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Effect of Pretreatment on the Activity of a Ru-Promoted Co/Al_2O_3 Fischer–Tropsch Catalyst

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The effect of calcination and reduction temperatures on the activity of a Ru-promoted Co/Al_2O_3 catalyst for the CO hydrogenation reaction has been studied. The catalyst was prepared by the incipient wetness impregnation method and calcined and reduced at various temperatures. Along with overall steady-state rate analysis, steady-state isotopic transient kinetic analysis was used to investigate the effect of the pretreatment conditions on the intrinsic activity and coverages of surface intermediates. Catalyst characterization techniques such as XRD, TPR, and hydrogen chemisorption were also used. The calcination temperature was found to have a pronounced effect on the overall activity of the catalyst but not on the intrinsic activity of the catalyst sites. On the other hand, the reduction temperature had only a negligible effect on the overall and intrinsic activities. The decrease in rate at high calcination temperatures was caused by a decrease in the number of surface active sites due to a decrease in the reducibility of the catalyst. Neither the reduction nor the calcination conditions had any effect on chain growth probability. Calcination temperature did have, however, a small effect on CH_4 selectivity.

INTRODUCTION

Cobalt is one of the most active metals used for the Fischer–Tropsch (F-T) synthesis, and a number of studies pertaining to the activities of cobalt catalysts have been recently reported (1–12). The preparation method and the pretreatment conditions used for a catalyst can have a great influence on the surface states of cobalt and cobalt oxide species formed, thus determining the catalytic properties. A number of studies have been reported concerning the effect of pretreatment conditions on catalysts containing cobalt (13–21). Different effects of the pretreatment conditions have been observed. The surface characteristics, such as the formation of tetrahedrally and/or octahedrally coordinated Co ions on Co/Al_2O_3, were found to be affected by the metal loading and the calcination temperature (13, 14). Only a few studies have reported the effect of reduction temperature on the performance of Co/Al_2O_3 catalysts (15–17). All of these studies reported an increase in the percent reduction with a concomitant increase in the overall rate for CO hydrogenation with increasing reduction temperature. Calleja *et al.* (18) have studied the pretreatment effects on the conversion of syngas to hydrocarbons over a Co/HZSM-5 catalyst. Calcination or reduction temperatures were found to have a very negligible effect on catalyst activity. However, Rathousky *et al.* (20) have shown that the pretreatment conditions affected the performance of Co/Al_2O_3 and Co/SiO_2 catalysts. Turn-over frequency (TOF) values for F-T synthesis decreased with increasing calcination temperature for Co/SiO_2 as well as for Co/Al_2O_3; however, the total hydrocarbon yield increased for Co/Al_2O_3 while it decreased for Co/SiO_2 (19–21). With the exception of a few papers (9, 11–12, 22), however, little focus has been directed toward understanding pretreatment effects on metal-promoted Co F-T catalysts, the new generation of Co formulations for Fischer–Tropsch synthesis (5–7, 23–25).

A previous comprehensive investigation in our laboratories (22) of various Ru-promoted Co F-T catalyst formulations had indicated how Ru promotion of Co/Al_2O_3 occurs as well as the optimal preparation technique for these catalysts. Ru, like other noble metal promoters, has been concluded to increase the reducibility of Co (11–12, 22, 26) and possibly preserve its activity by preventing the buildup of carbonaceous deposits (24). The increase in reduction of Co/Al_2O_3 upon promotion with Ru was accompanied by an increase in dispersion which was paralleled by an equivalent increase in the rate of CO hydrogenation yielding practically constant turnover frequencies (22). Thus, the Ru promoter apparently acts only as a reduction promoter for Co by increasing the reducibility and dispersion of cobalt. Ru-promoted Co/Al_2O_3 catalysts prepared by a co-impregnation aqueous technique exhibited the highest activity. This study addresses specifically the effect of various calcination and reduction conditions on the activity and selectivity of a Ru-promoted Co/Al_2O_3 catalyst prepared by the co-impregnation aqueous method. Along with steady-state kinetic measurements, steady-state isotopic transient kinetic analysis (SSITKA) was used to gain more understanding about the effect of pretreatment on the intrinsic

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activity and surface coverages of reaction intermediates. SSITKA studies have been used for many systems involving CO hydrogenation on metal catalysts and have been shown to provide excellent information about surface reaction parameters (27–30). The SSITKA technique is discussed in detail in a recent review paper (31). Characterization techniques such as temperature programmed reduction (TPR) and hydrogen chemisorption were also used to study the effect of pretreatment.

EXPERIMENTAL

Materials

Vista-B γ-Al_2O_3 (0–400 mesh) was used as the support. Impurities of Cu, Mg, Na, Mn, Zn, S, P, and Ca in the Al_2O_3 were found by ICP to be less than 0.01 wt%. Nitrogen adsorption at 77 K was used to determine the pore volume and the surface area of the support. The BET surface area of the alumina calcined at 500°C was found to be 240 m^2/g and its pore volume 0.49 cc/g. Cobalt nitrate (Alpha, 99.5%) and ruthenium (III) nitrosylnitrate (Alpha, Ru 28%) were used for the preparation of the catalyst.

Catalyst Preparation and Pretreatment

Cobalt (20 wt%) on γ-Al_2O_3 promoted with ruthenium (0.5 wt%) was used for this study. This catalyst was prepared by a single step, aqueous incipient wetness impregnation. The γ-alumina support was calcined at 500°C for 10 hr and cooled down to ambient temperature prior to its impregnation with an aqueous solution of cobalt nitrate and ruthenium (III) nitrosylnitrate. The catalyst precursor following incipient wetness impregnation was dried in air at 120°C for 5 hr before calcination.

The catalyst was calcined in several batches at different temperatures within the range 200–400°C. The calcination was carried out in flowing air using a temperature ramp of 1°C/min to the final temperature which was held for 10 hr. After calcination, the catalyst was cooled down to ambient temperature and stored in a dry atmosphere.

Before carrying out the CO hydrogenation reaction, the catalysts were reduced using flowing hydrogen at various reduction temperatures (300–400°C). A hydrogen flow rate of 30 cc/min was used with a temperature ramp of 1°C/min up to the final temperature which was held for 6 hr.

X-Ray Diffraction

A Phillips X'pert System X-ray diffractometer instrument with monochromatized Cu$K\alpha$ radiation was used for the XRD measurements in order to identify the most important CO phases present. The spectra were scanned at a rate of 2.4 deg/min. Since reduced and passivated samples did not exhibit any diffraction patterns for Co metal and only oxide phases could be observed, the catalysts were used in their calcined form to estimate the Co particle size. For this study, only the catalyst calcined at 300°C was examined by XRD. The crystallite size of the oxidized form of the cobalt was determined using the width at half maximum of the most intense peak of the spectrum of Co_3O_4.

Temperature Programmed Reduction (TPR)

An Altamira instrument AMI-1 was used for the temperature programmed reduction (TPR) experiments with catalysts calcined at different temperatures. A 50-mg sample of the calcined catalyst was initially flushed with argon flowing at 30 cc/min. The temperature was raised to 120°C with a ramp of 10°C/min and held for 30 min. After cooling the catalyst to room temperature, a reducing gas (5% H_2 in argon) was introduced at a flow rate of 30 cc/min. The temperature was then increased to 900°C at rate of 5°C/min, with a thermal conductivity detector (TCD) being used to determine the amount of H_2 consumed. The percentage reduction was calculated assuming that the cobalt oxide was in the form of Co_3O_4 and was reduced to Co metal.

Hydrogen Chemisorption

Hydrogen chemisorption measurements were carried out according to the method used by Reuel and Bartholomew (32). The catalyst was reduced with a hydrogen flow rate of 50 cc/min for 10 hr at 350°C following a temperature program of 1°C/min. After desorbing at 350°C for 2 hr under vacuum (10^{-6} Torr). The hydrogen chemisorption was then carried out at 100°C for 2 hr before determining the adsorption isotherm at room temperature. The number of surface Co metal atoms was determined using the total amount of hydrogen chemisorbed and assuming a stoichiometry of $H/Co_S = 1$.

Steady-State Reaction Studies

The catalysts calcined and reduced at various temperatures were tested for their steady-state activity and selectivity in a microreactor at 220°C. Differential conditions were used to avoid any mass transfer or heat transfer limitations. The catalyst amount used for various experiments was kept constant at 15 mg diluted with 15 mg of quartz powder. H_2 (Liquid Carbonic Specialty Gas Corporation, Ultra Pure, 99.999%) used for the reaction was further purified by passing through a molecular sieve trap. He (Liquid Carbonic Specialty Gas Corporation, Ultra Pure, 99.999%) was used without any further purification. A gas mixture of 5.13% Ar in CO was further purified by passing through a Matheson gas purifier unit. Reaction was carried out at 1.8 atm using a H_2/CO ratio of 10/1 (20 cc/min of H_2, 2 cc/min CO). A 10/1 H_2/CO ratio was used for both the steady-state reaction and SSITKA studies in order to minimize deactivation due to carbon deposition. A total reaction gas flow rate of 100 cc/min was used, having He as a diluent. An on-line gas chromatograph (Varian 3700) equipped with a Porapak Q column for product separation and a flame ionization detector (FID) was used for the analysis of the hydrocarbon products.

To determine the catalyst deactivation with time-on-stream, product samples were analyzed at various time intervals. Steady-state reaction was reached after approximately 7 hr of reaction.

Steady-State Isotopic Transient Kinetic Analysis

For SSITKA of CO hydrogenation, the same reaction setup was used as in the steady-state reaction studies. Transients of methane and CO were obtained by switching the flow of $^{12}CO/Ar$ to ^{13}CO without disturbing the stability of the reaction. Argon was used as a tracer to account for the gas phase hold-up of the system. The decay or increase of isotopically marked species was monitored by an on-line Leybold-Inficon Auditor-2 quadruple mass spectrometer. Average surface residence times for the carbon in CH_4 and CO were calculated from these transient studies. The number of surface intermediates which gave rise to CH_4 and the amount of reversibly chemisorbed CO were also calculated.

RESULTS

XRD

Only the catalyst calcined at 300°C was examined by XRD. Only Co oxide phases could be observed. No Co–Al compounds were detected. The average particle size for the oxide form of the metal in the calcined catalyst, determined from the XRD measurements using the Scherrer equation, was found to be 11 nm.

TPR

Figure 1 shows the TPR profiles for the catalyst calcined at different temperatures and also a profile for the uncalcined catalyst. Two different regions of reduction were observed: a lower temperature region (140–240°C) and a higher temperature region located between 270 and 500°C. For the uncalcined catalyst the majority of reduction was at lower temperature, occurring as two overlapping peaks. These peaks shifted to higher temperature with increasing calcination temperature and appeared to become one. The first of these low temperature peaks can be assigned to the decomposition of the Co nitrate (19). The absence of this lowest temperature peak for the calcined catalysts suggests that little Co nitrate remained after calcination. The higher temperature peak also shifted up in temperature with increasing calcination temperature. The peaks for the TPR of the calcined catalysts can be assigned to the decomposition of Co nitrate (lowest temperature peak and only observed for uncalcined samples), followed by the reduction of Co^{+3} to Co in two steps: Co^{+3} to CO^{+2} and Co^{+2} to Co (highest temperature peak) (19, 33).

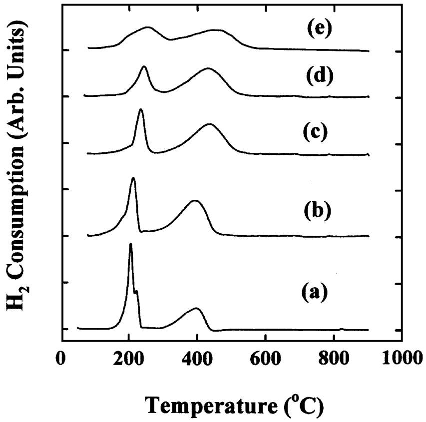

FIG. 1. TPR profiles for Ru-promoted Co/Al_2O_3 calcined at different temperatures: (a) uncalcined, (b) 250°C, (c) 300°C, (d) 350°C, (e) 400°C.

TABLE 1

Hydrogen Chemisorption and Percent Reduction as a Function of Calcination Temperature

T_C (°C)[a]	Total H_2 chemisorption[b] (μmole H_2/g cat.)	% Reduction[c]
Uncalcined	—	<64
250	188	77
300	165	65
350	121	61
400	88	59

[a] Temperature of calcination.

[b] Error in chemisorption measurements was ±10%.

[c] Calculated from TPR results (25–900°C).

From the TPR results it is observed that the degree of reduction of the catalysts decreased with increasing calcination temperature (Table 1). All the percent reducibilities were determined from the total hydrogen consumed during TPR. The value obtained for the uncalcined $Ru/Co/Al_2O_3$ can be considered maximum since any correction for the nitrate reduction would lower this value. The exact stoichiometry for Co nitrate reduction being unknown, no such correction was introduced here.

H_2-Chemisorption

Hydrogen chemisorption was carried out only for the catalysts calcined at 250–400°C. The results of the total hydrogen uptake obtained for various calcination temperatures are shown in Table 1. The total hydrogen chemisorption was found to decrease with increasing calcination temperature.

Steady-State Rates and Selectivities

Table 2 shows the reaction results obtained for the catalyst calcined at different temperatures. The initial rates were

TABLE 2

Effect of Calcination Temperature on CO Hydrogenation (Reduction Temperature = 300°C, H_2/CO = 10, T = 220°C, P = 1.8 atm)

	% CO conversion		Rate[d] (μmole/g Co_{Tot}/s)		CH_4 selectivity (%)		α		TOF[e] $\times 10^2$ (1/s)	
T_C(°C)[a]	Initial[b]	S-S[c]	Initial	S-S	Initial	S-S	Initial	S-S	Initial	S-S
Uncalcined	9.7	7.5	44.0	32.2	70	75	0.42	0.37	—	—
200	15.1	11.1	68.6	50.4	86	84	0.40	0.36	—	—
250	12.3	9.2	55.9	41.9	86	80	0.41	0.36	3.0	2.2
300	10.9	8.4	49.8	38.2	73	76	0.40	0.38	2.9	2.3
350	8.2	6.4	37.2	29.2	70	74	0.42	0.37	3.0	2.3
400	6.4	5.1	29.2	23.0	68	73	0.41	0.37	3.3	2.6

[a] Calcination temperature.
[b] After 5 min of reaction.
[c] After 7 hr of reaction.
[d] Error in rate measurement was ±5%.
[e] Based on total hydrogen chemisorption.

measured after 5 min of reaction, while steady-state rates were measured after 7 hr on stream. The overall rate of CO hydrogenation decreased with increasing calcination temperature. The selectivities for methane were as expected relatively high because of the high H_2/CO ratio used in this study. Catalysts calcined at higher temperatures resulted in lower selectivities for methane. The hydrocarbon products exhibited Anderson–Schulz–Flory distributions. The chain growth probabilities (α) determined did not vary with calcination temperature. Figure 2 shows the time-on-stream behavior of catalysts with various calcination conditions. The deactivation behavior was almost the same irrespective of pretreatment temperature. In all cases, there was a drop of about 20–25% in the activity from the initial value. The selectivity for methane in most cases increased slightly with reaction time. The TOF, calculated based on total hydrogen chemisorption, was found to be constant for all the calcination conditions. The rate of CO hydrogenation was lower for the uncalcined catalyst than for the ones calcined at $\leq$300°C.

Table 3 shows the reaction results obtained with the catalyst calcined at 300°C but reduced at various temperatures. The reduction temperature had little effect on the overall rate of CO hydrogenation. Only the catalyst reduced at the highest temperature, 450°C, exhibited a lower initial rate but its steady-state activity was within 5% of the values obtained with lower reduction temperatures. Figure 3 shows how the overall rate varied with the calcination and

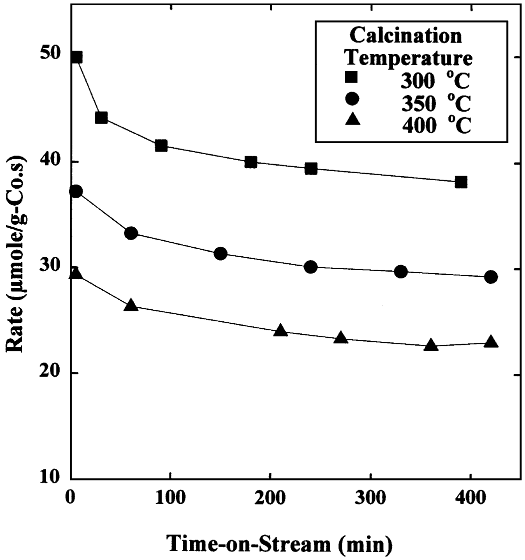

FIG. 2. Time-on-stream behavior of the overall rate of CO hydrogenation for the catalyst reduced at 300°C and calcined at various temperatures.

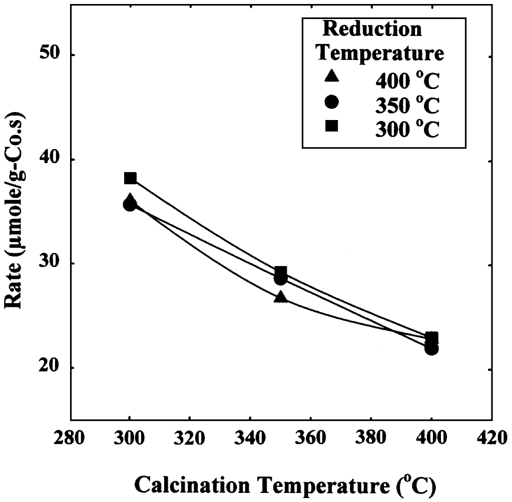

FIG. 3. Effect of pretreatment temperatures on overall catalyst activity of Ru/Co/Al_2O_3.

TABLE 3

Effect of Reduction Temperature on CO Hydrogenation (Calcination Temperature = 300°C, $H_2/CO = 10$, $T = 220$°C, $P = 1.8$ atm)

	% CO conversion		Rate[d] (μmole/g Co_{Tot}/s)		CH_4 selectivity (%)		α		TOF[e] × 10^2 (1/s)	
T_R (°C)[a]	Initial[b]	S-S[c]	Initial	S-S	Initial	S-S	Initial	S-S	Initial	S-S
300	10.9	8.4	49.8	38.2	73	76	0.40	0.38	3.0	2.3
350	10.3	7.9	47.0	35.7	82	79	0.41	0.38	2.8	2.1
400	11.1	7.9	50.4	36.1	71	73	0.41	0.39	3.0	2.2
450	8.3	7.0	41.7	34.7	73	77	0.40	0.36	2.5	2.1

[a] Reduction temperature.
[b] After 5 min of reaction.
[c] After 7 hr of reaction.
[d] Error in rate measurement was ±5%.
[e] Based on total hydrogen chemisorption.

reduction conditions used for this study. It is clear that the reduction temperature had no appreciable effect on the reaction even when the calcination temperature was varied.

SSITKA

Steady state isotopic transient kinetic analysis was used as a surface characterization technique to qualify the catalytic sites in terms of their number and activity and to gain more insight into the results obtained by steady-state reaction analysis. SSITKA enables one to calculate the surface concentration of intermediates and a measure of the intrinsic pseudo-first-order activity (k) (31, 34). Figure 4 shows a typical set of transients obtained during the steady-state switch from $^{12}CO/Ar$ to ^{13}CO in the reactant feed. The surface residence times for CO and CH_4 were determined by integrating the areas between the transient curves for Ar and CO or CH_4, respectively. A measure of the intrinsic activity for methanation was calculated by taking the inverse of the surface residence time of CH_4. This measure of the intrinsic activity is also the pseudo-frist-order rate constant for methanation.

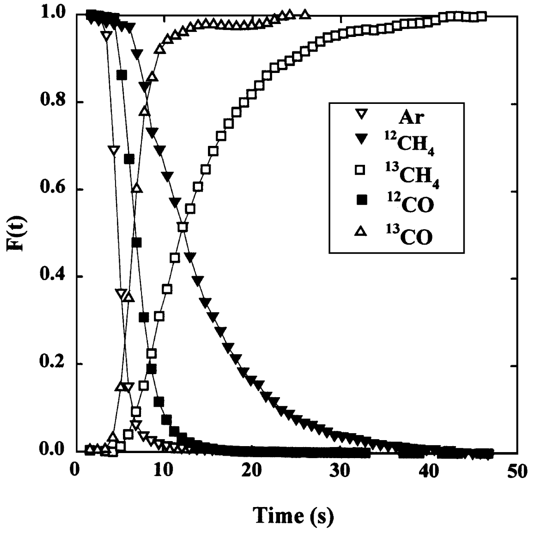

FIG. 4. Typical isotopic transients during a switch from $^{12}CO/Ar$ to ^{13}CO during CO hydrogenation on $Ru/Co/Al_2O_3$.

Table 4 shows the SSITKA results obtained for various calcination conditions. The surface residence time for the CH_4 intermediates remained unchanged with different calcination temperatures. This indicates that the mean activity of the sites producing methane was not affected by the temperature of calcination. There was an increase in the surface residence time of these intermediates with time-on-stream. This is typically due to deactivation of the most active sites with time-on-stream. The surface residence time for CO (τ_{CO}) was found to decrease with increasing calcination temperature. This suggests that the strength of CO adsorption decreased with increasing calcination temperature. τ_{CO} for the catalyst calcined at 400°C was similar to that for the uncalcined sample. The surface abundance of intermediates (N_M) leading to the formation of methane is calculated by

$$N_M = R_{M,SS} * \tau_M,$$

where $R_{M,SS}$ is the steady-state rate of methane formation. N_M decreased with increasing calcination temperature and with time-on-stream. The surface concentration of unreacted CO present on the surface (N_{CO}) also decreased with increasing calcination temperature.

The SSITKA results for different reduction temperatures are shown in Table 5. There was no significant change in the intrinsic activity, $1/\tau_M$, of the methane producing sites. In addition, the surface abundance for methane was unchanged within experimental error. The surface converages for methane intermediates (Θ_M) were found to be low (<0.2) as is typical, and they remained constant with increasing reduction and calcination temperatures.

TABLE 4

SSITKA Results for CO Hydrogenation for Catalysts Calcined at Different Temperatures (Reduction Temperature = 300°C, H_2/CO = 10, $T = 220$°C, $P = 1.8$ atm)

	τ_{M}^{b} (seconds)		τ_{CO}^{b} (seconds)		N_{M} (μmole/g cat)		N_{CO} (μmole/g cat)		Θ_{M}^{e}	
T_{C}(°C)[a]	Initial[c]	S-S[d]	Initial	S-S	Initial	S-S	Initial	S-S	Initial	S-S
Uncalcined	—	9.6	—	2.0	—	46.6	—	181.7	—	—
300	8.1	9.1	2.5	2.8	58.7	52.8	227.0	254.0	0.18	0.16
350	8.7	9.3	2.3	2.5	45.4	40.5	208.8	227.0	0.18	0.16
400	8.2	10.0	1.6	1.8	32.8	33.7	145.2	163.4	0.18	0.19

[a] Calcination temperature.
[b] Error in measurement of τ was ±8%.
[c] After 15 min of reaction.
[d] After 7 hr of reaction.
[e] Based on total hydrogen chemisorption.

Figure 5 shows the effect of calcination and reduction conditions on the intrinsic activity for methane, k_{M} ($k_{\mathrm{M}} = 1/\tau_{\mathrm{M}}$). This figure indicates that, in general, pretreatment conditions had a very insignificant effect on intrinsic activity.

DISCUSSION

The TPR results indicate that the reducibility of the catalyst decreased with increasing calcination temperature. This is similar to what has been reported by others for non-metal-promoted Co catalysts (13, 14, 19). It has been suggested that the lower reducibility may be the result of the formation of surface compounds through metal-support interactions at higher calcination temperatures (13). It has been reported that cobalt can be present on a catalyst surface as individual oxides, CoO or Co_3O_4, or as surface compounds with the support, with the amounts dependent upon the character of the support and on the temperature of calcination (14, 35). For alumina supports, the formation of surface compounds has been explained by the possible penetration of cobalt into the alumina lattice (35).

Hydrogen chemisorption has been found to be suppressed for catalysts which are poorly reduced (15–17). Our results show that the extent of reduction decreased with increasing calcination temperature and so did the total hydrogen uptake. Ho *et al.* (36) have also reported a decrease in chemisorption values with increasing calcination temperature for a Co/SiO_2 catalyst.

Lower reducibility has been reported to be one of the factors causing lower activity of cobalt catalysts for CO hydrogenation (37). Stable surface oxides which are highly inactive for CO hydrogenation may be present on the surface of the less reduced catalysts (16). Ho *et al.* (36) studied the effect of calcination temperature on the surface characteristics and CO hydrogenation activity of a Co/SiO_2 catalyst. They also did not observe any change in TOF with calcination temperature. However, the results presented

TABLE 5

SSITKA Results for CO Hydrogenation for Catalysts Reduced at Different Temperatures (Calcination Temperature = 300°C, H_2/CO = 10, $T = 220$°C, $P = 1.8$ atm)

	τ_{M}^{b} (seconds)		τ_{CO}^{b} (seconds)		N_{M} (μmol/g cat)		N_{CO} (μmol/g cat)		$\Theta_{\mathrm{CH_4}}^{e}$	
T_{R}(°C)[a]	Initial[c]	S-S[d]	Initial	S-S	Initial	S-S	Initial	S-S	Initial	S-S
300	8.1	9.1	2.5	2.8	58.7	52.8	227.0	254.0	0.18	0.16
350	7.3	8.9	2.9	2.4	56.3	50.0	263.3	218.0	0.17	0.16
400	8.5	10.1	2.6	2.8	60.7	53.5	236.1	254.2	0.18	0.16
450	7.7	8.6	2.1	2.2	47.1	45.8	195.4	196.3	0.14	0.14

[a] Reduction temperature.
[b] Error in measurement of τ was ±8%.
[c] After 15 min of reaction.
[d] After 7 hr of reaction.
[e] Based on total hydrogen chemisorption.

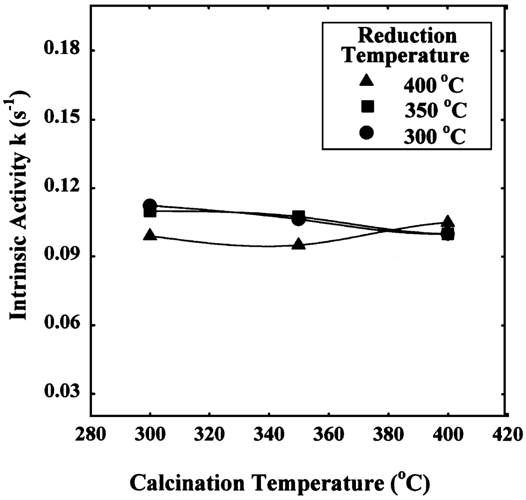

FIG. 5. Effect of pretreatment temperatures on intrinsic activity of Ru/Co/Al_2O_3 for methane formation.

here are in variance with the results obtained by Rathousky *et al.* (20). These workers observed an increase in total hydrocarbon yield for higher calcination temperatures. The argument for the observed increase was that the cobalt–aluminum mixed oxides formed due to high temperature calcination favored the increased yield of hydrocarbons. In contrast, Ihm *et al.* (16) reported that these stable surface oxides were highly inactive for CO hydrogenation. The approximately constant TOFs determined in this study suggest that the decrease in the activity was merely the result of a decrease in the number of active sites due to the lower reducibility of the catalyst with increasing calcination temperature. The SSITKA results confirm the TOF results that there was a decrease in the number of intermediates, and hence sites, with increasing calcination temperature. The lower activity of the uncalcined catalyst, which showed a lower number of surface intermediates compared to the catalyst calcined at 300°C, can also be explained by its lower reducibility. In addition, the TOF and SSITKA results confirm that the active sites were not affected by any additional amount of nonreduced cobalt oxide or cobalt/alumina compounds. This is indicated by the constant values of TOF and $k_M = 1/\tau_M$.

The calcination temperature did not have a significant effect on the selectivity of the catalyst. The chain growth probability remained essentially constant with increasing calcination temperature, although methane selectivity decreased somewhat. This additionally suggests that there was no change in the properties of the cobalt active sites.

The catalyst activity and selectivity were independent of reduction temperature. The only exception was the catalyst reduced at 450°C which showed a somewhat lower activity. This suggests that reduction temperature $\geq$450°C may cause a loss of active sites (confirmed by SSITKA for $T_R = 450°C$). This loss could be the result of inactive surface compounds formed at very high temperatures (15) or loss of dispersion. While Calleja *et al.* (18) did not observe any effect of reduction temperature of Co/HZSM-5 on the conversion of syngas to hydrocarbons, Fu and Bartholomew (17) found that the specific activity for a 3% Co/Al_2O_3 catalyst went through a maximum as the reduction temperature was varied. The trend in activity was related to a similar trend in the catalyst dispersion. They also did not observe any change in selectivity with increasing reduction temperature.

Other pretreatment techniques involving reduction/oxidation/reduction (ROR) of Ru-promoted catalysts have been suggested to result in an increased catalyst activity when compared to pretreatments involving calcination/reduction only (9, 23). However, in other parallel investigations of Co F-T catalysts in our laboratories, ROR was found to have no impact on catalysts prepared entirely by aqueous impregnation as were the ones used for this study (38). The preparation methods used in the other studies reported in the literature (9, 23) and which showed some effect of the ROR pretreatment on catalyst performance involved at least one organic impregnation step.

CONCLUSIONS

The effect of calcination and reduction temperatures on the activity of a Ru-promoted 20 wt% Co/Al_2O_3 catalyst for the CO hydrogenation reaction was studied by steady-state reaction and SSITKA. While reduction temperature in the range 300–450°C had at most a negligible effect, calcination temperature was found to have a significant effect on the overall activity of this catalyst. The overall catalyst activity decreased with increasing temperature of calcination. However, pretreatment temperatures did not affect the intrinsic activity of the catalyst sites. The decrease in CO hydrogenation rate with increasing calcination temperature was found to be attributable to a decrease in the number of surface active sites due to a decrease in the reducibility of the catalyst. The SSITKA results, which showed no change in the surface residence time for CH_4 intermediates with increasing calcination temperature, as well as the TOF results confirmed that there was no change in the intrinsic activity of the sites producing methane. Neither the reduction nor the calcination conditions had any effect on chain growth probability. Calcination temperature did have, however, a small effect on CH_4 selectivity.

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