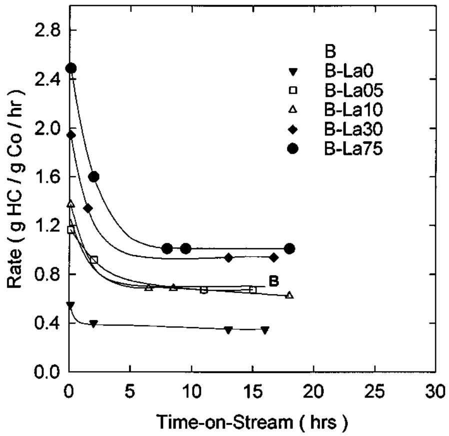

FIG. 1. Time-on-stream activities for CO hydrogenation on La-promoted Co/SiO$_2$ at 220°C and 1 atm (H_2/CO = 2).

(19). The total hydrogen uptake for the water-impregnated catalyst B-La0 was found to be much lower than that of the unimpregnated base catalyst B. The static hydrogen uptake increased significantly with La^{3+} addition up to La/Co = 0.3 after which it began to level off for higher loading catalysts ($0.3 \leq$ La/Co ≤ 0.75).

Table 2 presents the initial CO hydrogenation data for the base catalyst B, the water-impregnated base catalyst B-La0, and the La^{3+}-promoted catalysts. Rates in this study are expressed as per gram Co instead of per gram catalyst due to the significant variation in the wt% of Co with increasing loadings of La^{3+}. The water-impregnated catalyst B-La0 exhibited a significantly lower rate than that of catalyst B. On the other hand, water impregnation had no effects on either the chain growth probability, α, or the TOF (based on hydrogen chemisorption). The initial activity for CO hydrogenation was significantly enhanced upon La^{3+} addition to the Co/SiO$_2$ catalysts. The rate increased with increasing La^{3+} level. The initial activity for the most highly promoted catalyst (B-La75) was four times higher than that for B-La0 and was almost double that for B. On the other hand, the initial TOF values and the activation energies for the base catalysts (B and B-La0) and for the La^{3+}-promoted ones were essentially equivalent except perhaps for the highest promoted catalyst. Figure 1 shows the time-on-stream rates (in g HC/g Co/h) for these catalysts. The rates all decreased by approximately 50% during the first 5 h of reaction, typical for Co catalysts under these conditions. This deactivation was probably due to deposition of carbonaceous material on the catalyst surface and in the pores since the catalytic activities could be completely restored by H_2 at 220°C. Steady-state rates for the La^{3+}-promoted catalysts were superior to those of the base catalysts, especially the water-impregnated one (B-La0). The effect of La^{3+} promotion on rate of CO hydrogenation is similar to what has been seen for rate of ethane hydrogenolysis and discussed elsewhere (19). In particular, it was concluded in that paper based on extensive TPR results that the presence of La^{3+} in the aqueous solution moderates the strong Co–silica interactions that aqueous impregna-

TABLE 2

Initial CO Hydrogenation Reaction at 220°C for (La)/Co/SiO$_2$ Catalysts

Catalyst	CO conv. (%)	R_{CO}[a] (μmol/g Co/s)	TOF[b] × 10^2 (s^{-1})	Chain growth prob., α	Selectivity (wt%) C_1	C_2–C_4	C_5–C_{12}	C_{13+}	E_a (kcal/mol)
B	5.0	25	3.3	0.57	34	35	30	0.8	23
B-La0	4.0	11	2.4	0.56	31	33	35	1.0	24
B-La05	3.3	23	3.6	0.64	24	31	43	2	26
B-La10	3.7	26	3.6	0.7	18	27	48	6.6	25
B-La30	3.9	30	3.2	0.72	17	25	50	8	28
B-La75	4.8	41	4.2	0.71	17	26	50	7	30

[a] At 220°C, 1.0 atm, H_2/CO = 2/1.

[b] Based on hydrogen chemisorption.

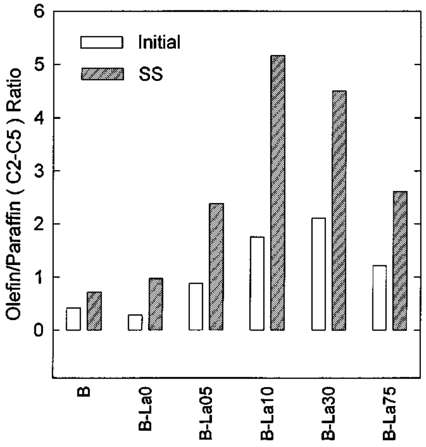

FIG. 2. C_2–C_5 olefin/paraffin ratios for La-promoted Co/SiO_2 Catalysts at 220°C and 1 atm ($H_2/CO = 2$).

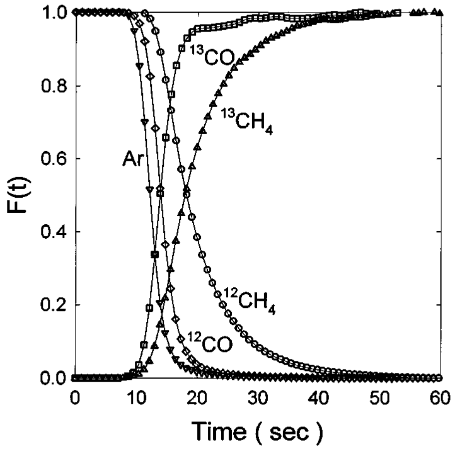

FIG. 3. Isotopic transients during methanation at 220°C on the base catalyst B ($H_2/CO = 10$).

tion and drying of a reduced/passivated Co/SiO_2 catalyst causes.

La^{3+} addition led to improved chain growth probability, α, for the Co/SiO_2 catalysts. α increased from 0.57 to 0.70 with increasing La^{3+} loading up to La/Co = 0.1 after which it leveled off. The olefin/paraffin ratio was essentially the same for both base catalysts (B and B-La0) (see Fig. 2). However, a marked increase in this ratio was observed with relatively low additions of La^{3+} corresponding to La/Co ≈ 0.05. This ratio was maximum for La/Co = 0.1. However, the ratio for even the highest La^{3+} loading catalyst B-La75 was still significantly higher than those of the base catalysts.

SSITKA of methanation was used to decouple the effects of La^{3+} on the rate of the formation of methane into contributions from the concentration of methane intermediates and from the average site/intermediate activity. The conditions for SSITKA (especially the high H_2/CO ratio) were chosen in order to minimize deactivation due to carbon deposition and resulted in methane selectivities >80%. A typical set of isotopic transients is shown in Fig. 3. Table 3 gives the initial and the steady-state SSITKA results for the unpromoted and the La^{3+}-promoted catalysts. A significant decrease in the rate and in the number of intermediates (N_M) leading to methane due to water impregnation alone (B-La0) was observed. The amount of reversibly adsorbed CO (N_{CO}) on the Co surface declined to a lesser degree with water impregnation. On the other hand, relative to hydrogen chemisorption, the water-impregnated unpromoted catalyst B-La0 exhibited an increase in CO surface coverage by about 35% over that for B.

La^{3+} did not appear to affect the intrinsic activity of the Co sites, since k_M (a measure of the "true" TOF for methane formation based on a pseudo-first-order rate assumption) was approximately constant for all the catalysts,

TABLE 3

SSITKA of CO Hydrogenation over (La)/Co/SiO_2 Catalysts at 220°C

Cat.	R_{CO}[a] (μmol/ g Co/s)		TOF[b] × 10^2 (s^{-1})		τ_{CO} (s)		τ_M (s)		k_M[c] (s^{-1})		N_{CO} (μmol/ g Co)		N_M (μmol/ g Co)		θ_{CO}[d]		θ_M[d]		$\theta_{(CO+M)}$[d]
	I[e]	SS[e]	I	SS	I	SS	I	SS	I	SS	I	SS	I	SS	I	SS	I	SS	SS
B	15	12	2	1.6	1.6	1.7	6.5	7.4	0.15	0.13	311	331	101	91	0.41	0.44	0.13	0.12	0.56
B-La0	7.0	5	1.5	1.1	1.3	1.2	5.4	7.5	0.18	0.13	253	233	39	38	0.56	0.52	0.09	0.08	0.60
B-La10	22	16	3.0	2.2	1.2	1.5	5.8	7.6	0.17	0.13	233	292	127	119	0.32	0.40	0.18	0.16	0.56
B-La30	32	24	3.5	2.7	1.3	1.3	5.6	6.3	0.18	0.16	253	253	180	154	0.28	0.28	0.20	0.17	0.45
B-La75	40	24	4	2.5	1.0	1.1	5	6.3	0.20	0.16	195	214	198	153	0.20	0.22	0.21	0.16	0.38

[a] At 220°C, 1.8 atm, $H_2/CO = 10$, $P_{H_2} = 0.2$, $P_{CO} = 0.02$.

[b] Based on static hydrogen chemisorption.

[c] $k_M = 1/\tau_M$, pseudo-first-order rate constant.

[d] θ_i is the surface coverage of intermediates = N_i/(total adsorbed H^b).

[e] I, initial, SS, steady-state.

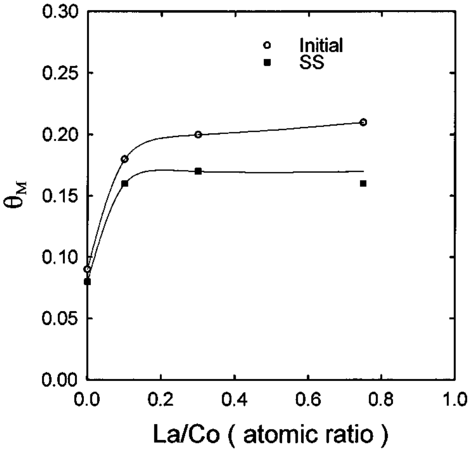

FIG. 4. Methane intermediates coverage versus La/Co atomic ratio at 220°C ($H_2/CO = 10$).

both unpromoted and La^{3+}-promoted. Similar to what was found at FT synthesis conditions (Table 2), there was also no significant effect on TOF (based on hydrogen chemisorption) for these catalysts at the reaction conditions used for SSITKA (Table 3). However, the concentration of surface intermediates leading to methane (N_M) during both initial and steady-state reaction increased significantly as a result of increasing La^{3+} loading, although it may have leveled off at the high loadings ($La/Co \geq 0.3$). Compared to B-La0, a three-fold increase in the methane intermediates with La^{3+} addition was observed for all La^{3+}-promoted catalysts. On a surface coverage basis (relative to H_2 chemisorption), however, there was only a twofold increase (Table 3, Fig. 4).

The La^{3+}-promoted catalysts exhibited a maxima in the amount of adsorbed CO relative to that of the base catalyst B-La0. However, a significant monotonic decrease in the CO surface coverage (based on H_2 chemisorption) with increasing La^{3+} loading was observed (see Table 3).

The total coverage of all surface species can be expressed as

$$\theta_T = \theta_{CO} + \theta_M + \theta_H + \theta_C + \theta_\square$$

where $\theta_{CO}, \theta_M, \theta_H, \theta_C$, and $\theta_\square$ are the coverages of reversibly adsorbed CO, active intermediates leading to methane, hydrogen, less reactive carbonaceous species, and vacant sites, respectively. It is highly likely that $\theta_\square$ was ca. 0 under the reaction conditions. Neither θ_H, the hydrogen coverage, nor θ_C, the carbonaceous deposits coverage could be determined under reaction conditions. Using $\theta_{CO+M} = \theta_{CO} + \theta_M$ as an indication of θ_T even though this quantity constituted only 40–60% of full coverage, it would appear that the total coverages of the unpromoted and the La^{3+}-promoted catalysts were probably essentially the same, except perhaps for the high La^{3+} loadings (see Table 3).

DISCUSSION

Effect of Aqueous Impregnation

The purpose for preparing the water-impregnated catalyst was to provide clues regarding the effects of aqueous impregnation in order to distinguish those effects relating to La^{3+} promotion itself from those relating to the "process" of adding the promoter. The formation of Co silicate and the resulting decline in the Co oxide phase was shown previously to occur as a result of aqueous impregnation of reduced Co/SiO_2 (18).

The results presented here show clearly that aqueous impregnation did not influence the nature of the Co active site for CO hydrogenation as evidenced by the similarity in TOFs, chain growth probabilities, and k_M for the base catalysts, B and B-La0. However, aqueous impregnation did lead to a decline in the number of active Co sites as shown by the significant decrease in H_2 chemisorption, the rate of CO hydrogenation, and the number of intermediates leading to methane (N_M) determined by SSITKA. This is also consistent with previous results for ethane hydrogenolysis (18).

Effect of La^{3+} on Co^0 Dispersion

A recent characterization study of these catalysts (19) has shown that La^{3+} addition to these catalysts leads to enhanced reducibility and to higher hydrogen uptakes. This has been suggested to be due to La^{3+} action in moderating the strong Co–SiO_2 interactions, resulting from the aqueous impregnation of these catalysts (18). Since La^{3+} addition did not change the activity of the Co sites as evidenced by the constant TOFs for F–T and methanation and since CO hydrogenation is not a structure-sensitive reaction, the observed increases in the F–T and the methanation rates are attributed to an increase in the number of active sites (as evidenced by an increase in N_M during methanation) probably due to an increase in the amount of Co^0 surface atoms (Co^0 dispersion) with increasing La^{3+} loading.

Effect of La^{3+} on Site Activity

CO hydrogenation results (Tables 2 and 3) show that the nature of the active site was not changed upon the addition of La^{3+} to the Co/SiO_2 catalysts, as evidenced by the constant TOFs (based on hydrogen chemisorption) for both F–T synthesis and methanation. SSITKA results provide an even better picture of the La^{3+} effects on the rate of CO hydrogenation. SSITKA can divide the rate results into contributions from intrinsic activity versus concentration of active intermediates. An examination of the SSITKA results (Table 3) reveals that the residence times of intermediates leading to CH_4, τ_M, and, consequently, the average pseudo-first-order rate constants, k_M, were essentially identical for the unpromoted and the La^{3+}-promoted catalysts,

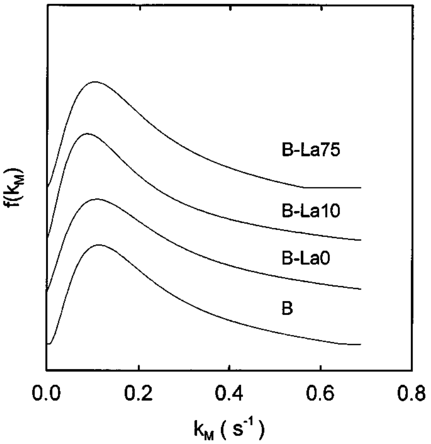

FIG. 5. Methanation activity distribution from SSITKA for La-promoted Co/SiO$_2$ at 220°C.

indicating also little or no change in the nature of the Co active sites. An extension of SSITKA, the T–F method (26), that employs a constrained standard Tikhonov regularization of the Fredholm equation of the first kind,

$$R_M(t) = N_M \int k_M e^{-k_M t} f(k_M) dk_M,$$

can be used for nonparametric determination of reactivity distribution functions, $f(k)$, from steady-state isotopic transients. $R_M(t)$ is the gas phase-corrected steady-state isotopic transient of methane. Analysis of the $^{12}CH_4$ transients of all the catalysts by this technique showed that the distribution functions of both the unpromoted and the La^{3+}-promoted catalysts were alike, indicating no effects of La^{3+} on the activity distribution of the Co sites (Fig. 5). The fact that the activation energies for the unpromoted and the La^{3+}-promoted catalysts were essentially the same also supports the conclusion that the sites were not significantly affected.

Effect of La^{3+} on Hydrogenation and Selectivity

Several researchers (27, 28) have indicated that, on a Co surface, the rate-determining step for CO hydrogenation is not the dissociation of CO but rather the reaction of CH$_x$ with hydrogen. A decrease in hydrogenation usually also entails a decrease in rate of CO hydrogenation such as seen upon K$^+$ promotion of Co (29). In the case of La^{3+} promotion, however, the rate of CO hydrogenation increased together with an increase in olefin/paraffin ratio. It would seem odd, also that hydrogenation would decrease but that the pseudo-first-order rate constant and TOF would remain constant. This perhaps indicates a compensation effect of some sort. An increase in the desorption rate of olefins could explain the increase in the olefin/paraffin ratio. However, there was no evidence for or against that possibility in the results presented here. Underwood and Bell (30) have suggested that La^{3+} cations interact with the oxygen end of CO adsorbed on a Rh/SiO$_2$ catalyst weakening the C–O bond and resulting in enhanced CO dissociation and, thus, in higher activity. However, in this paper, the residence times of CO on Co determined by SSITKA were constant, suggesting that the strength of adsorption of CO on both the unpromoted and the La^{3+}-promoted catalysts were essentially similar.

The answer to this question may lie with catalytic properties of La^{3+}. The catalytic properties of rare earth oxides have been investigated for dehydrogenation of cyclohexane (31, 32). Major products from these studies are aromatics and polyunsaturated olefins, but absolute activities are quite low and appreciable reactant conversions do not occur below ca. 450°C. However, it is possible that the interactions between Co and La^{3+} led to a higher dehydrogenation activity near the Co–La^{3+} interface than that for cyclohexane dehydrogenation on rare earth oxide. This would fit exactly with the increase in the olefin production.

It is well known that olefin readsorption can contribute to hydrocarbon chain growth in FTS. The production of high-molecular-weight hydrocarbons on Co catalysts has been reported to follow the readsorption of primary α-olefin products on Co catalysts (33). Thus, the increase in the chain growth probability, α, could be due to an increase in olefin reincorporation in the growing chains and a decrease in hydrogenation, as evidenced by the increase in the olefin/paraffin ratio. The implications of the maximum in olefin/paraffin ratio for a moderate level of La^{3+} can only be speculated on at this point.

The coadsorption of CO and H$_2$ at elevated temperatures on La^{3+} has been shown to lead to the formation of formate ions (34). Thus, it is possible that the Co–La^{3+} interface may have provided additional sites for olefin readsorption and chain growth to higher hydrocarbons.

CONCLUSIONS

While aqueous impregnation (the means of adding the promoter) of Co/SiO$_2$ catalysts resulted in a significant decrease in the number of Co surface sites for CO adsorption during CO hydrogenation, it is clear that it did not alter the nature of the active sites. La^{3+} addition, however, was found to lead to a significant increase in the activity for Fischer–Tropsch synthesis. Considering the similarity in the TOFs, the pseudo-first-order rate constants, k_M, the reactivity distribution functions, and the activation energies for the unpromoted and the La^{3+}-promoted catalysts, it can be concluded that La^{3+} did not change the nature of the active sites. However, La^{3+} promotion brought about the increase in CO hydrogenation rate by increasing the concentration of active sites/intermediates. La^{3+} addition also caused the chain growth probability and the olefin/paraffin ratio to increase substantially. It is speculated that La^{3+} may enhance olefin readsorption near the La^{3+}–Co interface, resulting in increased chain growth probability for these catalysts.

ACKNOWLEDGMENT

The authors thank the Department of Energy (Office of Fossil Energy) for funding this work under Contract DE-AC22-92PC92108.

REFERENCES

1. Kazi, A., Beddu-Adou, F., and Goodwin, J. G., Jr., *Prepr. Petr. Chem. Div.* **37**, 234 (1992).
2. Oukaci, R., Goodwin, J. G., Jr., Marcelin, G., Singelton, A., *Prepr. Div. Fuel Chem.* August 21–25 (1994).
3. Chen, Y. W., and Goodwin, J. G., Jr., *React. Kinet. Catal. Lett.* **26**, 453 (1984).
4. Gelthorpe, M. R., Mok, K. B., Ross, J. R. H., and Sambrook, R. M., *J. Mol. Catal.* **25**, 253 (1984).
5. Goodwin, J. G., Jr., *Prepr. ACS Div. Petr. Chem.* **36**, 156 (1991).
6. Eri, S., Goodwin, J. G., Jr., Marcelin, G., and Riis, T., U.S. patent 4,801,573 (1989).
7. Kibby, C. L., and Kobylinski, T. P., U.S. patent 4,497,903 (Feb. 5, 1985).
8. Eri, S., Goodwin, J. G., Jr., Marcelin, G., and Riis, T., U.S. patent 4,857,559 (1989).
9. Hoek, A., Joustra, A. H., Minderhoud, J. K., and Post, M. F., U.K. pat. appl. GB 2 125 062 A (1983).
10. Fiato, R. A., Iglesia, E., and Soled, S. L., U.S. patent 4,794,099 (1988).
11. Beuther, H., Kibby, C. L., Kobylinski, T. P., and Pannell, U.S. patent 4,613,624 (1986).
12. Vada, S., Kazi, A. M., Bedu-Addu, F. K., Chen, B., and Goodwin, J. G., Jr., *in* "Natural Gas Conversion" (H. E. Curry-Hyde, and R. F. Howe, Eds.), Vol. 2, Elsevier Science, Amsterdam, 1994.
13. Vada, S., Chen, B., and Goodwin, J. G., Jr., *J. Catal.* **153**, 224 (1995).
14. Barrault, J., and Guilleminot, A., *Appl. Catal.* **21**, 307 (1986).
15. Halvorsen, S., Vinje, K., Lofthus, S., and Dahl, I. M., *in* "Natural Gas Conversion" (A. Holmen *et al.*, Eds.), p. 281. Elsvier Science, Amsterdam, 1991.
16. Ledford, J. S., Houalla, M., Proctor, A., Hercules, D. M., and Petrakis, L., *J. Phys. Chem.* **93**, 6770 (1989).
17. Wang, D.-Z., Cheng, X.-P., Huang, Z.-E., Wang, X.-Z., and Peng, S.-Y., *Appl. Catal.* **77**, 109 (1991).
18. Haddad, G. J., and Goodwin, J. G., Jr., *J. Catal.* **157**, 25 (1995).
19. Haddad, G. J., Chen, B., and Goodwin, J. G., Jr., *J. Catal.* **160**, 43 (1996).
20. Happel, J., *Chem. Eng. Sci.* **33**, 1567 (1978).
21. Bennett, C. O., *Catal. Rev. Sci. Eng.* **13**, 121 (1976).
22. Biloen, P., *J. Mol. Catal.* **21**, 17 (1983).
23. Gallaher, G., Goodwin, J. G., Jr., Huang, Chen-Shi, and Houalla, M., *J. Catal.* **127**, 719 (1991).
24. Reuel, R. C., and Bartholomew, C. H., *J. Catal.* **85**, 63 (1984).
25. Zowtiak, J. M., and Bartholomew, C. H., *J. Catal.* **83**, 107 (1983).
26. Hoost, T. E., and Goodwin, J. G., Jr., *J. Catal.* **134**, 678 (1992).
27. Biloen, P., Helle, J. N., and Sachtler, W. M. H., *J. Catal.* **58**, 95 (1979).
28. Sachtler, W. M. H., *Chem. Ing. Tech.* **54**, 901 (1982).
29. Goodwin, J. G., Jr., Oukaci, R., Haddad, G. J., and Kogelbauer, A., unpublished results.
30. Underwood, R. P., and Bell, A. T., *J. Catal.* **111**, 325 (1988).
31. Briggs, R. A., and Taylor, H. S., *J. Am. Chem. Soc.* **63**, 2500 (1941).
32. Minachev, Kh. M., and Markov, M. A., *Sci. Select. Catal.* 248 (1968).
33. Iglesia, E., Reyes, S. C., and Soled, S. L., *in* "Computer-Aided Design of Catalysts and Reactors" (C. J. Pereira and R. E. Becker, Eds.), Dekker, New York, in press.
34. Hattori, H., and Wang, G. W., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984." Dechema, Frankfurt -am -Main, 1984.