Mechanistic Connections between CO₂ and CO Hydrogenation on Dispersed Ruthenium Nanoparticles

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1. INTRODUCTION

The thermodynamic stability of CO₂ molecules and their rising atmospheric levels render the upgrading of CO₂ to higher-value products a challenging but important catalytic endeavor. Metal nanoparticles, and even single metal atoms, have been shown to activate C≡O bonds in CO₂, thus providing direct catalytic routes for its hydrogenation to more valuable C₁ intermediates or products, such as CO, CH₄, and CH₃OH, at modest temperatures (443–673 K).1–4 The thermodynamics of CH₄ and CO formation from CO₂ and H₂ (methanation and reverse water-gas shift reactions, respectively) are far more favorable than CH₃OH synthesis reactions, which give low equilibrium yields at the temperatures required for practical rates (ΔG°methanation = +75 kJ mol⁻¹ for CH₃OH synthesis, −40 kJ mol⁻¹ for methanation, +14 kJ mol⁻¹ for reverse water-gas shift; per mole CO₂ 673 K). The significance of methanation and reverse water-gas shift in CO₂ utilization efforts and the promising catalytic routes for such reactions have attracted substantial attention in the recent literature.1–10

Previous attempts at relating catalytic properties to CO₂ hydrogenation rates and selectivities (to CO and CH₄) have led to persistent mechanistic questions that remain unresolved.11–14 These enduring controversies include the connections between the elementary steps that form CO and CH₄ during CO₂–H₂ catalysis on transition metal surfaces and which ones among those steps limit rates and selectivities. Ru nanoparticles are among the most active and selective catalysts for CO₂ methanation, leading to their preeminence as state-of-the-art catalysts in mechanistic studies of CO₂ hydrogenation.

Several recent studies on Ru-based catalysts concur that CO and CH₄ formation pathways occur on the same catalytic surfaces and that they are linked through the intervening formation of chemisorbed CO (CO*, where * denotes bound species)6,10,12 Steady-state and transient infrared spectroscopy and temperature-programmed desorption data10,13 show that surfaces are significantly covered by CO* as most abundant reactive intermediates during CO and CO₂ hydrogenation reactions. The minimum-energy paths that activate the first C≡O bond in CO₂ and the second C≡O bond (in CO), which differ markedly in strength (bond-
dissociation enthalpies of 532 kJ mol\(^{-1}\) for OC=O and 1075 kJ mol\(^{-1}\) for C=O in the gas phase, 298 K). Many studies suggest that CO\(*\) is formed along with a bound O atom (O\(*\)) as a product of direct dissociation of a C=O bond in CO\(_2\). H-assisted CO\(_2\) activation pathways that form bound COOH or HCOO intermediates, which undergo subsequent C=O cleavage to form OH\(*\) and CO\(*\), have also been previously proposed, but density functional theory (DFT)-derived barriers for such routes are higher than those for direct CO\(_2\) activation routes on oxophilic metals commonly used for CO\(_2\) methanation (e.g., Ru, Rh, Ni, and Co). The kinetic hurdles involved in direct CO\(_2\) activation pathways are the subject of enduring debate, however, with proposals for the kinetically relevant step that include CO\(*\) desorption and \(\text{H}_2\)O formation. The pathway involved in the activation of CO\(*\) (to ultimately form CH\(_2\)) on Ru surfaces also remains uncertain; some studies propose direct activation of C\(
abla\)O to form C\(*\) and O\(*\). While others suggest H-assisted pathways with CH\(_2\)O\(*\) formation or dissociation as kinetically-relevant steps.

In this study, we combine kinetic and isotopic measurements over a broad pressure range during CO\(_2\)−H\(_2\) reactions and in situ infrared spectroscopy during CO\(_2\)−CO−H\(_2\) reactions with theoretical treatments of C\(
abla\)O activation from previous studies in order to assess the identity and kinetic relevance of bound intermediates and elementary steps involved in forming CO, CH\(_2\) and \(\text{H}_2\)O from CO\(_2\)−H\(_2\) reactions on Ru nanoparticles dispersed on inert SiO\(_2\) supports. In doing so, we present an integral method of kinetic analysis that is essential to examine CO\(_2\) hydrogenation and other CO-forming reactions and to accurately assess reaction selectivities, which are often obscured by the ubiquitous strong inhibition by the CO molecules formed during such reactions. The infrared spectra measured during CO\(_2\)−H\(_2\) and CO−H\(_2\) catalysis on Ru/SiO\(_2\) are essentially identical and show high CO\(*\) coverages that are a single-valued function of CO pressure (0.75−1 mL CO\(*\), 0.05−0.85 kPa CO), irrespective of whether CO is used as a reactant (CO−H\(_2\) reactions) or formed as a product (CO\(_2\)−H\(_2\) reactions). The kinetic trends observed for CO\(_2\)−H\(_2\) reactions are also remarkably similar to those for CO−H\(_2\) reactions when prevalent CO pressures, which increase in the axial direction as CO is formed along the catalyst bed, are rigorously accounted for using integral analysis methods for plug-flow reactors. The results of this analysis show that CH\(_4\) formation rates during CO\(_2\)−H\(_2\) reactions are proportional to H\(_2\) pressure and described by the same rate equation as previously reported for CO−H\(_2\) reactions, providing compelling evidence for the inextricable links between CO\(_2\) and CO reactions with H\(_2\).

CH\(_4\) formation from both CO\(_2\)−H\(_2\) and CO−H\(_2\) reactants involves kinetically relevant H-assisted activation of the strong C\(
abla\)O bonds in CO\(*\) species that prevail as dense adlayers on Ru surfaces during steady-state catalysis. The weaker C\=
abla\)O bonds in CO\(_2\), in contrast, cleave via direct dissociation on exposed vacant sites (*) in quasi-equilibrated steps that form CO\(*\) and O\(*\) as products. CO\(_2\) conversion rates are limited by the removal of O\(*\) via sequential H-addition steps that ultimately form H\(_2\)O and complete the catalytic cycle. These mechanistic connections between CO\(_2\) and CO hydrogenation reactions bring together the mechanistic details of CO\(_2\) hydrogenation routes derived from this study with the knowledge gained from systematic studies of CO−H\(_2\) reactions on Ru and other metals in the context of Fischer-Tropsch synthesis reactions.

2. EXPERIMENTAL METHODS

2.1. Catalyst Synthesis and Characterization. Ru/SiO\(_2\) catalysts were prepared using ligand-assisted dispersion methods via incipient wetness impregnation of SiO\(_2\) powders with aqueous Ru(NO)(NO\(_3\))\(_2\) and triethanolamine (TEA) solutions. SiO\(_2\) (Davison 646, 300 m\(^2\) g\(^{-1}\)) was treated in flowing dry air (Praxair, 99.999%, 10.0 cm\(^3\) g\(^{-1}\) s\(^{-1}\)) by heating to 898 K at 0.033 K s\(^{-1}\) and holding for 5 h before impregnation. The impregnating solution, containing Ru(NO)(NO\(_3\))\(_2\) (Alfa Aesar, 31 wt % Ru) and TEA (Sigma-Aldrich, 99%), in deionized H\(_2\)O (1:5 Ru/TEA molar ratio), was added to the treated SiO\(_2\) support in amounts corresponding to its pore volume for each of the two catalyst samples. The impregnated solids (0.5 wt % Ru for one sample and 5 wt % Ru for the other) were treated in ambient air overnight at 373 K, then heated in flowing dry air (Praxair, 99.999%, 10.0 cm\(^3\) g\(^{-1}\) s\(^{-1}\)) to 548 K at 0.0167 K s\(^{-1}\), held for 4 h, and cooled to ambient temperature. Samples were then heated to 723 K at 0.0167 K s\(^{-1}\) in flowing 10% H\(_2\)/He (Praxair, 99.999%, 0.5 cm\(^3\) g\(^{-1}\) s\(^{-1}\)) and held for 3 h; these processes led to the formation of Ru nanoparticles, which were passivated by contact with flowing 2% O\(_2\)/He (Praxair, 99.999%, 1 cm\(^3\) g\(^{-1}\) s\(^{-1}\)) at ambient temperature before exposure to air.

The dispersion of the Ru nanoparticles, defined as the ratio of surface to total Ru atoms, was determined from the total uptakes of chemisorbed hydrogen measured volumetrically at 373 K, by assuming a 1:1 H/Ru adsorption stoichiometry. Prior to the H\(_2\) uptake measurements, catalyst samples were treated at 623 K in flowing H\(_2\) (Praxair, 99.999%, 1 cm\(^3\) g\(^{-1}\) s\(^{-1}\)) for 1 h, evacuated (≤10\(^{-9}\) mbar) for 1 h using a dual-stage rotary vane pump (Leybold, Trivac D2.5E) and a turbomolecular drag pump (Pfeiffer Vacuum, TMU 071P), and then cooled to 373 K. H\(_2\) was dosed stepwise into the adsorption chamber (0.02 to 80 kPa H\(_2\)), and total uptakes were determined from the constant uptake values measured above ~25 kPa H\(_2\). The adsorption chamber volume was determined by dosing He into the evacuated chamber using the same process as for H\(_2\). Surface-averaged particle diameters were determined from dispersion values by assuming spherical nanoparticles and the atomic density of bulk Ru metal.

2.2. Measurements of Infrared Spectra during CO\(_2\)−H\(_2\) and CO\(_2\)−CO−H\(_2\) Reactions. Infrared (IR) spectra were measured by averaging 64 scans (4000−600 cm\(^{-1}\) range, 2 cm\(^{-1}\) resolution) during CO\(_2\)−H\(_2\) and CO−H\(_2\) reactions using a Thermo Nicolet 8700 FT-IR spectrometer equipped with a liquid N\(_2\)-cooled MCT detector. Ru/SiO\(_2\) samples were pressed into self-supporting catalyst wafers (10 mg cm\(^{-2}\)) and placed within a quartz in situ flow cell fitted with KBr windows. The wafer temperature was measured using a K-type thermocouple (Omega) positioned within a thermowell in contact with the radial edge of the wafer; the cell temperature was maintained by using an electronic temperature controller (Watlow, Series 982) and resistive heating (AR Industries, BXX9RB38-4T).

These wafers were treated in flowing 10% H\(_2\)/He (Praxair, 99.999%, 30 cm\(^3\) g\(^{-1}\) s\(^{-1}\)) by heating to 698 K at 0.083 K s\(^{-1}\) and held for 1 h before cooling to 733 K. Background spectra were measured in flowing H\(_2\)/He before exposing the wafers to flowing CO\(_2\) (Praxair, 99.999%) or CO (Praxair, 99.999%, 1.0% CO/He); these background spectra, along with spectral contributions from gaseous CO and H\(_2\)O, were subtracted from all spectra measured during catalysis to extract the contributions from bound species. The components evident from these infrared bands were extracted from measured spectra using Gaussian−Lorentzian mixed functions. The reactant and product concentrations in the effluent stream were measured using a gas chromatograph (Agilent, 7890A) equipped with a capillary column (HP-Plot Q, 30 m × 0.53 mm × 40 μm), methanizer (Activated Research Company, Polysar), and a flame ionization detector (FID).

2.3. CO\(_2\) Hydrogenation Reactivity and Selectivity Measurements. Ru/SiO\(_2\) catalysts were diluted with additional SiO\(_2\) (Davison 646, 300 m\(^2\) g\(^{-1}\)) that was treated as described in section 2.1; these catalyst mixtures were pelleted and sieved to retain 150−250 μm aggregates and diluted further with quartz powder (Sigma-Aldrich, no. 204358) in order to eliminate heat and mass transfer corruptions. Further details about the elimination of transport artifacts are provided in section S1.3 of the Supporting Information. The mixtures were placed within a packed-bed tubular reactor (quartz, 4 mm i.d.) with
plug-flow hydrodynamics that was held within a three-zone resistively-heated furnace equipped with electronic controllers (Watlow, Series 988). Bed temperatures were measured with a K-type thermocouple in contact with the outer tube wall.

Inlet molar flow rates were metered using electronic mass flow controllers (Parker, 201) at ambient pressure. Ru/SiO2 samples were treated in flowing 10% H2/He (Praxair, 99.999%), 200 cm3 g−1 s−1 by heating to 698 K at 0.083 K s−1 and holding for 1 h before cooling to reaction temperature (573−673 K). The composition of the inlet stream was set by mixing CO2 (Praxair, 99.999%), H2 (Praxair, 99.999%), and He (Praxair, 99.999%) as balance to achieve CO2 pressures between 1 and 16 kPa and H2 pressures between 2 and 16 kPa. Concentrations of all species in the inlet and effluent streams were measured by gas chromatography (Agilent GC, 6890) using a packed column (Porapak Q, 2.74 m length, 2 mm i.d.) and a thermal conductivity detector (TCD). CO, CH4, and H2O were the main products detected; trace quantities of other hydrocarbons (C2H6 and C2H4) in the efluent were also detected (C2H4/CH4 molar ratio <0.005 across all conditions). CO and CH4 formation rates (rCO and rCH4, respectively) represent the net rates of formation for each product, and CO2 consumption rates (rCO2) represent the rate of conversion of CO2 to CO and CH4.

3. RESULTS AND DISCUSSION

3.1. In Situ Infrared Spectra during CO2−H2, CO−H2, and CO2−CO−H2 Reactions. The identity and coverages of bound species and their involvement as intermediates were assessed from infrared spectra measured during CO2 and CO hydrogenation on Ru/SiO2 catalysts with concurrent measurements of rates. The infrared spectra obtained during CO2 hydrogenation (573 K; 5 kPa CO2, 8 kPa H2, balance He) on 0.5 wt % Ru/SiO2 (Figure 1a) showed three bands corresponding to the C−O stretching modes of bound CO (CO*) at 2004, 1916, and 1670 cm−1. Backdonation of electron density from the metal into the CO antibonding 2π* orbital leads to the elongation and weakening of C−O bonds and to the observed shift to lower frequencies relative to that of gaseous CO (2140 cm−1). This effect becomes stronger as CO binds to larger metal ensembles, thus causing distinct spectral features for CO bound to metal ensembles of varying sizes; the three bands at 2004, 1916, and 1670 cm−1 (Figure 1a) correspond to CO* bound atop one Ru atom, bridging two Ru atoms, and interacting with several Ru atoms, respectively.36 Infrared features for bound formate (HCOO*) species, previously reported during CO2−H2 reactions on Ru nanoparticles dispersed on Al2O3 or TiO2 supports, were not detected on Ru/SiO2; such bound HCOO* species have been shown to act as mere spectators interacting with acid−base pairs on such supports12,18 and are not present at detectable coverages on SiO2 supports or Ru nanoparticles.

Figure 1b shows the infrared spectrum during reactions of CO−H2 on 0.5 wt % Ru/SiO2 at 573 K. In parts a and b of Figure 1, the samples are in contact with the same CO and H2 pressures (0.2 kPa CO, measured at the infrared cell outlet and equivalent to the pressure at the center of the wafer for the well-mixed cell compartment; 8 kPa H2); they differ only in the presence or substantial absence of CO2 (5 kPa, Figure 1a; <0.02 kPa, Figure 1b). The C−O bands are essentially identical, in frequency and intensity, for these two spectra, indicative of bound CO species that are similar, in type and coverage, whether CO is used as a
reactant or formed as a product in CO$_2$–H$_2$ reactions. CO pressures were varied from 0.05 to 0.9 kPa CO during CO–H$_2$ reactions, and the resulting spectra are shown in Figure 2. The combined integrated intensities of the three CO* bands increased by a factor of 1.3 as the CO pressure increased from 0.05 to 0.9 kPa, indicative of significant coverages of CO*, which form adlayers that reach near-saturation levels at ∼1 kPa CO. The CO* bands shift to higher frequencies as CO pressure increases, as previously reported, because of weaker backdonation from the metal into 2* dipole coupling among CO* species at higher coverages.

Figure 3 shows fractional CO* coverages, determined from the combined integrated intensities of the three CO* bands, during steady-state reactions of CO–H$_2$, CO–CO$_2$–H$_2$, and CO–H$_2$ mixture at 0.05–0.9 kPa CO pressures; such coverage estimates are normalized by the maximum integrated band intensities observed in this study (at 0.9 kPa CO), which represent saturation CO* coverages at 573 K. The CO* coverages derived from the spectra during CO$_2$–H$_2$ and CO–H$_2$ catalysis (shown at one condition in Figure 1) and at several other conditions in Figure 3) are a single-valued function of the CO pressure. CO–H$_2$ reactions (Figures 1a and 3) form CO* via surface-mediated steps that ultimately desorb CO, thus leading to CO* surface coverages that must equal (at equilibrium) or exceed (if desorption steps are not equilibrated) those expected at equilibrium with the contacting CO(g) pressure. During CO–H$_2$ reactions, CO* forms via adsorption of CO(g) (Figures 1b and 3); CO* coverages must therefore be equal to or below those in equilibrium with the contacting CO(g) pressure. Yet, CO* coverages are similar during CO–H$_2$, CO–H$_2$ and CO–CO$_2$–H$_2$ at each CO pressure, even at prevalent CO pressures that lead to submonolayer CO* coverages, indicative of CO adsorption–desorption quasi-equilibrium during both CO$_2$–H$_2$ and CO–H$_2$ reactions.

CO adsorption–desorption quasi-equilibrium requires that these steps occur in each direction at rates much higher than those for CO$_2$ or CO hydrogenation reactions. CO* desorption rates are given by

$$r_{\text{CO* desorption}} = \frac{k_B T}{h} e^{-\frac{\Delta S^{\text{des}}}{k_B} - \frac{\Delta H^{\text{des}}}{k_B T}} [\text{CO*}]$$

where $k_B$ and $h$ are the Boltzmann and Planck constants, $T$ is the absolute temperature, and $\Delta S^{\text{des}}$ and $\Delta H^{\text{des}}$ are the entropy and enthalpy components of the CO* desorption free energy barriers, respectively. A lower limit for CO* desorption rates can be estimated by assuming that desorption leads to the gain of one mode of translation and that desorption barriers equal the heat of CO adsorption (+100 kJ mol$^{-1}$ on 7 nm Ru nanoparticles at 0.6 ML CO*)$^{37,38}$; these assumptions lead to desorption rates of ∼10$^{-5}$ s$^{-1}$ at 573 K. CO$_2$ hydrogenation rates are much smaller (<1 s$^{-1}$); 0.6–9.0 ML CO*; 573 K; 1–25 kPa CO$_2$, 1–16 kPa H$_2$), consistent with quasi-equilibrated CO adsorption–desorption during CO$_2$–H$_2$ reactions. CO adsorption–desorption steps have also been shown to be fast and quasi-equilibrated during CO–H$_2$ reactions on Ru$^{27,28,30}$, Fe$^{40,41}$ and Co$_4$,42,43

The quasi-equilibrium of CO adsorption–desorption steps renders the CH$_4$ molecules that form before CO* desorption as kinetically indistinguishable from those that form after CO* desorbs and readsorbs. Measured CO formation rates ($r_{\text{CO,net}}$) during CO$_2$–H$_2$ reactions reflect the net rate of CO formation, as given by

$$r_{\text{CO,net}} = r_{\text{CO* des}} (1 - \eta)$$

$$\eta = \frac{[\text{CO}]^*}{k_{\text{CO*, des}}[\text{CO*}]}$$

Here, $r_{\text{CO*, des}}$ represents the forward CO* desorption rate, $\eta$ represents the approach to adsorption-desorption equilibrium, and $k_{\text{CO*, des}}$ represents the equilibrium constant of the CO* adsorption-desorption step. As CO* desorption approaches equilibrium ($\eta \rightarrow 1$), $r_{\text{CO,net}}$ becomes much smaller than $r_{\text{CO*, des}}$ and measured CO formation rates no longer reflect the intrinsic dynamics of CO* desorption–readsorption steps. Measured CO formation rates instead reflect the rate at which CO(g), present at pressures in equilibrium with the prevalent CO* coverages, leaves the reactor in the effluent stream. The quasi-equilibrated nature of CO* desorption precludes the use of CO formation rates as a meaningful "counter" of the rate at which CO forms via the elementary steps that activate CO$_2$ at Ru surfaces. CO$_2$ consumption rates ($r_{\text{CO}_2}$) and CH$_4$ formation rates ($r_{\text{CH}_4}$), the difference of which gives CO formation rates

![Figure 2](https://example.com/figure2.png)

**Figure 2.** In situ infrared spectra during steady-state CO–H$_2$ reactions (573 K, 0.05–0.9 kPa CO, 4 kPa H$_2$, balance He) on 0.5 wt % Ru/SiO$_2$.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Fractional CO* coverages as a function of CO pressure during steady-state CO–H$_2$ ( ), CO–CO$_2$–H$_2$ ( ), and CO–H$_2$ ( ) reactions determined from integrated IR bands on 0.5 wt % Ru/SiO$_2$. Fractional CO* coverages calculated by normalizing the integrated intensities of the three CO* bands to the maximum integrated intensities (at 0.9 kPa CO).
(\(r_{\text{CO}}\)), instead represent the simplest measures of reactivity for these catalytic events and are used to describe the intrinsic dynamics of CO\(_2\)--H\(_2\) reactions in the following sections.

### 3.2. Effects of Residence Time and Reactant Pressures on CO\(_2\) Consumption Rates and CH\(_4\) Formation Rates.

CO\(_2\) consumption and CH\(_4\) formation rates (\(r_{\text{CO}_2}\) and \(r_{\text{CH}_4}\), respectively; normalized per exposed Ru atom, determined from H\(_2\) chemisorption uptakes) were measured in a packed-bed reactor with plug-flow hydrodynamics at 573 K at different CO\(_2\) and H\(_2\) pressures (1−25 kPa CO\(_2\), 2−16 kPa H\(_2\)). Measured rates were unaffected by the mean diameter of the Ru/SiO\(_2\) porous aggregates (165 vs 215 \(\mu\)m) or by dilution of such aggregates with quartz (bed dilution ratio = 20−70), thus ruling out any corruptions of measured rates by intra-aggregate concentration gradients or bed-temperature gradients (section S1.3 in the Supporting Information). Forward CO\(_2\) consumption rates (\(r_{\text{CO}_2,f}\)) were obtained by correcting measured rates (\(r_{\text{CO}_2,\text{net}}\)) for the approach to equilibrium (\(\eta_1\)),

\[
\eta_1 = \frac{P_{\text{CO}_2}P_{\text{H}_2}O}{P_{\text{CO}_2}P_{\text{H}_2}K_{\text{EQ},1}}
\]

(6)

\[
r_{\text{CO}_2,\text{net}} = r_{\text{CO}_2,f}(1 - \eta_1)
\]

(7)

where \(K_{\text{EQ},1}\) is the equilibrium constant for CO\(_2\)--H\(_2\) conversion to CO and H\(_2\)O as products (reverse water-gas shift reaction) at the reaction temperature (\(\eta_1 = 0.005−0.1\) at 573 K in these experiments). CO\(_2\) conversion to CH\(_4\) and H\(_2\)O is far from equilibrium (\(\eta < 10^{-6}\)), thus requiring no corrections.

CO\(_2\) consumption and CH\(_4\) formation rates from CO\(_2\)--H\(_2\) reactants on Ru/SiO\(_2\) decrease with increasing residence time (ratio of catalyst mass to flow rate), even at CO\(_2\) and H\(_2\) conversions below 10% (Figure 4; 573 K; 8−16 kPa CO\(_2\), 8 kPa H\(_2\)). H\(_2\)O added to the inlet stream at pressures (1 kPa H\(_2\)O) ∼10-fold larger than indigenously formed did not lead to detectable decreases in rates (Figure S2), indicating that CO is the inhibiting product (linear average CO pressure from 0.04 to 0.09 kPa; Figure 4). Such effects are consistent with the high CO\(^*\) coverages evident from the infrared spectra measured during catalysis (0.05−1 kPa CO; Figures 1−3). CO\(^*\) binds to the Ru surface atoms required for the kinetically-relevant elementary steps that limit CO\(_2\) consumption and CH\(_4\) formation turnovers. Such inhibition effects are ubiquitous in CO hydrogenation studies, leading to rate equations that contain denominator terms that depend on CO pressures on Ru\(^{27,28,30}\) and Co\(^{40}\) catalysts and to the large fractional coverages of CO\(^*\) (\(\theta_{\text{CO}}\)) evident from CO\(^*\) infrared bands, even at very low CO pressures (e.g., 0.6, at 0.03 kPa CO; 598 K).\(^{28}\)

Figure 4. Effect of residence time (SV\(^{-1}\); SV denotes space velocity) on (a) CO\(_2\) consumption rates and (b) CH\(_4\) formation rates on 0.5 wt % Ru/SiO\(_2\) [573 K; 16 kPa CO\(_2\), 8 kPa H\(_2\), balance He (●); 8 kPa CO\(_2\), 8 kPa H\(_2\), balance He (○)]. Dashed lines are used to guide the eye.

Figure 5. CO\(_2\) pressure effects on (a) CO\(_2\) consumption rates and (b) CH\(_4\) formation rates on 0.5 wt % Ru/SiO\(_2\) (573 K; 1−25 kPa CO\(_2\), 2−8 kPa H\(_2\), balance He; 3.5 × 10\(^5\) cm\(^3\)/g-atoms Ru\(_2\)ks)/SV; CO\(_2\) conversion 0.006−0.12). Dashed curves represent the best regression fits of the rate data to the integrated forms of eqs 8 and 9.
Axial gradients in the concentration of CO products, combined with strong inhibition of rates by CO, lead to significant changes in rates along the catalyst bed as conversion occurs, even at relatively low CO2 conversions (<10%). Consequently, differential reactor formalisms, which rely upon the assumption of constant rates along the bed, cannot accurately describe intrinsic kinetic trends, which require instead integral reactor methods of analysis that rigorously account for axial CO concentration profiles. This also requires the simultaneous regression of rate data for both CO2 consumption and CH4 formation to a set of coupled rate equations in integral form (details provided in section S2.1 in the Supporting Information) because the prevalent CO pressures depend on the rates of both reactions, as they form and consume CO along the catalyst bed. Such methods and a systematic examination of plausible sequences of elementary steps and their respective rate equations have not been previously used in mechanistic and kinetic inquiries into CO2 hydrogenation reactions to our knowledge. These analysis methods are used next in order to describe the effects of CO2 and H2 pressures on intrinsic CH4 formation rates and CO2 consumption rates in terms of mechanism-based rate equations.

CH4 formation rates and (forward) CO2 consumption rates from CO2–H2 reactants are influenced by CO2 (Figure 5) and H2 (Figure 6) pressures at 573 K on Ru/SiO2. CO2 consumption rates increase monotonically with CO2 and H2 pressure (Figures 5a and 6a) for rates obtained at the same residence time; CH4 formation rates, in contrast, depend inversely on CO2 pressure (Figure 5b) and almost linearly on H2 pressure (Figure 6b). These observed kinetic trends reflect the consequences not only of the intended changes in CO2 and H2 pressures but also of the different prevalent CO pressures present along the bed for each condition.

The rate data in Figures 5 and 6 (and the additional data in section 3.5) were regressed to various sets of mechanism-based rate equations for CO2 consumption and CH4 formation (enumerated in Table S2) using integral methods. These rate equations reflect a range of potential mechanisms and kinetically relevant steps mediated by transition states that are bound to either one or two Ru surface sites, including unassisted CO2 activation (on bare Ru atoms), hydrogen-assisted CO2 activation, and O* removal steps as kinetically-relevant steps for CO2 consumption and hydrogen-assisted CO activation as the kinetically relevant step in CH4 formation. The observed kinetic trends are described most accurately by the following rate equations for CO2 consumption rates and CH4 formation rates,

\[
\begin{align*}
    r_{\text{CO}_2} &= \frac{r_{\text{CO}_2}^*}{1 + \beta \cdot \text{CO}} \\
    r_{\text{CH}_4} &= \frac{\gamma \cdot \text{H}_2 \cdot \text{CO}_2^*}{(1 + \beta \cdot \text{CO})^2}
\end{align*}
\]

where \( P_i \) represents the pressure of species \( i \) and \( \alpha, \beta, \) and \( \gamma \) represent lumped kinetic and thermodynamic parameters. The dashed curves in Figures 5 and 6 represent the regressed fit to the functional forms of eqs 8 and 9 with lumped parameters derived from integral reactor methods (section S2.1 in the Supporting Information) and all rate data (parity plots for all data in section 3.5). The unity terms in the denominators of eqs 8 and 9 become negligible when \( \beta \cdot \text{CO} \) is \( >1 \); bed-averaged values obtained for \( \beta \cdot \text{CO} \) ranged from 0.9 to 8.5, resulting in cross-correlation between the numerator and denominator terms at some of the conditions used in this study (section S2.4 in the Supporting Information). The functional forms of these rate equations are examined next in the context of the elementary steps that interconnect bound intermediates and transition states; such a mechanistic analysis assigns chemical significance to the \( \alpha, \beta, \) and \( \gamma \) parameters in eqs 8 and 9 for CO2 conversion (section 3.3) and CH4 formation (section 3.4).

### 3.3. Elementary Steps Involved in CO2 Consumption Reactions during CO2–H2 Reactions

The ability of eqs 8 and 9, which contain identical terms in their denominators, to accurately describe both CO2 consumption and CH4 formation rates demonstrates that these reactions, sometimes treated as independent routes on different active sites,44 occur instead via interlinked steps on the same catalytic surfaces. The two terms (1 and \( \beta \cdot \text{CO}_2 \) in eqs 8 and 9) are ubiquitous in CO hydrogenation rate equations27,28,30 and reflect the relative concentrations of bare surface atoms (*) and bound CO* in Langmuirian kinetic treatments. Such precise origins have been recently questioned28 based on discrepancies between the values of equilibrium constants for binding of molecular CO (\( K\text{CO}_2 \)) derived from regressions of rate data at high CO pressures (>1 kPa) and those determined from in situ infrared spectra and kinetic measurements. The functional forms of eqs 8 and 9 are used here to describe the consequences of CO2 and H2 pressures on intrinsic CH4 formation rates and (forward) CO2 consumption rates, as shown in Figure 6.

### Figure 6. H2 pressure effects on (a) CO2 consumption rates and (b) CH4 formation rates on 0.5% wt. Ru/SiO2 (573 K; 1–16 kPa CO2, 1–16 kPa H2, balance He; 3.5 × 10^3 cm^3/(g·atm·ks)/SV; CO2 conversion 0.006–0.12). Dashed curves represent the best regression fits of the rate data to the integrated forms of eqs 8 and 9.

\[P_i\] represents the pressure of species \( i \).
theoretical term. These discrepancies, caused by significant intermolecular repulsions within dense CO* adlayers, preclude accurate descriptions using Langmuirian treatments at the high CO pressures typical of CO methanation reactions (1–100 kPa CO) but not at the low CO pressures prevalent in this study (<0.1 kPa CO). In fact, CO hydrogenation rates at CO* coverages between 0.5 and 0.9 ML (0.01–0.1 kPa CO, 573 K) were accurately described by Langmuirian models, which gave values of $K_{\text{CO}}$ consistent with those determined independently from infrared spectra. The two terms in the denominators of the CO2 consumption and CH4 formation rate equations (eqs 8 and 9) likewise reflect * and CO* species, the relative concentrations of which are determined by $K_{\text{CO}}$ (represented by $\beta$). The values of $\beta$ obtained from the regression of rate data for CO2–H2 reactions are consistent with those obtained from kinetic data and in situ infrared spectra for CO–H2 reactions, as shown in section 3.5 for two catalysts with different mean nanoparticle diameters.

The absence of H2-dependent terms in the denominators of the rate equations (eqs 8 and 9) indicates that coverages of H2-derived species are negligible at the conditions used in this study. Previous kinetics studies of CO–H2 reactions have similarly found that the rate equations that describe such reactions do not contain H2-dependent terms in their denominators. DFT treatments have shown that Ru surfaces can bind H atoms at interstitial spaces present within CO* adlayers. Chemisorbed H atoms (denoted as H*) do not displace CO* species bound in atop configuration but reside instead at three-fold hollow sites on Ru surfaces containing significant CO* coverages.

The numerator term in the equation that describes CO2 consumption rates (eq 8) reflects the composition of the transition state (TS) that mediates the kinetically-relevant step for CO2 consumption during CO2–H2 reactions. It suggests a kinetically-relevant TS structure that contains one O atom and one H atom, a heuristic analysis confirmed by the kinetic treatment below. Chemisorbed O atoms (O*) and CO* form as products of CO2 activation on vicinal Ru atom pairs when it occurs without assistance by H2-derived species. Such CO2 activation steps have been suggested by DFT studies on Ru, Rh, and Ni surfaces. The CO* formed can desorb and readorb, thus establishing equilibrium with the contacting CO(g) phase, as shown in section 3.1. The O* species must ultimately react via sequential H-addition steps to form OH* and H2O* (Scheme 1); O* can also react with CO*, thus reversing its formation step before reacting with H* to form H2O. When this reverse step is fast relative to the step that forms H2O, unassisted CO2 activation steps become quasi-equilibrated. Taken together with the quasi-equilibrated nature of CO* adsorption–desorption, this would lead to O* coverages set by the following equation,

$$\frac{[O^*]}{[\text{]}]} = \frac{K_{\text{CO}}}{K_{\text{CO}}} \times \frac{P_{\text{CO}}}{P_{\text{CO}}}$$

(10)

where $K_{\text{CO}}$ is the equilibrium constant for CO2 dissociation to O* and CO*. CO*-saturated Ru surfaces bind both O* and H* at three-fold sites, but O atom binding requires displacement of CO*. whereas H atom binding occurs at interstitial sites within CO* adlayers. Consequently, the kinetically-relevant reaction of O* with H* to form OH* may involve a single Ru atom, which, together with the prevalence of CO* and * as the most abundant bound species, gives the rate equation for CO2 consumption (derivation in section S2.2 in the Supporting Information):

$$r_{\text{CO2}} = \frac{K_{\text{CO2}} \cdot K_{\text{H2}} \cdot k_{\text{OH}}}{K_{\text{CO}}} \times \frac{R_{\text{CO2}}}{P_{\text{H2}} + \frac{1}{K_{\text{CO2}}P_{\text{CO2}}}}$$

(11)

This equation has the functional form of eq 8 with $\alpha$ (in eq 8) given by $K_{\text{CO2}} \sqrt{K_{\text{H2}}} k_{\text{OH}} K_{\text{CO}}$ and $\beta$ (in eqs 8 and 9) corresponding to $K_{\text{CO}}$. The form of eq 8 is consistent with CO2 hydrogenation pathways that form O* and CO* as intermediates, but not with H-assisted CO2 activation pathways because such pathways directly form OH* and CO2 and thus do not involve any elementary steps that are mediated by TS structures containing only O and H atoms.

The sequence of elementary steps in Scheme 1 requires quasi-equilibrated CO2 activation steps to give the functional form of the rate equation that accurately describes measured CO2 consumption rates (eq 8). This occurs when reactions of O* with CO* are much faster than those with H* to form OH* (and ultimately H2O). Previous experimental and DFT studies of CO hydrogenation on Fe, Co, and Ru surfaces have shown that O*, formed in infrequent unassisted CO activation during CO–H2 reactions, reacts preferentially with CO* (to form CO2) instead of H* (to form H2O). Such a preference is consistent with the prevalence of CO2 over H2O as the predominant oxygen-rejection route, as well as with the prevalent, very large (CO*)/(H*) ratios on working surfaces.

The extent of equilibration of CO2 activation steps during CO2–H2 reactions was examined by measuring the CO2 isotopologues formed during C18O2–C13O2–H2 reactions with equimolar amounts of C16O2 and C18O2. Figure 7 shows the relative concentrations of C16O2, C18O2, and C16O18O at a fractional CO2 conversion of 0.02, a value within the range of conversions used in flow experiments in section 3.2 (0.01–0.05); the resulting distribution of isotopologues from equimolar mixtures of C16O2 and C18O2 is binomial. The CO2 fraction present as the mixed C18O2O C16O2O isotopologue (0.49) leads to a value for the approach to equilibrium of C16O2–C18O2 isotopic exchange (nHexa calculated as described in section 2.4) of 0.99 at conditions where the approach to equilibrium of CO2-consuming reactions is insignificant (<0.05). These results confirm that CO2 activation steps are quasi-equilibrated during CO2–H2 reactions, consistent with the form of the CO2 consumption rate equation (eq 8) and with the expectations

Scheme 1. Elementary Steps and Associated Thermodynamic and Kinetic Constants for CO2–H2 Reactions that Form CO and H2O on Ru Surfaces α
of faster O*-CO* reactions than O*-H' reactions set by previous CO hydrogenation studies. Next, we combine these CO2 conversion elementary steps with those for CH4 formation in order to determine the nature of the kinetically-relevant TS for both reactions.

3.4. Elementary Steps Involved in the Formation of CH4 from CO2−H2 and CO−H2 Reactants. The numerator in the CH4 formation rate equation (eq 9) reflects the stoichiometry of the transition state that mediates the kinetically-relevant step for CH4 formation during CO2−H2 reactions. CO, but not CO2, appears in this numerator, indicative of CH4 molecules that form through an intermediate present at coverages that reflect the contacting CO(g) pressure and that are insensitive to the concurrent presence or pressure of CO2. Such results are in agreement with infrared spectra (section 3.1) that show CO* to be the most abundant surface intermediate and to be present at coverages in quasi-equilibrium with CO(g) and independent of CO2 pressure. The involvement of CO* as an intermediate in CH4 formation for both CO2−H2 and CO−H2 reactions leads to the same rate equation for CH4 formation from CO2−H2 (eq 9) and CO−H2 reactions on Ru nanoparticles. CO* forms from CO2 via unassisted CO2 activation (section 3.3) and its coverage reaches quasi-equilibrium with the contacting CO(g) pressure along the bed. CH4 forms via H-assisted activation of CO* via the same intermediates and transition states as when CO is present at the inlet in CO−H2 reactions. The H2 dependence in the numerator of eq 9 thus reflects the prevalence of H-assisted routes for kinetically-relevant CO* activation, as shown for CO−H2 reactions on Ru over a much broader CO pressure range (0.001−100 kPa CO, 518−598 K) and also for Co29,40,48,49 and Fe catalysts.40

Scheme 2 depicts the sequence of elementary steps that accounts for the formation of CH4 and H2O as products of either CO2−H2 or CO−H2 reactants. Quasi-equilibrated adsorption of CO and H2 is followed by the quasi-equilibrated formation of formyl species (HC*O*) via H-addition to CO*. The kinetically relevant step involves the additional weakening of C−O bonds via another H-addition (to HC*O*), which forms hydroxymethylene species (HC*O*H) that cleave in a fast subsequent step to form CH* and OH*. These latter species react with additional H atoms in fast subsequent steps to form CH4 and H2O as the products of CO methanation. The CH4 species also act as monomers and initiators for chain growth in the Fischer-Tropsch synthesis.

Such hydrogen-assisted C−O activation routes form OH* instead of O* (formed in unassisted direct C−O activation), consistent with the prevalence of H2O over CO2 as the predominant O-rejection path on Ru and Co surfaces28,40 and with DFT-derived barriers for various plausible CH4 formation pathways for CO hydrogenation on Ru nanoparticles. DFT-derived energies on Ru201 nanoparticles at high CO* coverages (1.55 CO*/Ru, maximum CO* coverage that maintains atop CO* binding on terraces) have shown that hydrogen-assisted CO activation barriers (165 kJ mol−1) on (111) terraces are significantly smaller than those for unassisted direct CO* dissociation routes, which occur on bare Ru sites and form C* and O* as products (322−356 kJ mol−1).27

The hydrogen-assisted pathway depicted in Scheme 2, taken together with the assumptions of CO* and * as the most abundant surface intermediates, leads to an equation for CH4 formation rates with the functional form of eq 9 (derivation provided in section S2.3 in the Supporting Information):

\[

r_{CH4} = \frac{KHKCOKHCOKHOHKH2PRCO}{(1 + KCO)PCO}^2

\]

This equation assigns chemical significance to γ in eq 9.

Scheme 3 depicts the complete sequence of elementary steps involved in the formation of CO2, CH4 and H2O from CO2−H2 mixtures. Quasi-equilibrated CO2 and H2 dissociation steps form CO*, which subsequently desorbs molecularly, and O* and H', which combine to form OH* and ultimately H2O, thus completing a reverse water-gas shift catalytic turnover. CO* also undergoes H-addition steps before dissociation to form CH* and OH* fragments, which are hydrogenated to form CH4 and H2O, thus completing a methanation catalytic turnover. The next section explores the consequences of this mechanism in determining the selectivity to CH4 in CO2−H2 reactions.

3.5. Consequences of Mechanism and Ru Particle Size for Selectivity of CO2−H2 Reactions. The mechanism described in the preceding sections and depicted in Scheme 3...
gives a measure of CH₄ selectivity, defined here as the ratio of CH₄ rates to CO₂ consumption rates:

\[
\frac{r_{\text{CH}_4}}{r_{\text{CO}_2}} = \left( \frac{K_{\text{CO}H} K_{\text{COH}}}{K_{\text{CO}_H} K_{\text{COOH}}} \right) \frac{P_{\text{CO}_2}}{P_{\text{CO}_2}(1 + K_{\text{CO}_H} P_{\text{CO}_2})} \sqrt{\frac{P_{\text{H}_2}}{P_{\text{CO}_2}}}
\]

(13)

This equation reflects the combination of eqs 11 and 12 and relates such ratios to the prevalent pressures of reactants and products when surfaces are nearly saturated with CO* (\(K_{\text{CO}_H} P_{\text{CO}_2} \gg 1\)):

\[
\frac{r_{\text{CH}_4}}{r_{\text{CO}_2}} = \chi \frac{P_{\text{H}_2}}{P_{\text{CO}_2}}
\]

(14)

\[
\chi = \sqrt{\frac{K_{\text{H}_2} K_{\text{CO}_H} K_{\text{COH}}}{K_{\text{CO}_H} K_{\text{COOH}}}}
\]

(15)

The value of \(\chi\) represents a grouping of the relevant rate and equilibrium constants for the steps depicted in Scheme 3. Figure 8 shows measured CH₄ selectivities during CO₂–H₂ catalysis as a function of the expression in eq 14; the resulting relationship is nearly linear when average CO pressures are >0.04 kPa (closed circles), conditions that lead to high CO* coverages, in agreement with eqs 14 and 15 and indicative of the involvement and kinetic relevance of the proposed elementary steps (Scheme 3).

Previous studies have addressed the effects of nanoparticle size on CH₄ selectivity, with conclusions still subject to significant debate. Many reports show that small nanoparticles (<3 nm) and single atoms are highly selective for CH₄ formation, with other studies showing instead that small nanoparticles and single atoms exclusively form CO and H₂O from CO₂–H₂ reactants and that CH₄ selectivities become higher as nanoparticle size increases. The contradictions and other differences in reported selectivities are attributed to different and nonuniform nanoparticle structures among samples and to structural motifs formed in reaction environments. The mechanism-based integral reactor treatment shown here to be essential in the analysis of CO₂ hydrogenation rates and selectivities indicates that such contradictions also reflect differences in conversion and prevalent CO pressures among such studies. In the absence of such treatments, selectivity comparisons among catalysts become uninformative and often misleading, even when measured at low reactant conversions.

The value of \(\chi\) in eq 15 represents the intrinsic measure of selectivity that must be used to compare catalysts. The tenets of transition-state theory impose quasi-equilibrium between reactants and activated TS complexes, which gives the relationship between the kinetically-relevant transition states and their relevant precursors in the form of the following (nonelementary) reactions:

\[
\text{CO}_2(g) + \frac{1}{2}\text{H}_2(g) + \ast \neq \text{CH}_4(g) + \text{H}_2O(\ast) (16)
\]

\[
\text{CO}(g) + \frac{1}{2}\text{H}_2(g) + 2\ast \neq \text{H}_2(g) + \text{H}_2O(\ast) (17)
\]

The Gibbs free energy of formation of each TS from its gaseous precursors likewise determines the groupings of rate and equilibrium constants in the numerators of eqs 11 and 12 (\(K_{\text{CO}_H} \sqrt{K_{\text{CO}_H} K_{\text{COOH}}}\) and \(K_{\text{CO}_H} K_{\text{CO}_H} K_{\text{COOH}}\) respectively),

\[
K_{\text{CO}_H} \sqrt{K_{\text{CO}_H} K_{\text{COOH}}} = k_{\text{e}} \frac{T}{h} e^{-\frac{G_{\text{TS}}}{kT}} \frac{G_{\text{TS}}}{kT}
\]

(18)
The agreement between the measured and predicted rates in Figure 9 gives the following:

\[
K_{H_2}K_{CO}K_{HCO}K_{HCOH} = \frac{k_B T}{h} e^{-\frac{G_{HCOH} - G_{HCO} - G_{H_2}}{k_B T}}
\]  
(19)

where \(k_B\) and \(h\) are the Boltzmann and Planck constants, \(G_{O^*-H^f}\) and \(G_{HCO^*-H^f}\) are the free energies of the TS structures, and \(G_{CO}, G_{CO_2}\), and \(G_{H_2}\) are the free energies of gaseous CO, CO\(_2\), and H\(_2\) molecules, respectively. The combination of eqs 18 and 19 gives the following:

\[
\chi = \exp \left( \frac{G_{O^*-H^f} - G_{CO_2} + G_{CO} - \frac{1}{2} G_{H_2}}{RT} \right)
\]

\[-\frac{G_{HCO^*-H^f} - G_{CO} - G_{H_2}}{RT} + \frac{G_{CO^*} - G_{CO}}{RT} \]  
(20)

Within this equation, only \(G_{O^*-H^f}, G_{HCO^*-H^f}\), and \(G_{CO^*}\) (the Gibbs free energies of O\(^*\)–H\(^f\); HC*O\(^*\)–H\(^f\); and CO\(^*\), respectively) depend on the binding properties of nanoparticle surfaces. As a result, any differences in \(\chi\) among catalysts would indicate that the HC*O–H\(^f\) TS free energy differs from the combined free energies of CO\(^*\) and O\(^*\)–H\(^f\) TS. The value of \(\chi\) is given approximately by the slope in the linear region of Figure 8 (at high CO\(^*\) coverages) and more accurately by regression of all kinetic data to the functional form of eqs 11 and 12 and the insertion of the regressed parameters into eq 15.

Table 1 shows \(\chi\) values (and regressed parameters) on the catalyst used in the kinetic analysis of section 3.2 (0.5 wt % Ru/SiO\(_2\); 6 nm mean diameter particles) together with those on a catalyst with larger nanoparticles (5 wt % Ru/SiO\(_2\); 11 nm mean diameter). CH\(_4\) formation and CO\(_2\) consumption rates on both samples are accurately described by eqs 8 and 9, as shown by the agreement between the measured and predicted rates in Figure 9. The \(\chi\) values for the larger and smaller nanoparticles are essentially the same (21 ± 4 kPa\(^{-0.5}\) vs 24 ± 4 kPa\(^{-0.5}\)), suggesting that, within this range, nanoparticle size does not significantly affect product selectivities when the prevalent CO pressures for each selectivity measurement are taken into consideration.

The measured values of \(K_{CO}\) were 113 kPa\(^{-1}\) on 6 nm nanoparticles and 59 kPa\(^{-1}\) on 11 nm nanoparticles, consistent with the expected stronger binding of CO on smaller nanoparticles. Such \(K_{CO}\) values are also consistent with the results reported in previous infrared spectroscopic studies (~80 kPa\(^{-1}\) on 7.5 nm Ru nanoparticles; 0.001–0.1 kPa CO). The effective CH\(_4\) formation rate constants (\(K_{H_2}K_{CO}K_{HCO}K_{HCOH}\) eq 12) from CO–H\(_2\) reactions are slightly larger on 11 nm than 6 nm Ru nanoparticles (12.3 ± 1.3 kPa\(^{-2}\) s\(^{-1}\), 11 nm; 8.0 ± 0.5 kPa\(^{-2}\) s\(^{-1}\), 6 nm). These trends are directionally consistent with those reported for CO–H\(_2\) reactions on Ru\(^{47,59}\) and Co\(^{60}\) catalysts, for which turnover rates increase with increasing nanoparticle diameter up to ~10 nm. The similar effects of nanoparticle size on the rates of CH\(_4\) formation from CO–H\(_2\) and CO–H\(_2\) reactants represent the natural consequence of their mechanistic connections. The trends for CO–H\(_2\) reactions have been attributed to the decoration of coordinatively-unsaturated exposed atoms, which is more prevalent on smaller particles, by strongly bound CO\(^*\) or by C\(^*\) and O\(^*\) species formed via occasional CO\(^*\) dissociation events. Direct CO\(^*\) dissociation events do not contribute to measured rates, as shown by the functional form of the rate equation\(^{28,29,40,46,49}\) and by their large DFT-derived barriers on both terrace and corner Ru atoms\(^{27}\) (section 3.4); such infrequent events, however, render undercoordinated atoms unavailable for catalytic turnovers. This interpretation of the observed particle size effects is consistent with \(\chi\) values that are insensitive to particle diameter (24 ± 4 kPa\(^{-0.5}\), 6 nm; 21 ± 4 kPa\(^{-0.5}\), 11 nm).

---

**Table 1. Effects of Mean Ru Nanoparticle Size on Rate Parameters for CO\(_2\)–H\(_2\) Reactions on Ru/SiO\(_2\) Catalysts**

<table>
<thead>
<tr>
<th>Mean Ru nanoparticle size (nm)</th>
<th>(\chi) (kPa(^{-0.5}))</th>
<th>(K_{CO}) (kPa(^{-1}))</th>
<th>(K_{H_2}K_{CO}K_{HCO}K_{HCOH}) (kPa(^{-2}) s(^{-1}))</th>
<th>(K_{CO},V(K_{H_2}K_{CO}K_{HCO}K_{HCOH})) (kPa(^{-0.5}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>24 ± 4</td>
<td>113 ± 5</td>
<td>8.0 ± 0.5</td>
<td>(2.9 ± 0.5) × 10(^{-3})</td>
</tr>
<tr>
<td>11</td>
<td>21 ± 4</td>
<td>59 ± 3</td>
<td>12.3 ± 1.3</td>
<td>(9.7 ± 1.5) × 10(^{-3})</td>
</tr>
</tbody>
</table>

\(^{a}\)At 573 K; 1–25 kPa CO\(_2\), 1–16 kPa H\(_2\), balance He. \(^{b}\)Errors represent the 95% confidence intervals of the parameters obtained using bootstrapping methods. \(^{c}\)For 0.5 wt % Ru/SiO\(_2\) catalysts. \(^{d}\)For 5 wt % Ru/SiO\(_2\) catalysts.
and with the higher CO2 consumption rate constants measured on larger Ru nanoparticles (2.9 ± 0.5 × 10−3 kPa−0.5 s−1, 6 nm; 9.7 ± 1.5 × 10−3 kPa−0.5 s−1, 11 nm).

The connection between measured reaction selectivities and prevalent CO pressures highlights an important challenge associated with empirical approaches to catalytic design without a concomitant understanding of the underlying mechanistic details. The mechanistic insights gained in this work required a type of kinetic analysis that is seldom considered in comparing turnover rates and selectivities among catalysts, but which becomes crucial for sequential reactions that form strongly-bound intermediate products. Such formalisms, both in their use of sets of coupled rate equations and integral analysis of data, are essential in interpreting differences among catalysts and determining the effect of nanoparticle structure and support composition on reactivity and selectivity during CO2–H2 reactions.

4. CONCLUSIONS

This work brings together kinetic, isotopic, and spectroscopic data measured during CO2–H2 reactions with the knowledge gained from decades of experimental and theoretical studies of CO–H2 reactions to establish the identity and kinetic relevance of the elementary steps involved in CO2 hydrogenation at moderate conditions (573 K; 1–25 kPa CO2, 1–16 kPa H2). In doing so, we also present kinetic analysis methods that rigorously account for inhibition by CO, which is formed and consumed along the catalyst bed, through the regression of rate data to sets of coupled rate equations in their integrated forms. Such methods are essential to accurately assess the intrinsic reactivity of metal nanoparticles for CO2 hydrogenation (and other reactions that form strongly bound CO) and thus provide meaningful comparisons among different nanoparticle structures and compositions.

The combination of kinetic and isotopic evidence reveals that the kinetic hurdles in converting CO2 to hydrocarbons are not imposed by the chemical inertness of CO2, as typically claimed, but rather by the intermediate formation of CO2, which contains an even stronger C≡O bond and forms near-saturated adlayers on metal surfaces at typical reaction conditions. The strong C≡O bonds in chemisorbed CO are cleaved via kinetically-relevant hydrogen-assisted activation steps, while the weaker C≡O bonds in CO2 are cleaved through quasi-equilibrated steps that involve direct interactions with exposed metal atoms to form O* and CO*. O* species are removed via sequential H-addition steps, the first of which limits CO2 consumption turnovers. CO* species desorb and readsorb in quasi-equilibrated steps, as indicated by the similar CO* coverages obtained from infrared spectra measured during CO2–H2 and CO–H2 reactions at the same prevalent CO pressures. The observations presented in this work illustrate the mechanistic connections between CO and CO2 hydrogenation, which proceed via an identical sequence of elementary steps subsequent to the formation of CO* intermediates. These connections reward us with an ability to recycle the structure-function relationships developed in the context of Fischer-Tropsch synthesis to accelerate progress in the design of more active and selective catalysts for CO2 hydrogenation reactions.

■ ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c04298.

Infrared spectra at various H2 pressures, effect of cofeeding H2O during CO2–H2 reactions, testing for heat and mass transport effects, integral kinetic analysis methods, derivation of rate expressions for CO2 consumption and CH4 formation, and perturbation analysis to determine the extent of cross-correlation between numerator and denominator terms in the rate expressions (PDF)

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Notes

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■ REFERENCES


