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The Role of ZrO₂ in Promoting the Activity and Selectivity of Co-Based Fischer-Tropsch Synthesis Catalysts

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Abstract

The effects of Zr promotion on the structure and performance of Co-based Fischer-Tropsch synthesis (FTS) catalysts were investigated. Inclusion of Zr in the catalysts was found to increase the FTS turnover frequency and the selectivity to C_{5+} hydrocarbons and to decrease the selectivity to methane under most operating conditions. These improvements to the catalytic performance are a function of Zr loading up to an atomic ratio of $Zr/Co = 1.0$, above which the product selectivity is insensitive to higher concentrations of the promoter. Characterization of the Co nanoparticles by different methods demonstrated that the optimal Zr loading corresponds to half monolayer coverage of the Co surface by the promoter. Measurements of the rate of FTS at different pressures and temperatures established that the kinetics data for both the Zr-promoted and unpromoted catalysts are described by a two-parameter Langmuir-Hinshelwood expression. The parameters used to fit this rate law to the experimental data indicate that the apparent rate coefficient and the CO adsorption constant for the Zr-promoted catalysts are higher than those for the unpromoted catalyst. Elemental mapping by means of STEM-EDS provided evidence that Zr is highly dispersed over the catalyst surface and has limited preference for association with the Co nanoparticles. In situ X-ray absorption spectroscopy confirmed the absence of mixing between the Zr and Co in the nanoparticles. These results suggest that Zr exists as a partial layer of ZrO_2 on the surface of the Co metal nanoparticles. Accordingly, it is proposed that Zr promotion effects originate from sites of enhanced activity at the interface between Co and ZrO_2 . The possibility that ZrO_2 acts as a Lewis acid to assist in CO dissociation as well as to increase the ratio of CO to H adsorbed on the catalyst surface is discussed.

Keywords

Fischer-Tropsch Synthesis, Heterogeneous Catalysis, Cobalt, Zirconium, Promotion

1. Introduction

Fischer-Tropsch synthesis (FTS) continues to be an attractive option for the production of synthetic fuels (1). Much of the interest in FTS originates from the wide variety of carbon sources that can be used to produce synthesis gas, such as biomass, coal, or natural gas (2). Additionally, the hydrocarbons produced by FTS are compatible with existing vehicles and transportation infrastructure. Recent efforts have focused on the development of Co-based catalysts, which are ideal for producing the unbranched, long-chain hydrocarbons found in diesel fuels (3). A long-standing objective of this research is suppressing the formation of methane while shifting the product distribution toward C₅₊ hydrocarbons. To this end, extensive work has been devoted to exploring the effects of metal oxides as promoters. Particular interest has been devoted to ZrO₂, dating back to the 1980s (4) (5) (6). These early patents, which are well-summarized by Oukaci et al. (7), mention the role of Zr in moderating Co-support interactions and improving the catalyst stability. The suitability of ZrO₂ as a support (8) (9) or support modifier (10) (11) (12) has also been reported as well as the use of Zr as a promoter deposited along with the Co precursor onto supports during the catalyst preparation. For example, using catalysts in which Co and Zr precursors were impregnated onto SiO₂, Ali et al. found that Zr increased the turnover frequency for CO consumption and that at high promoter loadings, the presence of Zr resulted in improvements to the product selectivity (13). Similar studies have also demonstrated the ability of Zr promoters to enhance the activity and selectivity of Co-based FTS catalysts (14) (15) (16). However, it has also been reported that Zr promotion did not cause significant changes to the intrinsic activity of the catalyst (17) (18) and the product distribution (19). Without detailed information about the catalyst structure, especially regarding the structural and electronic interactions between Co and Zr, it remains difficult to fully reconcile these conflicting accounts.

At present, the effects of Zr promoters on catalyst performance remain ambiguous, and few studies have attempted to address the deeper question of whether Zr has any role beyond being a structural promoter. Ali et al. speculated that Co active sites at the interface with ZrO₂ may exhibit enhanced activity toward CO hydrogenation (13), a hypothesis that originates from studies of metal oxide-promoted Rh catalysts (20) (21). This hypothesis has also been used to rationalize the catalyst structure-performance relationships resulting from Mn promotion of Co-based FTS catalysts (22) (23). In this study, we demonstrate that Zr promotes the catalyst activity and selectivity in a manner analogous to promotion by Mn. Activity and selectivity data were collected over a range of operating conditions to assess the impact of Zr promotion on the intrinsic activity and CO adsorption properties of the catalyst.

The composition and structure of the catalyst was probed by elemental mapping and X-ray absorption spectroscopy to determine the extent to which the Zr promoter interacts with the Co nanoparticles within the catalysts. These data are consistent with the formation of highly dispersed nanoclusters of ZrO_2 over the surface of the Co nanoparticles, which produces interface sites that have higher activity toward FTS and interact more strongly with CO than unpromoted Co sites. ZrO_2 was determined to be a more effective promoter for improving product selectivity than MnO when the fraction of Co active sites at interface with the metal oxide promoter was close to unity. Since ZrO_2 is a stronger Lewis acid than MnO, these findings support the hypothesis that the role of the metal oxide promoter is to facilitate the binding and dissociation of CO through Lewis acid-base interactions.

2. Experimental Methods

2.1 Catalyst Synthesis

All catalysts were prepared by incipient wetness co-impregnation of porous SiO_2 (PQ Corporation) using aqueous solutions of $\text{Co}(\text{NO}_3)_2$ and $\text{ZrO}(\text{NO}_3)_2$ (Sigma-Aldrich, 99.999% purity). The concentration of the solutions were adjusted so as to achieve the targeted Zr/Co atomic ratio and a Co loading of 10 wt% with respect to the sum of the weights of SiO_2 and Co. On a watch glass, 1 g of the SiO_2 was spread evenly and about 1 mL of the metal impregnation solution was then added dropwise to the SiO_2 . The SiO_2 powder was then kneaded using a spatula until the SiO_2 had a dry, homogenous appearance, and the impregnation step was repeated until all the solution had been absorbed into the support. The SiO_2 with the deposited metals, henceforth referred to as the catalyst precursor, was dried for at least 12 h at ambient conditions. The catalyst precursor was then heated at 5 K/min in flowing H_2 to 723 K to decompose the deposited nitrates. After holding at 723 K for 2 h, the catalyst was cooled to ambient temperature, exposed to 500 ppm O_2 to passivate the metallic Co, and stored in a desiccator until use. ICP-OES (Galbraith Laboratories, Inc.) was used to confirm the Co and Zr loadings. The sequence of catalyst preparation steps is depicted as a flow diagram in Scheme S1 of the Supporting Information.

2.2 Temperature-Programmed Reduction

Temperature-programmed reduction (TPR) was conducted in a quartz tube reactor by heating the reactor from 298 K to 850 K at 5 K/min under a flow of 1% H_2 , 1% Ar, and 98% He (30 mL/min). The effluent from the reactor was analyzed by an MKS Minilab quadrupole mass spectrometer. The Ar in the feed was used as an internal standard to correct for variation in the reactor outlet flow rate during the

temperature ramp. TPR measurements were made on the catalyst precursors and the passivated catalysts (i.e. prior to the first and second pretreatment steps). Control measurements were made with SiO_2 and $\text{ZrO}(\text{NO}_3)_2$ deposited onto SiO_2 .

2.3 O_2 Titration

The extent of Co reduction was assessed by O_2 titrations of the passivated catalysts using the same apparatus that was used for TPR. For these measurements, pulses of air were dosed into the reactor and the reactor effluent was monitored by the mass spectrometer. In a typical experiment, a passivated catalyst sample was loaded into the reactor and subsequently reduced in H_2 at 723 K for 2 h. The system was then flushed with He to remove H_2 . Once the H_2 signal on the mass spectrometer returned to baseline values, a pulse of air was injected into the reactor using a sample loop on a 6-port valve. This step was repeated until O_2 peaks with equivalent area were observed. The O_2 signal as a function of time was integrated to calculate O_2 uptake.

2.4 H_2 Chemisorption

The exposed surface area of the metallic Co nanoparticles after reduction was quantified by static H_2 chemisorption using a Micromeritics 3Flex surface characterization analyzer. The catalysts were reduced in H_2 at 723 K, evacuated below 0.01 mbar for 2 h, and then cooled to 373 K. A known quantity of H_2 was then introduced into the sample tube and the pressure was allowed to equilibrate. This step was repeated until the pressure within the sample tube reached 0.66 bar in order to collect an H_2 adsorption isotherm. The adsorption temperature of 373 K was selected based on reports of this temperature being optimal for H_2 chemisorption measurements on Co (24). Moreover, the full H_2 uptake of a single adsorption isotherm, rather than the difference between initial and repeat isotherms, was used to determine metallic Co surface area because this method has been reported to correspond more closely to dispersions determined by TEM imaging and the expected 1/1 H/Co adsorption stoichiometry (24).

2.5 In Situ X-Ray Absorption Spectroscopy

The oxidation state of the promoter and the local environments of Co and Zr were probed by in situ X-ray absorption spectroscopy (XAS) experiments. These data were collected at beamlines 5-BM (DND-CAT) and 10-BM (MRCAT) at the Advanced Photon Source synchrotron at Argonne National Laboratory (25). All measurements were conducted in transmission mode using gas ionization detectors.

A Si(111) crystal monochromator, which was detuned to reject higher harmonics, was used to adjust the energy of the X-ray beam. Metal reference foils were used for energy calibration and sample spectra alignment. For these experiments, the passivated catalysts were pressed into pellets inside a sample holder that was placed into an in situ reactor cell. The cell was heated by a clamshell tube furnace and connected to a gas inlet manifold to flow He, H₂, and CO over the samples. After measuring spectra of the catalysts in the passivated state at ambient temperature, the catalysts were reduced in H₂ at 723 K. Spectra of the reduced catalysts were collected at 723 K and at ambient temperature. The samples were then re-heated to 493 K and exposed to syngas (2/1 H₂/CO) for 6 h before measuring a final set of spectra. Data analysis of the XAS spectra was performed using the Demeter software family (26), which uses IFFEFIT internally (27).

2.6 STEM Imaging and Elemental Mapping

The passivated catalysts were prepared for imaging by electron microscopy by grinding the catalysts with a mortar and pestle, suspending the ground catalysts in ethanol, and then drop-casting 5 μ l of the suspensions onto lacey carbon Cu TEM grids (Ted Pella, Inc.). The TEM grids were dried in a vacuum oven at 383 K for 1 h to fully evaporate the solvent. High-angle annular dark-field (HAADF) images of the Co nanoparticles were obtained using an FEI Titan electron microscope at the Molecular Foundry at the Lawrence Berkeley National Laboratory. Elemental maps were obtained by energy dispersive spectroscopy (EDS) using the same microscope, which was equipped with a Bruker, four-segment, silicon drift detector that collected the fluorescent X-ray spectrum from 0-20 keV with an energy resolution of 140 eV and a dispersion of 10 eV per channel. All imaging and mapping was done in scanning transmission mode with a 200 kV accelerating voltage. The Bruker Esprit software program was used to process and quantify the elemental map data using the Cliff-Lorimer method (28).

2.7 CO Temperature-Programmed Desorption

CO temperature-programmed desorption (TPD) measurements were made using a Micromeritics AutoChem II 2920 instrument. First, a catalyst sample was loaded into a sample tube and reduced in H₂ at 723 K. The sample was then cooled under He to 323 K and a series of 10% CO pulses were injected into the He carrier gas that was flowing through the sample tube. After saturating the catalyst surface with adsorbed CO, the system was flushed with He for 15 min to allow physisorbed CO to desorb and to clear the apparatus of gas phase CO. Then, the temperature of the sample was ramped at 10 K/min to 873 K while the thermal conductivity of the sample tube effluent was monitored.

2.8 Catalytic Reactions

Fischer-Tropsch synthesis was performed using a fix-bed reactor to assess the effects of Zr promotion on catalyst activity and selectivity. A quartz reactor was used for experiments at atmospheric pressure, and a 316 stainless steel reactor was used for experiments at elevated pressure. Each reactor was heated using a tube furnace, and the reactor temperature was regulated by a PID control loop incorporating a thermocouple inserted into the catalyst bed. Gas flow through the reactors were regulated by mass flow controllers. Pressure in the stainless steel reactor was measured with an electronic pressure transducer and controlled by a diaphragm back-pressure regulator. Sample collection vessels, maintained at 403 K, were installed below both reactors to collect liquid products, and the gaseous products were routed to an Agilent 6890N gas chromatograph for online composition analysis. The inlet and outlet of the reactors as well as all tubing between the liquid collection vessels and the gas chromatograph were heated to 503 K to prevent condensation of water and long-chain hydrocarbons.

Each experiment started with loading 50 to 100 mg of passivated catalyst diluted with calcined SiO_2 into the reactor. The catalyst was reduced in H_2 by heating from 298 K to 723 K at the rate of 5 K/min. The reactor was then flushed with He and cooled to 493 K before starting the FTS reaction. The catalyst was aged for 12 h in syngas (2/1 H_2/CO), after which the catalyst activity had stabilized. Following the aging step, measurements were conducted at various reaction conditions to observe the effects of temperature (483 to 503 K), reactant partial pressures (0 to 9.3 bar), and space velocity (20 to 100 mL/min). The background activities of the reactor, SiO_2 , and ZrO_2 deposited onto SiO_2 were found to be negligible, and the absence of transport limitations was determined by satisfying the Weisz-Prater criterion (29) and by carrying out a series of activity measurements at different space velocities and catalyst bed loadings. CO_2 production rates were below detectable levels, and oxygenates were less than 1% of the product fraction on a molar carbon basis.

The conversion of CO based on CO consumed, $X_{\text{CO}}^{\text{CO}}$, was calculated according to eq. 1, where C_{CO} and C_{Ar} are the molar concentrations of CO and Ar in the reactor effluent, respectively, and C_{CO}^0 and C_{Ar}^0 are the molar concentrations of the same species in the reactor inlet feed. The conversion was used to calculate the rate of CO consumption per gram of Co, given as $-r_{\text{CO}}$ in eq. 2, where Q_{in} is the volumetric flow rate of the reactor inlet feed and W_{Co} is the mass of Co in the catalyst bed. Ar was used as an internal standard and the concentrations of CO and Ar were determined using from the thermal conductivity detector response of the gas chromatograph.

$$X_{CO}^{CO} = \frac{\left(\frac{C_{CO}^0}{C_{Ar}^0}\right) - C_{CO}/C_{Ar}}{C_{CO}^0/C_{Ar}} \quad (1)$$

$$-r_{CO} = \frac{X_{CO}^{CO} C_{CO}^0 Q_{in}}{W_{Co}} \quad (2)$$

The CO conversion based on products formed, X_{CO}^{HC} , and the rate of hydrocarbon production per unit mass of Co on a molar C basis, r_{HC} , was determined from eqs. 3 and 4, respectively. Here, Q_{out} is the volumetric flow rate of the reactor effluent and C_i is the molar concentration of hydrocarbons containing i carbon atoms. CO consumption rates were relied upon for reaction conditions giving high conversions and significant liquid product selectivities, whereas the hydrocarbon production rates were more accurate at low conversions and conditions where the selectivity to wax products was negligible.

$$X_{CO}^{HC} = \frac{Q_{out} \sum_{i=1}^n i C_i}{Q_{in} C_{CO}^0} \quad (3)$$

$$r_{HC} = \frac{Q_{out} \sum_{i=1}^n i C_i}{W_{Co}} \quad (4)$$

Product selectivities were determined by the methods described by Dinse et al. (30). Briefly, for conditions at which the production of C_{12+} products was insignificant (e.g., high temperature and low pressure) the product selectivity could be determined by analyzing the composition of the gas phase products alone. However, at conditions yielding C_{13+} products, the presence of condensed hydrocarbons required the liquid phase product composition to be taken into account. As an alternative to collecting wax samples, the C_{5+} selectivity was determined by subtracting the rate of C_1 - C_4 production from the rate of CO consumption on a molar C basis. This approach permits timely acquisition of product selectivity data but forgoes the individual carbon number selectivities for the long-chain hydrocarbons.

3. Results

3.1 Temperature-Programmed Reduction

The consumption of H_2 during the first and second reduction steps of the Zr-promoted (Zr/Co = 1.0) and unpromoted (Zr/Co = 0) catalysts is shown in Figure 1, and data for the byproducts formed are provided in Figure S1 of the Supporting Information. As shown in Figure S1C, the decomposition of Co nitrate deposited onto SiO_2 produces peaks corresponding to NO, H_2O , and NO_2 between 430 K and 580 K. When Zr oxynitrate was deposited onto SiO_2 along with the Co nitrate, these decomposition product peaks occurred at higher temperatures between 450 K and 620 K, which provides evidence for chemical

interactions occurring between the Co and Zr precursors. The appearance of a peak at 395 K in the TPR profile for the co-impregnated catalyst precursor corresponds to Zr oxynitrate decomposition, which was observed in the profile for the control sample consisting of the Zr precursor deposited onto SiO₂ (Figure S1D). Interestingly, the TPR data for the control sample containing Zr oxynitrate had a peak 652 K, which was not present in the data for the co-impregnated catalyst precursor. On the basis of thermal gravimetric analysis, this peak has been attributed to restructuring of decomposed Zr precursor into crystalline ZrO₂ (31). However, the mass spectrometry data of the present study show evidence for NO production at this temperature, which demonstrates that full decomposition of Zr oxynitrate requires temperatures above 700 K. The absence of this peak from the co-impregnated catalyst precursor may indicate that the presence of the Co precursor lowers the temperature at which the Zr precursor fully decomposes.

The TPR profiles for the second reduction step of the Zr-promoted and unpromoted catalysts, which involved the pretreatment of the passivated catalysts prior to conducting FTS reactions, are shown in Figure 1. For the unpromoted catalyst, a single peak corresponding to the formation of Co metal is observed at 571 K. The data for the Zr-promoted catalyst showed two reduction events, possibly related to Co₃O₄ reduction to CoO and CoO reduction to Co metal at 485 and 680 K, respectively. Both catalysts also consumed H₂ over a broad temperature range starting at 650 K for the unpromoted catalyst and 775 for the promoted catalyst. Since slightly higher extents of reduction for the unpromoted catalyst were observed when the second reduction took place at 723 K compared to 673 K, it is reasonable to assume that this additional H₂ consumption is associated with the reduction of Co species that interacted strongly with the support (or the promoter for the Zr-promoted catalyst). This interpretation is corroborated by studies of Co reduction on both SiO₂ (32) and Al₂O₃ (33), which report the formation of mixed oxides of Co and the support that require similar temperatures to reduce. On the basis of the temperature required to decompose the Zr precursor and to form Co metal in the Zr-promoted catalyst, a reduction temperature of 723 K was chosen for both catalyst pretreatment steps used in this study.

3.2 O₂ Titration and H₂ Chemisorption

O₂ titration uptakes for the reduced Co-ZrO₂ catalysts are presented in Table 1, and the corresponding extents of Co reduction are given in Table 2. To calculate the fraction of Co in the metallic state following the reduction step, it was assumed that the reduced catalysts consisted of Co(0) and CoO, which were fully oxidized to Co₃O₄ during the O₂ titrations. Additionally, the promoter was

assumed to be in the form of ZrO_2 and to not undergo partial reduction during the pretreatment step, which was confirmed by XANES. Accordingly, the fraction of Co that was metallic after reduction, $f_{\text{Co},\text{metal}}$, was calculated from eq. 5 where U_{O_2} is the O_2 molar uptake and N_{Co} is the total moles of Co in the catalyst. For the unpromoted catalyst, 87% of the Co was reduced to Co metal following the second reduction pretreatment step. The extents of reduction decreased monotonically with Zr loading such that only 54% of the Co in the catalyst prepared with $\text{Zr/Co} = 1.0$ was metallic following reduction.

$$f_{\text{Co},\text{metal}} = \frac{2U_{\text{O}_2} - \left(\frac{4}{3} - 1\right)N_{\text{Co}}}{N_{\text{Co}}} \quad (5)$$

H_2 uptake values followed a more complex trend possibly owing to H spillover onto the promoter, a documented phenomenon for metal nanoparticles in contact with ZrO_2 (13) (34) (35). No uptake of H_2 onto control samples consisting of SiO_2 and ZrO_2 deposited onto SiO_2 was measured, but the interface between Co and ZrO_2 in the promoted catalysts may provide sites through which H can transfer onto the ZrO_2 . For catalysts with Zr/Co ratios between 0.01 and 0.1, the H_2 uptakes per gram of catalyst were comparable to that for the unpromoted catalyst. Taking into account the lower extents of reduction of these catalysts, the H_2 uptakes per mole of metallic Co were up to 10% higher than that of the unpromoted catalyst despite all catalysts having similar average nanoparticle sizes. This is an expected result if H spillover onto the ZrO_2 occurred. Nevertheless, the catalyst prepared with Zr/Co ratios greater than 0.25 showed a decrease in H_2 uptake as Zr loading increased, which is consistent with blockage of the Co surface by ZrO_2 . Assuming this blockage effect dominated over spillover at high Zr loading, it would make the most sense to use the total H_2 uptake when determining the number of Co active sites for catalysts within this loading regime, which is the approach used for this work. We note that this assumption may underestimate the turnover frequencies of the Zr-promoted catalysts with Zr/Co ratios greater than 0.25.

3.3 In Situ X-Ray Absorption Spectroscopy

Figure 2 shows the X-ray absorption near-edge structure (XANES) spectra at the Zr K-edge for the Zr-promoted Co catalysts acquired after passivation, reduction, and reaction. For all Zr loadings, the Zr edge energies for the passivated catalysts were consistent with that for the ZrO_2 standard, which implies that the apparent oxidation state of the Zr in these catalysts is 4+. Furthermore, no shifts in the Zr edge energy were observed following the reduction at 723 K or after subsequent exposure to syngas at 493 K for 6 h. This confirms that the ZrO_2 did not reduce, which is expected considering that unsupported ZrO_2 does not reduce in H_2 even at much higher temperatures (36). However, there were

noticeable differences in the shape of the XANES spectra as a function of Zr loading. Although the spectra of the catalysts with higher Zr loadings (e.g., Zr/Co = 1.0) matched that of the monoclinic ZrO₂ standard reasonably well, the lower loading sample (Zr/Co = 0.1) had a more prominent edge feature at 18,003 eV and differences in the relative peak heights immediately after the edge. These features are consistent with the reported XANES spectrum for tetragonal ZrO₂ (37). Hence, Zr appears to adopt a tetragonal crystal structure at low loadings, which is perhaps related to Zr being atomically dispersed over the SiO₂ surface, and higher loadings result in the emergence of monoclinic ZrO₂ structures. The transition of the XANES spectrum from that corresponding to the tetragonal structure to that for a predominantly monoclinic structure as a function of Zr loading is shown with greater detail in Figure S2 of the Supporting Information.

Analysis of the extended X-ray absorption fine structure (EXAFS) was carried out to gain additional structural information about the Co and Zr atoms in the catalysts. The EXAFS spectra for a Zr-promoted catalyst (Zr/Co = 1.0) and for an unpromoted catalyst, both in the reduced state, are shown in Figure 3. Fits of the data, represented by the dashed black lines, were performed for the data points within the shaded gray region of the plots. The modeling was done using a single energy shift for all paths and symmetric path expansion terms (i.e., k^*r_{eff}) for each crystal structure present in the fit. False peaks at radial distances less than 1 Å are visible in the Zr K-edge data, but it was not possible to remove them by changing the background function parameters without significantly attenuating the amplitude of the Zr-O scattering path. In Figure 3A, the spectra collected at the Co K-edge for the both catalyst contains peaks corresponding to scattering paths in Co metal (Co-Co at $R = 2.1$ Å) and CoO (Co-O at $R = 1.6$ Å and Co-Co at $R = 2.6$ Å). In the case of the Zr-promoted catalyst, a satisfactory fit was achieved without needing to substitute Zr atoms into the Co metal and CoO structures used to calculate the scattering paths. This finding is consistent with the Zr promoter not intermixing into the Co-containing phases in significant quantities. A major difference between the spectra for the two catalysts is that the magnitude of the peaks due to scattering in CoO are much larger relative to the magnitude of the peak for the first coordination shell of Co metal in the Zr-promoted catalyst than in the unpromoted catalyst. This feature suggests that a greater fraction of Co in the unpromoted catalyst was in the metallic state than in the Zr-promoted catalyst, reinforcing the conclusion based on O₂ titrations that the Zr-promoted catalyst had a lower extent of reduction following pretreatment.

Figure 3B shows a comparison between the Zr K-edge EXAFS spectrum and that of monoclinic ZrO₂. Both spectra contain two major peaks in the shaded region corresponding to the first and second

shell scattering paths. For the reference material, these peaks were clearly attributed to the Zr-O ($R = 1.58 \text{ \AA}$) and Zr-Zr ($R = 3.01 \text{ \AA}$) scattering paths of ZrO_2 . The first peak of the spectrum for the Zr-promoted catalyst matches expectations for the Zr-O scattering path, but the second shell peak is highly attenuated relative to the magnitude of the first peak. The smaller second peak suggests that there are fewer neighboring Zr atoms in this shell compared to the structure of bulk ZrO_2 , which would be the case if the Zr in the promoted sample were highly dispersed. Hence, these data suggest that even at this relatively high loading of promoter, the Zr did not form appreciable quantities of multilayered ZrO_2 .

3.4 Electron Microscopy

Electron microscopy was used to gain information about the size and structure of the Co nanoparticles as well as the location of the promoter relative to that of the Co. Table 1 lists the surface mean diameters of the Co nanoparticles as determined by TEM imaging for catalysts prepared with various loadings of Zr. The average particle sizes and the standard deviations of the size distributions were found to be independent of Zr loading. For all catalysts, the particle sizes were close to 10 nm, which corresponds to Co dispersions of about 9%. Because the Zr is highly dispersed over the catalyst surface, no features in the HAADF-STEM images could be attributed to Zr unambiguously. As a result it was necessary to use of analytical TEM imaging to locate the promoter. A representative image of the Zr-promoted catalyst prepared with $\text{Zr/Co} = 1.0$ is provided as Figure 4A. In this STEM-EDS elemental map, a number of Co nanoparticles, appearing as green clusters, are dispersed over a relatively thin region of the SiO_2 support. The promoter, which is represented visually by the color red, is shown to be spread across the support without correlation with the positions of the Co nanoparticles. Preferential spatial association between Co and Zr was not found in the catalysts prepared with lower loadings of Zr relative to Co. This qualitative finding was observed in all the elemental maps acquired for this study, and no evidence for homogenous, bimetallic nanoparticles was observed.

The conclusion that Zr does not associate preferentially with the Co was reinforced by the quantification of the nanoparticle compositions. For this analysis, the pixels constituting a Co nanoparticle and a 1 nm buffer around the nanoparticle were selected and the X-ray spectrum of these pixels were quantified by the Cliff-Lorimer method to determine the composition of the nanoparticle. The data from a set of images giving a sample size of over 100 nanoparticles were used to construct a histogram of nanoparticle compositions. This is presented in the form of nanoparticle Zr/Co atomic ratios for the catalyst prepared with $\text{Zr/Co} = 1.0$ in Figure 4B. The nanoparticle composition distribution is modeled accurately by a Gaussian function, and the median of the distribution is 0.63. The

discrepancy between the mean nanoparticle composition ($\text{Zr/Co} = 0.63$) and the bulk composition ($\text{Zr/Co} = 1.0$) indicates that a significant portion of the Zr promoter was not in contact with the Co nanoparticles. With the tendency of the Zr to spread over the support, a material balance calculation would overestimate the amount of promoter in contact with the Co given that the EDS maps are two-dimensional projections of a three-dimensional, porous material. Nevertheless, this analysis agrees well with the qualitative conclusions derived from visual inspection of the elemental maps.

3.5 CO Temperature-Programmed Desorption

The CO TPD profiles for a Zr-promoted catalyst ($\text{Zr/Co} = 1.0$) and for an unpromoted catalyst are shown in Figure 5. A profile for the SiO_2 support was also collected and used for background subtraction to remove the contribution from SiO_2 dehydroxylation, which occurred at temperatures above 700 K. ZrO_2 deposited onto SiO_2 did not show any CO uptake or additional desorption peaks. The unpromoted catalyst exhibited CO desorption peaks at 435 and 560 K, which establishes that there are at least two distinct Co sites on which CO can adsorb. Estimates of CO heats of adsorption were made using the Redhead model (38) assuming a typical pre-exponential factor of 10^{13} s^{-1} . These calculations suggest that the first desorption peak corresponds to a desorption activation energy of 93 kJ/mol whereas the higher temperature peak corresponds to 119 kJ/mol. The Zr-promoted catalyst had a prominent desorption peak at 460 K, which corresponds to a desorption activation energy of 98 kJ/mol. A smaller desorption peak also appeared at 680 K. The latter peak, which corresponds to a desorption activation energy of 143 kJ/mol, indicates the presence of a much more strongly bound CO species when the catalyst is Zr-promoted. While the desorption activation energies of the unpromoted catalyst are similar to typical CO heats of adsorption on Co, the activation energy for desorption of the strongly bound CO on the Zr-promoted catalyst is significantly higher than that reported for unpromoted Co (39) (40). It is possible that CO disproportionation occurs at temperatures exceeding those typically used for FTS. Therefore, the TCD peaks measured at such high temperatures may be a consequence of CO_2 formation more so than CO desorption. However, at lower temperatures, CO disproportionation does not occur and consequently the shift of the desorption peak to higher temperatures in this temperature range for the Zr-promoted catalyst suggests that the promoter strengthens CO adsorption.

3.6 Catalyst Activity

Measurements were made of the rate of FTS at 493 K under differential conversion using different partial pressures of H_2 and CO in order to determine the rate law for the kinetics of CO

consumption over Zr-promoted catalysts. As shown in Figure 6 for the catalyst prepared with Zr/Co = 1.0, it was found that CO consumption rates scaled linearly with the H₂ partial pressure and had a negative first-order dependence on the CO partial pressure. Within the data set for the CO partial pressure variation, the CO consumption rates increased monotonically as the CO partial pressure decreased. Since the rate must go to zero as P_{CO} approaches zero, a rate maximum must exist, which the data suggest occurs between 0 and 0.5 bar. All of these observations are in accordance with the two-parameter, Langmuir-Hinshelwood expression given by eq. 6 (41). In this equation, $-r_{CO}$ is the rate of CO consumption, a is an apparent rate coefficient, b is the CO adsorption constant, P_{CO} is the CO partial pressure, and P_{H_2} is the H₂ partial pressure. The unpromoted catalyst follows the same rate law as reported in our recent studies of similar catalysts (23).

$$-r_{CO} = \frac{abP_{CO}P_{H_2}}{(1+bP_{CO})^2} \quad (6)$$

Using this rate law, the dependence of CO consumption rates on total pressure and temperature was investigated. The unpromoted catalyst was found to be more active than the catalyst with Zr/Co = 1.0 at most conditions when compared on the basis of rates of CO consumption per gram Co (Figure S3 of the Supporting Information). This was most evident in the high pressure regime because the Zr-promoted catalyst was subject to stronger CO inhibition than the unpromoted catalyst. However, a different perspective is revealed when the H₂ uptake data from Table 1 is used to express the rates in terms of turnover frequencies on the basis of the number of Co atoms accessible to H₂ chemisorption. These data are shown in Figure 7 for the Zr-promoted (Zr/Co = 1.0) and unpromoted (Zr/Co = 0) catalysts. For most conditions, the Zr-promoted catalyst exhibits higher turnover frequencies than the unpromoted catalyst, which demonstrates that the promoter increases the intrinsic activity of the active sites that participate in FTS.

A deeper understanding of the effect of Zr on the rate law parameters was obtained by examining the parameters a and b appearing in the rate law. These parameters were obtained by nonlinear least-squares regression of the rate data, the fits are represented by the solid lines in Figures S3 and 7. The appropriateness of the rate law for modeling these kinetics data was confirmed by the high R² values of the parity plots in Figure S4 of the Supporting Information. The apparent rate coefficients and CO adsorption constants for the Zr-promoted catalyst (Zr/Co = 1.0) and unpromoted catalyst at 483, 493, and 503 K are given in Table S1 of the Supporting Information. At all temperatures, the apparent rate coefficients for the Zr-promoted catalyst are 3-4 times larger than those for the

unpromoted catalyst, which demonstrates that CO consumption per Co atom is faster on the promoted catalyst. The CO adsorption constants for the Zr-promoted catalyst are substantially larger than those of the unpromoted catalyst, which implies that the presence of the Zr leads to a stronger interaction between the adsorbed CO and the catalyst surface.

Arrhenius plots of the apparent rate coefficients and CO adsorption constants, presented in Figure S5 of the Supporting Information, were used to obtain estimates of the pre-exponential and energetic parameters of the constants according to eqs. 7 and 8. In these equations, A is the pre-exponential factor for the apparent rate coefficient for the rate-limiting step, E_A is the apparent activation energy for the rate limiting step, $K_{CO,0}$ is the pre-exponential factor for the adsorption constant, Q_{CO} is the CO heat of adsorption, R is the ideal gas constant, and T is the reaction temperature. Table 3 shows that the apparent activation energy for the rate limiting step for the unpromoted catalyst is about 15 kJ/mol higher than that for the Zr-promoted catalyst and the CO heat of adsorption for the Zr-promoted catalyst is about 27 kJ/mol larger than that for the unpromoted catalysts. The pre-exponential factors for the Zr-promoted catalyst were smaller than those for the unpromoted catalyst. We also note that the apparent activation energies for the rate-limiting step reported here appear to be significantly lower than those presented in the literature, which typically range between 90 and 105 kJ/mol (41). This discrepancy is largely due to the fact that most studies report an overall apparent activation energy that includes contributions from the heat of CO adsorption. Here, the parameter b has been fully separated from the apparent rate constant, resulting in a smaller apparent activation energy for the rate-limiting step. For pressures between 5 and 10 bar, the overall apparent activation energies for the unpromoted catalyst are between 99 and 107 kJ/mol, in good accord with values reported in the literature (41).

$$a = Ae^{\frac{-E_A}{RT}} \quad (7)$$

$$b = K_{CO,0}e^{\frac{Q_{CO}}{RT}} \quad (8)$$

Although the rate law used in this study modeled the catalyst activity quite well in the limit of 0% CO conversion, discrepancies emerged at higher conversion. The rate law implies that CO consumption should decrease as conversion increases owing to the depletion of the CO and H₂. As shown in Figure 8, this behavior was observed qualitatively with the Zr-promoted catalyst at 1 bar; however at 10 bar, the catalyst activity was independent of CO conversion. These findings are similar to those previously reported for unpromoted and Mn-promoted Co-based catalysts (30). A likely

explanation for these effects is the higher partial pressure of water encountered when operating the reactor at a higher total pressure. Multiple researchers have reported that the formation of water has a positive effect on FTS activity for certain ranges of water partial pressure (42) (43). Additionally, the re-adsorption of olefins onto the catalyst surface and their incorporation into or initiation of chain growth may contribute to the positive deviation from the rate law as conversion increases. We have demonstrated previously that this reaction pathway is negligible at low pressure and significant at high pressure for Co/SiO₂ and Mn-promoted Co/SiO₂ (30).

3.7 Catalyst Selectivity

The dependence of catalyst selectivity on Zr loading was explored at 1 bar and 493 K under differential conversions using a series of catalysts prepared with Zr/Co ratios between 0 and 2 (Figure 9). It was found that methane selectivity decreased from about 35% to 14% as the Zr/Co ratio increased from 0 to 1.0. Over this range of Zr loading, the C₅₊ selectivity increased from 31% to 59%. Figure 9B shows the increase in the carbon number-weighted olefin to paraffin ratio of the C₂-C₄ fraction as a function of Zr loading. Both the carbon number selectivities and the olefin to paraffin ratio became insensitive to the promoter loading at a Zr/Co ratio close to 1. This diminishment in the effects of the promoter with increasing promoter loading is quite similar to that reported for Mn-promoted catalysts (23). However in the case of Zr promotion, ten times as much promoter on an atomic basis is required to reach the selectivity plateau.

Experiments at elevated pressure and different temperatures were also conducted. As shown in Figure 10, selectivity toward methane decreased and that for C₅₊ increased as total pressure increased from 1 bar to 10 bar for both catalysts. The effect was more pronounced for the unpromoted catalyst, which has about twice the selectivity toward methane and half as much toward C₅₊ at 1 bar compared to the Zr-promoted catalyst. Increasing the pressure gave diminishing improvements to the product distribution, and at 10 bar the carbon number selectivities were relatively insensitive to pressure. Still, the Zr-promoted catalyst had a lower methane selectivity (10%) and higher C₅₊ selectivity (79%) than the unpromoted catalyst (16% and 73%, respectively) at 10 bar. More detailed presentations of the methane, C₂-C₄, and C₅₊ selectivity data for the Zr-promoted and unpromoted catalysts are given in Figure S6 of the Supporting Information. Higher temperature elevated the selectivity toward methane at the expense of C₅₊ selectivity for both catalysts, and the effects of pressure on the carbon number selectivities were similar at all temperatures.

The effects of CO conversion on product selectivity were dependent on the total pressure at which the reaction was operated. Figure 11 shows the dependence of methane and C₅₊ selectivities on CO conversion at pressures ranging from 1 bar to 10 bar for the Zr-promoted catalyst. At atmospheric pressure, the selectivities did not change as CO conversion increased, which is identical to the behavior seen with the unpromoted and Mn-promoted catalysts (30). At higher pressures, the methane selectivity decreased and C₅₊ selectivity increased as the conversion increased. This effect was quite substantial at 10 bar for which methane selectivity decreased from 10 % to 5.3% and C₅₊ selectivity increased from 80% to 89%. An extrapolation of these data suggest that C₅₊ selectivities higher than 95% could be achieved by operating at a CO conversion higher than 50%, which is quite typical for industrial FTS reactors.

4. Discussion

4.1 Effects of Zr Promotion on the Co Nanoparticle Structure

The empirical evidence presented above shows that promotion of Co/SiO₂ with ZrO₂ has an effect on the intrinsic activity of Co and on the distribution of products. To identify the cause for these effects, it is important to first consider whether or not ZrO₂ affects the Co nanoparticle size and morphology. It is well-established that turnover frequencies and product selectivities are sensitive to particle size when the Co nanoparticle diameters are smaller than 6 to 10 nm (44) (45) (46). Accordingly, it is important to have the average Co particle size close to 10 nm in order to maximize activity per gram Co while avoiding particle size effects. The catalysts used for this study were prepared by co-impregnation of Co and Zr precursors onto SiO₂ followed by direct reduction in H₂. This catalyst preparation strategy was motivated by our recent investigations of Co-MnO catalysts which have demonstrated that this approach results in spherical Co nanoparticles that are insensitive to promoter loading and are close to 10 nm in diameter (23). The same phenomenon was observed for the Co-ZrO₂ catalysts of the present study where the average particle sizes for all catalysts were within 2 nm of 10 nm and the predominant nanoparticle geometry was spherical. Hence, the absence of particle size and shape differences as a function of Zr loading eliminates one source of structural promotion effects.

Another aspect of the Co nanoparticle structure that must be considered is the oxidation state of Co and whether or not the presence of Zr leads to the formation of mixed phases of Co and Zr. The local environment of the Co atoms in the Zr-promoted catalyst as determined by EXAFS is consistent with the Co being a mixture of CoO and Co metal phases. Thus, there are no indications of neighboring

Zr atoms within the coordination shells around the Co atoms. Likewise, the Zr spectra did not show signs of neighboring Co atoms. These data suggest that the presence of Co-Zr mixed oxides after reduction does not appear to be substantial. Any ZrO_2 in contact with the Co would likely be on the surface of the nanoparticles rather than mixed into the nanoparticle bulk. Evidence for this morphology in the Co EXAFS spectrum is not detectable because only about 5% of the Co was on the surface of Co metal nanoparticles. Even if the Co nanoparticles were encapsulated by ZrO_2 , the signals from the oxidized Co and the subsurface metallic Co would obscure the signal from the Co that coordinates with ZrO_2 . The Zr EXAFS spectrum would also not reveal signs for this morphology because the tendency of the Zr to disperse over the SiO_2 support would result in Si rather than Co atoms dominating in the second coordination shell of Zr. Nevertheless, interactions between the Co and Zr could be inferred from the TPR profiles in which the temperature of Co reduction increased markedly with inclusion of the Zr promoter.

The higher Co reduction temperature and lower Co extent of reduction for the Zr-promoted catalyst is unexpected given the abundance of literature reporting that Zr facilitates the reduction of Co. Feller et al. (14) and Moradi et al. (15) have shown that Zr promotion resulted in substantial improvements to the extents of Co reduction for SiO_2 -supported Co. These observations were rationalized in terms of the replacement of Co-Si interactions by weaker Co-Zr interactions, thereby permitting Co atoms to separate more readily from the oxide phase and form metallic nanoparticles. More recently, these reducibility trends were observed for Co on Al_2O_3 (17). However, not all reports claim that Zr improves Co reducibility. For example, Ali et al. have noted that the addition of Zr to SiO_2 -supported Co catalysts did not cause significant changes to the TPR profiles and extents of Co reduction (13). Likewise, Rohr et al. have reported that no improvements in Co reducibility result from Zr promotion of Al_2O_3 -supported catalysts (18). Variations in the level of interaction between Co and Zr due to differences in catalyst preparation methods or pretreatment conditions could account for the assortment of effects that Zr promotion has been reported to have on Co reducibility. In the present study, the coverage of the Co nanoparticle surface by a partial layer of ZrO_2 likely impedes the reduction of Co.

4.2 Structure and Chemical State of the Zr Promoter

Prior work on Zr promotion has assumed, either by chemical intuition or thermodynamics calculations, that Zr forms ZrO_2 . However, it has been reported that Zr can undergo partial reduction in certain systems so it is important to verify whether ZrO_2 persists following reduction and during reaction

(47). As demonstrated by the in situ XANES data, the Zr promoter had an apparent oxidation state of 4+, which did not change during pretreatment in H₂ or with exposure to syngas. These data indicate that, within the limits of detection by XANES, the promoter was present as oxide structures, for which ZrO₂ is the most likely candidate at all levels of Zr promotion. On the basis of the edge features in the Zr XANES spectrum, it appears that the promoter transitions from a tetragonal to monoclinic structure as its loading increases. However, this phenomenon is not obviously connected to the observed effects of Zr promotion. Measurable improvements in the product distribution occurred as the Zr loading increased while ZrO₂ was present in the tetragonal phase, and the ZrO₂ became predominantly monoclinic before the product selectivity became insensitive to Zr loading at higher loadings.

The monoclinic structure of the promoter at a Zr/Co ratio of 1.0 was consistent with analysis of the EXAFS data (Figure 3). The diminished intensity of the second shell peak relative to the first shell peak is consistent with the ZrO₂ being highly dispersed. However, the fit of the second peak in the spectrum of the Zr-promoted catalyst was of notably lower quality than that of the first shell. Various alternative structures to monoclinic ZrO₂ were considered as a result. Working from the assumption that the Zr was highly dispersed over the SiO₂ support, substitutions of Si for Zr atoms in the second shell of ZrO₂ were made. For these fits, additional parameters for the path degeneracy, path expansion length, and mean squared displacement of the Si were introduced. Substitution of Si atoms into the ZrO₂ structure yielded minor improvements to the fit, which is expected considering the presence of additional fitting parameters. With no clear boundary between meaningful fit improvements and overfitting of the data, the identity and position of the second shell neighboring atoms remains ambiguous. Nevertheless, the most plausible fits involving Si yielded second shell path degeneracies that were about half of the values for the bulk structure, which is suggestive of monolayer, or near monolayer, coverage of ZrO₂ over the catalyst surface.

The hypothesis that Zr is highly dispersed over the entire catalyst surface agrees well with the elemental maps obtained by STEM-EDS. The representative map shown in Figure 4A illustrates the lack of spatial association between the Zr and Co as well as an absence of ZrO₂ nanoparticles. Most studies of Zr-promoted Co catalysts report a similar lack of large ZrO₂ domains, which generally has been inferred from the lack of peaks corresponding to ZrO₂ in XRD spectra (48). The extent to which ZrO₂ associates with the Co versus the support has been investigated less rigorously though. The nanoparticle composition histogram given in Figure 4B indicates that less Zr is in contact with the nanoparticles than would be expected from the bulk Zr/Co ratio of the catalyst, which is a clear sign that partial segregation

between the Co and ZrO₂ occurred. While quantitative elemental mapping is quite useful in this regard, the technique is less than adequate for inferring what fraction of the nanoparticle surface was covered by the promoter. To address this question, H₂ uptake and TEM particle size data were used to estimate θ_{Zr} , the fraction of the nanoparticle surface that was inaccessible for H₂ chemisorption due to coverage by ZrO₂. These values were calculated for catalysts with different Zr loadings using eq. 9, where U_{H_2} is the molar H₂ uptake and D is the Co nanoparticle dispersion determined by TEM imaging. The unpromoted catalyst showed good agreement between the dispersion determined by TEM and by H₂ chemisorption so no corrections were applied for blockage of the nanoparticle surface by the support.

$$\theta_{Zr} = 1 - \frac{2U_{H_2}}{N_{Co}f_{Co,metal}D} \quad (9)$$

As reported in Table 2, the fraction of the nanoparticle surface covered by ZrO₂ increases with Zr loading such that the catalyst prepared with Zr/Co = 1.0 is half covered by the promoter. The apparent lack of ZrO₂ coverage in the catalysts prepared with Zr/Co ratios less than 0.25 may have been an artifact of H₂ spillover onto the ZrO₂. While this effect would also be present in the catalysts prepared with higher Zr loading, the decreased Co metal surface area of these catalysts appears to dominate. To determine whether these coverage estimates are reasonable, a separate validation was performed using N₂ adsorption isotherms. Here, the surface area that ZrO₂ would occupy assuming it forms a partial monolayer was compared to the total catalyst surface area determined by BET surface area analysis. The quantity of Zr in the Zr/Co = 1.0 catalyst would have a surface area of 112 m²/g_{cat} if it were in the form of single layer of ZrO₂, and the surface area of the unpromoted catalyst was determined to be 238 m²/g_{cat}. These values suggest that 47% coverage of the catalyst surface by ZrO₂, which is quite close to being a half monolayer in agreement with the estimates from TEM and chemisorption data.

The primary motivation for direct reduction of the catalyst precursors in H₂, rather than first calcining them in air, was our finding that the former pretreatment leads to better spatial association between Co and MnO in Mn-promoted Co/SiO₂ (22). In contrast to Zr, Mn has a high affinity for Co and deposits almost exclusively onto the Co nanoparticle surface until a significant fraction of the surface is covered. While the same catalyst pretreatment approach was used in the present work, it was found that Zr has a much lower affinity for associating with Co compared with SiO₂. We propose that the limited association between the two metals may be related to the relative inability of their precursors to form mixed oxide phases. Co(II) and Zr(IV) have similar ionic radii so there is more reason to think that structural mismatches may play a role in this phenomenon. CoO and MnO both adopt the rock-salt

structure, but ZrO_2 has a monoclinic crystal structure under most conditions. With a sufficiently high loading of Zr, the weaker tendency of the ZrO_2 to associate with the Co can be overcome and a substantial interface between Co and the ZrO_2 can form.

4.3 Influence of Zr Promotion on Activity and the Reaction Mechanism

Although the activity for Zr-promoted Co-based catalysts at atmospheric (13) (17) and elevated (14) pressure has been reported previously, the evaluation of rate laws with the aim of identifying the effects of the promoter on the rate parameters has not been conducted yet. In this study, it was determined that the Zr-promoted catalyst kinetics follow a rate law that is consistent with H-assisted CO dissociation as the rate-limiting step. As reported previously, the same rate law holds for the unpromoted catalyst (23). Differences in the activities of the Zr-promoted and unpromoted catalysts originate from differences in the apparent rate coefficients and CO adsorption constants. For the Zr-promoted catalyst, both these parameters, a and b , are larger than those for the unpromoted catalyst. The larger apparent rate coefficient, a , suggests that ZrO_2 near the Co plays a role in facilitating CO dissociation, but this parameter combines the rate constant for the rate determining step along with the H_2 adsorption constant and the equilibrium constants for any quasi-equilibrated elementary reactions in the mechanism that occur prior to the rate determining step. Consequently, it is difficult to attribute the large apparent rate coefficient for the Zr-promoted catalyst solely to accelerated CO dissociation. A more important contributor to the differences in the turnover frequencies is the CO adsorption constant, which was 3 to 4 times larger with Zr promotion depending on the reaction temperature.

The appearance of the CO adsorption constant in the numerator of the rate law results in a significant increase of the turnover frequency for the Zr-promoted catalyst at low pressures. At 10 bar, the CO adsorption constant in the denominator of the rate law dominates such that Zr promotion yields turnover frequencies comparable to those for the unpromoted catalyst, especially at lower temperatures. These trends demonstrate that whether the promoter increases or decreases the catalytic activity depends significantly on the temperature and pressure at which the system is operated. The heat of CO adsorption on the Zr-promoted catalyst, determined by parameter fitting of the kinetics data, is twice the magnitude of that for the unpromoted catalyst. However, these values are much smaller than the heats of adsorption inferred from the CO TPD profiles by the Redhead model. These differences likely result from the differences in CO surface coverages that occur during steady-state FTS and TPD measurements. Whereas the Co surface is largely saturated by CO under FTS, the catalyst surface becomes comparatively vacant during a desorption profile. Lateral interactions between

neighboring CO adsorbates on the CO saturated surface are responsible for the lower heat of CO adsorption deduced from the FTS data (49). Nevertheless, both perspectives are in qualitative agreement that CO binds more strongly to the Zr-promoted catalyst compared to the unpromoted catalyst.

While there is consensus in the literature that Zr promotion of Co-based FTS catalysts increases rates of CO consumption per gram Co, there is less certainty regarding whether this is due to enhanced activity of the active sites or simply a greater abundance of active sites. Based on SSITKA experiments, Jongsomjit et al. concluded that Zr promotion increases the number of active surface intermediates without changing the average surface residence time of these intermediates (17). Similarly, Rohr et al. found no improvements to the intrinsic activity of active sites within a Zr-promoted catalyst using the same experimental methods (18). However, the catalysts used for these studies were not prepared with the intention of depositing ZrO_2 over the surface of the Co nanoparticles, and the reported H_2 chemisorption data do not show clear signs that the Co nanoparticle surfaces were covered by the promoter. If the active sites at the interface between Co and ZrO_2 were to exhibit enhanced activity for FTS, then these catalysts may have been unsuitable for identifying this phenomenon. In the present study, the lower apparent activation energy for FTS suggests that ZrO_2 plays a role in facilitating the rate determining step of CO dissociation.

4.4 Relationship between Zr Promotion and Product Selectivity

The shift of the product distribution toward higher molecular weight hydrocarbons follows from the larger CO adsorption constant for the Zr-promoted catalyst. With a stronger interaction between CO and the catalyst surface when the Zr promoter is present, a higher coverage of CO on the catalyst surface should occur on the promoted catalyst compared to the unpromoted catalyst, provided that the promoter does not also strengthen the adsorption of H. This phenomenon would also decrease the availability of H on the catalyst surface, and in turn suppress the formation of methane and decreases the probability of chain termination to paraffins by α -hydrogen addition. The secondary hydrogenation of olefins to paraffins would become slower with less H availability, which would result in a higher olefin to paraffin ratio at a fixed CO conversion. These effects are also achieved by increasing total pressure owing to competitive adsorption between CO, which adsorbs molecularly, and H_2 , which adsorbs dissociatively (30). As pressure increases, the surface coverage of adsorbed CO will increase, which decreases the H availability and leads to a more olefinic product distribution having a higher average

molecular weight. Accordingly, Zr promotion is analogous to operating at a higher pressure, at least with respect to its effects on product selectivity.

Increasing the total pressure improves the product selectivity of the Zr-promoted catalyst, but the promoted catalyst is less sensitive to the pressure changes than is the unpromoted catalyst. This is understandable considering that product selectivity is heavily related to the coverage of the Co surface by CO, which has an upper limit dictated by saturation. The Zr-promoted catalyst, with its larger CO adsorption constant, starts with a higher CO surface coverage at low pressure than does the unpromoted catalyst. As pressure increases, the CO surface coverages for both catalysts increase and converge toward unity, which also causes the product selectivities of the catalysts to converge. Operating at higher CO conversions leads to further product selectivity improvements, but only when at elevated pressure (Figure 11). These results can be explained by the same principles that account for the connection between turnover frequencies and CO conversion (Figure 8). For a given CO conversion, reactors operated at higher pressure will have higher water partial pressure. Along with increasing catalyst activity, elevated water concentrations have been documented to yield more C_{5+} and less methane (50). Furthermore, the suppression of olefin secondary hydrogenation at high pressure permits olefins to re-adsorb and to reinitiate chain growth. The beneficial effects of higher CO conversion on product selectivity also apply to the unpromoted catalyst (30). Consequently, the C_{5+} selectivities for both catalysts would probably be quite similar at pressures and CO conversions near 10 bar and 50%, respectively. For this reason, it may be more appropriate to consider Zr promotion as a tool for achieving a target product selectivity at a lower operating pressure rather than as a means for improving dramatically the highest attainable C_{5+} selectivity.

4.5 Interaction between Zr and the Co Active Sites

The dependence of the catalyst selectivity on the Zr loading can be rationalized with the following model. It is assumed, as shown in Scheme S2 of the Supporting Information, that the surface of Co comprises two types of sites, Co atoms on the perimeter of ZrO_2 moieties covering the Co surface and Co sites that are not adjacent to the ZrO_2 . The sites on the perimeter of the ZrO_2 moieties are assumed to be more active and have a higher affinity toward CO than those located farther away. As the coverage of Co by ZrO_2 increases, the number of the less active Co sites unaffected by ZrO_2 will decrease monotonically, whereas the number of more active Co sites adjacent to ZrO_2 will increase. Given the highly dispersed nature of the ZrO_2 , it is reasonable to assume that Zr might deposit randomly on the catalyst surface. Under this assumption, the total number of active sites along the ZrO_2 perimeter would

be maximized when the ZrO_2 covers half the Co surface (51). The fraction of active Co sites that are adjacent to the ZrO_2 would be close to unity at this level of coverage. Higher loading of ZrO_2 would decrease the number the sites available for catalysis by covering up the remainder of the Co surface.

Since the observed product selectivity is the average of the selectivities of all active sites weighted their activity, the product distribution will improve as the fraction of sites adjacent to the ZrO_2 becomes larger. This behavior is observed for catalysts prepared with Zr/Co ratios between 0 and 1.0 where the product distribution shifts toward higher molecular weight and the olefinic content of the light hydrocarbon product fraction increases as the Zr loading increases (Figure 9). Once all Co sites are adjacent to ZrO_2 , the observed product selectivity will be equivalent to the intrinsic selectivity of an active site at the Co- ZrO_2 interface, which represents an upper limit to the product selectivity improvements resulting from Zr promotion. This onset of the insensitivity of product selectivity toward Zr loading occurs at a Zr/Co ratio of 1.0. The percentage of the Co nanoparticle surface that is covered by ZrO_2 at this loading is about 50%, which agrees with the theoretical expectation for the ZrO_2 perimeter to be maximized at half monolayer coverage of the catalyst surface. Additional Zr did not alter the product selectivity, which is consistent with most active sites being adjacent to the ZrO_2 and the additional promoter depleting the number of such sites by covering the nanoparticle surface.

The same conclusion was reached in our recent work with Mn-promoted Co, which demonstrated that the optimal amount of Mn promoter corresponds to the loading required to form a half monolayer of the promoter on the Co nanoparticle surface (23). A key difference between the two promoters is that the optimal loading for the Zr promoter is $\text{Zr/Co} = 1.0$ whereas the Mn-promoted catalysts only require $\text{Mn/Co} = 0.1$. This difference is attributable to the different level of spatial association between the two promoters and Co. Mn has a strong probability of associating with the Co such that a half monolayer of MnO on the Co nanoparticle surfaces is established before Mn deposits elsewhere. In the Zr-promoted catalysts, the Zr disperses randomly over the catalyst such that a half monolayer on the Co nanoparticles is reached at a loading that places a half monolayer over the entire catalyst surface. These results demonstrate the importance of controlling for differences in the degree of contact between the Co and the promoter when comparing different metal oxide promoter elements.

The differences between MnO and ZrO_2 promoters extend beyond performance-loading relationships. The highest attainable C_{5+} selectivity at low pressure, where the promotion effects were most apparent, was higher for ZrO_2 (59%) than for MnO (48%). Moreover, the apparent rate coefficient and CO adsorption constant for the Zr-promoted catalyst were larger than those of the Mn-promoted

catalysts. These comparisons, made under conditions for which the interface between Co and the promoter was maximized, suggest that Zr is intrinsically a more effective promoting element. A periodic trend that likely accounts for the higher performance of the Zr-promoted catalyst is the higher Lewis acidity of Zr(IV), which is largely a result of the higher oxidation state of the Zr compared to the Mn under FTS (52). Metal oxide promoters functioning as Lewis acids has been hypothesized in the literature (53) (21). In this proposal, the CO is envisioned to be adsorbed onto the Co through the C atom while interacting simultaneously with the nearby promoter cation via the O atom, which helps to bind and weaken the carbonyl bond. Although it is difficult to find direct evidence for this intermediate, there are findings in the present work that support this hypothesis. The CO TPD profile for the Zr-promoted catalyst (Figure 5) contains a high temperature CO desorption peak, which may be related to chemisorbed CO that interacts with the Zr. Additionally, the pre-exponential factor of the CO adsorption constant for the Zr-promoted catalyst was two orders of magnitude smaller than that for the unpromoted catalyst. This is consistent with the hypothesis of simultaneous interaction of the adsorbed CO with both the Co and Zr, which should result in the adsorbed CO being more vibrationally constrained leading to a significant decrease in entropy.

5. Conclusions

The present work establishes that Zr promotion can be an effective tool for improving the activity and product selectivity of Co-based FTS catalysts. Higher turnover frequencies were observed for the Zr-promoted catalysts at most operating conditions, which resulted from the larger FTS apparent rate coefficient and CO adsorption constant for the promoted catalysts. Adding Zr to the catalyst suppressed the formation of methane and shifted the product distribution in favor of the C₅₊ hydrocarbons. The effects of pressure on the product selectivity of the promoted and unpromoted catalysts demonstrate that Zr promotion was analogous to operating at a higher pressure owing to the larger CO adsorption constants of the promoted catalysts. Stronger interactions between CO and the catalyst surface would increase the ratio of CO to H on the catalyst surface. With less H availability at the active sites of the Zr-promoted catalysts, termination to paraffins is suppressed and the growth of longer hydrocarbon chains can occur.

Structurally, the Zr promoter formed highly dispersed ZrO₂ under reaction conditions. Furthermore, it appears that Zr did not form mixed alloys or oxides with the Co. Instead, the ZrO₂ existed as a near monolayer dispersed over the catalyst surface with limited preference for associating

spatially with the Co nanoparticles versus the support. The relationship between catalyst selectivity and Zr loading is consistent with the formation of enhanced active sites at the interface between the Co metal and the ZrO₂ promoter. As ZrO₂ begins to cover the catalyst nanoparticles as Zr loading increases, the fraction of active sites adjacent to the promoter increases. Eventually, the fraction of active sites that are promoted approaches unity, with evidence suggesting that this occurs near a Zr/Co atomic ratio of 1, and no further improvements to the product selectivity result from higher Zr loading. The structure and catalytic behavior of the Zr-promoted catalysts are very similar to those of Mn-promoted catalysts, but for catalysts in which the Co-promoter interfaces were maximized, Zr promotion results in stronger enhancements to the CO dissociation rates and adsorption. Accordingly, these findings support the hypothesis that the Lewis acidity of the promoter is the relevant descriptor for metal oxide promotion effects.

Supporting Information

The Supporting Information is available free of charge on the Internet at <http://pubs.acs.org>. Flow diagram of catalyst preparation steps, TPR profiles, Zr K-edge XANES spectra, specific activity, parity plots, rate constants and adsorption constants, Arrhenius plots, product selectivity data, and hypothesized structure of the Co-ZrO₂ nanoparticles.

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Table 1. Physical characterization data for the Co-ZrO₂ catalysts.

Zr/Co Atomic Ratio	Co Loading ^a (wt %)	d(Co) ^b (nm)	O ₂ Uptake (mmol g _{cat} ⁻¹)	H ₂ Uptake (mmol g _{cat} ⁻¹)
0	9.8	11 ± 3	1.0	0.063
0.01	9.8	10 ± 2	0.96	0.067
0.05	9.7	11 ± 3	0.90	0.060
0.10	9.5	10 ± 4	0.86	0.060
0.25	9.4	10 ± 3	0.82	0.053
0.5	8.9	9 ± 3	0.72	0.037
1.0	7.7	10 ± 3	0.57	0.017
2.0	6.6	9 ± 4	0.43	0.008

^a Compositions were determined by ICP-OES, and the Co wt % were approximately constant at 10 wt% with respect to mass of Co and SiO₂.

^b Surface mean diameter.

Table 2. Co extents of reduction, nanoparticle dispersions, and coverages of the nanoparticle surfaces by ZrO₂.

Zr/Co Atomic Ratio	Co(0) ^a (%)	Dispersion ^b (%)	ZrO ₂ Coverage ^c (%)
0	87	9.1	—
0.01	82	9.5	0 ± 10
0.05	76	8.7	0 ± 10
0.10	73	9.3	0 ± 10
0.25	69	9.4	0 ± 10
0.5	63	10.8	30 ± 10
1.0	54	9.3	50 ± 10
2.0	44	10.2	70 ± 20

^a Percentage of Co in the metallic state after reduction.

^b Determined by particle sizes assuming a site density of 14.6 Co atoms/nm².

^c Percentage of the metallic Co nanoparticle surface area covered by ZrO₂.

Table 3. Fitted kinetics parameters for the Zr-promoted and unpromoted catalysts.

Zr/Co Atomic Ratio	A ($\text{bar}^{-1} \text{s}^{-1}$)	E_A (kJ/mol)	$K_{\text{CO},0}$ (bar^{-1})	Q_{CO} (kJ/mol)
0	7×10^7	84	3×10^{-4}	35
1.0	6×10^6	68	1×10^{-6}	62

Figure 1. TPR profiles of the Co and Co-ZrO₂ (Zr/Co = 1.0) catalysts. The curves labeled “1st” correspond to the initial decompositions of the dried catalyst precursors. The curves labeled “2nd” correspond to the second reductions of the passivated catalysts that would occur prior to conducting FTS reactions. The catalyst synthesis process and its relation to these TPR data is illustrated in Scheme S1 of the Supporting Information.

Figure 2. In situ XANES spectra of the Co-ZrO₂ catalysts collected at the Zr K-edge. Spectra for catalysts prepared with low (Zr/Co = 0.1) and high (Zr/Co = 1.0) promoter loadings were collected at three conditions: passivated state at ambient temperature (Pass.), after reduction with H₂ at 723 K for 2 h and cooling to 493 K (Redu.), and in 2/1 H₂/CO syngas at 493 K (FTS). A more detailed view of the effect of Zr loading on the spectra is included in Figure S2 of the Supporting Information.

A)

B)

Figure 3. EXAFS spectra of Co and Co-ZrO₂ catalyst samples at the (A) Zr K-edge and (B) Co K-edge. The spectra were measured at ambient temperature and pressure in He. Before collecting the spectra, the catalyst samples were reduced in H₂ at 723 K (the ZrO₂ reference was used without pretreatment). The solid colored lines in the plots are the k^2 -weighted Fourier transforms of the EXAFS spectra, and the dashed black lines are fits to these data within the shaded gray region.

A)

B)

Figure 4. STEM-EDS elemental map (A) and nanoparticle composition histogram (B) of the Co-ZrO₂ catalyst prepared with a Zr/Co = 1.0 atomic ratio. The dashed curve in the histogram is a Gaussian function fitted to the data, and the vertical lines in the histogram indicate the mean nanoparticle composition (dotted) and the bulk catalyst composition (dashed).

Figure 5. CO temperature-programmed desorption spectra for the Zr-promoted ($\text{Zr/Co} = 1.0$) and unpromoted ($\text{Zr/Co} = 0$) catalysts. The CO adsorption took place at 323 K and the desorption temperature ramp rate was 10 K/min. The plotted data are the instrument thermal conductivity signals as a function of sample temperature.

Figure 6. Dependence of the CO consumption rate for the Zr-promoted catalyst (Zr/Co = 1.0) on (A) H₂ and (B) CO partial pressures. The variation of H₂ partial pressure was done with a constant CO partial pressure of 1.55 bar; the variation of CO partial pressure was done with a constant H₂ partial pressure of 3.1 bar. The data for both figures were collected at 493 K and were extrapolated to 0% conversion. The curves in the plot correspond to the rate law from eq. 6 fitted to the data.

Figure 7. Dependence of FTS turnover frequencies on temperature and pressure for (A) Zr-promoted (Zr/Co = 1.0) and (B) unpromoted (Zr/Co = 0) catalysts. These data were collected using a 7% Ar, 31% CO, and 62% H₂ reactor inlet feed composition, and the data points were extrapolated to 0% conversion. The curves in the plots are fits to the data using the rate law from eq. 6.

Figure 8. FTS turnover frequencies as a function of CO conversion for the catalyst prepared with $\text{Zr/Co} = 1.0$. These data were collected at 493 K with a 7% Ar, 31% CO, and 62% H_2 reactor inlet feed composition. The lines in the plot are for visual aid.

A)

B)

Figure 9. Effect of Zr loading on product selectivities at 1 bar and 493 K. (A) Methane, C_2 – C_4 , and C_{5+} selectivities at 0% conversion as a function of Zr loading. (B) Olefin to paraffin ratio within the C_2 – C_4 product fraction interpolated to 3% CO conversion as a function of Zr loading. All data points were collected with a reactor inlet feed composition of 7% Ar, 31% CO, and 62% H_2 . The curves in each plot are cubic splines added for visual aid.

A)

B)

Figure 10. Comparison of (A) CH₄ and (B) C₅₊ selectivities as a function of pressure for Zr-promoted (Zr/Co = 1.0) and unpromoted (Zr/Co = 0) catalysts. The data were collected at 493 K with a 7% Ar, 31% CO, and 62% H₂ reactor inlet feed composition. The plotted data points were extrapolated to 0% conversion. The curves in each plot are cubic splines added for visual aid.

Figure 11. Selectivities toward (A) methane and (B) C₅₊ for the catalyst prepared with Zr/Co = 1.0 as a function of CO conversion. These data were collected at 493 K with a 7% Ar, 31% CO, and 62% H₂ reactor inlet feed composition. The lines in the plot are for visual aid.

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