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Zr Promotion of Co/SiO$_2$ for Fischer–Tropsch Synthesis

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Zr has been proposed in the patent literature as an important promoter for Co/SiO$_2$ Fischer–Tropsch synthesis (FTS) catalysts. This paper reports on an investigation of the influence of Zr promotion of 20 wt% Co/SiO$_2$ on FTS using catalysts prepared in different ways and having different loadings of Zr (up to 8.5 wt%). The catalysts were investigated using FTS (H$_2$/CO = 2), H$_2$–D$_2$ exchange, and CO dissociation to provide insight into how Zr modifies the Co properties. The Zr-promoted catalysts exhibited higher overall rates of FTS compared to unpromoted Co/SiO$_2$. The sequentially impregnated Co/Zr/SiO$_2$ catalysts appeared to be the most active. However, the coimpregnation method of preparation appeared to result in higher cobalt dispersion. While Zr promotion did not appear to promote or inhibit H$_2$ activation, hydrogen spillover may have been partly responsible for enhancing the activity of the sequentially impregnated Zr/Co/SiO$_2$ catalysts. Zr also possibly created an active interface with Co that increased catalyst activity by facilitating CO dissociation. Although high levels of promotion tended to increase the selectivity for higher hydrocarbons, Zr appears to be primarily an excellent rate promoter for Co/SiO$_2$. © 1995 Academic Press, Inc.

INTRODUCTION

Cobalt has been one of the most commonly used metals for Fischer–Tropsch catalysts since the 1930s because of its high activity (1). It has received alot of attention recently (2–8, and others) due to its usefulness in converting CO to liquid hydrocarbons.

Catalyst modifiers affect the activity and/or the selectivity of catalysts. Such modifiers for metal catalysts have been hypothesized to act by structural modification of the metal surfaces induced by the promoter (9–12), by blockage of the active catalytic sites by the modifier (13), by charge transfer between the modifier and the metal (14, 15), by direct chemical interactions between the modifier and the active intermediates (16), and/or by the effect of the electrostatic field of the modifier ions (17–19). If a modifier improves the catalyst performance it is called a promoter. While many promoters for Fischer–Tropsch synthesis (FTS), such as the alkali series, have been extensively studied, others, such as Zr, have not. A number of FTS studies have been reported in the literature for ZrO$_2$-supported Co (1, 20), Ni (20), Ni/Co (20), and Pd (21). The use of ZrO$_2$ as the support for these different active metals has been found to increase the higher hydrocarbon selectivity. In addition, a number of patents by Shell (22, 23) have involved Zr promotion of Co/SiO$_2$.

The purpose of this study was to examine the effects of Zr as a promoter for SiO$_2$-supported Co. X-ray diffraction (XRD), temperature-programmed reduction (TPR), and H$_2$ chemisorption were used to characterize the catalysts before reaction. The catalytic properties of the catalyst were investigated using the H$_2$–D$_2$ exchange, CO dissociation, and CO hydrogenation (H$_2$/CO = 2).

EXPERIMENTAL

Materials

The surface area and the pore volume of the SiO$_2$ used (Davison 952), obtained by nitrogen physisorption at 77 K, were found to be 219 m^2/g and 0.51 cc/g, respectively. The impurities in the SiO$_2$ and their concentrations were determined by ICP to be Mg (150 ppm), Na (570 ppm), Ca (750 ppm), Ti (120 ppm), Al (220 ppm), Fe (96 ppm), P (83 ppm), K (160 ppm), and S (30 ppm). Cobalt nitrate (Alfa Mathey), zirconium tetra-*n*-propoxide (Alfa Mathey), and zirconium nitrate (Aldrich) were used for preparing the catalysts.

Catalyst Nomenclature

The nomenclature used for the catalysts in this study consists of three parts: (S or CI) ([A/B] or [$A + B$])(.XX). The first part refers to how the catalyst was prepared: "S" indicates sequential impregnation, and "CI" indicates coimpregnation. The second part gives the order of impregnation of the metal salts: [A/B] means that "A" was impregnated into the support after "B", and [$A + B$] means that they were coimpregnated. "B(O)" means that an organic compound of B was used instead of the nitrate, in which case the impregnating solution was nonaqueous. The

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TABLE 1

Preparation Details for the Zr-Promoted Co/SiO_2 Catalysts

Catalyst	wt% Co	wt% ZrO_2	Atomic ratio Zr/Co	Step 1[a]		Step 2[a]	
				Method	Solution	Method	Solution
[Co].00	20	0.0	0.0	Kneading[b]	Aqueous(Co)	—	—
S[Zr/Co].02	20	0.7	0.023	Kneading[b]	Aqueous (Co)	Inc. wetness	Aqueous (Zr)
S[Zr/Co].04	20	1.4	0.045	Kneading[b]	Aqueous (Co)	Inc. wetness	Aqueous (Zr)
S[Zr/Co].28	20	8.5	0.28	Kneading[b]	Aqueous (Co)	Inc. wetness	Aqueous (Zr)
S[Co/Zr(O)].28	20	8.5	0.28	Inc. wetness	Organic (Zr)	Inc. wetness	Aqueous (Co)
S[Co/Zr].28	20	8.5	0.28	Inc. wetness	Aqueous (Co)	Inc. wetness	Aqueous (Co)
CI[Zr + Co].02	20	0.7	0.023	Kneading[b]	Aqueous (Co + Zr)	—	—
CI[Zr + Co].28	20	8.5	0.28	Kneading[b]	Aqueous (Co + Zr)	—	—
[Zr].00	0.0	8.5	—	Inc. wetness	Aqueous (Zr)	—	—

[a] Following this step, the catalyst was dried in an oven for 5 h at 115°C and then calcined for 2 h at 300°C.

[b] See Ref. (22, 23).

last part, ".XX," denotes the Zr/Co atomic ratio. The unpromoted Co catalyst and Zr/SiO_2 are referred to as [Co].00 and [Zr].00, respectively. While Zr was present in all cases in the catalysts in compound form (probably primarily as ZrO_2), it is denoted as "Zr" for simplicity of notation.

Catalyst Preparation

Co/SiO_2 catalysts (20 wt%) having different amounts of Zr (up to 8.5 wt% of ZrO_2) were prepared (see Table 1). SiO_2, calcined at 500°C for 10 h prior to catalyst preparation, was loaded with Co and/or Zr by either a one- or two-step process of impregnation. In order to maintain a constant wt% of Co, the amount of SiO_2 was adjusted according to the amount of Zr used. Aqueous solutions of cobalt nitrate and/or zirconium nitrate were used to prepare all the catalysts except S[Co/Zr(O)].28, for which a solution of zirconium tetra-*n*-propoxide in a mixture of *n*-propanol, toluene, and acetyl acetone was used to impregnate the SiO_2 with Zr in the initial impregnation step. In the case of one-step impregnations, the catalysts [Co].00 and CI[Zr + Co].*XX* were prepared by kneading (22, 23) the aqueous metal precursor solution–support mixture for 3.5 h. For the sequentially impregnated catalysts ([Zr/Co].*XX*), kneading was used in the initial step followed by use of the incipient wetness method for the impregnation of Zr (22, 23). For the sequentially impregnated S[Co/Zr].*XX* catalysts, on the other hand, the incipient wetness method was used in both steps. After the first impregnation step, the catalyst was dried in an oven for 5 h at 115°C with occasional stirring. Then, it was calcined in air by raising its temperature to 300°C with a heating rate of 1°C/min and holding that temperature for 2 h. Also, after the second step of impregnation (if used) the catalyst was dried and calcined as in the first step. The catalysts were reduced under H_2 at 250°C for 10 h, following a 1°C/min ramp, prior to H_2 chemisorption or reaction.

X-Ray Diffraction

A Phillips X'pert System X-ray diffractometer instrument with monochromatized Cu$K\alpha$ radiation was used for the X-ray measurements. The calcined catalysts were examined by XRD, using a scan rate of 2.4°/min. The resulting X-ray diffraction patterns were examined to determine the most important phases present. In addition, the average crystallite sizes of the oxidized form of the catalysts were determined using the half-width at half-height of the most intense peak of the diffraction pattern and the Scherrer equation.

Due to the low intensities of the Co metal peaks, it was not possible to use the reduced form of a given catalyst in order to estimate the average size of the metal crystallites by a physical technique. Therefore, the calcined catalysts were studied using XRD to determine Co phases present and to estimate differences in Co dispersion brought about by the different methods of preparation and the different loadings of Zr.

Temperature-Programmed Reduction

An Altamira Instrument AMI-1 system was used for performing temperature-programmed reduction experiments. A 50-mg sample of the calcined catalyst was initially flushed with Ar flowing at 30 cc/min as the temperature was increased at a rate of 10°C/min to 120°C where it was held for 30 min. Then, the reducing gas (5% H_2 in Ar) was switched on at 30 cc/min, and the temperature was raised at a rate of 5°C/min until it reached 900°C. A thermal conductivity detector (TCD) was used to determine the amount of H_2 consumed. In order to evaluate the fraction of Co reduced under the normal reduction conditions at 250°C, TPR was also performed for the calcined catalysts after an initial *in situ* reduction at 250°C for 10 h.

Hydrogen Chemisorption

Hydrogen chemisorption measurements were carried out according to the method used by Reuel and Bartholomew (4). The catalyst was reduced with hydrogen flowing at a rate of 60 cc/min for 10 h at 250°C following a 1°C/min ramp. Then, desorption of hydrogen from the cell was done at 220°C for 1.5 h to achieve a vacuum of less than 10^{-6} mm Hg. Hydrogen was then introduced into the cell containing the reduced catalyst and allowed to equilibrate with the Co surface for 5 h at 100°C. The total adsorption isotherm data were then collected at room temperature (25°C) by the decreasing pressure method. Each sequential datum of the isotherm was obtained after $\frac{1}{2}$ h. Total hydrogen chemisorbed was calculated by extrapolating the total adsorption isotherm to zero pressure. After determination of the total adsorption isotherm, the cell was evacuated for 15 min at room temperature, and the reversible desorption isotherm measured at 25°C. The number of vacant Co metal atoms at the surface was determined using the total amount of hydrogen chemisorbed and the relationship $H/Co_s = 1$ (4).

H_2–D_2 Exchange

A fixed-bed microreactor (loaded with 0.035 g of a catalyst sample) was used to study the H_2–D_2 exchange reaction. This exchange reaction was carried out (after standard reduction of the catalyst) in the temperature range of 25–175°C at 1.8 atm and in the presence of CO in order to evaluate the effect of Zr promotion on H_2 activation under conditions related to CO hydrogenation, where CO competes with H_2 for adsorption sites. H_2, D_2, CO, and He flow rates of 10, 10, 2, and 78 cc/min, respectively, were used. A Leybold–Inficon Auditor-2 mass spectrometer (MS) was used to determine the amount of exchange.

CO Dissociation

Unsteady-state CO dissociation was performed (also after standard reduction) in a fixed-bed microreactor loaded with 0.035 g of catalyst using CO and He flows of 2 and 20 cc/min, respectively. An MS was used to follow the CO and CO_2 transient after switching from a stream containing only He to one containing CO and He. The amount of CO dissociated before deactivation of the catalysts was determined.

Carbon Monoxide Hydrogenation

A fixed-bed microreactor was used for studying this reaction, and differential conditions were employed to avoid mass and heat transfer limitations. A flow of 60 cc/min of H_2 was used first to rereduce 0.350 g of a catalyst, ramping the temperature by 1°C/min to 250°C and holding for 10 h. After the rereduction was completed, the reaction was started at 220°C and 1.3 atm by setting the initial flows of H_2 and CO at a ratio of 2/1 and adding Ar as a balance gas to get a total flow rate of 90 cc/min (STP). During the start-up period, the H_2 and CO components of the input stream were increased gradually from zero to 90 cc/min total flow with $H_2/CO = 2$. A slow start-up procedure was utilized to prevent exotherming during the initial reaction period. Product analysis was carried out with a gas chromatograph which was equipped with a 30-m DB-5 capillary column. The reaction reached a pseudo-steady state after 10 h and was usually followed for more than 24 h.

RESULTS AND DISCUSSION

Sequentially Impregnated Zr/Co Catalysts

The calcined catalysts exhibited only one detectable phase of cobalt oxide, Co_3O_4, as also found by Okamoto *et al.* (24). The XRD results (Table 2) suggest that Zr was highly dispersed on Co/SiO$_2$ since no Zr compound phases were detected. Using XRD line broadening, it was found that all the calcined S[Zr/Co].*XX* catalysts, as well as [Co].00, exhibited similar average crystallite sizes for Co_3O_4 (28 ± 1 nm).

As can be seen in Fig. 1, there were two regions in the TPR profile for the reduction of [Co].00. One region was located between 200 and 320°C and the other was located between 320 and 500°C, having peaks at 300 and 345°C, respectively, as previously found by Lapidus *et al.* (25). The TPR profiles (Fig. 1) for the sequentially impregnated Zr/Co catalysts (S[Zr/Co].*XX*) were comparable to the [Co].00 profile, but indicated slightly higher degrees of reduction. The two peaks observed have been identified as the conversion of Co^{3+} to Co^{2+} followed by the conversion of Co^{2+} to Co (25). It is important to note that, for the methods of preparation used in this study, no "reducible" surface compounds were formed between Co and SiO$_2$ during preparation of the catalysts, as evidenced by the lack of high-temperature reduction regions (below 900°C) in the TPR profiles. Such reducible Co silicate compound formation has been noted after aqueous impregnation of prereduced Co/SiO$_2$, and appears to require the presence of Co metal (26). All the tabulated reducibilities were determined after subtracting the TPR profile for SiO$_2$ by

TABLE 2

Characterization Results[a]

Catalyst	H$_2$ chemisorption				TPR		XRD
	Total (μmol H$_2$/g catalyst)	Irreversible (μmol H$_2$/g catalyst)	Average d_p[b] of Co^0 (nm)	% Co Disp.[c]	% Reduction 25–900°C	% Reduction[d] at 250°C	Co$_3$O$_4$ d_p (nm)
[Co].00	82	70	16	4.8	75	75	27
S[Zr/Co].02	141	122	10	8.3	80	80	28
S[Zr/Co].04	149	122	9	8.8	81	81	27
S[Zr/Co].28	122	98	11	7.2	81	81	29
S[Co/Zr(O)].28	87	72	15	5.1	75	75	31
S[Co/Zr].28	93	77	14	5.5	75	75	27
CI[Zr + Co].02	67	50	16	4.0	64	64	20
CI[Zr + Co].28	125	115	11	7.3	77	77	24
[Zr].00	0	0	0	0.0	0	0	0

[a] All the results were within ±5%.

[b] Based on the reduced cobalt, assuming H/Co$_s$ = 1 and d_p = 5/(metal surface area)/(g catalyst)/(metal density).

[c] Based on the total cobalt.

[d] Represents percentage of metal reduced after the standard reduction procedure (ramp 1°C/min to 250°C, hold for 10 h).

itself (blank experiment). It was also found that all the catalysts used in this study were reduced to the maximum degree (defined as % Co reduced during TPR to 900°C) during the standard reduction procedure at 250°C. Any Co not reduced during TPR has been categorized as "irreducible" Co silicate (26).

The irreversible H$_2$ uptakes measured during H$_2$ chemisorption were equal to or greater than 75% of the total H$_2$ uptake, suggesting that hydrogen was strongly adsorbed on the catalyst surfaces. The impregnation of Zr onto Co/SiO$_2$ increased the H$_2$ chemisorption up to a maximum point (possibly at a Zr/Co atomic ratio of 0.04). However, higher loadings of Zr acted to partially block the Co^0 sites. Much of it also may have existed only on the support. ZrO$_2$ ([Zr].00) by itself did not chemisorb hydrogen.

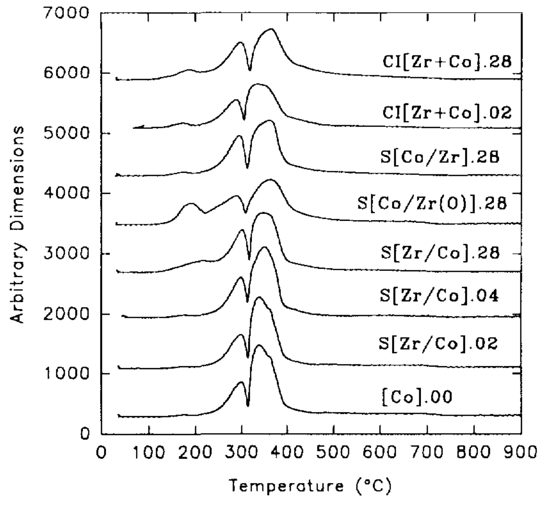

FIG. 1. TPR profiles for the unpromoted and the promoted catalysts.

Calculations were made using the Co$_3$O$_4$ XRD results (by converting Co$_3$O$_4$ to Co^0) in order to get an approximation of the average size of the Co metal crystals for reduced S[Zr/Co].*XX* having the same shape. While such estimations are subject to significant errors because of the assumptions which must be made, they are useful for comparison purposes. The S[Zr/Co].*XX* catalysts would be expected to have average Co metal particle sizes of 15 ± 1 nm, which is equal (within experimental error) to the average crystallite size determined for [Co].00. However, H$_2$ chemisorption results suggest that the average Co metal sizes for S[Zr/Co].*XX* were equal to 10 ± 1 nm, which is smaller than the average size for [Co].00 (16 nm). Thus, the addition of Zr to Co/SiO$_2$ caused an apparent underestimation of the average Co crystallite size (or in other words, an overestimation of Co dispersion) based on H$_2$ chemisorption. Hence, it is possible that H$_2$ spillover occurs due to Zr promotion. Given the similarity in XRD results for the calcined catalysts (including [Co].00), it is unlikely that the increase in hydrogen uptake for this series of catalysts can be explained by the formation of higher dispersed Co^0 due to Zr addition.

Borer *et al.* (27) reported that ZrO$_2$ can be partly reduced

TABLE 3

FTS Results for $H_2/CO = 2$[a]

Catalyst	% CO conversion		Total rate ($g\ CH_2/g$ catalyst/h)		TOF_H[b] (s^{-1}) × 10^3		CH_4 selectivity (wt%)		α	
	Initial	SS[c]	Initial	SS	Initial	SS	Initial	SS	Initial	SS
[Co].00	3.3	2.7	0.11	0.09	13.3	10.9	22	22	0.58	0.61
S[Zr/Co].02	4.7	3.8	0.15	0.12	10.6	8.4	23	27	0.57	0.55
S[Zr/Co].04	5.6	3.8	0.18	0.12	12.0	8.0	23	28	0.61	0.56
S[Zr/Co].28	5.2	3.9	0.17	0.13	12.8	10.6	26	29	0.67	0.67
S[Co/Zr(O)].28	8.8	5.7	0.28	0.18	31.9	20.5	28	29	0.64	0.62
S[Co/Zr].28	8.3	5.0	0.27	0.16	28.8	17.1	19	24	0.65	0.63
CI[Zr + Co].02	4.8	3.6	0.15	0.11	22.2	16.3	24	28	0.58	0.56
CI[Zr + Co].28	5.7	4.6	0.18	0.15	14.3	11.9	21	22	0.70	0.69

[a] The reaction conditions were 220°C, 1.3 atm, $H_2/CO = 2$. Error of measurement was ±5%.

[b] Based on total H_2 chemisorption.

[c] Steady state.

to Zr^{3+} and suggested that ZrO_2 may exhibit SMSI. However, Bruce and Mathews (28) reported that Ni supported on ZrO_2 did not show any signs of SMSI. In addition, Tauster and Fung (29) found that reduction up to 700°C did not significantly affect H_2 chemisorption for Ir supported on ZrO_2. Thus, for Co catalysts reduced at the temperature (250°C) used for this study, it is unlikely that ZrO_2 promotion would cause any SMSI-type behavior.

As can be seen from Table 3, for the S[Zr/Co].*XX* catalysts, there appeared to have been little additional effect of Zr loading on FTS rate beyond Zr/Co = 0.04, although even a loading of Zr/Co = 0.02 had a significant impact on rate. The increase in the Zr/Co ratio caused an increase in the value of α. No significant effect of Zr promotion on the TOF (based on H_2 chemisorption results) for CO hydrogenation was measured for S[Zr/Co].*XX* over that for [Co].00. Such a result is contrary to the conclusion that H_2 spillover occurred, since one would expect TOF as calculated to decrease. This may be explained by the outcome of two competing effects on the value of TOF—H_2 spillover and Zr–Co interactions. While H_2 spillover would lead to a decrease in the value of TOF, the presence of Zr–Co interactions could lead to an increase.

The time-on-stream results (Fig. 2) indicate that the reduction in activity of the promoted catalysts was more than 35% compared to only 20% for [Co].00, although the promoted catalysts still remained significantly more active at steady state.

Sequentially Impregnated Co/Zr Catalysts

The XRD results for both the sequentially impregnated Co/Zr and Zr/Co catalysts were similar. Bruce *et al.* (20) have reported that almost all Co and Ni catalysts (with metal loadings less than 13 wt%) prepared using ZrO_2 as the support were XRD amorphous. In this study, Co on Zr/SiO_2 did not seem to exhibit such a high dispersion effect, perhaps due to large expanses of bare SiO_2 surfaces.

The TPR profile of S[Co/Zr(O))].28 (Fig. 1) exhibited a peak in a very-low-temperature range (between 100 and 220°C). By comparing the TPR profiles for both S[Co/Zr(O)].28 and S[Co/Zr].28, it is obvious that the latter peak is related to the removal of organic species not removed during the calcination of S[Co/Zr(O)].28. This peak that appeared in the very-low-temperature range was ex-

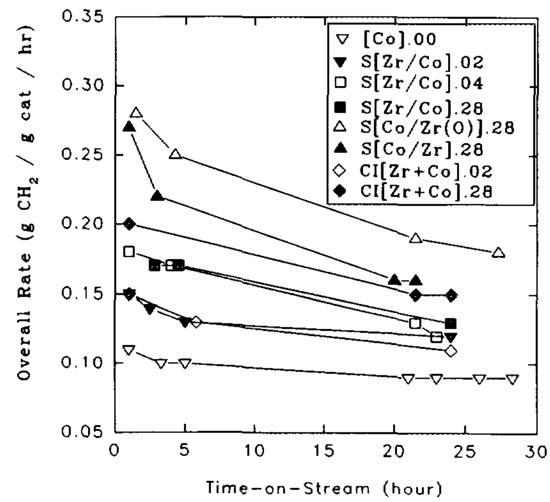

FIG. 2. Overall rate vs time-on-stream during FTS ($H_2/CO = 2$).

cluded in the estimation of the % reduction of the Co, leading to equality in the degree of reduction between the sequentially impregnated Co/Zr catalysts (S[Co/Zr].28 and S[Co/Zr(O)].28). The sequentially impregnated Co/Zr catalysts had the same degrees of reduction as the unpromoted catalyst.

The impregnation of Co onto Zr/SiO_2 did not appear to have any significant effect on Co_3O_4 dispersion or on H_2 chemisorption compared to [Co].00, which suggests that no H_2 spillover occurred for catalysts prepared by impregnation of Co/Zr.

The S[Co/Zr].28 catalysts, prepared by either aqueous or nonaqueous impregnation, showed the highest activities (by having the highest overall rates of reaction and TOFs) for FTS with moderate values of α. Withers *et al.* (1) have also found an increase in activity for FTS with increasing Zr/Co ratio for Co on Zr/SiO_2 using a slurry-phase reactor, with the optimum Zr/Co ratio being equal to 2. Hence, the results would seem to suggest that the activity of Co sites might have increased due to the presence of Zr in this series of catalysts. Zr may create an active interface with Co that is responsible to some extent for the enhancement in Co activity by facilitating CO dissociation. If the C atom of CO forms a chemical bond with an active surface metal atom of the catalyst while the O atom of CO bonds to an adjacent positive ion, such as Zr, as has been proposed by a number of other authors (12, 27, 30), a facilitation of CO dissociation would occur, which could lead to an increase in reaction rate without a change in H_2 activation.

Coimpregnated Zr + Co Catalysts

The XRD results for the calcined coimpregnated catalysts showed that they had smaller average Co_3O_4 crystallite sizes (22 + 2 nm) compared to the other catalysts, possibly due to a decrease in Co sintering during initial decomposition and calcination.

The coimpregnated Zr and Co catalysts CI[Zr + Co] has three regions of reduction with peaks at 185, 290, and 350°C (Fig. 1). This additional peak at 185°C, due to the reduction of residual cobalt nitrate (25), was also excluded from the estimation of the % reduction of the Co. This retention of Co nitrate in the CI[Zr + Co].*XX* catalysts was related to the fact that only a single calcination step was used for preparing these catalysts, whereas the sequentially impregnated catalysts were calcined twice. The degrees of reduction of the coimpregnated catalysts were within experimental error of the value for the unpromoted catalyst.

The H_2 uptake for the coimpregnated catalysts increased upon increasing the Zr/Co ratio; the highest H_2 uptake was for CI[Zr + Co].28. That the amount of metal surface area was greater for this latter catalyst compared to [Co].00 is confirmed by the CO dissociation results (Table 4). The amount of CO able to be dissociated by CI[Zr + Co].28 before deactivation was 70% higher than that by [Co].00 (see Table 4), while [Zr].00 did not activate CO for dissociation at all. The number of CO molecules dissociated before deactivation was equal (within experimental error) to the total number of chemisorbed H atoms. It can be speculated that the coimpregnation of Zr and Co onto SiO_2 during the course of preparation may have resulted (especially for the catalysts with high loadings of Zr) in the formation of smaller Co crystallites.

From Table 3, the increase in the loading of Zr led to an increase of catalyst activity for FTS and a noticeable increase in the value of α, without a significant effect on TOF values. These results could mean that Zr did not increase the site activity for the coimpregnated Zr + Co catalysts (especially CI[Zr + Co].28) as much as increase the number of active sites.

No significant differences in either the conversion or the rate of the H_2–D_2 exchange reaction in the presence of CO (see Table 4) were detected between the promoted catalyst (CI[Zr + Co].28) and the unpromoted catalyst ([Co].00), even upon changing the temperature. Zr/SiO_2 by itself ([Zr].00) showed no exchange activity whatsoever under the conditions used.

CONCLUSIONS

Both XRD and TPR results showed no discrete Zr phase, which indicates that Zr did not form a separate bulk phase, regardless of the method of preparation and the loading of Zr. Although the Co covered only a small portion of the SiO_2 surface, Zr obviously showed an affinity for interaction with the metal phase. This is commonly seen for promotion of Group VIII metals with Group IA, IIA, and rare earth species (31–34).

Zr promotion of Co/SiO_2 increased both the initial and steady-state rates of FTS for all Zr-promoted catalysts, with the largest increase in the rate of FTS at steady state being 100%. It should be noted that FTS is a structure-insensitive reaction and as such would not be expected to exhibit order-of-magnitude changes in activity. Thus, the increase seen upon Zr promotion should be considered to be significant. It was found that by increasing the Zr-to-Co ratio from 0.02 to 0.28, α (at steady state) increased by almost 20%, except for the catalysts prepared by sequential addition of Co to Zr/SiO_2. This enhancement in the value of α is significant when one considers the effect on product distribution.

Although the method of preparation of ZrO_2-promoted Rh/SiO_2 has been reported not to have any effect on catalyst activity (27), the contrary was found here. It appears that the extent of Zr promotion depended on the method of preparation and the Zr/Co ratio. H_2 spillover may have been the main reason for the enhancement of the activity

TABLE 4

H_2–D_2 Exchange and CO Dissociation Results[a]

	H_2–D_2 exchange[b]										CO dissociation[c]
	25°C		100°C		130°C		150°C		175°C		(μmol (CO)/g catalyst)
Catalyst	%C[d]	Rate[e]	%C	Rate	%C	Rate	%C	Rate	%C	Rate	
[Co].00	0.0	0.0	4.6	18.2	20.0	79.0	38.6	152.4	41.2	162.7	165
CI[Zr + Co].28	0.0	0.0	4.4	18.8	20.2	86.4	31.8	136.1	34.3	146.8	282
[Zr].00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0

[a] All the results were within ±10%.

[b] $H_2:D_2:CO:He = 10:10:2:78$ (cc/min), 1.8 atm.

[c] Total amount of CO dissociated before catalyst deactivation for $CO:He = 2:20$ (cc/min), 1.8 atm.

[d] Percent conversion of H_2 to HD.

[e] Overall rate of HD formation (μmol HD/g cat/s).

of Zr/Co catalysts for FTS. For these catalysts it appears that there was an optimum Zr/Co ratio, beyond which some Co site blockage may have occurred. In the case of Co/Zr catalysts the interactions between Co and Zr seemed to enhance the activity of Co sites for FTS. The coimpregnation of Zr and Co, on the other hand, resulted in a true increase in Co dispersion, as shown by XRD and H_2 chemisorption results and confirmed by CO-dissociation experiments.

The FTS results indicate that Zr is basically a rate promoter for Co/SiO$_2$; however, high loadings also appear to increase the selectivity for higher hydrocarbons. While the presence of Zr facilitated CO dissociation, Zr by itself has no activity for CO hydrogenation or H_2 activation. The activated and/or the created sites due to the presence of Zr seem to be more easily deactivated, probably by carbon deposition.

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