

Fischer-Tropsch Chemistry

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Evidence of Structure Sensitivity in the Fischer–Tropsch Reaction on Model Cobalt Nanoparticles by Time-Resolved Chemical Transient Kinetics

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Abstract: The Fischer–Tropsch process, or the catalytic hydrogenation of carbon monoxide (CO), produces long chain hydrocarbons and offers an alternative to the use of crude oil for chemical feedstocks. The observed size dependence of cobalt (Co) catalysts for the Fischer-Tropsch reaction was studied with colloidally prepared Co nanoparticles and a chemical transient kinetics reactor capable of measurements under non-steady-state conditions. Co nanoparticles of 4.3 nm and 9.5 nm diameters were synthesized and tested under atmospheric pressure conditions and $H_2/CO = 2$. Large differences in carbon coverage (Θ_{C}) were observed for the two catalysts: the 4.3 nm Co catalyst has a Θ_C less than one while the 9.5 nm Co catalyst supports a Θ_C greater than two. The monomer units present on the surface during reaction are identified as single carbon species for both sizes of Co nanoparticles, and the major CO dissociation site is identified as the B_5 -B geometry. The difference in activity of Co nanoparticles was found to be a result of the structure sensitivity caused by the loss of these specific types of sites at smaller nanoparticle sizes.

he catalytic hydrogenation of carbon monoxide (CO) to longer chain hydrocarbons—the Fischer–Tropsch (FT) reaction—is industrially and scientifically important. Common catalysts used for this surface-catalyzed polymerization are cobalt (Co) and iron (Fe). Catalysts based on Co are valued for their ability to produce a higher quantity of longer chains; however, the mechanism of the FT process remains elusive.

A fundamental goal in the field of heterogeneous catalysis is to control the product selectivity, and to this end, an understanding of the FT mechanistic pathway is needed. Additionally, work on Co catalysts for the FT reaction have shown the reaction to be structure-sensitive; below catalyst particle sizes of 8–10 nm, the activity decreases.^[1,2] Several reasons for the activity loss of small particles have been proposed, such as easier re-oxidation of smaller particles,^[3,4] loss of necessary ensemble sites, and surface reconstructions.^[5]

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To understand the origin of the structure sensitivity, information is needed about individual or intermediate steps. Furthermore, an idea as to the true active site or active ensemble is necessary. Because the FT reaction has a complex reaction network, a variety of types of active sites are likely to exist; CO dissociation sites, H_2 dissociation sites, monomer formation sites, and chain-growth sites are all possibilities.

Through the use of transient reactor systems,^[6,7] information such as intermediate residence times, surface coverages, and site reactivity distributions can be obtained. Various transient techniques have been developed, such as isotopic reactant exchange at steady state (SSITKA),^[8–10] pulsed techniques (TAP),^[11,12] and various step-change experiments.^[13,14] Previous transient experiments on Co catalysts have shown evidence for two distinct surface carbon precursors to methane,^[13] evidence for the CO insertion mechanism,^[15] steric hindrance on the surface,^[16] and irreversibly adsorbed CO on smaller Co particles.^[17]

This article presents our work using chemical transient kinetic experiments of CO/H2 gas over size-controlled Co model catalysts. The chemical transient kinetic system observes the catalysts as it approaches a new steady statea type of relaxation method where the effect of CO appearance or disappearance is studied. By synthesizing the Co nanoparticles using colloidal chemistry methods, we can ensure a proper size measurement^[18] so as to correlate the structure of the Co nanoparticle catalysts with the observed catalytic trends. It was found that the Co surface of smaller (4.3 nm) particles could not support as much carbon as larger (9.5 nm) particles by more than 1 carbon per Co surface atom. The monomer unit that gives rise to chain growth is found to be a single carbon species on both small and large Co particles. Additionally, the CO dissociation site is identified as the B₅-B site, and the observed activity difference of Co nanoparticles is attributed to structure sensitivity caused by a decrease in B₅-B sites at smaller nanoparticle sizes.

The Co nanoparticles were imaged by transmission electron spectroscopy (TEM) after synthesis and prior to introduction to the mesoporous silica (MCF-17) support. Over 1000 particles were counted to obtain the size distributions. The average particle size and standard deviation are reported in Table 1, along with other physical properties of the prepared catalysts. Figure 1 gives representative TEM images with the corresponding size distributions. Synthesis details, procedures, and TEM images of both fresh and spent catalysts can be found in the Supporting Information.

A layer of organic capping agent (oleic acid) is present at the surface because of the colloidal method used to prepare the Co nanoparticles. The capping agent is removed under

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Table 1: Physical properties of the prepared Co nanoparticle MCF-17 catalysts.

| | Nanoparticle diameter ^[a] [nm] | Co loading [wt%] ^[b] | BET surface area ^[c] [m ² g ⁻¹] | Metallic Co surface sites ^[d] |
|--------------------------------|---|---------------------------------------|---|--|
| Catalyst A | 4.3 ± 0.8 | 8.4 | 635 | 1.88×10 ²⁰ |
| Catalyst B 9.5 nm Co | 9.5 ± 1.0 | 9.2 | 632 | 1.10×10 ²⁰ |

[a] Derived from TEM. [b] As determined by ICP-AES. [c] Surface area of supported catalysts. [d] Calculated using values from TEM, ICP, and 14.6 atoms Co nm^{-2.[19]}



Figure 1. Transmission electron micrographs of catalyst **A** (left), catalyst **B** (middle), and the corresponding size distributions (right) with a Gaussian fit (dotted lines). Scale bar: 50 nm.

oxidative treatment, while a subsequent reduction step produces the Co metal. To follow these changes and to confirm removal of the capping agent, in situ X-ray spectroscopies were employed to characterize the catalyst surface under pretreatment and reaction conditions. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and Co K-edge X-ray absorption spectroscopy (XAS) data can be found in the Supporting Information.

The chemical transient reactor (see the Supporting Information for a schematic) allows for step changes in the gaseous composition, and the experimental data is characterized by two distinct transient periods: the forward transient, in which a switch from He + H₂ to CO + H₂ turns the reaction "on"; and the backward transient, where a switch from CO + H₂ to He + H₂ turns the reaction "off". The partial pressure of H₂ is kept constant, while the partial pressure of He equals the partial pressure of CO.

After the forward transient switch, the online mass spectrometry (MS) signals typically stabilize after approximately 120 s on stream, marking the beginning of steadystate FT operation. The steady-state conversion and selectivity data for both catalyst **A** and **B** are similar to existing literature on size-controlled Co catalysts for FT.^[1,2] Table 2 gives the steady-state data for both catalysts.

Figure 2 gives an example of the forward transient response of catalyst **A**. The CO gas bottle contains 10% Ar as a tracer, which allows for the characterization of the

Table 2: Steady-state reaction data at 230°C, H₂/CO=2.

| | , | | | | |
|--------------------|-------------------|-----------------------------|---------------------------|--|--------------------|
| Catalyst | Conversion [%] | TOF [×10 ⁻²] | CH4 ^[a] [%] | C ₂₋₄ ^[a] [%] | O/P ^[b] |
| A 4 3 nm | 15.5% | 0.45 | 44.7 | 40.2 | 0.07 |
| В | 24.7% | 1.04 | 41.6 | 42.7 | 0.35 |
| 9.5 nm | | | | | |

[a] Selectivity on a carbon basis. [b] Olefin:paraffin ratio.

gas-phase response of the reactor. The t = 0 time point in each of the figures in this article are referenced to the appearance (or disappearance in the back transient) of Ar in the outlet flow. Because Ar is inert it can be used to evaluate the



Figure 2. Forward transient switch to reaction conditions. Inset: the first 15 s of the reaction magnified.

theoretical response of CO in the case of no adsorption/ reaction occurring—labeled "theoretical CO" in Figure 2.

Using the Ar reference, we can separate the filling of the reactor with adsorption on the surface of the catalyst in the first seconds of the forward transient. The appearance of CO at the outlet is delayed in time from the theoretical response and exhibits a different slope, which indicates the CO is undergoing adsorption and probably dissociation at the surface. The difference between the "theoretical CO" and CO outlet flow values in Figure 2 represent the total number of CO molecules that have been adsorbed by the surface. Figure 3 shows the normalized outlet flow of CO during the forward transient for both catalysts. Comparing the outlet flow for catalysts A and B, it is obvious that the adsorption profiles are very different. Although catalyst A has more total metallic surface area than catalyst **B**, the surface adjusts to the new conditions much faster, as indicated by the steeper slope in the CO outlet flow and the faster time to reach steady-state

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Figure 3. Normalized outlet flow of CO and theoretical CO for both 9.5 nm and 4.3 nm Co catalysts.

CO consumption. The 4.3 nm Co particles reach their steadystate consumption of CO after about 20 s, whereas the 9.5 nm Co takes closer to 100 s. The faster equilibration implies that CO adsorption on smaller nanoparticles is either faster, more energetically favorable, or limited by available sites for adsorption.

Similar to previous results on a CoMgO catalyst,^[20] the hydrocarbons appear in order of increasing carbon number; Figure 4 shows the selectivity of the catalysts plotted in time. Sequential appearance of the hydrocarbons confirms that a single carbon atom species is the monomer unit on both 4.3 nm and 9.5 nm Co catalysts. Our observations agree with theoretical models, which predict the product distribution according to addition of a single carbon monomer; namely the Anderson–Schulz–Flory distribution.^[21,22]

The product distributions are similar on both nanoparticle sizes regardless of whether the actual monomer units are the same. Both catalysts produce a small amount of CO_2 , with CO_2 appearing early after the forward switch but stabilizing very quickly to a steady-state selectivity of about 1%. No alcohol formation was observed in this study. The major difference between catalyst **A** and **B** lies in the olefin production. The olefin to paraffin (O/P) ratio makes this clear; catalyst **A** has an O/P of 0.07, while catalyst **B** has an O/P ratio of 0.35, indicating that the hydrogenation ability of the 4.3 nm Co is much higher than that of the 9.5 nm Co.^[17]

Using data from both online MS and offline GC-MS, the full carbon balance can be followed in time (see the Supporting Information for calculations). From the AP-XPS data, a clean, metallic Co surface is prepared before exposure to CO (Supporting Information, Figure S1). Figure 5 shows the carbon coverage ($\Theta_{\rm C}$) versus time for both catalysts. The $\Theta_{\rm C}$ initially increases steadily for both catalysts, with the 9.5 nm Co particles accumulating slightly more carbon than the smaller nanoparticles. Both Co nanoparticle sizes show a change in the $\Theta_{\rm C}$ profile around 15 s, with the small particles stabilizing around $\Theta_{\rm C} = 0.5$ while the larger particles continue to accrue carbon with $\Theta_{\rm C}\,{=}\,1.5$ at 80 s. A $\Theta_{\rm C}$ value above 1 can be rationalized by considering that the growing chains will have multiple carbon atoms. We propose that a monomer pool is being formed in the initial seconds of the forward transient period and that the $\Theta_{\rm C}$ value of 0.5 is a critical value at which the surface concentration of C and H favor



Figure 4. Carbon selectivity as a function of time for catalyst A) **A** and B) **B**; hydrocarbons appear in carbon number order.



Figure 5. Carbon coverage (Θ_c) for 9.5 nm and 4.3 nm Co catalysts.

chain-growth kinetics, producing larger hydrocarbons. Once this initial monomer pool is created, the reaction starts producing larger quantities of heavier hydrocarbons.

During the initial adsorption of CO, no products appear until 5 s after the switch to $CO + H_2$. The first products to appear are CH_4 and CO_2 . To understand what is occurring we consider the starting state of the catalyst. Under $H_2 + He$, the Co nanoparticle surface should be covered in atomic hydrogen, as the Co surface is metallic and can easily dissociate H_2 . Upon the switch to $H_2 + CO$, the hydrogen coverage (Θ_H)

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should be much higher than typical FT conditions; thus, we can expect a higher methanation rate at the initial onset of the reaction. Once a pool of carbon has built up on the surface, the values of Θ_{C} and Θ_{H} favor chain growth rather than methanation/termination. The smaller nanoparticles have a smaller carbon pool and exhibit less activity, whereas the larger nanoparticles have a larger amount of carbon on the surface and have higher activity (see Table 1). Even though catalyst A has a large metallic surface area, the number of sites for carbon seems to be limited; the 9.5 nm Co has a higher $\Theta_{\rm C}$ and is still more active. It appears that, to promote chain propagation on Co, more carbon must be available on the surface. The idea of a carbon pool is not new;^[7-9] however, our results show that the carbon pool is not a by-product of the FT reaction but rather a necessary requirement for the reaction to occur.

Theoretical studies have shown agreement with the high $\Theta_{\rm C}$ values on fcc Co under FT conditions,^[23] and that CO or deposited carbon can induce restructuring.^[24,25] Recent work by van Helden et al. demonstrated the variation of surface sites with fcc Co nanoparticle size;^[26] interestingly, they showed that the site fractions of certain edge, step, and kink sites can actually increase with increasing nanoparticle size. Within the perspective of our present work, we propose that small variations in site fractions of B₅-A, B₅-B, and B₆ (Co (211), (221), and (321), respectively) sites of different size nanoparticles lead to large changes in the relative surface coverage of C and H atoms, as evidenced by the surface coverage of carbon. More specifically, these low coordination B₅-A, B₅-B, and B₆ sites must correspond to either CO dissociation or chain-growth sites.

In addition to monitoring the forward transient, the back transient also provides interesting information. An example of the back transient period is given in Figure 6; zero time corresponds to the disappearance of Ar at the reactor outlet. Once the switch is operated and the CO inlet flow is stopped, the H₂ consumption decreases correspondingly. Interestingly, both CH₄ and H₂ exhibit a peak during the back transient period. Figure 6 gives a representative example of the back transient period from catalyst **A**.

At the onset of the back transient period, the switch from $CO + H_2$ to $He + H_2$ creates a pseudo zero-order hydrogen environment for the surface bound species. We assume that

any and all carbon species on the surface are hydrogenated during the back transient period; clean C 1s spectra (Supporting Information, Figure S3) prove that carbon removal from the surface is complete during the back transient period. From Figure 6 it is clear that methane increases substantially after CO is removed from the reactor, and this phenomenon is observed for both catalysts. This is additional proof that the most abundant species on the surface during steady-state FT operation appears to be a single carbon monomer.

Interestingly, the consumption of molecular hydrogen as a reactant shows a distinct peak after the back transient switch (Figure 6). The surface flux calculation is detailed in the Supporting Information, using a negative sign convention for adsorption and positive for desorption. Overall, the catalysts are adsorbing hydrogen (Figure 6, negative value, right axis); however the upward facing peak can only be obtained by surface species desorbing. The slow increase of H_2 over 80 s in Figure 6 corresponds to emptying of the surface of remaining carbon monomer units, which is why CH_4 exhibits a similar time-dependent tailing.

To understand why there is an observed peak in H_2 desorption from the surface, we must assume a supply of hydrogen exists that is similar to the carbon pool proposed earlier. Some of this surface hydrogen is used for chain propagation and growth, while some hydrogen is used for dissociation of CO.^[27,28] When the back transient switch is operated, the CO flow stops, cutting off the carbon reactant supply to the surface. Once CO stops, the hydrogen pool that has been used to help dissociate CO is not needed and desorbs from the surface. By integrating the area of the hydrogen desorption peak, an estimate on the number of CO dissociation sites available on each catalyst is obtained.

To identify the specific CO dissociation site corresponding to the observed H_2 desorption peak, normalizing the integrated H_2 desorption peak by the number of dissociation sites for each size nanoparticle should give equal values. Figure 7 gives the ratio of desorbed hydrogen to the type of surface site (using estimates of surface site fractions from van Helden et al.). When normalizing the H_2 peak by B_5 -B sites, both 4.3 nm and 9.5 nm Co give a similar value. Given that the



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Figure 6. Back transient switch from $CO + H_2$ to $He + H_2$.



Figure 7. Integrated H_2 surface flow normalized by the corresponding type of site for both catalysts.

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reaction conditions are kept constant and assuming the absence of large energetic differences in reactant absorption, then the B_5 -B site should correspond to the major CO dissociation site on Co nanoparticles.

The loss of activity with smaller Co nanoparticles can now be explained by the structure sensitivity of the FT reaction to specific Co sites. Theoretical work has shown that B₅-B sites continue to increase in concentration with increasing nanoparticle size^[26] and this increase in CO dissociation sites leads to higher $\Theta_{\rm C}$ values and thus higher activity. Our data confirms that it is a structural factor that influences the activity of the catalyst, as H₂-assisted CO dissociation sites are present in larger quantities for larger particles.

Experimental Section

Synthesis of Co nanoparticles, MCF-17, and X-ray spectroscopy data and fitting details are included in the Supplementary Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cobalt nanoparticles · Fischer–Tropsch · surface chemistry · time-resolved measurements · X-ray absorption spectroscopy

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Communications

Fischer–Tropsch Chemistry

W. T. Ralston, G. Melaet, T. Saephan, G. A. Somorjai* _____ IIII--IIII

Evidence of Structure Sensitivity in the Fischer–Tropsch Reaction on Model Cobalt Nanoparticles by Time-Resolved Chemical Transient Kinetics



Size it up: Size-dependent activity of cobalt nanoparticles in Fischer–Tropsch synthesis is correlated with loss of carbon monoxide dissociation sites on small nanoparticles. Transient kinetic experiments and synchrotron spectroscopy reveal greater carbon accumulation on large nanoparticles. Carbon monoxide dissociation sites occur on face-centered cubic cobalt (221) steps.

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