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Mechanism of Cobalt-Catalyzed CO Hydrogenation: 1. Methanation

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Supporting Information

ABSTRACT: The mechanism of CO hydrogenation to CH4 at 260 °C on a cobalt catalyst is investigated using steady-state isotopic transient kinetic analysis (SSITKA) and forward and backward chemical transient kinetic analysis (CTKA). The dependence of CH4 residence time is determined by 12CO/H2 → 13CO/H2 SSITKA as a function of the CO and H2 partial pressure and shows that the CH4 formation rate is mainly controlled by CH4 hydrogenation rather than CO dissociation. Backward CO/H2 → H2 CTKA emphasizes the importance of H coverage on the slow CH4 hydrogenation step. The H coverage strongly depends on the CO coverage, which is directly related to CO partial pressure. Combining SSITKA and backward CTKA allows determining that the amount of additional CH4 obtained during CTKA is nearly equal to the amount of CO adsorbed to the cobalt surface. Thus, under the given conditions overall barrier for CO hydrogenation to CH4 under methanation condition is lower than the CO adsorption energy. Forward CTKA measurements reveal that O hydrogenation to H2O is also a relatively slow step compared to CO dissociation. The combined transient kinetic data are used to fit an explicit microkinetic model for the methanation reaction. The mechanism involving direct CO dissociation represents the data better than a mechanism in which H-assisted CO dissociation is assumed. Microkinetics simulations based on the fitted parameters confirms that under methanation conditions the overall CO consumption rate is mainly controlled by C hydrogenation and to a smaller degree by O hydrogenation and CO dissociation. These simulations are also used to explore the influence of CO and H2 partial pressure on possible rate-controlling steps.

KEYWORDS: cobalt, methanation, mechanism, SSITKA, rate-limiting step

1. INTRODUCTION

Fischer–Tropsch synthesis is a heterogeneously catalyzed reaction whereby synthesis gas (a mixture of carbon monoxide and hydrogen) is converted into liquid fuels and chemicals. Known since the seminal works of Franz Fischer and Hans Tropsch in the 1920s, the Fischer–Tropsch (FT) reaction has led to large-scale industrial applications to upgrade carbonaceous feedstock such as coal and natural gas into more valuable liquid products. Supported cobalt is the preferred catalyst for the FT reaction due to its high activity, high chain-growth probability, low water–gas shift activity, and moderate deactivation. A key challenge of FT technology in practice is to combine high yield of long-chain hydrocarbons with low methane selectivity. Even for methane, the simplest hydrocarbon product of the FT reaction, the exact reaction mechanism has not been resolved yet. Mechanisms proposed for the FT reaction are often based on postulated rate-determining steps leading to Langmuir–Hinshelwood equations or have been developed using empiric rate equations. Some of these models for the FT reaction are very sophisticated in their ability to describe important kinetic parameters such as CO consumption rate, chain-growth probability, and other aspects such as olefin readsorption and hydrogenation. Nevertheless, given the complexity of the FT reaction—the large number of involved reactants, products and reaction intermediates, and the uncertainty about the reaction mechanism—there is a great need to investigate this important reaction in more detail.

Detailed insight into reaction mechanism, specifically into the way particular elementary reaction steps control reaction rate and selectivity, can be obtained by transient experiments. Transient techniques involving isotopes were developed by Happel, Bennett and Biloen. Steady-state isotopic transient kinetic analysis (SSITKA) allows extracting kinetic information under steady-state conditions. The unique feature of SSITKA is that the chemical composition of the surface is not changed by the abrupt replacement of one reactant by its isotope. Using this technique surface coverages and kinetic parameters con...
SSITKA has already been used before to investigate the mechanism of FT catalysts. The majority of these studies focused on methanation, because the involved molecules are small enough to be traced online by mass spectrometry and also because the reaction network leading to methane can be formulated robustly in terms of elementary reaction steps. Regarding cobalt-catalyzed FT synthesis, it is usually assumed that CO dissociation is the rate-determining step based on the observation that the reaction order with respect to CO is negative. Matsumoto and Biloen made early attempts to understand the FT mechanism by transient kinetics. Another important work by Winslow and Bell combined isotopic transient kinetic analysis with in situ infrared spectroscopy to investigate the FT mechanism for supported ruthenium. Winslow and Bell showed the existence of two different carbon species, one being a reactive surface intermediate and the other one involved in deactivation. These two pools of carbidic carbon have also been observed by others such as Happel et al. for nickel and van Dijk et al. for cobalt albeit that, different from the work of Winslow and Bell, all of the species could be hydrogenated to methane. Van Dijk et al. reported that C hydrogenation is the slow step in the mechanism of CO hydrogenation to methane by supported cobalt. More recently, Yang et al. attributed the H partial pressure dependence of the methanation reaction to the H-assisted CO dissociation. Den Breejen et al. and Yang et al. interpreted the cobalt particle size effect in terms of strongly bonded C and O atoms on small cobalt particles on the basis of SSITKA data. SSITKA investigations of promoter effects of rhenium and zinc on cobalt were reported by Yang et al. and Enger et al. respectively. Recent progresses in understanding the FT mechanism by SSITKA has been reviewed by Qi et al.

An important related aspect of the FT mechanism in this regard is the mode of CO dissociation. With the advent of density functional theory, the sensitivity of dissociation of molecules like CO, NO, and N₂ to the topology of metal surfaces that enclose catalytic nanoparticles has been extensively investigated. Accordingly, it has been realized that direct CO dissociation is highly likely on step-edge sites, because the terrace sites, which dominate the surface of sufficiently large nanoparticles, are not reactive enough. Another view is that CO activation takes place on terrace sites through an H-assisted mechanism. Although it is difficult to disprove an H-assisted CO dissociation mechanism on a surface that contains adsorbed CO and H, we have recently demonstrated by isotopic exchange of a ¹²C¹⁸O/¹³C¹⁸O mixture that CO dissociation is fast and reversible on an empty cobalt surface.

The purpose of the present work is to provide new mechanistic insight into the CO methanation reaction based on direct CO dissociation employing transient kinetic techniques. We discuss an interpretation of the H partial pressure dependence of the methanation reaction that is different from H-assisted CO dissociation. We employ two different types of transients, a SSITKA switch involving a change in the isotopic labeling of the feed, and forward and backward CTKA transients involving Ne → CO/H₂, Ne/H₂ → CO/H₂ and CO/H₂ → Ne/H₂ switches. The coverage dependence of the kinetic parameters extracted from these transient measurements was evaluated by varying the CO and H₂ pressures. The obtained steady-state and transient data are modeled using the two CO dissociation mechanisms. The direct CO dissociation model that describes the data better is then used to carry out microkinetics simulations to identify the elementary reaction steps that control the CO consumption rate. An important corollary of this study will be that CO dissociation is not the rate-controlling step under methanation conditions at 260 °C. Instead, hydrogenation of O and especially of C atoms deriving from CO dissociation are identified as the slow steps. The consequences of applying different conditions (H₂/CO ratios and partial pressures) on surface composition and major rate-controlling steps will be discussed.

2. EXPERIMENTAL SECTION

Preparation and Basic Characterization. A silica-supported Co catalyst promoted by Pt was prepared by incipient wetness impregnation of SiO₂ (Shell, sieved fraction 120–250 μm, 136 m²/g determined by BET) with an aqueous solution of Co(NO₃)₂·6H₂O (Merck, 99.99%) and Pt(NH₃)₄(NO₃)₂ (Alfa Aesar, 99.995%). Pt was added as a reduction promoter. The impregnated silica was dried at 110 °C for 12 h and then calcined at 350 °C in static air for 2 h before heating to this temperature at a rate of 1 °C min⁻¹. The catalyst contained 17.1 wt % Co and 0.04 wt % Pt as determined by ICP-OES analysis (Spectroblue, AMETEK, Inc.). Co dispersion was measured by H₂-chemisorption ( ASAP 2010, Micromeritics), which was carried out at 110 °C after reduction at 450 °C (heating rate 1 °C min⁻¹) for 6 h and evacuation at 470 °C for 3 h. During this process, the degree of reduction as measured by TPR ( ASAP 2920 II, Micromeritics), the particle size determined by extrapolating the straight-line portion of the adsorption isotherm to zero pressure was 19 nm. From TEM imaging (FEI Tecnai 20, LaB6, 200 kV), a volume-averaged particle size determined by in situ XRD (D/max-2600, Rigaku) of the reduced catalyst by use of the Scherrer equation was 14.7 nm.

Catalytic Activity Measurements. Catalytic activity measurements were performed in a setup that is capable of transient experiments. Two identical gas-feeding units were connected to a four-way valve, which allows rapidly switching between the two feed flows. Great care was taken to keep flow perturbations minimal during switching. This was done by imposing similar pressure drop over the system between the two flow lines and the use of properly regulated mass flow controllers. A low dead-volume stainless-steel tubular reactor of 5 mm inner diameter and 80 mm bed length was used. The catalytic activity in steady state was determined by online gas chromatography (VARIAN CP-3800 equipped with TCD and FID).

Typically, 20 mg of sample diluted with SiC was loaded in the stainless-steel reactor. Prior to reaction, the sample was in situ reduced in a diluted H₂ flow (10% H₂ in Ar, 50 mL min⁻¹ in total) at 450 °C using a heating rate of 2 °C min⁻¹ and atmospheric pressure for 16 h. Subsequently, the sample was cooled to 260 °C in an Ar flow and the pressure was increased to 1.5 bar. Thereafter, the feed was switched to a flow containing a mixture of ¹²CO, H₂, and Ar for 16 h to obtain steady-state conversion of the synthesis gas feed.

Transient Kinetic Experiments. Three types of transient kinetic analyses were performed, i.e., forward and backward chemical transient kinetic analysis (CTKA) involving a change in the chemical composition of the gas phase (forward transient involving Ne → CO/H₂ or Ne/H₂ → CO/H₂; backward transient involving CO/H₂ → Ne/H₂) and a steady-state conversion of the synthesis gas feed.
state isotopic transient kinetic analysis (SSITKA) involving a change in the isotopic labeling of the feed \((12\text{CO}/\text{H}_2/\text{Ar} \rightarrow 13\text{CO}/\text{H}_2/\text{Ne})\). In CTKA experiments, the Ne flow was used as balance to keep the total flow rate unchanged after switch. In SSITKA, the Ne was used as tracer to determine the gas-phase hold-up of the reactor. In all the experiments, an additional Ar flow was used as balance to keep \(\text{H}_2\) partial pressure and total flow rate at 50 mL min\(^{-1}\) when the \(\text{CO}/\text{H}_2\) ratio was varied. The concentrations of \(\text{H}_2\) \((m/z = 2)\), \(\text{H}_2\text{O}\) \((m/z = 18)\), \(\text{12CO}\) \((m/z = 28)\), \(\text{13CO}\) \((m/z = 29)\), \(\text{12CH}_4\) \((m/z = 15)\), \(\text{13CH}_4\) \((m/z = 17)\), Ne \((m/z = 22)\), and Ar \((m/z = 40)\) were monitored by an online quadrupole mass spectrometer (GeneSys).

The CO residence time \((t)\) was calculated via the area under the normalized transient curves \(N_{\text{CO}}(t)\), and corrected for the gas phase hold-up with the use of the Ne inert tracer.

\[
\tau_{\text{CO}} = \int_0^\infty (N_{\text{CO}} - N_{\text{Ne}})dt
\]

The CH\(_4\) (surface intermediates leading to methane) residence time was first determined in a similar way as CO, but corrected for the chromatographic effect of CO by subtracting half of the CO residence time.\(^{18}\)

\[
\tau_{\text{CH}_4} = \int_0^\infty (N_{\text{CH}_4} - N_{\text{Ne}})dt - \frac{1}{2}\tau_{\text{CO}}
\]

The number of reversibly adsorbed CO and adsorbed CH\(_4\) species can be determined from the residence time and exit flow of the corresponding species. Taking into account the dispersion (the value derived from \(\text{H}_2\)-chemisorption), the surface coverage of CO and CH\(_4\) can be calculated.

\[
\theta_{\text{CO}} = \frac{\tau_{\text{CO}} F_{\text{CO}}(1 - X_{\text{CO}})}{A_{\text{co}}}
\]

\[
\theta_{\text{CH}_4} = \frac{\tau_{\text{CH}_4} F_{\text{CO}} X_{\text{CO}} S_{\text{CH}_4}}{A_{\text{co}}}
\]

where \(F_{\text{CO}}\) refers to the CO feed rate, \(A_{\text{co}}\) is the number of accessible Co surface atoms determined by \(\text{H}_2\)-chemisorption, and \(X_{\text{CO}}\) and \(S_{\text{CH}_4}\) are CO conversion and CH\(_4\) selectivity, respectively.

3. RESULTS AND DISCUSSION

3.1 Steady-State Kinetic Measurements. We first investigated the steady-state kinetics of the Co/SiO\(_2\) catalyst at a temperature of 260 °C in order to determine reaction orders with respect to CO and \(\text{H}_2\). The dependences of the reaction rates (expressed as turnover frequency, TOF) of CO consumption, CH\(_4\) formation, C\(_2+\) formation, CO\(_2\) formation and the chain-growth probability on CO and \(\text{H}_2\) partial pressures are presented in Figure 1. The CO and \(\text{H}_2\) partial pressures were varied between 15 and 150 mbar and 270–1350 mbar, respectively. At 260 °C, the main product of CO hydrogenation is CH\(_4\). Under such methanation conditions, the chain-growth probability is low. Apparent reaction orders with respect to CO and \(\text{H}_2\) are listed in Table 1. In line with literature,\(^{30}\) the methanation rate decreases with increasing CO partial pressure, while the reverse holds true for the dependence on \(\text{H}_2\) partial pressure. The negative reaction order with respect to CO can be interpreted in terms of a decrease in free sites needed for CO dissociation.\(^{30}\) An alternative interpretation is a lack of H atoms needed for methanation. The reaction order with respect to \(\text{H}_2\) is slightly higher than unity, implying that hydrogenation of CO or hydrogenation of C or O atoms are rate-controlling steps. We observe that the reaction order with respect to \(\text{H}_2\) based on the CH\(_4\) formation rate is higher than the corresponding reaction order based on the formation rate of C\(_2+\)-hydrocarbon products. This suggests that the \(\text{H}_2\) partial pressure dependence at least in part originates from the rate-controlling nature of hydrogenation of C atoms, as less C hydrogenation steps for each C atom are involved in the formation of C\(_2+\)-hydrocarbon products than in the formation of CH\(_4\). The rate of CO\(_2\) formation increases with CO partial pressure and decreases with \(\text{H}_2\) partial pressure. These

| rate based on | reaction order |
|--------------|----------------|
| CO           | \(r_{\text{CO}}\) |
| \(r_{\text{H}_2}\) | 1.09 |
| CO \(p_{\text{H}_2} = 450\) mbar, \(p_{\text{CO}}\) varied from 15 mbar to 150 mbar. \(p_{\text{CO}} = 90\) mbar, \(p_{\text{H}_2}\) varied from 270 mbar to 1350 mbar. \(C_{\text{2+}}\) refers to all hydrocarbons containing two or more carbon atoms. |
Figure 2. Residence times (left panels) and equivalent coverages (right panels) of CO (squares), CH₄ (circles), and extra-CH₄ (triangles, defined in Figure 4) as a function of CO partial pressure (a) and H₂ partial pressure (b). Conditions: T = 260 °C, P₄H = 450 mbar at varying CO partial pressure, P_{CO} = 90 mbar at varying H₂ partial pressure.

dependencies point to competition of O removal pathways via CO₂ and H₂O. Although CO₂ formation cannot be neglected especially at high CO partial pressure, the dominant O removal pathway is via H₂O. It is interesting to note that the chain-growth probability only changes significantly with CO partial pressure, implying a strong influence of surface coverage on the chain-growth process. This observation will be discussed in more detailed in a companion paper that focuses on similar measurements under FT conditions at a temperature of 220 °C.

Steady-State Isotopic Transient Kinetic Analysis (SSITKA). After attaining steady state in a ¹²CO/H₂ mixture, the catalyst was subjected to a SSITKA switch from ¹³CO/H₂ → ¹³CO/H₂ in order to determine residence times (τ) of CO and CH₄ (intermediates leading to CH₄) by use of eqs 1 and 2. Long residence time indicates low activity, and vice versa. Together with the site-normalized rates, CO and CH₄ coverages can then be obtained by use of eqs 3 and 4. These residence times and coverages are plotted as a function of the CO and H₂ partial pressure in Figure 2. In good agreement with other studies,²⁰ a higher CO partial pressure leads to a longer residence time of CH₄. The reverse holds for changes in the H₂ partial pressure. As widely assumed in literature, CH₄ formation rate is a pseudo-first-order process with respect to the coverage of CH₄ (θ_{CH₄}),²²,²⁸–³⁴

\[ r_{CH₄} = k'_{CH₄} \theta_{CH₄} \]  

where k’ is a pseudo-first-order rate constant and, together with eq 4, we can state that

\[ k'_{CH₄} = \frac{1}{r_{CH₄}} \]  

However, the pseudo-first-order assumption is not valid as the residence time also depends on the reactant partial pressure. Accordingly, we employed a more detailed analysis of the SSITKA results in which we assume that either C hydrogenation or CO dissociation is limiting the rate of CH₄ formation. The first assumption leads to decoupling of the pseudo-first-order rate constant via

\[ r_{CH₄} = k'_{CH₄} \theta_{CH₄} = k_{CH₄} \theta_{H} \theta_{CH₄} \]  

where k_{CH₄} is the rate constant of hydrogenation and θ_{H} the H coverage. Therefore

\[ k_{CH₄} \theta_{H} = \frac{1}{r_{CH₄}} \]  

Although the pseudo-first-order assumption leads to decoupling of the reaction rate from the CO coverage (Figure 1). We therefore conclude that CH₄ formation under methanation conditions is most likely controlled by hydrogenation steps that involve H atoms rather than by a CO dissociation step that involves vacancies. We also emphasize that the surface coverage plays an important role in determining the rate-controlling steps. It is to be expected that the FT reaction will occur in a different regime as CO coverage will be higher at the typically used lower temperature. SSITKA results obtained at 260 °C (this study) show the coverage of CO, the most abundant surface species, is typically no more than 0.3, which is lower than the value obtained at FT condition in a companion paper (typically 0.4 at 220 °C) and in literature (0.48 and 0.45 at 210 °C). We should take care here, as analysis based on SSITKA alone is not able to distinguish an H-assisted CO dissociation mechanism from C hydrogenation as the rate-determining step, because both depend on the H coverage. As outlined above, we have demonstrated that direct CO
dissociation on the same Co/SiO₂ catalyst is possible and can be correlated to a minority site at the surface. Therefore, the minor increase in CO coverage will significantly influence the reaction kinetics. This scenario will be discussed in a companion paper.

The SSITKA results reveal the strong influence of hydrogenation on the overall CO consumption rate. Both C and O hydrogenation should be considered. We therefore combine the results from SSITKA with those obtained in forward and backward CTKA and use them to fit a microkinetic model for CO hydrogenation to CH₄. From this analysis, we can identify rate-controlling steps.

**Backward Chemical Transient Kinetic Analysis.** The backward CTKA experiment comprises a CO/H₂ → Ne/H₂ switch. Figure 3 shows that this switch leads to an increase in the CH₄ formation rate followed by a decline toward zero. This phenomenon was first observed for a fused iron catalyst by Matsumoto and Bennett. Later, Cant et al. reported similar behavior for a Ru catalyst, attributing the increased methane formation rate to increased H coverage. Biloen also observed the same for a Ru catalyst and suggested that the initial increase in rate of methane formation is due to an increasing pseudo-first-order rate constant of methane formation. Kruse and co-workers discussed similar backward transient phenomena for a Co/MgO catalyst. They interpreted these CTKA data as evidence for the CO-insertion mechanism. More recently, Ralston et al. explained cobalt particle size-dependent CTKA data in terms of structure sensitivity, i.e., lack of B₅-B sites for CO dissociation on small Co nanoparticles.

The CTKA transients obtained at different CO and H₂ partial pressures are shown in Figure 3. The maximum CH₄ formation rates during the transient coincide with an optimum surface coverage ratio of vacancies, CO, CH₄, and H₂, of which the latter two determine the CH₄ formation rate. At constant H₂ pressure, the H coverage will depend linearly on the fraction of free sites according to the adsorption equilibrium of H₂. Accordingly, the optimum rate is achieved at optimum ratio of θ_CH₄ and θ_H₂. This ratio is independent of the initial steady-state coverage of CO, but is reached later in time when the starting coverage is higher (Figure 3a). However, when the CO partial pressure is constant and the H₂ partial pressure is varied, the H₂ adsorption equilibrium will lead to increasing H coverage at higher H₂ partial pressure. This will lead to higher and earlier maximum CH₄ formation rate (Figure 3b). Evidently, the CH₄ formation rate is highly dependent on the H coverage.

Here, we combine for the first time SSITKA with backward CTKA in order to construct Figure 4. In this figure, we compare CH₄ formation from two different transient experiments, viz. SSITKA and backward CTKA measurements. As only CH₄ formed during SSITKA can be assigned to CH₄ species present on the surface during steady state, we define the difference as “extra-CH₄”. We quantified this amount and converted it to an equivalent surface coverage by using the available Co surface area as determined by H₂-chemisorption. This surface coverage of species generating extra-CH₄ is compared to the CO coverage as determined by SSITKA. These data are displayed in Figure 2. Notably, at sufficiently high H₂/CO ratios (either at relatively low CO partial pressure or relatively high H₂ partial pressure), the amount of extra-CH₄ is equivalent to the amount of CO adsorbed on the Co surface during the steady state preceding the CTKA switch. This result indicates that the extra-CH₄ formed during the backward CTKA switch at high H₂/CO ratio can be attributed solely to conversion of adsorbed CO to methane. At low H₂/CO ratio, the amount of extra-CH₄ is slightly higher than the amount of adsorbed CO. This cannot be accounted for by higher hydrocarbon fragments present on the surface that would dissociate and hydrogenate to CH₄ because even at the lowest H₂/CO ratio the CH₄ selectivity is higher than 60% with the CH₄ coverage being approximately 5% (Figure 2). As higher hydrocarbons formation typically follows an Anderson–Schulz–Flory distribution, the coverage of C₃−products must

Figure 3. Backward transient at different CO partial pressures (a) and H₂ partial pressures (b) after a switch from CO/H₂ to H₂. Conditions: T = 260 °C, p_H₂ = 450 mbar at varying CO partial pressure, p_CO = 90 mbar at varying H₂ partial pressure.

Figure 4. Normalized responses in SSITKA and backward CTKA. The extra-CH₄ is defined by as the filled area between SSITKA CH₄ (squares) and backward CTKA CH₄ (circles) responses. Steady-state conditions: T = 260 °C, p_H₂ = 450 mbar, p_CO = 90 mbar.
be even lower than 5%. In this way, a pool of higher hydrocarbons cannot explain the extra-CH₄ formed relative to the amount of adsorbed CO.

Another point worth mentioning about the data in Figure 4 is that the CO signal during the SSITKA switch exhibits a delay of 1 s with respect to the inert tracer gas. This delay is caused by the adsorption/desorption equilibrium of CO in the catalyst bed, also known as the chromatographic effect. The CO response in the CO/H₂ → H₂ backward CTKA switch did not exhibit this delay. Close inspection reveals that the CO signal precedes the inert tracer signal. It implies that all CO adsorbed on the Co surface is consumed and leaves the reactor predominantly as CH₄. An important corollary of this finding is that the overall barrier for CO hydrogenation to CH₄ is lower than the CO desorption energy under methanation condition.

In order to understand the deviation between the amount of extra-CH₄ and adsorbed CO, we carried out temperature-programmed hydrogenation (TPH) experiments in which the flow was switched from CO/H₂ to Ar, followed by flushing in Ar for 6 h at 260 °C. After cooling to room temperature, a TPH experiment was carried out. As shown in Figure 5, there are likely two carbon-containing surface species that are hydrogenated at relatively low temperature, which is below 220 °C. The data show that this carbon pool is not present at high H₂/CO ratio, but is formed in increasing amounts when the H₂/CO ratio is lowered. The nature of these carbon-containing surface intermediates remains unclear, but a particular property is that they can only be hydrogenated at sufficiently high H coverage as occurs during TPH and during the backward CTKA. Clearly, the surface will also contain even less-reactive C species as demonstrated by the reduction feature above 300 °C. Similar observations have been reported by Winslow and Bell.35 Flushing a working Ru catalyst in He followed by temperature-programmed reduction in D₂ led to two CD₄ peaks designated as C₊ and C₋, which are assigned to reactive intermediate and less reactive species causing deactivation, respectively.

**Forward Chemical Transient Kinetic Analysis.** We use forward CTKA to distinguish between rates of C and O hydrogenation. As the H coverage during methanation is high, both C and O hydrogenation reactions are fast. It is thus difficult to differentiate between the rates of these two reactions. Therefore, we decreased the H₂ partial pressure (200 mbar) and increased CO partial pressure (200 mbar) to amplify differences in C and O hydrogenation. The results of the forward CTKA switch are given in Figure 6. For these measurements, we analyzed both CH₄ and H₂O as primary products. Analyzing H₂O during transient measurements is a challenge, because H₂O will relatively strongly interact with various parts of the setup outside the catalyst bed (mainly with the stainless-steel capillary). Accordingly, we carefully established the systematic delay due to these nonspecific interactions (see the Supporting Information). The H₂O delay values discussed below have been corrected for this systematic delay, as well as the delay caused by the chromatographic effect of CO. As before, the CH₄ delay has also been corrected for the chromatographic effect of CO.

As a reference case, we performed the forward CTKA switch on an empty cobalt surface. We obtained this state by flushing the in situ reduced Co catalyst in Ar for 2 h, followed by cooling to reaction temperature in Ar. The forward transient involved an Ar/Ne → H₂/CO switch. Figure 6a shows that CH₄ formation was delayed 2.5 s with respect to Ne, while H₂O was not detected above 200 mbar, indicating that CH₄ is also consumed when the H₂ coverage is low. The specific evolution of the CH₄, H₂O, and H₂ signals also evidence that H₂ is more rapidly consumed for hydrogenation of C toward CH₄ on an initially empty cobalt surface.

The same transient experiment was also performed on a catalyst that was precovered by H₂ followed by a H₂/Ne → CO/H₂ switch. In this case, the H coverage before the switch is much higher than that at reaction condition. The corresponding results in Figure 6b show a shorter H₂O delay of 0.5 s, while the decrease in the CH₄ delay (2 s) is less pronounced. This comparison implies that the H₂O delay on an empty surface is
caused by a lack of adsorbed H, and that the O hydrogenation profits more from higher H coverage than C hydrogenation.

We also carried out an experiment in which we precovered the surface with 13C atoms by exposure to 13CO flow at 260 °C for 0.5 h, followed by Ar flushing to remove adsorbed 13CO. As demonstrated earlier, this procedure results in the deposition of C atoms on the Co surface.64,65 As shown in Figure 6c, the forward transient Ar/Ne → H2/CO of this 13C atom precovered surface results in a significant longer H2O delay of 10 s, 3.5 s longer than on the empty surface and 9.5 s longer than on the H precovered surface. This increase in H2O delay is caused by two factors. On one hand, since the surface was partially due to the low H2/CO ratio in this case. The stress that the competition between C and O hydrogenation is cobalt surface (6 s) as compared to the empty surface (4 s). We reaction order with respect to H2.

formation on the H coverage significantly contributes to the H2O delay with respect to12CH4 on a 13C precovered surface results in a significant increase in H2O delay. The correspondence between the H2 and 13CH4 signals shown in Figure 6b represents the strong dependence of C hydrogenation on H coverage. On the other hand, the preadsorbed 13C depletes H coverage. In line with the observation that an increase in H coverage effectively shortens the H2O delay, the extra consumption of adsorbed H atoms caused by hydrogenation of precovered 13C results in a longer H2O delay with respect to 13CH4 on a 13C precovered cobalt surface (6 s) as compared to the empty surface (4 s). We stress that the competition between C and O hydrogenation is partially due to the low H2/CO ratio in this case. The findings above also suggest that the strong dependence of H2O formation on the H coverage significantly contributes to the reaction order with respect to H2.

Microkinetic Modeling. A common approach to distinguish mechanisms is to fit steady-state catalytic data to a microkinetic model based on a mechanism consisting of elementary reaction steps. A major limitation of transient kinetic studies of CO hydrogenation is that the H coverage cannot be explicitly measured. This dependence is therefore often lumped into hydrogenation reaction rate constants. Here, we take a different approach in which we use transient data to fit a microkinetic model for CO hydrogenation involving H explicitly as a surface species. The elementary reaction steps that make up the microkinetic model for CO hydrogenation is given in Figure 7. The alternative kinetic model that involves H-assisted CO dissociation is provided in the Supporting Information. We will first discuss the set of coupled nonlinear differential equations that describes the transient coverages of surface adsorbed species, which are the reaction intermediates.

The balance for CHx species involves CH4 hydrogenation/dehydrogenation steps and also the CO dissociation for the C intermediate:

\[
\frac{d\theta_{\text{CO}}}{dt} = k_{\text{ads,CO}} \theta_{\text{v}} - k_{\text{des,CO}} \theta_{\text{CO}} - k^{f}_{\text{CH}} \theta_{\text{CH}} + k^{b}_{\text{H}} \theta_{\text{H}}
\]

\[
\frac{d\theta_{\text{H}}}{dt} = 2k_{\text{ads,H}} \theta_{\text{v}} - 2k_{\text{des,H}} \theta_{\text{H}}
\]

The balance for OHx intermediates involves CO dissociation, removal of O via H2O and CO2:

\[
\frac{d\theta_{\text{OH}x}}{dt} = -k^{f}_{\text{OH}} \theta_{\text{OH}x} - k_{\text{H2O}} \theta_{\text{H2O}} - k^{b}_{\text{H}} \theta_{\text{H}}
\]

The balance for adsorbed COx is given by

\[
\frac{d\theta_{\text{CO}x}}{dt} = k^{f}_{\text{CO}} \theta_{\text{CO}} - k^{b}_{\text{CO}} \theta_{\text{CO}} - k^{b}_{\text{CO}} \theta_{\text{CO}}
\]

Finally, we provide the balance for the H surface intermediate

\[
\frac{d\theta_{\text{H}}}{dt} = 2k_{\text{ads,H}} \theta_{\text{v}} - 2k_{\text{des,H}} \theta_{\text{H}}
\]

where \( \theta_{\text{v}} \) refers the vacant sites on surface.

The surface coverage of CO can be described as follows:

\[
\frac{d\theta_{\text{CO}}}{dt} = k_{\text{ads,CO}} \theta_{\text{v}} - k_{\text{des,CO}} \theta_{\text{CO}} - k^{f}_{\text{CH}} \theta_{\text{CH}} + k^{b}_{\text{H}} \theta_{\text{H}}
\]

\[
\frac{d\theta_{\text{H}}}{dt} = 2k_{\text{ads,H}} \theta_{\text{v}} - 2k_{\text{des,H}} \theta_{\text{H}}
\]

where \( \theta_{\text{v}} \) refers the vacant sites on surface.

The additional constraint is that the sum of all coverages is unity:

\[
\theta_{\text{CO}} + \theta_{\text{CH}} + \theta_{\text{CH}_2} + \theta_{\text{CH}_3} + \theta_{\text{CO}} + \theta_{\text{OH}} + \theta_{\text{H}_2} + \theta_{\text{H}} = 1
\]
backward CTKA). We choose transient data obtained at a high H₂/CO ratio of 15 ($p_{\text{CO}} = 30 \text{ mbar}, p_{\text{H}_2} = 450 \text{ mbar}$ and $T = 260 ^\circ \text{C}$) so as to ensure a high CH₄ selectivity of approximately 90% and a chain-growth probability smaller than 0.1. A least-squares objective function is used as following

$$
\varepsilon = \sum (f_{\text{model, forward}} - f_{\text{exp, forward}})^2 + \sum (f_{\text{model, SSITKA}} - f_{\text{exp, SSITKA}})^2 + \sum (f_{\text{model, backward}} - f_{\text{exp, backward}})^2 + \sum (\theta(n_{\text{model}} - n_{\text{exp}})^2)
$$

in which $f$ denotes the normalized transient response of methane, $n$ the reaction order, and $w$ is a factor for giving a similar weight to the reaction orders as that to the transient data. To decrease the number of unknown variables, we introduced equilibrium constants for several surface reactions based on DFT calculations for the Co(112) surface (Table S1 in the Supporting Information). Finally, a total of 16 rate constants were fitted. The boundary conditions and the details about the fitting procedure are discussed in the Supporting Information. The fitting results are listed in Table 2 (the results based on H-assisted CO dissociation are listed in Table S2).

The good correspondence between the model and the experimental data is shown in Figure 8. The goodness of fit for the microkinetic model based on direct CO dissociation ($R^2 = 0.95$) is higher than the one on H-assisted CO dissociation ($R^2 = 0.88$). We emphasize that this criterion alone is not sufficient to rule out that a H-assisted mechanism occurs in parallel with direct CO dissociation. Therefore, we discuss the fitting results for a model based on H-assisted CO dissociation in the Supporting Information.

Based on the fitted data, we then analyzed the different kinetic regimes of the CO hydrogenation reaction by determining the degree of rate control (DRC, see the Supporting Information). By doing so, one can identify to what extent particular elementary reaction steps control the overall CO conversion rate. A positive DRC value ($X_{\text{DRC}}$) indicates that the overall reaction rate increases when the rate of elementary step $i$ is increased. On the contrary, steps with a negative $X_{\text{DRC}}$ are rate-inhibiting steps that slow down the overall rate. The results are presented in Table 3 in terms of lumped DRC parameters for key reaction steps in the CO hydrogenation mechanism. A detailed list of DRC values is provided in the Supporting Information. Table 3 shows that C hydrogenation steps control the methanation reaction most. The other reaction that controls the overall rate is O hydrogenation for which we identify a $X_{\text{DRC}}$ of 0.24. The DRC for the C–O bond scission step is only 0.15, emphasizing its weak rate-controlling nature with the hydrogenation steps. The DRC analysis based on the H-assisted CO dissociation mechanism shows qualitatively similar results (Table S3), suggesting that the conclusion of slow C and O hydrogenation at methanation conditions is independent of the CO dissociation mechanism. These conclusions are in good agreement with a recent theoretical study and also the forward transient experiments in this study.

An important conclusion from this kinetic analysis is that CO dissociation is not the rate-limiting step on cobalt at sufficiently high H₂/CO ratio and high temperature (pertaining to a relatively empty surface). Instead, the hydrogenation of the O and especially C species deriving from CO dissociation control

Table 2. Rate Constants Determined by Model Fitting

| reaction          | $k_1$ (s⁻¹) | $k_6$ (s⁻¹) |
|-------------------|-------------|-------------|
| adsorption/desorption |             |             |
| CO + * $\rightleftarrows$ CO* | 4.8 x 10⁵ | 8.1 x 10⁻¹ |
| H₂ + 2 * $\rightleftarrows$ 2 H* | 7.2 x 10⁴ | 2.5 x 10⁶ |
| H₂O* $\rightleftarrows$ H₂O + * | 7.7 x 10⁵ | 7.7 x 10⁵ |
| CO₂* $\rightleftarrows$ CO₂ + * | 7.7 x 10⁵ | 7.7 x 10⁵ |
| CO dissociation |             |             |
| COO* + * $\rightleftarrows$ C* + O* | 5.2 x 10⁻¹ | 7.3 x 10³ |
| CH₄ formation |             |             |
| C* + H* $\rightleftarrows$ CH* + * | 2.3 x 10⁴ | 2.6 x 10³ |
| CH₆* + H* $\rightleftarrows$ CH₅* + * | 1.9 x 10⁴ | 2.2 x 10⁴ |
| CH₅* + H* $\rightleftarrows$ CH₄* + * | 2.8 x 10⁴ | 1.0 x 10⁵ |
| CH₄* + H* $\rightleftarrows$ CH₄ + 2 * | 8.7 x 10⁴ |             |
| H₂O formation |             |             |
| O* + H* $\rightleftarrows$ OH* + * | 1.7 x 10⁵ | 9.3 x 10⁻³ |
| OH* + H* $\rightleftarrows$ H₂O* + * | 4.7 x 10⁵ | 1.5 x 10⁻¹ |
| 2 OH* $\rightleftarrows$ H₂O* + O* | 2.8 x 10⁵ | 2.1 x 10⁴ |
| CO₂ formation |             |             |
| COO* + O* $\rightleftarrows$ CO₂* + * | 1.1 x 10⁻¹ | 5.9 x 10⁻⁸ |

Figure 8. Combined transient data (points) and model fitting (line) based on direct CO dissociation mechanism. Steady-state conditions: $T = 260 ^\circ \text{C}, p_{\text{H}_2} = 450 \text{ mbar}, p_{\text{CO}} = 30 \text{ mbar}.$

Table 3. Lumped Degree of Rate Control Values Obtained at 30 mbar CO and 450 mbar H₂

| reaction          | $X_{\text{DRC}}$ |
|-------------------|------------------|
| CO adsorption     | $-4.9 \times 10^{-2}$ |
| H₂ adsorption     | $3.6 \times 10^{-4}$ |
| CO dissociation   | 0.15             |
| C hydrogenation   | 0.62             |
| O hydrogenation   | 0.24             |
| CO₂ formation     | $3.2 \times 10^{-2}$ |
the reaction rate. This finding is consistent with the experimental observation that the absolute value of $H_2$ reaction order for $CH_4$ formation is larger than that of $CO$ reaction order, implying $H_2$ partial pressure affects the reaction more strongly than $CO$ does. The influence of $H_2$ partial pressure on the reaction rate is larger, as the $H$ coverage is directly related to the $H_2$ partial pressure; the influence of $CO$ partial pressure is smaller as it indirectly influences the reaction by hindering $H_2$ adsorption.

The present work demonstrates that multiple elementary reaction steps can contribute to the rate control of the methanation reaction. The positive order with respect to $H_2$ is due to the rate-controlling nature of $C$ and $O$ hydrogenation steps. The negative CO reaction order is due to the competition between CO and $H_2$ adsorption, in which an increase in CO coverage decreases the $H$ coverage that is needed for catalyzing the rate-controlling $C$ and $O$ hydrogenation steps.

**Microkinetics Simulations.** We employ the fitted microkinetic model to explore the effect of a wider range of $CO$ and $H_2$ partial pressures, that is, from 0.06 to 20 bar and 0.03–10 bar, respectively. The output of these microkinetic simulations is presented in Figure 9 in the form of a DRC analysis, surface coverages, and $CO_2$ selectivity. Four regimes can be distinguished on the basis of the DRC values. In regime 1, the $H_2$ partial pressure is substantially higher than the CO partial pressure. Consequently, $CO$ coverage is low and $H$ coverage high. In this regime, $C$ and $O$ atoms derived from CO dissociation are rapidly removed as $CH_4$ and $H_2O$, respectively, and $CO$ dissociation becomes increasingly rate-controlling with increasing $H_2$ pressure. Thus, $C$ and O hydrogenation steps do not limit the $CO$ conversion rate, but $CO$ dissociation does. In regime 2, the surface contains a significant amount of $CH_x$ intermediates as the lack of $H$ atoms limits their hydrogenation. Regime 3 presents the conditions with moderate $H_2/CO$ ratio (the diagonal lines in Figure 9 refer to a $H_2/CO$ ratio of 2), a condition close to the FT condition. $CO$ dissociation and $C$ hydrogenation steps largely contribute to the overall rate control. Due to the accumulation of $OH_x$ intermediates on the surface (Figure 9g), $H_2O$ formation considerably controls the $CO$ conversion rate in this regime. This is in line with recent DFT-based microkinetics simulations. Meanwhile, Regime 4 refers to the lean H condition, under which the cobalt surface is fully covered by $CO$ (Figure 9h). In this case, $O$ is
predominantly removed as CO₂ (Figure 9i), as the surface lacks H atoms for O hydrogenation.

These regimes provide us some insight into the different kinetic regimes one might encounter when varying the H₂/CO ratio. Notably, regime 4 is an extreme case, stemming from the higher CO₂ selectivity observed at 260 °C than at the actual FT temperature. As expected, the rate-controlling steps at conditions close to FT conditions (upper right corner in Figure 9) differ from those under methanation conditions (lower right corner in Figure 9). It appears that the very different composition of the surface adsorbed layer at lower temperature will have a significant impact on the rate-controlling nature of the different elementary reaction steps. These aspects are the focus of our companion paper which uses similar transient methodologies to interrogate the reaction mechanism of the Co/SiO₂ catalyst under conditions close to those encountered in practical FT synthesis.

**CONCLUSIONS**

The mechanism of CO hydrogenation to CH₄ at 260 °C on a cobalt catalyst is interrogated by different types of transient kinetic measurements including SSITKA and backward and forward CTKA. The dependence of CH₄ residence time as determined by SSITKA (¹³CO/H₂ → ¹³CO/H₂) on CO and H₂ partial pressure indicates that the CH₄ formation rate is mainly controlled by CH₄ hydrogenation rather than CO dissociation. The backward CO/H₂ → H₂ CTKA emphasizes the importance of H coverage on the slow CH₄ hydrogenation step. The H coverage strongly depends on the CO coverage, which is mainly determined by CO partial pressure. By combining SSITKA and backward CTKA, it is established that the additional CH₄ obtained during CTKA in comparison to SSITKA is nearly equal in amount to the amount of CO adsorbed on the cobalt surface. This implies that under the given conditions the overall barrier for CO hydrogenation to CH₄ is lower than the CO adsorption energy. Forward CTKA measurements also qualitatively show that O hydrogenation is relatively slow compared to CO dissociation. The combined transient kinetic data are captured in an explicit microkinetic model for the methanation reaction. The model fitting shows that a mechanism involving direct CO dissociation better represents the data than a mechanism in which H-assisted CO dissociation is assumed. Microkinetics simulations based on the fitted parameters show the highest DRC for C hydrogenation and lower DRC for O hydrogenation and CO dissociation at typical methanation conditions. These simulations are also used to explore different conditions depending on CO and H₂ partial pressure. This leads to four kinetic regimes in which CO consumption rate is controlled by CO dissociation, C hydrogenation, O hydrogenation, and CO₂ formation.

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