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Transient Isotopic Studies and Microkinetic Modeling of CO Methanation over Nickel Catalysts

Davide Lorito, Pascal Fongarland, and Yves Schuurman*

ABSTRACT: The methanation of CO over a 20 wt % Ni/Al₂O₃ catalyst was studied with different transient experiments. CO dissociation was found to be reversible and faster than the formation of methane. SSITKA experiments showed that two pools of surface intermediates lead to the formation of methane. The transient experiments could be adequately described by a microkinetic model based on two distinct adsorbed CO species. One CO species proceeds through direct dissociation, and the other, through hydrogen assisted dissociation to a common CH* intermediate that leads to methane. The model is consistent with literature DFT studies that show that the direct CO dissociation occurs over edge or step sites and hydrogen assisted dissociation occurs over terrace sites.

INTRODUCTION

CO methanation over nickel supported catalysts has great potential for the production of synthetic natural gas from syngas generated from coal, biomass, or waste.^{1,2} Nickel supported catalysts can also be used to produce longer chain hydrocarbons by Fischer–Tropsch (FT) synthesis.³ The mechanism of CO hydrogenation over transition metals is still debated in the literature.⁴ In the case of CO hydrogenation over nickel, some mechanistic studies propose “enol-like” intermediates, while other studies suggest a carbide mechanism based on direct CO dissociation.^{5–17} In the Fischer–Tropsch literature the direct and hydrogen-assisted CO dissociation are still being strongly debated, supported by DFT studies.^{18–22}

The reactive intermediates, like the enol species, are present on the surface at very small concentrations. In situ spectroscopic methods such as FTIR or DRIFTS are not sensitive enough to identify these surface species. Although methoxy and formate species are observed by in situ FTIR, they can be located on the support and often are considered to be spectators. In order to distinguish reactive intermediates from spectators, dynamic experiments are necessary and most spectroscopic cells are not very well suited for transient operation due to the presence of dead volumes and the difficulty to operate in the absence of temperature and concentration gradients. This is especially the case for exothermic reactions like CO methanation.

Steady State Isotopic Transient Kinetic Analysis (SSITKA) and chemical transient kinetics (CTK) have been used to investigate the kinetics of the methanation over nickel catalysts.^{6,7,26–35} Transient kinetics allow estimating amounts of relevant surface species and kinetic constants and decouple these two quantities. In the SSITKA technique, the reactant is replaced by its isotopic counterpart, giving a transient response of the isotopically labeled reactants and products, while

preserving steady-state operation. CTK switches between different reactant concentrations, while going from one steady state toward another one. Information on the reaction intermediates can be obtained by carefully tracking the balance of C₁H₄O or the isotopically labeled element as a function of time.^{7,26,27,29} While transient methods lead to better insights into the reaction mechanism, the modeling of the data is a much more complex task than for steady-state experiments. The steady-state hypothesis is no longer valid, and the continuity equations for surface intermediates need to be solved explicitly. This will lead to a much larger number of kinetic parameters to be estimated.^{36–38}

An often common observation in SSITKA studies of CO hydrogenation over transition metals is the presence of at least two pools of intermediates for the production of methane.^{35,39–44} However, few studies address the nature of these intermediates. In this paper we explore if the combination of the direct and hydrogen-assisted CO dissociation is compatible with these two intermediates by developing a microkinetic model based on SSITKA and CTK experiments.

EXPERIMENTAL SECTION

Catalyst. All experiments were performed over a well-dispersed 20 wt % Ni/Al₂O₃ catalyst. Catalyst characterization was reported in ref 45. The BET surface area was approximately 100 m²/g. A mean nickel particle size of 5 nm

was observed by Transmission Electron Microscopy. From hydrogen adsorption experiments, a nickel surface site concentration of 0.68 mol/kg was estimated, in line with the mean nickel particle size of 5 nm. Additional nonsteady-state experiments were carried out over a 10 wt % Ni/SiC catalyst with a BET surface area of 30 m²/g and a mean nickel particle size of 6 nm.

Catalyst Testing. Steady-state, nonsteady state, and SSITKA experiments were performed in a fixed-bed reactor (I.D. = 7 mm) filled with 0.2 g of catalyst diluted with SiC. The catalyst pellet size was in the range 100–200 μm. A thermocouple was located inside the catalyst bed. The reactor was 20 cm long, but the catalyst bed was approximately 1.5 cm. The reactor volume before the catalyst bed was filled with silicon carbide particles. After the catalyst bed the reactor diameter was reduced to 3 mm. The catalyst bed void fraction was estimated at 0.45. The Ni catalyst was reduced in situ at 500 °C for 10 h, with a temperature increasing rate of 1 °C/min. A mixture of 20% H₂/80% Ar with a flow rate of 100 smL/min was used. After the reduction the catalyst was exposed to the reaction mixture of 15% CO/60% H₂/25% Ar with a flow rate of 100 smL/min for at least 24 h. Switches between reaction mixtures were realized using a two-position four-way Valco-valve. Krypton was added to analyze the gas hold up. The effluents were monitored by an online INFICON quadrupole mass spectrometer. All the experiments were performed at 210 °C, a pressure of 1.2 bar, and a H₂/CO ratio equal to 4. The CO conversion under these conditions amounted to approximately 3%, and the only observed products were methane and water; no carbon dioxide or higher hydrocarbons were observed in any significant amount.

SSITKA Data Treatment. From the integration of the transient response, the concentration, N_i (mol/kg), of reversibly adsorbed CO* and partly dissociated CO* as well as active CH_x* and/or COH_x* intermediates leading to methane can be calculated by²⁶

$$N_i = \frac{1}{W} \int_0^\infty |F_i(t) - F_{tr}(t)| dt \quad (1)$$

where W is the catalyst mass (kg), t is the time (s), $F_i(t)$ is the time-dependent outlet flow of species i (mol/s), and $F_{tr}(t)$ is the outlet flow of the tracer gas (mol/s). The surface lifetimes $\tau_{i,r}$ (s) were calculated by²⁶

$$\tau_{i,r} = \frac{N_i}{R_i(\infty)} \quad (2)$$

where $R_i(\infty)$ (mol/s/kg) is the steady-state consumption or production rate.

The “net” surface lifetimes τ_i (s) are obtained after correcting the average residence time by the inert tracer. Kr represents the hold-up of the reactor system:

$$\tau_{CO} = \tau_{CO,r} - \tau_{Kr,r} \quad (3)$$

$$\tau_{Cl} = \tau_{Cl} - \frac{1}{2} \tau_{CO} - \tau_{Kr,r} \quad (4)$$

In the last equation, which is of empirical nature, the surface lifetime of methane is further corrected for the chromatographic effect of CO in a plug-flow reactor, as is custom in the literature.²⁶

The following compartment models were used to fit the methane decay ($E(t)$) during SSITKA experiments for one pool (eq 5) and two parallel pools (eq 6):³⁵

$$E(t) = N \exp\left(-\frac{t}{\tau}\right) \quad (5)$$

$$E(t) = N_1 \exp\left(-\frac{t}{\tau_1}\right) + (1 - N_1) \exp\left(-\frac{t}{\tau_2}\right) \quad (6)$$

The derivation of these equations is based on differential conditions and an ideal step response input.

Modeling. The transient model is based on a one-dimensional pseudohomogeneous fixed bed reactor, thus assuming no radial and no external and internal mass- and heat transfer limitations. The gas velocity is assumed to be constant. The continuity equations are then given for the gas phase and adsorbed phase respectively as

$$\epsilon_b \frac{\partial C_i}{\partial t} = -u_s \frac{\partial C_i}{\partial z} + D_{ax,i} \frac{\partial^2 C_i}{\partial z^2} - (1 - \epsilon_b) L_t (k_{ads,i} P_i \theta_i - k_{des,i} \theta_i) \quad (7)$$

$$\frac{\partial \theta_i}{\partial t} = \sum_j v_{ij} k_j P_i^n \prod_{j'} \theta^{m_j} \quad (8)$$

where L_t is the number of active sites per catalyst volume (mol/m³_{cat}), u_s the superficial gas velocity (m_r/s), D_{ax} the axial diffusion coefficient (m_g³/m_r/s), ϵ_b the bed void fraction (m_r³/m_r³), C_i the gas phase concentration of each species (mol/m_r³), P_i the partial pressure of each species (bar), $k_{ads,i}$ the adsorption constant for the gas phase species (bar⁻¹ s⁻¹), $k_{des,i}$ the desorption constant for the gas phase species (s⁻¹), and z the reaction axial coordinate (m).

The following initial and boundary conditions are applied for all gas phase species i :

$$t = 0 \wedge 0 \leq z \leq L: C_i = 0 \wedge \theta_i(z) = 0 \quad (9)$$

$$t > 0 \wedge z = 0: C_i = C_i^0 \left(\frac{1 - \exp(-At)}{1 + \exp(-At)} \right) \quad (10)$$

$$t > 0 \wedge z = L: \frac{dC_i}{dt} = 0 \quad (11)$$

where L is the reactor length (m). This set of partial differential equations is transformed into a set of ordinary differential equations by the methods of lines and integrated numerically using the ODEPACK library.⁴⁶ The axial dispersion coefficient was calculated by the well-known correlation given in ref 47.

The reaction kinetics were calculated by using the law of mass action. This implies that the exponents n and m in eq 8 correspond to the number of species involved in each elementary step given in Table 2, except for step 1a which was considered to be first order, as Derrouiche and Bianchi⁴⁸ observed similar sorption kinetics for linear and bridged carbonyl species. Thus, the rate for step 1a in Table 3 is calculated as

$$r_{1a} = \overrightarrow{k}_{1a} P_{CO} \theta_v - \overleftarrow{k}_{1a} \theta_{CO^{**}} \quad (12)$$

Regression analysis based on a Marquardt–Levenberg algorithm including statistical analysis was used to estimate the kinetic parameters.^{49,50} The Kr tracer was fitted first to estimate the value of the constant A (9.9 s⁻¹) in eq 10. For the SSITKA experiments, the outlet flows of ¹²CO and ¹²CH₄ were

Figure 1. Isotopic scrambling experiments over 20 wt % Ni/Al₂O₃ in the presence (left) and absence (right) of hydrogen.

used in the objective function, while, for the nonsteady-state experiments, the outlet flows of CO, CH₄, and H₂O were used.

To check the intrinsic reaction conditions during the reforming experiments the appropriate criteria were evaluated by using the EUROKIN spreadsheet for assessment of transport limitations in gas–solid fixed beds.⁵¹ The steady-state CO consumption rate at 210 °C of 0.018 mol/kg/s was used. The results are reported in Table S1. The criteria indicated the absence of heat and mass transfer limitations.

Campbell's degree of rate control (DRC) was applied to the methane formation at steady state.⁵² This method is used in microkinetic models to evaluate the degree to which reaction steps are rate-controlling. This is accomplished by increasing both forward and reverse rate constants for the specific step and calculating the resulting fractional increase in the overall rate, as expressed by the following equation:

$$\text{DRC} = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (13)$$

where the partial derivative is taken holding constant the rate constants, k_j , for all other steps $j \neq i$ and the equilibrium constant, K_i , for step i . The larger the value of DRC_i is for a given step, the more the influence its rate constant has on the overall reaction rate r . A positive value indicates that increasing k_i will increase the net rate r . A negative value indicates the opposite; such steps are inhibition steps.

RESULTS

Isotopic Exchange Experiments. Figure 1 shows the ¹²C¹⁶O and ¹³C¹⁸O responses from a mixture of ¹²C¹⁸O and ¹³C¹⁶O in both the presence and absence of hydrogen (Figure 1). In both cases equal amounts of ¹²C¹⁶O and ¹³C¹⁸O are formed, with a lower amount of both products in the presence of hydrogen, due to the fact that part of the adsorbed CO species will react with hydrogen to form methane. The early ¹²C¹⁶O response in the absence of hydrogen might be an experimental artifact, amplified by the logarithmic scale of Figure 1. In both the presence and absence of hydrogen, CO dissociates reversibly over the nickel catalyst. The disappearance rate of ¹²C¹⁶O and ¹³C¹⁸O, when removing ¹³C¹⁶O from the feed, is rather similar for both cases, characterized by time

constants of 25 and 30 s in the presence and absence of hydrogen, respectively.

SSITKA Experiments. Figure 2 shows the CO and methane responses upon a switch from ¹²CO/H₂ to ¹³CO/

Figure 2. SSITKA experiments for a switch of 15% ¹²CO/60% H₂/20% Ar/5% Kr to 15% ¹³CO/60% H₂/25% Ar over 20 wt % Ni/Al₂O₃ at 210 °C. Symbols are experimental data; lines model to microkinetic model simulation. The inset serves to better visualize the Kr and ¹²CO transient responses.

H₂ at 210 °C. A symmetric upward response was observed for the 13 carbon labeled components, although the noise-to-signal ratio was higher. A delay in the CO response with respect to the Kr tracer can be noticed. This is due to the reversible adsorption of CO on the nickel surface. The methane response is even further delayed and decreases slowly. Table 1 summarizes the residence times and surface coverages estimated from the ¹²CO/H₂ SSITKA experiments.

Table 1. Surface Amounts and Coverages of CO_{ads} and C_{1,ads} Based on the Integration of the Transients Shown in Figure 2 with $N_s = 0.68 \text{ mol}_{\text{Ni}} \cdot \text{kg}_{\text{cat}}^{-1}$

τ_{CO} (s)	τ_{C1} (s)	N_{CO} (mol/kg)	N_{C1} (mol/kg)	Θ_{CO}	Θ_{CHx}
8	99	0.44	0.16	0.65	0.23

The N_{CO} corresponds to surface species that desorb as CO, which might contain species that have been dissociated on the surface, as the CO adsorption is reversible. The N_{C1} species correspond to CH_x species leading to the formation of methane. Note that CO scrambling ($t = 28$ s) is faster than the formation of methane ($t = 100$ s), consistent with the fact that CO dissociation is not the rate-limiting step.

The rate of methane formation was further inspected by tracing the $^{12}CH_4$ decay on a semilog plot, as shown in Figure 3. The decay rate, and therefore also the rate of methane

Figure 3. Decay of $^{12}CH_4$ normalized response during SSITKA experiments for a switch of 15% $^{12}CO/60\%$ $H_2/20\%$ Ar/5% Kr to 15% $^{13}CO/60\%$ $H_2/25\%$ Ar over 20 wt % Ni/ Al_2O_3 at 210 °C. Symbols are experimental data; lines correspond to eq 5 (blue dashed line) and eq 6 (green dashed dotted line), to microkinetic model (red full line).

formation as SSITKA responses are symmetric, is downward convex, indicating a parallel formation or a buffer step involving two species. Figure 3 also shows the calculated rates for a single pool ($\tau_{C1} = 100$ s) and a two-pool parallel model.³⁵ The parallel pool model describes the data adequately with the parameters reported in Table 2. One pool of 57% of the N_{C1} species has a characteristic time of 58 s, while the other 43% has a characteristic time of 178 s.

Table 2. Parameter Estimates from Regression Analysis of Equation 6 to the Normalized Decay of $^{12}CH_4$ (Shown in Figure 3)

N_i	τ_1 (s)	τ_2 (s)
0.57	58	178

Nonsteady-State Experiments. The catalyst was initially reduced under a H_2/He (60 vol %/40 vol %) flow at 400 °C, and then the reactor temperature was lowered to 210 °C. Figure 4 shows the transient responses when switching from the H_2/He (60 vol %/40 vol %) feed to a $^{12}CO/H_2/Ar$ (15 vol %/60 vol %/25 vol %) mixture. At the moment of the switch, gas phase hydrogen is released. An initial “overshoot” in the methane response is observed, followed by a steady state production. On the other hand, the water formation is strongly delayed. This is due to a retention of the water by the alumina

Figure 4. Step response experiment of a switch of 40 He/60 H_2 to 25 Ar/60 $H_2/15$ CO over 20 wt % Ni/ Al_2O_3 at 210 °C. Symbols are experimental data; lines correspond to microkinetic model simulation.

support. This was further verified by conducting the same experiment over a 10 wt % Ni/SiC catalyst. SiC is more hydrophobic than alumina and will have less interaction with water. As shown in Figure 5, now an initial “overshoot” in the water response is observed, while the methane response increases gradually to steady state.

Figure 5. Step response experiment of a switch of 40 He/60 H_2 to 25 Ar/60 $H_2/15$ CO over 10 wt % Ni/SiC, at 225 °C.

DISCUSSION

Methane production by a two-pool parallel route, as evidenced here over Ni/ Al_2O_3 by SSITKA experiments, has been observed over a large number of methanation and Fischer–Tropsch catalysts.^{35,39–44} Soong et al.³² were the first to analyze their data over Raney nickel catalysts in terms of a two-pool parallel model. Several research groups refer to the two pools as C_α and C_β ^{39–41} whereas de Pontes et al.⁴² report that C_α corresponds to atomic carbon and C_β to alkyl fragments. C_α is more reactive, while the C_β fraction increases for catalysts with a higher growth probability. Yang et al.⁴¹ proposed that the C_α and C_β pools correspond, respectively, to CH_2O^* and CH_x species, based on a combined kinetic and DFT study for syngas conversion over a 20 wt % Co supported on carbon nanotubes.

Table 3. Elementary Steps for CO Methanation over 20 wt Ni/Al₂O₃ with the Corresponding Parameter Values and the Degree of Rate Control for the Methane Production at 210°C and H₂/CO = 4^a

Step no.	Reaction step	forward rate constant (bar ⁻¹ s ⁻¹ or s ⁻¹)	reverse rate constant (bar ⁻¹ s ⁻¹ or s ⁻¹)	Degree of rate control
1a	CO + 2* ⇌ CO**	(1.8 ± 0.25) × 10 ³	5.4	0.00
1b	CO + * ⇌ CO*	(2.0 ± 0.4) × 10 ³	5.4	0.00
2	H ₂ + 2* ⇌ 2H*	2.0 × 10 ⁴	99.9	0.01
3	CO** + * ⇌ C** + O*	(1.5 ± 0.25) × 10 ²	34.3	0.00
4	C** + H* ⇌ CH* + 2*	1.0 ± 0.25	0.7	0.00
5	CH* + H* ⇌ CH ₂ * + *	(1.1 ± 0.2) × 10 ²	51.8	0.01
6	CH ₂ * + H* ⇌ CH ₃ * + *	1.4 ± 0.2	1.5	0.09
7	CH ₃ * + H* ⇌ CH ₄ * + 2*	(2.4 ± 0.45) × 10 ²	5.1 × 10 ⁻³	0.00
8	CO* + H* ⇌ HCO* + *	0.1 ± 0.01	3.1	0.14
9	HCO* + H* ⇌ HCOH* + *	2.4 ± 0.45	1.2	0.05
10	CHOH* + * ⇌ CH* + OH*	2.5 ± 0.25	1.2 × 10 ²	0.36
11	O* + H* ⇌ OH* + *	0.1 ± 0.02	19.4	0.31
12	OH* + H* ⇌ H ₂ O* + 2*	(1.2 ± 0.35) × 10 ²	3.7 × 10 ²	0.04
13	H ₂ O + # ⇌ H ₂ O#	(5.4 ± 0.55) × 10 ²	2.4 × 10 ⁵	0.00

^a *: Nickel surface site. #: Alumina support site. Numbers preceded ± by are the 95% confidence intervals. Parameters listed without a confidence interval were fixed at their value during regression analysis.

By using IR spectroscopy, Derrouiche and Bianchi⁴⁸ identified both linear and bridged (or multibonded) reversibly adsorbed CO species with similar heats of adsorption over reduced 20 wt % Ni/Al₂O₃. The reaction mechanism of methanation over nickel catalysts has been the subject of numerous studies^{5-17,27-35} and are briefly summarized in ref 1. It is generally admitted in all the proposed reaction mechanisms that reversible dissociative hydrogen and reversible molecular CO adsorption takes place over reduced nickel surface sites.⁵⁻¹⁷ The differences in the mechanisms given in refs 5-17 concern the different carbon species present on the surface and the nature of the dissociation of CO. Either direct CO dissociation into surface carbon and surface oxygen occurs or the formation of an “enol-like” CH_xO intermediate has been proposed. The CH_xO then dissociates into CH_x and OH_y species that are further hydrogenated into methane and water. Alstrup⁵ developed a microkinetic model based on direct CO dissociation and was able to fit the data over single nickel crystals and foils. Aparicio,⁶ on the other hand, developed a microkinetic model based on transient experiments over a Ni/MgO-MgAl₂O₄ catalyst, via a **CHO intermediate. In an attempt to reconcile these views, we developed a microkinetic model based on direct CO dissociation and hydrogen assisted CO dissociation, through HCO* and HCOH* intermediates, consistent with the observed two-pool parallel methane production from SSITKA experiments. Yadav and Rinker³⁴ already proposed a mechanism based on these two routes to explain their nonsteady-state data, but did not quantify their data, nor showed that two pools of intermediates were present on their catalyst.

Table 3 lists the elementary reactions of the microkinetic model. The only difference with the mechanisms proposed previously⁵⁻¹⁷ is that the mechanism given in Table 3 is based on both the route for direct CO* dissociation (step 3) and the formation of an “enol-like” intermediate CH_xO steps (8 and 9). CO adsorption takes place as either linear (CO*) or bridged or multibonded (CO**) species, as shown by IR spectroscopy.⁴⁵ An asterisk * indicates a nickel surface atom,

and # indicates a site on the alumina support. The surface species do not necessarily bind through the element that is preceding the asterisk in the notation of the reaction steps in Table 3. This is especially the case for the HCO* species, which are reported as OHC* as well as HCO*.²⁰ The bridged CO** undergoes direct dissociation into C** and O*, which are then hydrogenated to CH* and OH*. The linear CO* undergoes hydrogenation via HCO* to HCOH*, which then dissociates into CH* and OH*. Here the two parallel routes join to form methane and water through further consecutive surface hydrogenation steps. An additional step for water adsorption on the support was necessary to describe the delayed water transient response. Both the transient and SSITKA experimental data were used for parameter estimation. The SSITKA data alone were not sufficient to estimate the model parameters statistically significantly. On the other hand, the transient data alone can be fitted with a single methane production route. Fitting the SSITKA data with one single route resulted for both routes in a straight line fit of the methane decay in a semilog plot similar to that of eq 5, as shown in Figure 3. The solid lines in Figures 2 and 4 show the microkinetic model descriptions. A good fit of the model is found, especially for the SSITKA data, but the main features of the transient responses are well captured by the model. Figure 3 compares the model to the experimental decay of the methane for the SSITKA experiment. The model shows an adequate fit of the decay, confirming the two parallel routes.

Confidence intervals in the range 10–30% were estimated as reported in Table 3. The confidence intervals were determined by regression of the SSITKA data only, except the parameter for step 13, which was determined from the nonsteady state experiment. No strong parameter correlation was observed. The highest value of 0.84 was found between the forward rate constants for steps 1a and 8. The values of the rate constants for step 2 were obtained from independent hydrogen adsorption experiments and therefore were fixed during regression analysis. The rate parameters for the backward

Table 4. Calculated Steady-State Surface Coverages during the SSITKA Experiment at 210°C and H₂/CO = 4 Based on the Microkinetic Model

H*	O*	OH*	CO**	CO*	C*	CH*	CH ₂ *	CH ₃ *	HCO*	HCNH*
1.3×10^{-3}	0.16	4.3×10^{-4}	0.18	0.25	1.7×10^{-2}	1.7×10^{-3}	3.5×10^{-2}	2.0×10^{-4}	2.0×10^{-2}	0.17

steps were fixed at values determined from initial regression analysis of both SSITKA and nonsteady-state data.

Calculating the relative contribution of the two routes to the production of methane shows that 65% of the methane is produced through the hydrogen assisted route and 35% through direct CO dissociation. DFT calculations for the dissociation of CO over nickel surfaces show that, in the absence of hydrogen, direct CO dissociation occurs over only undercoordinated sites, such as steps.²¹ In the presence of hydrogen, CO dissociation takes place through a COH surface intermediate and can take place over terrace sites, but is still most favorable over undercoordinated sites.²¹ Our results show that on supported nickel particles both routes coexist, their relative importance probably depending on the number and types of undercoordinated Ni sites. Table 4 gives the surface coverages during the SSITKA experiment. The total CO coverage amounts to 0.43, while the sum of all other carbon-containing species is equal to 0.25. The model underestimates the total CO coverage compared to the experimental value given in Table 1. This might be due to a slight misfit of the CO response and/or the correction of the experimental data by the chromatographic effect. A significant O* coverage is given by the model, which might be due to the underestimation of the rate of water formation. This rate is “masked” by the strong interaction of water with the alumina support. The CO** coverage of 0.18 corresponds well with the fraction of 0.2 of steps and edges of a truncated octahedron particle with a diameter of 5 nm.⁵³ Thus, the bridged CO species might be located at the steps and edges where direct CO dissociations are favored according to DFT studies.²¹

To further analyze the microkinetic model, the degree of rate control was calculated for all steps in the mechanism and given in Table 3. There is not a single rate-controlling step, but the dissociation of the CHOH* intermediate has the highest coefficient of 0.36, closely followed by the formation of hydroxyl species (0.31). The reaction orders are 0.33 for hydrogen and −0.93 for CO, in agreement with the reaction orders reported in the literature that range for hydrogen from 0.2 to 0.82 and for CO from −0.8 to 0.8.^{11,13}

CONCLUSIONS

The use of different transient methods has revealed some specific features of CO methanation over an alumina supported nickel catalyst. In both the presence and absence of hydrogen, CO dissociates reversibly over the nickel catalyst with similar rates. These rates are faster than the rate for the formation of methane. SSITKA experiments show that the working catalyst is mainly covered by adsorbed CO species and that methane is formed through two parallel routes. Non-steady-state experiments show an increase in methane production at high surface hydrogen coverage and a strong interaction of the alumina support with water. Based on these observations, a quantitatively microkinetic model for CO methanation has been developed. Notably, it includes two parallel routes for methane production, one based on direct CO dissociation likely over edge and step sites and one through hydrogen assisted CO dissociation likely on terrace

sites. The existence of parallel pools of CH_x species has been observed over different CO hydrogenation catalysts, like iron, cobalt, and ruthenium. These catalysts are used for the synthesis of long chain hydrocarbons and are often structure sensitive. If one of these species can be linked to the desired products, proper catalyst design can then lead to higher selectivities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c05885>.

Evaluation of different criteria to assess the intrinsic kinetic conditions. (PDF)

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Notes

The authors declare no competing financial interest.

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