Mechanism of CO₂ reduction by H₂ on Ru(0001) and general selectivity descriptors for late-transition metal catalysts

Talin Avanesian ^a, Gabriel S. Gusmão ^b, Phillip Christopher ^{a,c,d*}

^a Department of Chemical & Environmental Engineering, University of California, Riverside, Riverside, CA 92521, USA.

^b Renewable Technologies, Braskem S.A., Campinas, SP 13086-530 Brazil

^c Program in Materials Science, University of California, Riverside, Riverside, CA 92521, USA.

^d UCR Center for Catalysis, University of California, Riverside, Riverside, CA 92521, USA.

^{*}Email: Christopher@engr.ucr.edu

Abstract:

The mechanism of CO₂ reduction by H₂ at atmospheric pressure was investigated on Ru(0001) by coupling density functional theory (DFT) calculations with mean-field microkinetic modeling. The initial CO₂ hydrogenation step leading to CH₄ production was shown to occur through CO₂ dissociation and subsequent hydrogenation of CO* to CHO*. The dissociation of CHO* to form CH* and O* was identified as the rate limiting step for CH₄ formation, while the rate limiting step for CO production through the reverse water gas shift reaction was identified as CO* desorption. Based on a scaling relations analysis of competing CHO* dissociation and CO* desorption, O* adsorption energy was found to be an effective descriptor of differences in selectivity between CO and CH₄ production previously observed on late-transition metal catalysts. These mechanistic insights provide critical information to guide the design of catalysts with tunable selectivity for CO₂ reduction by H₂ at atmospheric pressure.

Keywords: CO₂ hydrogenation, Methanation, Reverse Water Gas Shift, DFT, Microkinetic model, Selectivity

1. Introduction

More than 85% of the current global energy need is provided by combustion of fossil fuels, which is accountable for continuously increasing atmospheric concentrations of CO₂ and accompanying climate change effects.[1] The search for approaches to reduce atmospheric CO₂ concentration has become a high priority research area. Recent efforts show the potential promise of directly sequestering CO₂ from the atmosphere using amine based sorbent materials, among other methods.[2–6] If approaches to directly sequester CO₂ from the atmosphere prove successful, it will be important to develop efficient, low temperature and pressure processes for converting CO₂ to higher value hydrocarbon feedstocks for chemical and fuel production. The coupling of CO₂ sorption technologies with solar-based H₂ production through catalytic reduction processes would provide an energy efficient, environmentally friendly and carbon neutral approach for chemical and fuel production. This approach relies, in part, on the development of materials that facilitate catalytic conversion of CO₂ and H₂ into desired products with high selectivity.

Because of high energy requirements, C-C coupling reactions are rare at low temperature and pressure and it is expected that C1 molecules (CO, CH₃OH and CH₄) will be the dominant products of environmentally friendly CO₂ reduction processes. CH₃OH synthesis from CO₂ and H₂ on Cu and “Cu-like” catalysts has received significant attention, due the extensive use of CH₃OH as a precursor for production of chemicals and liquid fuels. However, CH₃OH is a minimal side product under low pressure CO₂ hydrogenation conditions.[7–9] On the other hand, highly selective catalytic CH₄ and CO production has been demonstrated at low temperature (as low as 150 °C) and atmospheric pressure over a range of supported transition metal catalysts (eg. Ni, Ru, Rh, Pd, Pt).[10–15] Supported Ru

1 and Rh catalysts are consistently observed to exhibit high activity and selectivity for CO₂
2 methanation ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) at moderate temperatures and atmospheric
3 pressure. Pt and Pd have been shown to facilitate CO production through the reverse Water
4 Gas Shift reaction (rWGS, $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) and Ni has exhibited a combination of CO
5 and CH₄ selectivity.[10–14,16–23] In spite of extensive theoretical and experimental
6 studies of catalytic reduction of CO₂ by H₂ on late transition metal catalysts, outstanding
7 mechanistic questions remain, including most importantly the elementary steps and factors
8 that control catalytic performance and selectivity.[10–14,16–22,24–33]

9 Based on the excellent reactivity of Ru for CO₂ methanation and extensive
10 experimental evidence, we use this system as a base case to develop mechanistic insights.
11 Three main initial CO₂ hydrogenation mechanisms have been proposed in literature on late
12 transition metal catalysts: (1) direct hydrogenation of CO₂ to HCOO* or COOH* (adsorbed
13 species are denoted by a star), (2) CO₂ dissociation followed by hydrogenation of
14 CO*,[18,21,29,34,35] and (3) dissociation of CO₂, followed by direct dissociation of CO* and
15 hydrogenation of surface bound C*.[14,36] Surface formates (HCOO*) have been observed
16 by *in-situ* Fourier Transform Infrared (FTIR) spectroscopy, however results have shown
17 that these species are most likely spectators on the support.[37–39] Further, the relatively
18 low barrier for CO₂ dissociation on Ru indicates that direct CO₂ hydrogenation to form
19 COOH* is not a primary reaction pathway on Ru.[31,40,41] *In-situ* FTIR studies of CO₂
20 hydrogenation on Ru have repeatedly shown adsorbed CO* to be the dominant surface
21 species, [11–13,17,25,35–37,42,43] suggesting that hydrogenation following CO₂
22 dissociation is more feasible than direct hydrogenation of CO₂. Therefore it is likely that the
23 main reaction pathway involves hydrogenation of CO*, which has led to the suggestion that

CO₂ hydrogenation follows similar mechanism to CO hydrogenation after CO₂ is dissociated on the surface. However experiments have shown that CO and CO₂ hydrogenation kinetics differ considerably in terms of partial pressure dependences and activation barriers, suggesting important mechanistic differences.[17,22] As discussed in the Results and Discussion sections, this can be attributed to differences in the surface coverage of CO* on Ru under CO and CO₂ hydrogenation reaction conditions. CO* hydrogenation can evolve through formation of COH* or CHO* intermediates. Theoretical studies based on density functional theory (DFT) calculations favor CHO* route over COH* formation. [31,32,44–46] A few studies report traces of elemental carbon (C*), which can be a result of direct CO* dissociation, however both theoretical and experimental studies have agreed that the H-assisted CO* dissociation is the more energetically favorable route. [21,32,33,44,46–48]

Although there has been significant experimental analysis of the mechanism of CO₂ reduction by H₂ on late transition metal catalysts, there is no consensus on the initial hydrogenation pathway, or the rate-limiting step (RLS) of the reaction. The most commonly proposed RLS's are direct CO* bond breaking, or in more recent studies H-assisted CO* dissociation through formation of CH_xO*.[26,37,46] Importantly, there is also no consensus on what properties of late transition metals dictate selective CO production through rWGS (Pt, Pd) versus CH₄ production through methanation (Ru and Rh). A recent study showed that the catalytic metal d-band center energy trends with competing selectivity for CO and CH₄ production. However, significant variations in the trends observed in this study suggest that d-band center correlation cannot completely describe previously observed variations in selectivity among late transition metal catalysts. [19]

In this work we utilize DFT calculations coupled with mean-field microkinetic modeling to develop molecular level insights into the mechanisms that control performance and selectivity of Ru catalysts in CO₂ reduction by H₂ at atmospheric pressure. Mean-field microkinetic models have been proven successful in describing reaction kinetics semi-quantitatively and have been repeatedly used in computational screening of catalyst materials.[7,49–51] To investigate the mechanism of CO₂ hydrogenation reaction at realistic operating conditions, without a known rate expression and a priori assumption of RLS, it is essential to conduct a detailed microkinetic analysis using temperature and pressure corrected free energies and entropies. In this study the thermodynamic and kinetic parameters are obtained from DFT calculations and used to build a microkinetic model of competing rWGS and methanation pathways on Ru(0001). The microkinetic model captures experimentally observed trends in reaction selectivity and the impact of reactant partial pressures on catalytic rate and surface coverage of reaction intermediates, validating mechanistic insights gained from the model. The initial CO₂ hydrogenation pathway on Ru catalysts was shown to occur through CO₂ dissociation on the catalyst surface and subsequent hydrogenation of CO* to CHO*, in-line with recent FTIR results.[11–13,17,25,35–37,42,43] Using Campbell's degree of rate control analysis it was identified that the RLS for CH₄ formation on Ru(0001) is the dissociation of CHO* to form CH* and O*, while the RLS for the competing CO production through rWGS is CO* desorption.[52,53] Insights into competing RLS's for CO and CH₄ production on Ru, coupled with linear scaling and Brønsted–Evans–Polanyi (BEP) relationships that extend insights on Ru to Rh, Ni, Pt and Pd catalysts,[54–57] establish that the O* adsorption energy is an effective descriptor of competing selectivity between CO and CH₄ production on late-

transition metal catalysts. That is, more exothermic oxygen adsorption energy is associated with higher selectivity towards CH₄ production. This relationship derives from the impact of the O* adsorption energy on the exothermicity of CHO* dissociation, the resulting influence on the CHO* dissociation barrier (the RLS for CH₄ formation), and the lack of significant variation in CO* binding energy on late transition metal surfaces. The use of oxygen adsorption energy as a selectivity descriptor for CH₄ versus CO production in CO₂ reduction by H₂ accurately explains experimentally observed variations in selectivity on late transition metal catalysts.

2. Methods

2.1. DFT calculations

DFT calculations were carried out with the real space grid-based projector-augmented wave method (GPAW) code.[58] The Revised Perdew–Burke–Ernzerhof (RPBE) form of the generalized gradient approximation (GGA) was used to approximate exchange and correlation effects.[59] The BEEF-vdW functional was also investigated for geometry optimization of larger intermediate molecules.[60] Comparisons between RPBE and BEEF-vdW calculated results are provided in the Results and Discussion section (see section 3.1). The Ru(0001) termination was selected to represent the catalyst surface, because it has been demonstrated that larger catalyst particles (>5 nm diameter) have higher activity and selectivity towards CH₄ production, indicating that CO₂ hydrogenation occurs preferably on well-coordinated surfaces of metal catalyst particles.[61–63] It is important to note that, the support materials such as TiO₂ can have important effects on catalytic behavior of transition metals catalysts, by participating in the reaction mechanism or inducing the well-known metal-support interactions, which are not considered in our

1 model. However the results derived with our model are expected to be comparable with
2 the experiments conducted on support materials such as Al_2O_3 , which have shown
3 negligible influence on catalyst activity.[64]

4 The Ru(0001) surface was modeled as a $3\times 3\times 4$ periodically repeated unit cells in x
5 and y directions with 15 Å vacuum space between consecutive metal slabs in z direction. A
6 grid space of $h=0.2$ was used. The Brillouin zone was sampled with a $4\times 4\times 1$ Monkhorst-
7 Pack k -point set.[65] Geometry optimization calculations were performed for single
8 adsorbed species by adding 1/9 Mono Layer (ML) of adsorbate molecules to the top surface
9 of the slab and fixing the lower two layers. The optimized configurations of co-adsorbed
10 reactant and products of the elementary steps were also obtained using similar slab
11 geometry and addition of 2/9 ML of adsorbates on the top surface. The transition state
12 geometries and energy barriers for reaction elementary steps were obtained using the
13 climbing image nudged elastic band method (CI-NEB).[66] All geometry configurations
14 were allowed to relax using a quasi-Newton algorithm until the forces on all atoms
15 converged to less than 0.1 eV/Å. The calculated energies of optimized geometries for
16 considered species are provided in the supplemental information Tables S1-S3.

17 Relevant elementary steps in the reaction mechanism were identified by a thorough
18 analysis of possible reaction pathways based on DFT calculated energetics and previously
19 postulated mechanisms in literature.[31–33,37,44,46–48,67,68] Further discussion on
20 competing pathways is provided in the Results and Discussion section (see section 3.1). To
21 analyze the reaction mechanism under realistic experimental operating conditions, the
22 thermodynamic and kinetic parameters of elementary steps obtained from DFT
23 calculations were extended to enthalpies and free energies at a temperature of 500 K and

atmospheric pressure using statistical thermodynamics. Enthalpies and Gibbs free energies were calculated for gas phase and adsorbed species (including transition states) by applying zero-point energy, thermal energy and entropic corrections using DFT calculated vibrational frequencies and statistical mechanics correlations (details are provided in Supplementary Material). Vibrational frequency calculations were performed for gas phase, adsorbed species and transition states, using a finite-difference approximation of the Hessian matrix as implemented in Atomic Simulation Environment (ASE), a Python package used by GPAW to describe molecular configurations and run atomic simulations.[69] Activation barriers of all molecular adsorption steps were assumed to be zero. Free energies of weakly adsorbed species (H₂O, CO₂ and CH₄) were estimated as an average of gas phase and chemisorbed species Gibbs free energies. The heat of reactions and energy barriers of elementary steps used in the microkinetic model were calculated in terms of enthalpy as $\Delta H_{\text{rxn}} = \sum H(\text{products}) - \sum H(\text{reactants})$ and $\Delta H^\ddagger = H^\ddagger - \sum H(\text{reactants})$, respectively. DFT-derived entropies of reactants, products and transition states were used to calculate the pre-exponential factors of surface reactions. The pre-exponential factors of molecular adsorption were calculated assuming a sticking coefficient of 1 for all adsorption steps.[50] In Table S4, activation barriers, reaction energies and pre-exponential factors are provided for all considered elementary steps. The associated discussion with Table S4 in the Supplementary Materials provides additional details on the calculation of enthalpies and pre-exponential factors.

2.2. Microkinetic analysis

A mean-field microkinetic model was constructed based on 18 elementary steps (See Table S4 for details on all considered elementary steps). It was assumed that all elementary reactions are microscopically reversible and follow Langmuir-Hinshelwood type mechanisms. The reaction rates of elementary steps were described by Arrhenius expressions using DFT-calculated activation barriers and estimated pre-exponential factors.[70,71] All values used in the microkinetic analysis were enthalpies. No assumptions of RLS were made. A pseudo steady state hypothesis was used in the microkinetic model, where the accumulation of surface species as a function of time was considered to be zero ($d\theta_i/dt=0$). This is comparable to the steady state condition of a differential reactor. Mole balances on adsorbed intermediate species and vacant catalyst sites provide a set of non-linear algebraic equations. An in house MATLAB code based on a quasi-Newtonian scheme was used to solve a linearized set of the mole balances.[72] At any given temperature, pressure and set of reactant concentrations the surface coverage of the adsorbed species were obtained and used in rate expressions to calculate the instantaneous reaction rates.

The RLS's were identified using Campbell's degree of rate control ($X_{RC,i}$) as shown in equation 1.[52,53] In this approach, the impact of small variations in elementary step activation barriers on the overall reaction rate is analyzed to identify elementary steps that have the most impact on the overall mechanism. In equation 1, k_i is the rate constant of an elementary step and r is the overall reaction rate. Degree of Selectivity control ($X_{SC,i}$) for all elementary steps was also calculated in a similar manner to $X_{RC,i}$ using equation 2. In our definition of $X_{SC,i}$, the impact of small variations in elementary step activation barriers on

the difference in apparent activation barriers for CH₄ and CO production is analyzed. It should be noted that $X_{RC,i}$ and $X_{SC,i}$ are calculated at instantaneous reaction conditions.

$$X_{RC,i} = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_i} \right)_{K_i, k_{j \neq i}} \quad K_i = const \quad (1)$$

$$X_{SC,i} = \frac{k_i}{S} \left(\frac{\partial S}{\partial k_i} \right)_{K_i, k_{j \neq i}} \quad K_i = const \quad (2)$$

3. Results and Discussion

3.1. CO₂ methanation and rWGS mechanisms on Ru(0001)

First we address an un-resolved question of the initial hydrogenation step in the mechanism of CO₂ methanation on Ru catalysts. The potential energy diagram shown in Figure 1 compares three competing free energy pathways; direct hydrogenation of physisorbed CO₂*, hydrogenation of CO* after dissociation of adsorbed CO₂* to CO* and O*, [18,21,34,35] and hydrogenation following complete dissociation of CO₂* to C* and 2O*. [14,36] Our calculated electronic energies are in good agreement with similarly calculated energies on Ru(0001) surfaces. [31–33,40,41] A comparison between direct and hydrogen assisted CO₂* dissociation paths in Figure 1 (blue and red lines, respectively) shows that the first hydrogenation step for CO₂ methanation is more favorable through the dissociation of CO₂* to CO* and O* and subsequent hydrogenation of CO* to CHO*. This is due to the considerably lower activation barrier for CO₂* dissociation, compared to CO₂* hydrogenation to COOH* ($\Delta G^\ddagger = 0.45$ eV compared to $\Delta G^\ddagger = 1.42$ eV), and more stable products (1.1 eV more stable). However, the elementary steps involving COOH* species were also included in our microkinetic model and their impact on the overall reaction mechanism will be discussed in the sensitivity analysis section (see section 3.3). It is

important to note that CO₂ hydrogenation through HCOO* formation was excluded from our analysis based on ample experimental data proving that formates (HCOO*) are spectator species and don't impact the mechanism of the CO₂ hydrogenation on Ru.[37–39]

Figure 1: Potential energy diagram for competing initial hydrogenation steps in the CO₂ + H₂ reaction on Ru(0001). All energies are reported relative to the free energy of CO₂* + 8 H* on Ru(0001). Free energies were calculated at 500 K and atmospheric pressure.

As discussed in the introduction, the initial hydrogenation mechanism following CO₂* dissociation, has been proposed to proceed by two main pathways: (1) direct CO* dissociation, and (2) H-assisted CO* dissociation. CO* activation on Ru and other transition metal surfaces has been studied extensively in the context of CO hydrogenation (Fischer Tropsch) reaction. While a majority of theoretical calculations show CO* hydrogenation to form COH* or CHO* are energetically more favorable compared to direct CO* dissociation on terrace sites, direct CO* dissociation has been shown to have a lower activation barrier on under-coordinated sites such as step sites of (211) and corrugated sites of (1121) facets on Ru catalysts.[73–75] However, as mentioned previously, CO₂ hydrogenation is known to occur primarily at terraces on Ru nanoparticles. [61–63] The significant CO* dissociation barrier on Ru terrace sites ($\Delta G^\ddagger=2.5$ eV), relatively low barrier for CO₂* dissociation and

CO* hydrogenation to CHO*, and strong CO* signals observed by in-situ FTIR studies, [11–13,17,25,35–37,42,43] suggest that CO* is the main intermediate in both the methanation and rWGS reaction pathways and that it is reasonable to exclude the CO* dissociation step from our kinetic studies.

Although CO and CO₂ hydrogenation mechanisms are hypothesized to both evolve through the common pathway of CO* hydrogenation, we suggest differences in CO* coverage during these reactions, as observed via in-situ FTIR measurements, leads to different minimum energy pathways for CO* hydrogenation to form CH₄. Comparison of CHO* and COH* formation pathways under both high and low CO* coverage have shown CHO* formation to be the more favorable route. [31,44] Comparison of CHO* hydrogenation and dissociation pathways in figure S1, based on energies calculated under low CO* coverage, shows CHOH* to have higher energy compared to CHO* dissociation products (by 1.2 eV) and larger activation barrier compared to CHO* dissociation pathway (1.16 vs 0.91 eV). Therefore CHO* dissociation pathway is proposed to be the main pathway towards CH₄ formation in CO₂ hydrogenation mechanism. However, under high CO* coverage (conditions more relevant for CO hydrogenation on Ru), CHOH* formation has been identified to be the most relevant (rate limiting) step in the mechanism of CO hydrogenation.[44] It is suggested that under CO hydrogenation reaction condition, where the Ru surface is saturated with CO*, repulsive forces increase CHO* dissociation barrier by weakening the final state O*-Ru bond. Similarly, H*-Ru bonds are weakened due to high CO* coverage, which facilitate H*-Ru bond breaking and CHO*-H* bond formation. Thus, it seems that the differences in the CO* coverage under CO and CO₂ hydrogenation reaction

conditions on Ru, drive the hydrogenation of CO* to CH₄ to occur through different reaction pathways. [44]

The parallel pathways of CO* hydrogenation through COH* and CHO* formation are compared in the potential energy diagram plotted in Figure 2. In this Figure the complete energetic pathways of CO₂ methanation, and the competing rWGS reaction are mapped out at 500 K and atmospheric pressure. The calculated free energy pathways are in good agreement with similarly calculated free energy pathways for CO₂ conversion on Ru and other metal surfaces.[30–33,45,46] Based purely on the thermodynamics of competing COH* and CHO* pathways, the more favorable route toward CH₄ formation after CO₂* dissociation is the formation of CHO* and its dissociation to CH* and O* (green line in Figure 2). Although energetically, CO* desorption (i.e. rWGS pathway) is more favorable than either COH* and CHO* formation, the larger pre-exponential factors for the latter create a competition between methanation and rWGS that cannot be predicted based purely on the free energy landscapes in Figure 2, and will be discussed below in the results of the microkinetic model. The overall energy diagram identifies CO* and CH* as the most stable free energy states in the mechanism. It would be expected that CO* is the most abundant surface species under reaction conditions due to the lower energy barrier of CO₂* dissociation to form CO* ($\Delta G^\ddagger=0.45$ eV), compared to barriers of CO* hydrogenation (CO*+H*→CHO* $\Delta G^\ddagger=1.42$ eV) and CH* formation (CHO*+*→CH*+O* $\Delta G^\ddagger=0.93$ eV). Also, CH* can easily overcome the small barrier of 0.63 eV to form CH₂*. Based on a simple examination of the calculated competing free energy surfaces for rWGS and CO₂ methanation on Ru(0001), it would be expected that the most abundant surface intermediate would be CO*, although the favored reaction pathway (CO vs. CH₄ production)

1 and rate and selectivity controlling steps cannot be predicted based on the shape of the free
2 energy landscapes alone.

3
4 **Figure 2:** Potential energy diagram of competing pathways for CO₂ reduction by H₂ on Ru(0001). The rWGS
5 (CO formation) and methanation (CH₄ formation) pathways are shown. The most favorable pathways for CO₂
6 methanation and rWGS are shown in green. The elementary steps in red are associated with product
7 evolution from the catalyst. The pathways shown in light blue are competing potential pathways for the initial
8 hydrogenation of CO₂ and conversion of CO* to CH*. All energies are reported relative to CO₂* + 8 H*. Gibbs
9 free energies were calculated at 500 K and atmospheric pressure.

10 The inclusion of van der Waals forces in DFT calculations has shown to stabilize
11 larger molecules on catalytic surfaces and have little effect on the adsorption energies of
12 smaller molecules.[76] To analyze the effect of van der Waals forces in the CO₂ conversion
13 pathways on Ru(0001), the BEEF-vdW functional was used in the calculation of possible
14 CHO* hydrogenation pathways that included larger intermediate molecules. The results
15 (provided in Supplementary Material, Figure S1) agree well with calculations performed
16 using the RPBE functional. Both functionals predict that pathways involving larger
17 intermediates (such as CHOH* and CH₂O*) are less favorable, in comparison to the routes
18 with smaller molecules (CH* and OH*) and can be excluded from kinetic studies of reaction

mechanism. Based on this comparison, the RPBE calculated values were used in the microkinetic modeling.

3.2. Microkinetic model

A steady state microkinetic model of the 18 elementary step reaction system (listed in Table S4) was solved for the surface coverage of all reaction intermediates. Figure 3a shows the surface coverage of the most abundant (>0.1% coverage) surface species as a function of temperature (480-520 K) at atmospheric pressure and stoichiometric methanation reactant concentrations (CO₂:4H₂, no inert is included). Figure 3a shows that in the temperature range of 480-520 K, the Ru(0001) surface is predominantly covered by CO* (46%-68%) and H* (31%-53%). CO* and H* are the two main species competing for the surface adsorption sites under atmospheric conditions explored here. Because CO₂* dissociation ($\Delta H_{rxn} = -1.0$ eV) is slightly more exothermic than H₂ dissociative adsorption ($\Delta H_{rxn} = -0.91$ eV), the forward energy barrier of CO* hydrogenation steps are relatively high ($\Delta H^\ddagger_{H-CO^*} = 1.31$ eV and $\Delta H^\ddagger_{CO-H^*} = 1.77$ eV) and H* and O* are easily consumed by elementary steps with lower activation energies (O*+H*→OH*+*, $\Delta H^\ddagger = 1.15$ eV and OH*+H*→H₂O*+*, $\Delta H^\ddagger = 1.03$ eV), CO* is the dominant surface species at temperature below 510 K and $P_{H_2} < 0.7$ bar. These results agree with *in-situ* FTIR spectroscopic measurements that consistently show strong signals of CO* compared to smaller intensities of other surface species.[11–13,17,25,35–37,42,43] It is also important to point out that H* vibrational modes cannot be detected in FTIR measurements. Although it was postulated earlier that CH* may be a significant surface species based on an inspection of the free energy pathway, the formation of CH₄ from CH* apparently occurs with low enough energy barriers to minimize

CH* coverage under reaction conditions. The low surface concentrations of other key intermediates in the methanation pathway, such as CHO* and CH_x* species, indicate that these species are highly reactive and it can be expected that their identification in spectroscopic experiments would be difficult. Figure 3a also shows that with increasing temperature the concentration of CO* decreases while H* coverage increases, which can be attributed to the increased number of adsorbed CO* crossing the hydrogenation reaction barrier to form CHO* and eventually CH₄. The lower CO* concentration provides more adsorption sites available for H* species to bind.

Figure 3: Microkinetic model predictions of surface coverage for the most abundant surface species (> 0.01 fractional coverage), a) as a function of temperature at 1 bar total pressure and stoichiometric methanation feed composition (CO₂:4H₂), b) as a function of CO₂ partial pressure at 500K and constant H₂ partial pressure (P_{H2}=0.1 bar), and c) as a function of H₂ partial pressure at 500 K and constant CO₂ partial pressure (P_{CO2}=0.1 bar).

Figures 3b and c show the most abundant surface species coverage as a function of CO₂ and H₂ partial pressures, respectively. The surface coverages were calculated at a temperature of 500 K and total pressure of 1 bar. The partial pressure of CO₂ (H₂) was varied in the range of 0.1-0.9 bar while the partial pressure of the other reactant was kept constant at 0.1 bar (varying amount of inert gas is assumed to balance the total pressure).

The results show that under atmospheric reaction conditions, regardless of the feed composition explored, CO* and H* are the most abundant surface species. It can be seen in Figure 3b that as CO₂ partial pressure is increased from 0.1 to 0.9 bar, CO* coverage increases slightly by replacing surface H* ($\Delta\theta=0.16$). Conversely, Figure 3c shows that a higher concentration of H₂ in the reactant mixture results in an increase in H* coverage and decrease in CO* coverage ($\Delta\theta=0.26$). While the absolute magnitude of the coverage changes was small, the relative change in H* coverage with varying reactant partial pressure is significant, which is expected to have an impact on the reactivity of the surface.

Experimental FTIR studies have shown the surface coverage of CO*, the most abundant FTIR-detectable species, is about 20%-40% of saturation coverage. Therefore it is expected that there should be a considerable number of vacant sites present on the surface under reaction condition, which is not captured by our model. We believe this is because the destabilizing effects of increasing surface coverage on CO* and H* binding energies was not considered in our microkinetic model. It has been shown that at high CO* coverages, >50%, repulsive interactions of surface species can have a significant effect on binding energies. [77] As the CO* coverage during CO₂ reduction reaction is not expected to exceed 40%, this is not expected to significantly impact mechanistic insights gained from the study. However, we believe including an accurate account of surface coverage effects in the calculation of binding energies would improve the calculated free site concentrations. A rigorous study to include the correct coverage dependent surface kinetic would require kinetic Monte Carlo (kMC) simulations which involves numerous DFT calculations to account for various adsorbate configurations and is computationally expensive and outside the scope of this work.[78]

To investigate the effect of feed composition on the CH₄ production rate, the turn over frequency (TOF) for CH₄ formation was calculated as a function of H₂ partial pressure at 500 K, 1 bar total pressure, constant CO₂ partial pressure of 0.1 bar and varying amounts of inert gas depending on H₂ partial pressure. Variations in the calculated TOF and CO* coverage as a function of H₂ partial pressure in the feed stream are shown in Figure 4a. CH₄ TOF is positively correlated with the variation in H₂ partial pressure, where a change in H₂ partial pressure from 0.1 to 0.6 bar causes a 27% increase in the TOF for CH₄ formation (from 1.67×10^{-4} to 2.12×10^{-4} s⁻¹). The coupled inverse correlation of CO* coverage and positive correlation of CH₄ TOF with the H₂ partial pressure in the feed stream observed in Figure 4a was also observed experimentally by Prairie et al.[36] In this study, CO₂ reduction by H₂ on Ru catalysts was investigated under similar reaction conditions as Figure 4a (H₂ partial pressure varying in the range of 0.1-0.6 bar at temperature of 463 K, atmospheric pressure and CO₂ partial pressure of 0.13 bar), using *in situ* diffuse reflectance FTIR spectroscopy (DRIFTS). CO* coverage was quantified by normalizing the band integrals associated with CO* during the hydrogenation reaction to the value for the CO* saturated catalyst.[36] A 70% increase in the CH₄ production rate (from 7.4 to 12.6 μmol/g.s) and 7% decrease in relative CO* coverage was measured with a change in H₂ partial pressure from 0.1-0.6 bar, as shown in Figure 4b.[36] The agreement between trends in theoretical and experimentally derived changes in CH₄ TOF (30% versus and 70% increase) and relative CO* coverage (7% versus 28%) as a function of H₂ partial pressure provide confidence in the microkinetic model for qualitatively describing experimental systems.

Figure 4: a) Microkinetic model predictions of TOF for CH₄ production (1/s) and CO coverage as a function of H₂ partial pressure in the reactant mixture at 1 bar total pressure, 500 K, and fixed CO₂ partial pressure (P_{CO₂} = 0.1 bar). b) Experimentally measured CH₄ production rate (μmol/g/s) and CO coverage as a function of H₂ partial pressure at 1 bar total pressure, 463 K, and fixed CO₂ partial pressure (P_{CO₂} = 0.13 bar), adapted from Prarie et al.[36]

Experimentally measured reaction orders with respect to H₂ partial pressure are in the range of 0.5-1.0,[17,27,79] which are larger than the value calculated based on the data in Figure 4a (about 0.13). The dependence of CH₄ production on CO₂ partial pressure was also investigated through its variation in the range of 0.1- 0.9 bar at temperature of 500 K, total pressure of 1 bar and constant H₂ partial pressure of 0.1 bar (data not shown here). The reaction order with respect to CO₂ partial pressure for CH₄ formation was found to be -0.32, which is lower than reported values in the range of 0.1-0.5. The apparent activation energy calculated with our model is about 47 Kcal/mol which is larger than experimentally measured apparent barriers in the range of 19-25 Kcal/mol.[17,27] We believe the discrepancies observed between the calculated and experimentally measured partial

1 pressure dependence and apparent activation barriers are mainly related to the
2 underestimation of vacant sites, which will be discussed more in detail in section 3.3.

3 It is important to note that the absolute values of TOF obtained from DFT-based
4 microkinetic modeling are known to have uncertainties of several orders of
5 magnitudes.[80] In addition, as discussed above, the exclusion of coverage dependence of
6 adsorption energies for surface species is believed to cause an underestimation of vacant
7 site concentration by the microkinetic model. Furthermore, the magnitude of adsorbate
8 coverage is also difficult to quantify through *in-situ*, spectroscopy. While calculated rates,
9 reaction orders and coverages are difficult to quantitatively relate to experimental values,
10 it is possible to quantitatively compare the trends of the calculated rates and coverage with
11 experimental measurements under similar reaction conditions due to a cancellation of
12 errors in DFT calculations. Thus, we believe that the reasonable agreement between
13 experimental observed trends and our model predictions in Figure 4 and the justifiable
14 differences between measured and predicted reaction orders and activation enthalpies
15 (see more discussion below) provide evidence that the microkinetic model is a reasonable
16 representation of experimental systems.

17 As mentioned in the Introduction, Ru catalysts are known to be highly selective
18 towards CH₄ production, rather than catalyzing rWGS. To ensure that the microkinetic
19 model accurately captures this behavior, catalytic selectivity toward CH₄ production
20 ($S_{CH_4} = r_{CH_4} / (r_{CH_4} + r_{CO})$) was calculated as a function of temperature and CO₂ partial pressure.
21 Under stoichiometric feed composition (CO₂:4H₂) and 1 bar total pressure, in the
22 temperature range of 480-520 K, Ru(0001) exhibits a high CH₄ selectivity in the range of
23 97% to >99%, increasing with temperature, Figure 5a. These results are in agreement with

experimentally measured selectivity of Ru catalyst particles towards CH_4 formation and observed temperature dependence of the selectivity.[10,14,17,35,36] Figure 5b shows the dependence of CH_4 selectivity on CO_2 partial pressure, calculated at a temperature of 500 K, atmospheric pressure and H_2 partial pressure of 0.1 bar. Ru(0001) is calculated to be selective for CH_4 production in the entire range of explored CO_2 partial pressures, but shows an negative correlation with the increasing CO_2 partial pressure. The calculated CH_4 selectivity drops from 98% to 95% as CO_2 partial pressure increases from 0.1 to 0.9 bar. This is consistent with the conclusions drawn in the previous sections regarding the correlation of CH_4 production rate with H^* surface coverage and its inverse correlation with CO^* surface coverage and CO_2 partial pressure.

Figure 5: Microkinetic model prediction of CH_4 selectivity, a) as a function of temperature at 1 bar total pressure and stoichiometric methanation feed composition ($\text{CO}_2\text{:4H}_2$) and, b) as a function of CO_2 partial pressure at 1 bar total pressure, 500 K and constant H_2 partial pressure ($\text{P}_{\text{H}_2}=0.1$ bar).

To summarize, the calculated microkinetic model predicted high selectivity (>95%) to CH_4 for CO_2 reduction by H_2 on Ru(0001) at atmospheric pressure for a wide range of reactant partial pressures and temperatures of 480-520 K. Over the range of considered conditions, the surface was covered predominantly by CO^* and H^* . It was found that there

is a positive correlation between H^* coverage and CH_4 production rate. The observed trends were in good agreement with various experimental reports, providing confidence in mechanistic conclusions drawn from the calculated microkinetic model.

3.3. Sensitivity Analysis

To determine the RLS for CH_4 production in the microkinetic model, $X_{RC,i}$ was calculated for all elementary steps in a temperature range of 480-520 K, at 1 bar total pressure and stoichiometric feed composition ($CO_2:4H_2$), Figure 6a. Under these reaction conditions CHO^* dissociation was identified as the primary RLS for CH_4 formation. This is consistent with previous experimental and theoretical studies that have suggested H-assisted CO bond cleavage is the slowest step in CO_2 hydrogenation towards CH_4 production.[26,37,46] The results from the degree of rate control analysis, coupled with previous studies, provide strong evidence that CO_2 methanation on Ru occurs through CHO^* formation and has a RLS of CHO^* dissociation.

Figure 6: a) Degree of rate control, X_{RC} , for elementary steps that exhibit significant control ($|X_{RC,i}| > 0.01$) for the CH_4 formation rate. b) Degree of selectivity control, X_{SC} , for elementary steps that exhibit significant control ($|X_{SC,i}| > 0.01$) of selectivity for CH_4 formation. $X_{RC,i}$ and $X_{SC,i}$ were calculated at a total pressure of 1 bar and stoichiometric methanation feed composition ($CO_2:4H_2$) in the temperature range of 480-520 K.

The elementary step, $O^* + H^* \rightarrow OH^*$, has slight negative $X_{RC,i}$ at lower temperatures. This indicates that an increase in the rate of this step will have an impeding effect on the CH_4 formation rate. All other elementary steps have $X_{RC,i}$ values close to zero ($<10^{-3}$), indicating that they have little or no effect on the overall CH_4 formation rate. The negligible impact of $COOH^*$ formation and dissociation steps on the overall reaction rate ($X_{RC,4,5} < 10^{-3}$) further substantiates the assertion made in previous section that CO_2 dissociation followed by hydrogenation is the more feasible CO_2 activation route compared to the direct CO_2 hydrogenation pathway on Ru.

The degree of selectivity control, $X_{SC,i}$, for CH_4 formation was calculated for all elementary steps using equation 2. It should be noted that a modified selectivity definition ($S_{CH_4} = r_{CH_4}/r_{CO}$) was used in the $X_{SC,i}$ calculations, compared to how selectivity was calculated in Figure 5. Defining selectivity as the ratio of CH_4 and CO formation rates, makes it possible to directly analyze the impact of a change in the activation barrier of a single elementary step on the difference of apparent activation barriers for competing CO and CH_4 formation, ($X_{SC,i} = \ln(r_{CH_4}/r_{CO})/\ln(k_i) \approx (\Delta H_{CH_4}^\ddagger - \Delta H_{CO}^\ddagger)/\Delta H_i^\ddagger$). Figure 6b shows the calculated $X_{SC,i}$ values of the elementary steps that have the largest impact on selectivity for CH_4 formation in the temperature range of 480-520 K and 1 bar total pressure with a feed composition of $CO_2:4H_2$. The degree of selectivity control for CH_4 formation has primarily a strong positive correlation with the CHO^* dissociation step, consistent with the degree of rate control analysis in Figure 6a. The CO^* desorption step has a large negative degree of selectivity control for CH_4 formation indicating that CO^* desorption is the primary RLS for CO production in the rWGS pathway. From these results it can be concluded that the two main elementary steps determining selectivity of late transition metal catalysts (those with

similar electronic structure to Ru) for methanation versus the rWGS reaction are CHO* dissociation and CO* desorption.

Based on the identified RLS, $\text{CHO}^* \rightarrow \text{CH}^* + \text{O}^*$, a rate expression was derived for the CH_4 formation reaction in the form of equation 3 where r_{CH_4} is the CH_4 production rate, P_{CO_2} , P_{H_2} and $P_{\text{H}_2\text{O}}$ are partial pressures of CO_2 , H_2 and H_2O , respectively and α , β and γ are kinetic parameters (for details see section 5 of Supplementary Material).

$$-r_{\text{CH}_4} = \frac{\alpha P_{\text{CO}_2} P_{\text{H}_2}^{1.5}}{P_{\text{H}_2\text{O}} \left(1 + \beta \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} + \gamma P_{\text{H}_2}^{0.5} \right)^2} \quad (3)$$

It is important to note that equation 3 is derived for CH_4 formation pathway only with the assumption of a single RLS, CHO* dissociation. The contributions of other elementary steps that have a smaller impact on the kinetics of the reaction system and CO production route are not captured with this rate expression. The derived rate expression can be used to explain the wide range of reaction orders and activation barriers reported in the literature for CH_4 formation reaction on Ru, which will strongly depend on the experimental conditions and relative concentration of dominant surface species.[17,27,79] The discrepancies observed between the calculated and experimentally measured partial pressure dependences and activation barriers, as well as among the experimental measurements alone, can be explained based on the following analysis of the rate expression in equation 3 (see section 5 of Supplementary Material for a detailed analysis). The three terms inside the parentheses in the denominator of equation 3 represent surface concentration of vacant sites (*), CO* and H* respectively, which are expected to be present at similar concentrations during reaction conditions. The underestimation of surface

vacant site concentration in our model, $\theta^* \sim 0$, increases CO* and H* concentrations and the contribution of the second and third terms inside the parentheses to the reaction rate. The increased negative contribution of these two terms will reduce the order of reaction with respect to P_{CO_2} and P_{H_2} (see details in section 5 in Supplementary Material), hence the microkinetic model predicts reaction orders that are smaller than experimentally measured values ($n_{CO_2} = -0.32$ and $n_{H_2} = 0.13$, compared to experimental values of $n_{CO_2} = 0.1-0.5$ and $n_{H_2} = 0.5-1$). In a similar analysis in the Supplementary Material (section 5.1) it is shown that variations in the contribution of the CO* and H* concentration terms in the rate expression can significantly influence the calculated apparent activation barrier, which we believe is the main reason for the overestimated activation barrier obtained from the microkinetic model ($\Delta H_{app} = 47$ Kcal/mol compared to experimental values of 19-25 Kcal/mol). We expect that a model, where surface coverage effects are incorporated accurately, will predict more accurate vacant site concentrations and improved reaction orders and apparent activation barriers.

To understand how the competition between CHO* dissociation and CO* desorption can be used to explain the trend in selectivity for late transition metals (CO production on Pt and Pd and CH₄ production on Rh and Ru), reaction free energies and barriers of the two steps were calculated for Pt, Pd, Ni, Rh and Ru. The free energies in Figure 7 were calculated using DFT-derived formation energies of C* and O* elements on (211) surface terminations by Medford et al.[56] Formation energies for surface species are equivalent to adsorption energies calculated relative to common gas phase reference molecules H₂, H₂O and CH₄. These energies were coupled with scaling relations to calculate adsorption energies of CH* and CHO*, and the HC-O* transition state energy. It is critical to mention

1 that while scaling relations applied here were developed using calculations on stepped
 2 (211) surfaces and our calculations were done on a flat (0001) surface, there is strong
 3 evidence that the coordination number of the active site only impacts the y-intercept of the
 4 scaling relations, rather than the slope.[81] Thus the trend in the adsorption energies and
 5 activation barriers of the selectivity controlling steps predicted by (211) or flat surface
 6 scaling relations should be identical (within error of the scaling relations themselves) and
 7 simply offset by a constant value. As a result, because we are looking only to identify a
 8 trend in the energetics of the two competing elementary steps that correlates with the
 9 experimentally observed trend in selectivity, we believe our use of (211) scaling relations
 10 to perform this analysis is fully justified and would provide identical conclusions compared
 11 to scaling relations developed on flat surfaces. It can be seen in Figure 7a that CO*
 12 desorption free energies (red bars in Figure 7a) for the five metals are similar and vary in
 13 the range of 0.27-0.71 eV. Furthermore, the CO* desorption free energy is essentially
 14 identical (0.57, 0.56 and 0.63 eV) for Pd, Ni and Rh, which have been shown to exhibit very
 15 different selectivity in CO₂ reduction by H₂ at atmospheric conditions, as mentioned
 16 previously. Thus, CO* desorption energy alone cannot be used as a descriptor to predict the
 17 tendency of a metal to promote CO₂ methanation or rWGS. Conversely, CHO* dissociation
 18 activation energies (blue bars in Figure 7a) are significantly different for the investigated
 19 metals. There is a difference greater than 1 eV in the energy barriers of CHO* dissociation
 20 on Pt ($\Delta G^\ddagger=2.51$ eV) and Pd ($\Delta G^\ddagger=2.55$ eV) with the barriers on Ni ($\Delta G^\ddagger=1.44$ eV), Rh
 21 ($\Delta G^\ddagger=1.43$ eV) and a difference of 1.4 eV with that of Ru ($\Delta G^\ddagger=1.18$ eV). The CHO*
 22 dissociation free energies (orange bars in Figure 7a), which are linearly correlated with
 23 activation energies based on BEP relationships,[54,55] show the same trend. Comparison

of the CHO* dissociation free energies shows that the dissociation step switches from endothermic on Pd ($\Delta G=0.64$ eV) and Pt ($\Delta G=0.64$ eV) to exothermic on Ni ($\Delta G=-0.72$ eV), Rh ($\Delta G=-0.75$ eV) and Ru ($\Delta G=-1.07$ eV).

Figure 7: a) Comparison of free energy for CO* desorption, CHO* dissociation activation barrier, and free energy for the CHO* dissociation reaction on Pt, Pd, Ni, Rh and Ru surfaces. b) Comparison of free energy of formation for CHO*, C*, CH* and O* on Pt, Pd, Ni, Rh and Ru (211) surfaces. Values were derived from previously developed scaling relations and DFT calculated formation energies of C* and O*. See Supplementary Material for details on the calculations.[56]

The switch from endothermic to exothermic CHO* dissociation free energies agrees well with experimentally observed selectivity trends. CHO* dissociation is difficult on Pd and Pt surfaces due to its endothermic reaction energy and high activation barrier; hence these are superior rWGs catalysts. Whereas on Ni, Rh and Ru surfaces, CHO* dissociation is exothermic, the barrier for CHO* dissociation is comparable to CO* desorption (an endothermic step) and thus CH₄ is the dominant CO₂ hydrogenation product. Furthermore, Ru exhibits the most exothermic CHO* dissociation free energy of the compared metals and is consistently shown to be the best monometallic methanation catalyst. It is worth mentioning that the mechanism of rWGS on late transition metals was recently shown to occur through COOH* formation and dissociation on Pt and Pd and via direct CO₂

dissociation on Rh and Ru.[30] These mechanistic differences are consistent with our results and do not impact our analysis, because regardless of the mechanism, CO* desorption remained the RLS for rWGS on all metals.

Differences in free energies of the CHO* dissociation elementary step among the compared metals can be decomposed into the impacts of constitutive species. The free energy of CHO* formation, remember this is essentially the adsorption energy of this species, for the considered late transition metals is shown in Figure 7b. Minimal differences exist between the CHO* formation energies on the compared metals due to a direct correlation of the free energy of CHO* formation to the free energy of C* formation (shown in green color bars on Figure 7b), which also varies little on the compared metals. The story is similar for the formation free energy of CH*, due again to direct correlation to C* formation energy, where minimal variation across the compared metals cannot account for the switch from endothermic to exothermic free energy of the CHO* dissociation step. Finally, Figure 7b shows that variations in the O* formation free energy exhibit a significant, ~1 eV, difference comparing Pt and Pt to Ni, Ru and Rh. Clearly the change in O* formation free energy across the late transition metals is primarily responsible for the trends in CHO* dissociation free energy (and as a result CHO* dissociation activation barrier) and thus dictates the switch in CO₂ reduction selectivity from CO to CH₄ observed in this series of late transition metal catalysts. The competition between CO and CH₄ production in CO₂ reduction by H₂ seems to be controlled by the strength of the atomic oxygen-metal surface interaction, which induces a thermodynamic bias towards CH* formation thereby facilitating the kinetics for CH₄ production, without significantly impacting the CO production kinetics.

1 It is interesting to consider our results in light of previous studies that implicate the
2 role of atomic oxygen adsorption energy for understanding CO₂ reduction on metal
3 surfaces. As mentioned above, it was recently shown that the mechanism of rWGS differs
4 on late transition metals switching from a COOH* mediated CO₂ dissociation on Pt, Pd and
5 Ag to direct CO₂ dissociation on Ni, Rh and Cu.[30] It was observed that the increased
6 oxygen adsorption energy on more reactive metals facilitated the direct CO₂ dissociation
7 pathway through the relationship between the oxygen adsorption energy and the CO₂
8 dissociation barrier. Further, a recent report of descriptor based design of catalysts for CO₂
9 hydrogenation to CH₃OH found that an optimum oxygen adsorption energy exists to
10 maximize CH₃OH selectivity that is similar to the oxygen adsorption energy on Cu.[7] This
11 occurs due to the relationship between most intermediates in the CH₃OH synthesis
12 pathway and oxygen adsorption energy through scaling relations. Coupling these results
13 with ours, we observe that increasing oxygen adsorption energy among late-transition and
14 noble metal catalysts is related to increasing levels of CO₂ reduction by H₂. For example, the
15 weakest oxygen adsorption occurs on Ag, Pt and Pd where CO (a 2e⁻ reduction from CO₂) is
16 the dominant product. Cu is the next weakest O* adsorbing metal and produces a
17 combination of CO and CH₃OH (a 6e⁻ reduction from CO₂). Finally the stronger O* adsorbing
18 metals (Ni, Rh and Ru) produce predominantly CH₄ (8e⁻ reduction from CO₂). The higher
19 exothermicity of the CO_x hydrogenation steps induced by increasing O* adsorption energy
20 and the resulting impact on the kinetics of the reaction, determines the level of CO₂
21 reduction past the mildest reduction product, CO. Fundamentally this can be understood by
22 considering that reduction of CO₂ occurs effectively via the breaking of C-O bonds, whereby
23 strong interactions between the metal surface and O* coupled with reasonable H*

coverage, facilitates the breaking of C-O bonds and the hydrogenation of intermediates. It is worth noting that even if the primary reaction pathway towards CH₄ formation on less reactive metals (Pd and Pt) does not proceed through CHO* formation and dissociation, it must always involve a dissociation step resulting in an adsorbed O* or OH* species on the catalyst surface. Thus, the strength of the metal-O* interaction will always dictate the relative thermodynamic favorability of CH₄ formation pathway and the kinetics of the reaction.

Summarizing these findings, the C* formation free energy varies little across late transition metals and as a result, the CO*, CH* and CHO* formation free energies also vary by only a small amount due to correlations between the formation free energy of C* and these species. Because of these minimal variations, the energetics of the RLS for rWGS, CO* desorption, are similar for late transition metals. However, the O* formation free energy varies with a step function like behavior moving from Pt and Pd to Ni, Rh and Ru and due to existing scaling relations a similar step-function change in the free energy and activation energy for CHO* dissociation exists. This causes a switch in selectivity among late transition metals when CHO* dissociation kinetics become more favorable than CO* desorption. The difference in trends associated with the adsorption energy of species binding through C* and O* was recently associated with a difference in the dominant forces controlling the strength of adsorbate metal binding (attraction for C* based species adsorption and repulsion for O* based species adsorption) [56,82–85] It was shown that while the adsorption energy of species binding through C* and O* both trend with the d-band energy of metal surfaces to a varying degree, the p-band characteristics also are important in controlling adsorption energies. Variations in the relative contribution of d-

band and p-band interactions account for variations in the trends of adsorption energies of species binding through O* and C* across late transition metals and therefore selectivity in CO₂ reduction by H₂. Our mechanistic conclusions agree with a recent assertion that selectivity in CO₂ reduction can be correlated with the d-band center.[19] However, we point to the importance of differentiation between adsorbates binding through C* and O* on the kinetics of competing rWGS and methanation steps and the role that both d-band and p-band characteristics play in dictating this differentiation.

4. Conclusions

The mechanism of CO₂ reduction was investigated over Ru(0001) using DFT calculations and mean field microkinetic modeling. A reaction mechanism consisting of 18 elementary steps was proposed. Energetic pathways of competing reactions were explored and direct CO₂ dissociation followed by hydrogenation of CO* to CHO* was identified as the prominent pathway for CH₄ production. The microkinetic model successfully predicted experimentally observed trends of surface coverage variations with temperature and reactant partial pressures, as well as CH₄ selectivity and rate dependence on feed composition. It was demonstrated through sensitivity analysis that CHO*→CH*+O* is the RLS in CH₄ formation, whereas CO* desorption is the RLS for CO production via rWGS. Although CHO* dissociation and CO* desorption steps control selectivity, comparison of these species binding energies among late transition metal catalysts does not explain experimentally observed differences in selectivity. On the other hand, the tendency of the late transition metals for CH₄ formation was found to correlate well with the affinity of the metals for O* binding. It is shown that depth of catalytic CO₂ reduction by H₂ on late transition metal catalysts is directly related to the catalysts' oxygen adsorption strength,

where weaker oxygen binding metals can only reduce CO₂ mildly to CO, whereas stronger oxygen binding metals reduce CO₂ more deeply to CH₄.

Acknowledgements

P.C. acknowledges funding from University of California, Riverside and the National Science Foundation Grant, CHE-1301019. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575.

References

- [1] A.T. Bell, B.C. Gates, D. Ray, Basic Research Needs: Catalysis for Energy, Washington D.C., 2008. doi:10.2172/927492.
- [2] R.A. Khatri, S.S.C. Chuang, Y. Soong, M. Gray, Thermal and chemical stability of regenerable solid amine sorbent for CO₂ capture, *Energy and Fuels*. 20 (2006) 1514–1520. doi:10.1021/ef050402y.
- [3] J.C. Hicks, J.H. Drese, D.J. Fauth, M.L. Gray, G. Qi, C.W. Jones, Designing adsorbents for CO₂ capture from flue gas-hyperbranched aminosilicas capable of capturing CO₂ reversibly, *J. Am. Chem. Soc.* 130 (2008) 2902–2903. doi:10.1021/ja077795v.
- [4] C.W. Jones, CO₂ Capture from Dilute Gases as a Component of Modern Global Carbon Management, *Annu. Rev. Chem. Biomol. Eng.* 2 (2011) 31–52. doi:10.1146/annurev-chembioeng-061010-114252.
- [5] C.H. Yu, C.H. Huang, C.S. Tan, A review of CO₂ capture by absorption and adsorption, *Aerosol Air Qual. Res.* 12 (2012) 745–769. doi:10.4209/aaqr.2012.05.0132.
- [6] K.M.K. Yu, I. Curcic, J. Gabriel, S.C.E. Tsang, Recent advances in CO₂ capture and utilization., *ChemSusChem*. 1 (2008) 893–899. doi:10.1002/cssc.200800169.
- [7] F. Studt, I. Sharafutdinov, F. Abild-Pedersen, C.F. Elkjær, J.S. Hummelshøj, S. Dahl, et al., Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol, *Nat. Chem.* 6 (2014) 320–324. doi:10.1038/nchem.1873.
- [8] C. Liu, B. Yang, E. Tyo, S. Seifert, J. DeBartolo, B. von Issendorff, et al., Carbon Dioxide Conversion to Methanol over Size-selected Cu₄ Clusters at Low Pressures, *J. Am. Chem. Soc.* 137 (2015) 8676–8679. doi:10.1021/jacs.5b03668.
- [9] M. Behrens, F. Studt, I. Kasatkin, S. Köhl, M. Hävecker, F. Abild-pedersen, et al., The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts, *Science*. 336 (2012) 893–897.
- [10] T. Abe, M. Tanizawa, K. Watanabe, A. Taguchi, CO₂ methanation property of Ru

- nanoparticle-loaded TiO₂ prepared by a polygonal barrel-sputtering method, *Energy Environ. Sci.* 2 (2009) 315–321. doi:10.1039/b817740f.
- [11] M. Jacquemin, A. Beuls, P. Ruiz, Catalytic production of methane from CO₂ and H₂ at low temperature: Insight on the reaction mechanism, *Catal. Today*. 157 (2010) 462–466. doi:10.1016/j.cattod.2010.06.016.
- [12] A. Beuls, C. Swalus, M. Jacquemin, G. Heyen, A. Karelovic, P. Ruiz, Methanation of CO₂: Further insight into the mechanism over Rh/γ-Al₂O₃ catalyst, *Appl. Catal. B Environ.* 113–114 (2012) 2–10. doi:10.1016/j.apcatb.2011.02.033.
- [13] A. Karelovic, P. Ruiz, Mechanistic study of low temperature CO₂ methanation over Rh/TiO₂ catalysts, *J. Catal.* 301 (2013) 141–153. doi:10.1016/j.jcat.2013.02.009.
- [14] F. Solymosi, A. Erdöhelyi, Hydrogenation of CO₂ to CH₄ over alumina-supported noble metals, *J. Mol. Catal.* 8 (1980) 471–474. doi:10.1016/0304-5102(80)80086-1.
- [15] K. Ravindranathan Thampi, J. Kiwi, M. Grätzel, Methanation and photo-methanation of carbon dioxide at room temperature and atmospheric pressure, *Nature*. 327 (1987) 506–508.
- [16] F. Solymosi, A. Erdöhelyi, T. Bánsági, Methanation of CO₂ on Supported Rhodium Catalysts, *J. Catal.* 68 (1981) 371–382. doi:10.1016/S0167-2991(08)64768-0.
- [17] F. Solymosi, A. Erdöhelyi, M. Kocsis, Methanation of CO₂ on Supported Ru Catalysts, *J. Chem. Soc., Faraday Trans. 1*. 77 (1981) 1003–1012.
- [18] D.E. Peebles, D.W. Goodman, J.M. White, Methanation of carbon dioxide on Ni(100) and the effects of surface modifiers, *J. Phys. Chem.* 87 (1983) 4378–4387. doi:10.1021/j100245a014.
- [19] M.D. Porosoff, J.G. Chen, Trends in the catalytic reduction of CO₂ by hydrogen over supported monometallic and bimetallic catalysts, *J. Catal.* 301 (2013) 30–37. doi:10.1016/j.jcat.2013.01.022.
- [20] K. Yaccato, R. Carhart, A. Hagemeyer, A. Lesik, P. Strasser, A.F. Volpe, et al., Competitive CO and CO₂ methanation over supported noble metal catalysts in high throughput scanning mass spectrometer, *Appl. Catal. A Gen.* 296 (2005) 30–48. doi:10.1016/j.apcata.2005.07.052.
- [21] G.D. Weatherbee, C.H. Bartholomew, Hydrogenation of CO₂ on Group VIII Metals, II. Kinetics and Mechanism of CO₂ Hydrogenation on Nickel, *J. Catal.* 77 (1982) 460–472. doi:10.1016/0021-9517(81)90040-3.
- [22] P. Panagiotopoulou, D.I. Kondarides, X.E. Verykios, Selective methanation of CO over supported noble metal catalysts: Effects of the nature of the metallic phase on catalytic performance, *Appl. Catal. A Gen.* 344 (2008) 45–54. doi:10.1016/j.apcata.2008.03.039.
- [23] J.C. Matsubu, V.N. Yang, P. Christopher, Isolated Metal Active Site Concentration and Stability Control Catalytic CO₂ Reduction Selectivity, *J. Am. Chem. Soc.* 137 (2015) 3076–3084. doi:10.1021/ja5128133.
- [24] W. Wang, S. Wang, X. Ma, J. Gong, Recent advances in catalytic hydrogenation of carbon dioxide, *Chem. Soc. Rev.* 40 (2011) 3703–3727. doi:10.1039/c1cs15008a.

- [25] P. Panagiotopoulou, D.I. Kondarides, X.E. Verykios, Mechanistic aspects of the selective methanation of CO over Ru/TiO₂ catalyst, *Catal. Today*. 181 (2012) 138–147. doi:10.1016/j.cattod.2011.05.030.
- [26] W. Wei, G. Jinlong, Methanation of carbon dioxide: an overview, *Front. Chem. Sci. Eng.* 5 (2011) 2–10. doi:10.1007/s11705-010-0528-3.
- [27] M. Kuśmierz, Kinetic study on carbon dioxide hydrogenation over Ru/ γ -Al₂O₃ catalysts, *Catal. Today*. 137 (2008) 429–432. doi:10.1016/j.cattod.2008.03.003.
- [28] M.R. Gogate, R.J. Davis, Comparative study of CO and CO₂ hydrogenation over supported Rh-Fe catalysts, *Catal. Commun.* 11 (2010) 901–906. doi:10.1016/j.catcom.2010.03.020.
- [29] A. Trovarelli, C. Mustazza, G. Dolcetti, J. Kašpar, M. Graziani, Carbon dioxide hydrogenation on rhodium supported on transition metal oxides, *Appl. Catal.* 65 (1990) 129–142. doi:10.1016/S0166-9834(00)81593-6.
- [30] L. Dietz, S. Piccinin, M. Maestri, Mechanistic Insights Into CO₂ Activation via Reverse Water-Gas Shift On Metal Surfaces, *J. Phys. Chem. C*. 119 (2015) 4959–4966. doi:10.1021/jp512962c.
- [31] S. Akamaru, T. Shimazaki, M. Kubo, T. Abe, Density functional theory analysis of methanation reaction of CO₂ on Ru nanoparticle supported on TiO₂ (101), *Appl. Catal. A Gen.* 470 (2014) 405–411. doi:10.1016/j.apcata.2013.11.016.
- [32] S.-T. Zhang, H. Yan, M. Wei, D.G. Evans, X. Duan, Hydrogenation mechanism of carbon dioxide and carbon monoxide on Ru(0001) surface: a density functional theory study, *RSC Adv.* 4 (2014) 30241–30249. doi:10.1039/C4RA01655F.
- [33] D.R. Alfonso, Further Theoretical Evidence for Hydrogen-Assisted CO Dissociation on Ru(0001), *J. Phys. Chem. C*. 117 (2013) 20562–20571. doi:10.1021/jp403828y.
- [34] J.L. Falconer, E. Zağli, Adsorption and Methanation of Carbon Dioxide on a Nickel/Silica Catalyst, *J. Catal.* 62 (1980) 280–285.
- [35] M. Marwood, R. Doepper, A. Renken, In-situ surface and gas phase analysis for kinetic studies under transient conditions The catalytic hydrogenation of CO₂, *Appl. Catal. A Gen.* 151 (1997) 223–246. doi:10.1016/S0926-860X(96)00267-0.
- [36] M.R. Prairie, A. Renken, J.G. Highfield, K. Ravindranathan Thampi, M. Grätzel, A fourier transform infrared spectroscopic study of CO₂ methanation on supported Ruthenium, *J. Catal.* 129 (1991) 130–144. doi:10.1016/0021-9517(91)90017-X.
- [37] S. Eckle, H.-G. Anfang, R.J. Behm, Reaction Intermediates and Side Products in the Methanation of CO and CO₂ over Supported Ru Catalysts in H₂-Rich Reformate Gases, *J. Phys. Chem. C*. 115 (2011) 1361–1367.
- [38] D. Cheng, F.R. Negreiros, E. Aprà, A. Fortunelli, Computational Approaches to the Chemical Conversion of Carbon Dioxide, *ChemSusChem*. 6 (2013) 944–965. doi:10.1002/cssc.201200872.
- [39] E. Vesselli, M. Rizzi, L. De Rogatis, X. Ding, A. Baraldi, G. Comelli, et al., Hydrogen-Assisted Transformation of CO₂ on Nickel: The Role of Formate and Carbon Monoxide, *J. Phys. Chem. Lett.* 1 (2010) 402–406. doi:10.1021/jz900221c.

- [40] H. Falsig, B. Hvolbæk, I.S. Kristensen, T. Jiang, T. Bligaard, C.H. Christensen, et al., Trends in the catalytic CO oxidation activity of nanoparticles, *Angew. Chemie - Int. Ed.* 47 (2008) 4835–4839. doi:10.1002/anie.200801479.
- [41] C.J. Zhang, P. Hu, A. Alavi, A density functional theory study of CO oxidation on Ru(0001) at low coverage, *J. Chem. Phys.* 112 (2000) 10564–10570. doi:10.1063/1.481690.
- [42] M.A. Henderson, S.D. Worely, An infrared study of the hydrogenation of carbon dioxide on supported rhodium catalysts, *J. Phys. Chem.* 89 (1985) 1417–1423. doi:10.1021/j100254a023.
- [43] N.M. Gupta, V.S. Kamble, V.B. Kartha, R.M. Iyer, K. Ravindranathan Thampi, M. Grätzel, FTIR Spectroscopic Study of the Interaction of CO₂ and CO₂+H₂ over Partially Oxidized Ru/TiO₂ Catalyst, *J. Catal.* 146 (1994) 173–184.
- [44] B.T. Loveless, C. Buda, M. Neurock, E. Iglesia, CO chemisorption and dissociation at high coverages during CO hydrogenation on Ru catalysts, *J. Am. Chem. Soc.* 135 (2013) 6107–6121. doi:10.1021/ja311848e.
- [45] J.L.C. Fajín, J.R.B. Gomes, M.N. D. S. Cordeiro, Mechanistic Study of Carbon Monoxide Methanation over Pure and Rhodium- or Ruthenium-Doped Nickel Catalysts, *J. Phys. Chem. C.* (2015) 150710111820004. doi:10.1021/acs.jpcc.5b01837.
- [46] O.R. Inderwildi, S.J. Jenkins, D.A. King, Fischer-Tropsch Mechanism Revisited: Alternative Pathways for the Production of Higher Hydrocarbons from Synthesis Gas, *J. Phys. Chem. C.* 112 (2008) 1305–1307. doi:10.1021/jp710674q.
- [47] M.P. Andersson, F. Abild-Pedersen, I.N. Remediakis, T. Bligaard, G. Jones, J. Engbæk, et al., Structure sensitivity of the methanation reaction: H₂-induced CO dissociation on nickel surfaces, *J. Catal.* 255 (2008) 6–19. doi:10.1016/j.jcat.2007.12.016.
- [48] M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, CO activation pathways and the mechanism of Fischer-Tropsch synthesis, *J. Catal.* 272 (2010) 287–297. doi:10.1016/j.jcat.2010.04.012.
- [49] F. Abild-Pedersen, Computational catalyst screening: Scaling, bond-order and catalysis, *Catal. Today.* (2015). doi:10.1016/j.cattod.2015.08.056.
- [50] L.C. Grabow, M. Mavrikakis, Mechanism of Methanol Synthesis on Cu through CO₂ and CO Hydrogenation, *ACS Catal.* 1 (2011) 365–384. doi:10.1021/cs200055d.
- [51] J.K. Nørskov, F. Abild-Pedersen, F. Studt, T. Bligaard, Density functional theory in surface chemistry and catalysis., *Proc. Natl. Acad. Sci. U. S. A.* 108 (2011) 937–43. doi:10.1073/pnas.1006652108.
- [52] C.T. Campbell, Micro- and macro-kinetics: their relationship in heterogeneous catalysis, *Top. Catal.* 1 (1994) 353–366. doi:10.1007/BF01492288.
- [53] C.T. Campbell, Finding the Rate-Determining Step in a Mechanism, *J. Catal.* 204 (2001) 520–524. doi:10.1006/jcat.2001.3396.
- [54] J.N. Brønsted, Acid and Basic Catalysis, *Chem. Rev.* 5 (1928) 231–338.
- [55] M.G. Evans, M. Polanyi, Further Considerations on the thermodynamics of chemical

- equilibria and reaction rates, *J. Chem. Soc., Faraday Trans. 1*. 32 (1936) 1333–1359.
- [56] A.J. Medford, A.C. Lausche, F. Abild-Pedersen, B. Temel, N.C. Schjødt, J.K. Nørskov, et al., Activity and Selectivity Trends in Synthesis Gas Conversion to Higher Alcohols, *Top. Catal.* 57 (2014) 135–142. doi:10.1007/s11244-013-0169-0.
- [57] A.J. Medford, A. Vojvodic, J.S. Hummelshøj, J. Voss, F. Abild-Pedersen, F. Studt, et al., From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis, *J. Catal.* 328 (2015) 36–42. doi:10.1016/j.jcat.2014.12.033.
- [58] J. Enkovaara, C. Rostgaard, J.J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, et al., Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method, *J. Phys. Condens. Matter*. 22 (2010) 253202. doi:10.1088/0953-8984/22/25/253202.
- [59] B. Hammer, L.B. Hansen, J.K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, *Phys. Rev. B*. 59 (1999) 7413–7421. doi:10.1103/PhysRevB.59.7413.
- [60] J. Wellendorff, K.T. Lundgaard, A. Møgelhøj, V. Petzold, D.D. Landis, J.K. Nørskov, et al., Density functionals for surface science: Exchange-correlation model development with Bayesian error estimation, *Phys. Rev. B*. 85 (2012) 235149. doi:10.1103/PhysRevB.85.235149.
- [61] P. Panagiotopoulou, D.I. Kondarides, X.E. Verykios, Selective methanation of CO over supported Ru catalysts, *Appl. Catal. B Environ.* 88 (2009) 470–478. doi:10.1016/j.apcatb.2008.10.012.
- [62] H. Abrevaya, M.J. Cohn, W.M. Targos, H.J. Robota, Structure Sensitive Reactions Over Supported Ruthenium Catalysts during Fischer Tropsch Synthesis, *Catal. Letters*. 7 (1990) 183–189.
- [63] A.M. Abdel-Mageed, S. Eckle, R.J. Behm, High selectivity of supported Ru catalysts in the Selective CO Methanation - Water makes the difference, *J. Am. Chem. Soc.* (2015) 150626152444002. doi:10.1021/jacs.5b03689.
- [64] P. Panagiotopoulou, D.I. Kondarides, Effect of the nature of the support on the catalytic performance of noble metal catalysts for the water–gas shift reaction, *Catal. Today*. 112 (2006) 49–52. doi:10.1016/j.cattod.2005.11.026.
- [65] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B*. 13 (1976) 5188–5192. doi:10.1103/PhysRevB.16.1748.
- [66] G. Henkelman, B.P. Uberuaga, H. Jónsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, *J. Chem. Phys.* 113 (2000) 9901–9904.
- [67] Y.-A. Zhu, D. Chen, X.-G. Zhou, W.-K. Yuan, DFT studies of dry reforming of methane on Ni catalyst, *Catal. Today*. 148 (2009) 260–267. doi:10.1016/j.cattod.2009.08.022.
- [68] A. a. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J.K. Nørskov, How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels, *Energy Environ. Sci.* 3 (2010) 1311–1315. doi:10.1039/c0ee00071j.
- [69] S.R. Bahn, K.W. Jacobsen, An object-oriented scripting interface to a legacy electronic

- structure code, *Comput. Sci. Eng.* 4 (2002) 56–66.
- [70] A.A. Gokhale, S. Kandoi, J.P. Greeley, M. Mavrikakis, J.A. Dumesic, Molecular-level descriptions of surface chemistry in kinetic models using density functional theory, *Chem. Eng. Sci.* 59 (2004) 4679–4691. doi:10.1016/j.ces.2004.09.038.
- [71] J. a. Dumesic, D.F. Rudd, L.M. Aparicio, J.E. Rekoske, A.A. Trevino, *The Microkinetics of Heterogeneous Catalysis*, Washington DC, 1993.
- [72] G.S. Gusmão, P. Christopher, A General and Robust Approach for Defining and Solving Microkinetic Catalytic Systems, *AIChE J.* 61 (2015) 188–199. doi:10.1002/aic.
- [73] I.M. Ciobîcă, V. Santen, Carbon monoxide dissociation on planar and stepped Ru(0001) surfaces, *J. Phys. Chem. B.* 107 (2003) 3808–3812. doi:10.1021/jp030010x.
- [74] S. Shetty, A.P.J. Jansen, R.A. van Santen, Direct versus hydrogen-assisted CO dissociation, *J. Am. Chem. Soc.* 131 (2009) 12874–12875. doi:10.1021/ja9044482.
- [75] H. Li, G. Fu, X. Xu, A new insight into the initial step in the Fischer-Tropsch synthesis: CO dissociation on Ru surfaces, *Phys. Chem. Chem. Phys.* (2012) 16686–16694. doi:10.1039/c2cp43176a.
- [76] F. Studt, F. Abild-Pedersen, J.B. Varley, J.K. Nørskov, CO and CO₂ Hydrogenation to Methanol Calculated Using the BEEF-vdW Functional, *Catal. Letters.* 143 (2013) 71–73. doi:10.1007/s10562-012-0947-5.
- [77] L.C. Grabow, A. a. Gokhale, S.T. Evans, J. a. Dumesic, M. Mavrikakis, Mechanism of the Water Gas Shift Reaction on Pt: First Principles, Experiments, and Microkinetic Modeling, *J. Phys. Chem. C.* 112 (2008) 4608–4617. doi:10.1021/jp7099702.
- [78] L.C. Grabow, B. Hvolbæk, J.K. Nørskov, Understanding Trends in Catalytic Activity: The Effect of Adsorbate–Adsorbate Interactions for CO Oxidation Over Transition Metals, *Top. Catal.* 53 (2010) 298–310. doi:10.1007/s11244-010-9455-2.
- [79] M.S. Duyar, A. Ramachandran, C. Wang, R.J. Farrauto, Kinetics of CO₂ methanation over Ru/ γ -Al₂O₃ and implications for renewable energy storage applications, *J. CO₂ Util.* 12 (2015) 27–33. doi:10.1016/j.jcou.2015.10.003.
- [80] A.J. Medford, J. Wellendorff, A. Vojvodic, F. Studt, F. Abild-pedersen, K.W. Jacobsen, et al., Assessing the reliability of calculated catalytic ammonia synthesis rates, *Science.* 345 (2014) 197–200. doi:10.1126/science.1253486.
- [81] F. Calle-Vallejo, D. Loffreda, M.T.M. Koper, P. Sautet, Introducing structural sensitivity into adsorption – energy scaling relations by means of coordination numbers, *Nat. Chem.* 7 (2015) 403–410. doi:10.1038/nchem.2226.
- [82] M.M. Montemore, J.W. Medlin, A Unified Picture of Adsorption on Transition Metals through Different Atoms, *J. Am. Chem. Soc.* 136 (2014) 9272–9275.
- [83] M.M. Montemore, J.W. Medlin, Predicting and comparing C-M and O-M bond strengths for adsorption on transition metal surfaces, *J. Phys. Chem. C.* 118 (2014) 2666–2672. doi:10.1021/jp5001418.
- [84] J. Greeley, J.K. Nørskov, M. Mavrikakis, Electronic structure and catalysis on metal

1 surfaces, *Annu. Rev. Phys. Chem.* 53 (2002) 319–348.
2 doi:10.1146/annurev.physchem.53.100301.131630.
3 [85] H. Xin, S. Linic, Exceptions to the d-band model of chemisorption on metal surfaces:
4 The dominant role of repulsion between adsorbate states and metal d-states, *J. Chem.*
5 *Phys.* 132 (2010) 221101. doi:10.1063/1.3437609.

6