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C-O Bond Activation and C-C Bond Formation Paths in Catalytic CO Hydrogenation

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Publication Date
2012

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C-O Bond Activation and C-C Bond Formation Paths in Catalytic CO Hydrogenation

By

Brett Thomas Loveless

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemical and Biomolecular Engineering in the Graduate Division of the University of California, Berkeley

Committee in charge:

Professor Enrique Iglesia, Chair
Professor Alexis T. Bell
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Fall 2012
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Abstract

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Professor Enrique Iglesia, Chair

Fundamental mechanistic details regarding C-O bond activation and C-C bond formation remain unknown in catalytic CO hydrogenation to heavy hydrocarbons (Fischer-Tropsch synthesis, FTS). This study combines infrared spectroscopic and density functional theory methods (DFT) to first identify relevant surface CO coverages during FTS; reaction energy profiles are then calculated using DFT to determine the most facile path for C-O bond activation on Ru cluster surfaces. Kinetic responses of CO conversion rates and product selectivities to changes in H₂ and CO pressures are measured in a packed-bed reactor at differential conversions on supported Ru catalysts to develop kinetic rate equations for FTS and corresponding sets of elementary reaction steps consistent with such equations. The effects of Ru cluster size on CO turnover rates, CO adsorption equilibrium constants, and CO conversion activation energies are also investigated to identify the Ru coordination environment in which C-O bonds are activated during FTS. C-C bond formation paths are then probed by measuring the effects of H₂ and CO pressures on chain termination parameters, which provide a direct comparison between chain termination and chain propagation rates for all hydrocarbon products. DFT simulations of chain termination and chain propagation reactions as a function of carbon number are also performed to elucidate relevant C-C bond formation paths and to explain the apparent difficulty in forming the initial C-C bond during FTS.

Calculated CO adsorption energies decrease with increasing CO coverage on flat extended Ru(0001) surfaces and on 201-atom Ru cluster surfaces (Ru₂₀₁) due to repulsive intermolecular CO-CO interactions; such repulsive interactions are alleviated on convex Ru₂₀₁ cluster surfaces, which can also accommodate CO coverages above a stoichiometric monolayer by forming geminal di-carbonyl species (also identified by infrared spectroscopy of CO adsorbed on Ru/SiO₂ catalysts) at under-coordinated corner and edge Ru atoms. DFT-derived activation barriers for H-assisted CO activation paths on Ru atoms in high-coordination environments are much smaller than such barriers for direct CO bond cleavage, suggesting that CO species can be activated via H-assistance on low-index surfaces. Direct CO activation barriers on under-coordinated corner and step-edge sites are larger than those on high-coordination sites because of unfavorable interactions between di-carbonyl species and vicinal C-O activation transition states. DFT results also show that C-O bond activation during FTS is irreversible, and any direct CO
dissociation path, as a result, is inconsistent with the reported effects of H\(_2\) and CO pressures on FTS rates.

Kinetic responses of CO conversion turnover rates and oxygen rejection selectivities (in the form of H\(_2\)O/CO\(_2\) formation rate ratios) are consistent with CO activation occurring predominantly via H-assisted paths on Ru catalysts, irrespective of Ru cluster size. CO adsorption equilibrium constants and CO conversion activation energies, measured during FTS reactions, are the same for both small and large Ru clusters, suggesting that CO activation occurs in similar environments on both particle sizes. Turnover rates are smaller on small (~ 1 nm) Ru clusters than rates on large (~ 7 nm) Ru clusters when rates are normalized by the total number of exposed Ru atoms. Such differences in turnover rates become much smaller, however, when rates are normalized by the number of exposed Ru atoms in low-index (111) planes; CO activation reactions, as a result, likely occur on Ru atoms in high-coordination environments on both small and large Ru clusters.

Increases in H\(_2\) pressures increases CH\(_4\) selectivities and decreases C\(_{5+}\) selectivities because chain termination is proportional to the concentration of surface hydrogen atoms (H*); chain growth reactions are favored at high CO pressures where termination is suppressed. Chain termination parameters for C\(_1\) species (to CH\(_4\)) are much larger than such parameters for C\(_2\), species; these parameters depend exponentially on the difference in chain termination and chain propagation barriers for each carbon number. DFT-derived activation barriers for termination reactions (via hydrogenation of surface alkyl species) are small and independent of chain length because such reactions are exothermic and proceed via early transition states; chain propagation reactions (via alkyl migration to vicinal CO* species), however, proceed through late transition states where surface-alkyl bonds are broken completely. Surface methyl (CH\(_3\)) species are bound to surfaces much more strongly than ethyl (C\(_2\)H\(_5\)) and propyl (C\(_3\)H\(_7\)) species; C\(_1\) propagation barriers, as a result, are much larger than such barriers for C\(_2\), hydrocarbons, a result that is consistent with measured chain termination parameters on supported Ru catalysts. A steady-state treatment of reactive intermediates shows that CO conversion rate equations must include terms for CO consumption via CO activation as well as for consumption via chain growth with CO* monomers.

This study unites experiment and theory to investigate fundamental C-O bond activation and C-C bond formation reactions on relevant catalyst surfaces during FTS. Kinetic and selectivity measurements remain vital in the understanding of elementary steps involved in bond making and bond breaking events in FTS reactions; theoretical tools can be used to investigate elementary reactions under conditions inaccessible to experimental techniques. Theoretical investigations of FTS reactions must be performed on cluster surfaces at high CO* coverages that prevail during relevant conditions because CO* coverages affect thermodynamic and kinetic parameters included in apparent activation energies. High CO* coverages also weaken Ru-CO bonds, consistent with quasi-equilibrated CO adsorption-desorption processes during FTS. This study is an important example of how theoretical calculations performed on relevant surfaces at relevant coverages are an invaluable compliment to experimental studies of metal-catalyzed chemical reactions.
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Acknowledgements

I would like to thank, first and foremost, Professor Enrique Iglesia for his guidance throughout the entire dissertation process; his tenacious pursuit of knowledge has shown me how science should really be done. The methods that I have developed under his tutelage, with the help of past and current Iglesia group members, will be an invaluable set of skills that I will carry with me throughout my career. I would also like to thank Professor Matt Neurock and his research group at the University of Virginia for taking the time to share their expertise in computational chemistry with an experimentalist like myself.

The graduate school life would not have been the same without the friendship and camaraderie within the group of individuals in my incoming class. I would like to thank especially Rob Carr, Dana Nadler, Ted Amundsen, Bryan McCulloch, Keith Beers, Adam Gross, Colin Cerretani, Megan Hoarfrost, Joanna MacKay, Adrienne Rosales, Hannah Murnen, Maureen Tang, and Sean Dee for making graduate school a one of a kind experience. I’d also like to thank Raj Gounder, Dave Flaherty, Sebastian Kunz, Dante Simonetti, Brian Weiss, Will and Megan Vining, Jarred Ghilarducci, Kevin Haas, Penny Gunterman, Andrew and Kristen Jones, Will Knaeble, Stephanie Paquin, Michele Sarazen, Allie Landry, and Stan Herrmann for their friendship, technical expertise, and in many cases, both. I am also forever indebted to my family and non-Berkeley friends for their support prior to, and continuing beyond, graduate school.

Last, but certainly not least, I’d like to thank Alexandra Naastad for enduring 3+ years of a long-distance relationship with a struggling PhD. student. Benefits of such a relationship included (but were not limited to) countless late-night phone calls due to the two-hour time difference, expensive flights from North Dakota to California (and back), and many birthdays and other important events shared only by a phone call or a care package. Her patience, caring, and flexibility are unparalleled; I could not have asked for a better best friend, and I look forward to spending the rest of my life with her.
Chapter 1

Unresolved Mechanistic Details of C-O Bond Activation and C-C Bond Formation in Catalytic CO Hydrogenation

Fischer-Tropsch synthesis (FTS) is a well-known industrial process that converts synthesis gas mixtures (CO + H$_2$) on Group VIIIB metals (Fe, Co, Ru) to long-chain, linear hydrocarbons, which can be utilized directly as liquid transportation fuels or converted to other chemicals in downstream processes [1, 2]. FTS is an attractive alternative to fuels and chemicals production from conventional crude oil feedstocks, because synthesis gas can be generated from sources like biomass [3], coal [4], and natural gas [5]. Large-scale FTS processes are operated currently in South Africa and Malaysia [6]; fundamental chemical details regarding C-O bond activation and C-C bond formation in FTS, however, remain unclear despite significant research efforts [7, 8, 9]. This study uses a combination of rigorous experimental (kinetic and selectivity studies, infrared spectroscopy) and theoretical (density functional theory (DFT)) techniques to investigate C-O bond activation and C-C bond formation reactions on Ru catalysts at industrially-relevant conditions.

C-O bond activation in FTS can occur either before or after hydrogen addition to surface-bound CO molecules (CO*). Direct C-O bond cleavage was suggested first by Fischer and Tropsch themselves [10], and many experimental [11, 12, 13] and theoretical [14, 15] studies have since proposed such unassisted CO activation paths. Hydrogenated intermediates in FTS containing intact C-O bonds (H$_x$CO) were also postulated to exist by workers as the U.S. Bureau of Mines [16]; such H-assisted CO activation paths were later supported by results showing incorporation of oxygenated probe molecules into larger hydrocarbon products [17, 18], as well as by theoretical investigations of C-O bond activation on model surfaces at low [19, 20] CO* coverages. Unassisted and H-assisted CO activation paths and subsequent oxygen-removal reactions in FTS are shown in Scheme 1.1. Recent studies have shown kinetic data, oxygen-removal selectivities, and DFT studies at moderate CO* coverages that are consistent with CO activation occurring via H-assistance on Fe and Co catalysts [19]; this work extends to FTS on Ru nanoclusters nearly saturated with CO* species, an important detail that has been identified in previous infrared [21] and isotopic transient [22] studies of FTS but one that has been largely overlooked in both interpreting experimental data and modeling relevant FTS surfaces.

Details regarding C-C bond formation paths are as equally unclear as those regarding C-O activation in FTS. Numerous reactions, including CH$_x$-CH$_x$ coupling [11], H$_x$CO condensation [16], and CO insertion [23] have been proposed to explain hydrocarbon chain growth, and more recent theoretical work has investigated chain growth processes at low CO* coverages [24, 25, 26, 27]. A general chain growth scheme is shown in Scheme 1.2, in which adsorbed hydrocarbon intermediates (C$_n$*) undergo chain termination and chain propagation reactions in FTS [28]. Chain growth can be described rigorously by measuring chain termination parameters, which include chain termination and chain propagation rates, for each carbon number in the product.
distribution [28]. Previous studies have shown that C$_1$ chain termination parameters are much greater than those for larger hydrocarbons [28, 29], indicating that initial C-C bond formation reactions are more difficult than subsequent C-C bond forming reactions. A fundamental understanding of chain growth in FTS requires insights regarding the identity of the growth monomer as well as the mechanism for growth; this study utilizes DFT studies of C-C bond formation reactions on Ru clusters at relevant CO* saturation coverages, coupled with measured chain termination parameters and the effects of H$_2$ and CO on such parameters to investigate how C-C bonds form on catalyst surfaces during FTS.

CO* coverage effects on CO adsorption and CO activation paths are addressed in Chapter 2, in which DFT simulations and infrared spectroscopy are used to show Ru nanoclusters can accommodate CO* coverages above a stoichiometric monolayer (ML) by the formation of geminal di-carbonyl species at low-coordination corner and edge atoms. These near-saturation CO* coverages decrease CO* binding energies and are consistent with quasi-equilibrated CO adsorption-desorption steps during FTS; DFT-derived activation energies are consistent with CO activation occurring via H-assisted paths on high-coordination atoms in (111) terraces on Ru cluster surfaces. Unassisted CO dissociation does not occur to any appreciable extent on CO*-saturated Ru clusters, even on low-coordination sites, where transition states for direct CO dissociation are destabilized via repulsion from vicinal CO* species. Kinetic data, oxygen-rejection selectivities, and apparent activation energies presented in Chapter 3 are consistent with H-assisted paths being the predominant route for CO activation on Ru clusters, irrespective of Ru cluster size. Measured CO adsorption equilibrium constants and effects of Ru cluster size on CO conversion turnover rates suggest that CO activation occurs in similar environments on high-coordination sites on both small (~ 1 nm) and large (~ 7 nm) Ru clusters.

The effects of H$_2$ and CO pressures on product selectivities, primary alkene to n-alkane ratios, and FTS chain termination parameters for Ru catalysts are reported in Chapter 4. Reactions of surface alkyl species (C$_n$H$_{2n+1}$*) with CO* monomers are proposed as the chain growth mechanism in FTS; DFT-derived activation energies for such reactions show that CH$_3$* + CO* reactions are relatively slow because Ru-CH$_3$* bonds, which are broken completely in transition states for chain propagation reactions, are much stronger than Ru-C$_2$, alkyl bonds. Chapter 4 also includes, for the first time, the consequences of CO* chain growth monomers on observed CO conversion rate equations along with preliminary data on the effects of H$_2$ and CO pressures on such equations.

This dissertation combines experiment and theory to resolve longstanding questions regarding C-O bond activation and C-C bond formation reactions in FTS. Rigorous kinetic measurements, rate equation and selectivity analyses, and infrared spectroscopy are coupled with state-of-the-art DFT calculations on nano-scale Ru clusters nearly saturated with CO* to investigate elementary chemical process and to generate conclusions that have been overlooked by previous studies on systems that are less faithful to reality.
Scheme 1.1  H-assisted (blue) and direct (red) CO activation paths during Fischer-Tropsch synthesis; reaction steps are denoted as quasi-equilibrated (\( \rightarrow \)) or irreversible (\( \not\rightarrow \)).

Scheme 1.2  Primary and secondary reactions of adsorbed hydrocarbon chains (\( \text{C}_n^* \)) in FTS reactions (taken from [28]).
References

Chapter 2

CO Chemisorption and Dissociation at High Coverages during CO Hydrogenation on Ru Catalysts

Abstract

Density functional theory (DFT) and infrared spectra are combined here with mechanism-based rate equations to assess the structure and thermodynamics of chemisorbed CO (CO*) and its activation pathways during the Fischer-Tropsch synthesis (FTS). CO* binding becomes weaker with increasing coverage because of strong intermolecular repulsion on flat extended Ru(0001) surfaces and on surfaces of cubo-octahedral clusters with 201 Ru atoms (Ru$_{201}$, 5.3 – 5.6 Å edge length). On Ru(0001), saturation occurs at much lower coverages (CO*/Ru = 0.75) than on Ru$_{201}$ surfaces (CO*/Ru = 1.55), because curvature allows the relaxation of adsorbed adlayers and weakens repulsive interactions. Ru$_{201}$ clusters achieve stable supramonolayer CO* coverages (CO*/Ru > 1) by forming geminal di-carbonyls at corner and edge sites of low coordination. The infrared spectra of CO* on Ru/SiO$_2$ catalysts (~ 7 nm mean diameter) indeed detect mobile CO* adlayers that anneal into dense structures with multiple binding modes, including geminal species, at saturation. Mechanistic interpretations of FTS rate equations provide estimates of activation energies that reflect surfaces at saturation CO* coverages in quasi-equilibrium with CO(g) at catalytic conditions; thus, rigorous comparisons between experiments and theory require that we consider and analyze the dynamics and thermodynamics of adsorbed species at relevant coverages on surfaces resembling those present on catalytic solids. DFT estimates of activation energies show that CO* bond activation occurs predominantly on CO*-saturated (111) terraces and through the essential kinetic assistance of coadsorbed H*, consistent with measured effects of H$_2$ and CO on FTS rates, with oxygen rejection selectivities and with the ubiquitous effects of Ru cluster size on FTS turnover rates. Direct CO* dissociation via reactions with vicinal vacant metal sites show much higher activation barriers on both (111) terraces and on low-coordination exposed Ru atoms, including those at step-edge sites previously claimed as uniquely active and essential for direct CO* dissociation during FTS. Low-coordination sites are rendered unreactive at near-saturation coverages on Ru$_{201}$ clusters because di-carbonyl structures at such sites interact unfavorably with C-O bond activation transition states. DFT-derived activation barriers also show that direct CO* dissociation is irreversible, an observation that is inconsistent with measured FTS rates, which require that such dissociation paths be quasi-equilibrated irrespective of activation site. The prevalence and modest barriers of H-assisted CO* dissociation routes remove the need for the special low-coordination sites otherwise required for direct pathways, which are, in fact, inconsistent with the higher observed reactivity of larger Ru clusters. We expect that these conclusions are also relevant for FTS reactions on Co and Fe surfaces, which show similar rate equations and cluster size effects and on which theory and experiment also support the prevalence of H-assisted CO* dissociation pathways. This study illustrates the feasibility and relevance of theoretical treatments of
the dynamics and thermodynamics of adsorbed species on curved and crowded cluster surfaces, which reflect the state of most relevant catalytic surfaces as turnovers occur and which differ in structure and coverage, and consequently in reactivity, from sparsely-covered extended flat surfaces.

2.1 Introduction

Catalysis on supported metal clusters often occurs at conditions of near-saturation adsorbate coverages, for which coverages significantly influence the binding energies of adsorbed species and their reactivity in surface-catalyzed reactions. In alkane oxidation reactions, for example, changes in surface oxygen coverages cause sharp transitions in kinetic behavior and mechanisms [1, 2, 3]. High coverages favor reactions of intermediates with co-adsorbed species instead of reactions involving vicinal vacant sites; for instance, O₂ dissociation on CO-covered Pt clusters occurs via direct reactions with adsorbed CO (CO*) [4] instead of O₂ reactions with vacant site pairs [5, 6, 7] during CO oxidation at low temperatures. CO hydrogenation to form large hydrocarbons (Fischer-Tropsch synthesis, FTS) also occurs on CO*-covered surfaces, as shown by previous kinetic [8, 9, 10, 11], infrared (IR) spectroscopic [12] and transient isotopic [13] data. The matter of whether C-O bonds are activated directly on vicinal vacant sites (*) or via reactions with co-adsorbed hydrogen atoms (H*) in FTS reactions remains the subject of active debate and significant controversy. Here, we use density functional theory (DFT) and infrared studies to first assess the CO* coverages that prevail during FTS and then to probe the effects of CO* coverages on adsorption energies and C-O bond activation paths on Ru clusters and extended Ru surfaces.

CO consumption rates in FTS reactions decrease strongly with decreasing cluster size on Co [14], Fe [15], and Ru [16] catalysts, indicating that low-coordination metal atoms, prevalent in small clusters [17], are either less reactive than atoms with higher coordination in exposed low-index planes or that these low-coordination sites become unavailable because of strong interactions with adsorbed species during catalysis. In spite of these cluster size effects on FTS rates, several studies have proposed that low-coordination sites are required for direct CO dissociation during FTS reactions [18, 19, 20, 21, 22, 23]. Direct CO dissociation routes are expected to be slow on CO*-covered surfaces, irrespective of the coordination of exposed atoms, because of the dearth of vacancies (*) during FTS reactions at the conditions of high H₂ and CO pressures required for hydrocarbon chain growth. CO* species are much more likely to reside vicinal to chemisorbed hydrogen atoms (H*) than to vacancies (*) because of high H₂ pressures and quasi-equilibrated H₂ adsorption during FTS reactions; as a result, reactions of CO* with H* have been studied as an alternate CO activation route [9, 11, 18, 24, 25, 26]. Such H-assisted routes allow facile CO dissociation on low-index planes of Co and Fe surfaces and are consistent with measured effects of H₂ and CO on FTS rates, with DFT simulations of direct and H-assisted dissociation reactions, and with the preferential formation of H₂O instead of CO₂ on these catalysts as the primary oxygen carrier [9, 10]. FTS rate equations, oxygen rejection selectivities, and chain termination parameters [8, 11, 27] on Ru-based catalysts are similar to those found on Co, suggesting that H-assisted CO dissociation routes also prevail during FTS reactions on Ru cluster surfaces.
Theoretical treatments have been used previously to infer mechanistic details that are inaccessible to direct verification by experiments at the high reactant pressures required for significant chain growth in FTS [18, 21, 24, 28]. These theoretical studies have invariably used extended surfaces with exposed low-index planes at CO* coverages well below saturation. These coverages (CO*/M_{surface} < 0.75) are consistent with the maximum coverages reported from thermal desorption studies of CO* on Co(0001) [29] and Ru(0001) [30] single crystals.

Repulsive intermolecular CO*-CO* interactions at high CO* coverages cannot be relieved on flat extended surfaces via lateral relaxation of adsorbed CO* [30, 31], as typically occurs on metal cluster surfaces with small domains of exposed crystal planes and convex shape [4]. Single crystals can accommodate high adsorbate coverages only via surface reconstruction [19, 32], whereas metal clusters stabilize high adsorbate coverages instead via relaxation of the surface adlayer itself. High adsorbate coverages weaken surface-adsorbate bonds [4]; these effects enhance the mobility of the adsorbed species involved in adlayer relaxation and avoid metal surface reconstruction otherwise required to stabilize high adsorbate coverages.

Here, we explore CO chemisorption on Ru clusters with 201 atoms (diameter = 1.8 nm, Ru_{201}) and containing exposed atoms of diverse coordination. These clusters can achieve monolayer (and even supramonolayer) CO* coverages and allow us to probe the effects of site coordination on the binding and reactivity of CO* on surfaces that represent working catalysts more faithfully than extended flat surfaces with CO* coverages well below monolayer coverages. The effects of CO* coverage on the CO binding strength on these cluster surfaces are compared here with those on extended Ru(0001) surfaces to examine the roles of surface curvature, loosely defined by the differently oriented surface domains of small size, and binding site coordination on CO adsorption energies and CO* dissociation paths.

Ru_{201} cluster surfaces expose low-coordination atoms at corner and edge sites, and DFT treatments indicate that these atoms can interact with more than one CO* molecule which results in CO-to-surface atom (CO*/Ru_{201} \theta_{CO}) ratios significantly greater than unity. These ratios are consistent with the detection of high frequency C-O stretching vibrations associated with Ru carbonyl species [33, 34, 35] on Ru/SiO_{2} catalysts at near-saturation CO* coverages and with the known stability of Ru carbonyls [36]. DFT-derived activation energies for direct and H-assisted CO dissociation paths on CO*-covered Ru_{201} clusters at relevant CO* coverage are then used to assess the extent to which direct and H-assisted CO* dissociation paths contribute to FTS rates on Ru cluster surfaces. Our results show that CO* activation occurs primarily via H-assisted paths on high-coordination Ru atoms in CO*-covered (111) terraces of Ru_{201} cluster surfaces, consistent with FTS rate equations, oxygen rejection selectivities, and cluster size effects on FTS rates; low-coordination sites are not necessary for CO* dissociation when H-assisted paths are available. Direct CO dissociation is unlikely to occur on high-coordination or low-coordination Ru atoms at near-saturation CO* coverages and in any case is inconsistent with reported FTS rate equations.

2.2 Theoretical and Experimental Methods
2.2.1 Computational Procedures

Plane-wave, gradient-corrected periodic DFT calculations were carried out using the Vienna \textit{Ab-initio} Software Package (VASP) [37, 38, 39] with a plane-wave energy cutoff of 396 eV. All calculations used the revised Perdew-Burke-Ernzerhof (RPBE) [40] form of the generalized gradient approximation (GGA) and Vanderbilt ultrasoft pseudo-potentials to describe the core-valence electron interactions [41]. The effects of CO\textsuperscript{*} coverage on CO binding energies were investigated on flat two-dimensional extended Ru(0001) surfaces and on three-dimensional 201-atom Ru clusters (Ru\textsubscript{201}), which expose atoms of different coordination and with potentially different adsorbate binding and catalytic properties. The face-centered cubic (fcc) arrangement of cuboctahedral Ru\textsubscript{201} structures was used because it is the most stable configuration for Ru clusters with \(>\ 140\) atoms [42]; this cluster exposes surface atoms with coordination numbers ranging from six at corner sites to nine at (111) terraces [17]; as a result, Ru\textsubscript{201} clusters seem well-suited to probe the effects of coordination on the binding and reactivity of chemisorbed CO.

Periodic Ru(0001) surfaces were treated as four layers of Ru atoms in a (3x3) unit cell. Adsorbed species and the uppermost two metal layers were fully relaxed, while the bottom two metal layers were fixed at an Ru-Ru distance of 0.2706 nm, estimated as the equilibrium distance by energy optimizations for bulk Ru lattices; these distances agree well with the lattice spacings measured in large Ru crystals (0.27058 nm) [43].

A (3x3x1) gamma-centered \(k\)-point mesh was used to sample the first Brillouin zone for Ru(0001) surfaces; a single gamma-centered \(k\)-point was used for the Ru\textsubscript{201} cluster with a 25 x 25 x 25 Å\textsuperscript{3} unit cell that provided enough vacuum space to avoid interactions between the periodic cluster images. All atoms in the Ru\textsubscript{201} cluster were allowed to relax until electronic energies varied by < 1 \times 10^{-4} \text{ eV} and the forces on all atoms were < 0.05 \text{ eV Å}^{-1}; these convergence criteria were deemed adequate, because a more stringent force convergence criterion (0.01 \text{ eV Å}^{-1}) resulted in CO adsorption energies that were less than 2 \text{ kJ mol}^{-1} different from those carried out using the initial (0.05 \text{ eV Å}^{-1}) criterion on both the bare and CO\textsuperscript{*}-covered Ru\textsubscript{201} surfaces.

The structures and energies of reactants, products, and transition states were calculated for both direct and H-assisted CO\textsuperscript{*} activation paths on (111) terraces of the Ru\textsubscript{201} cluster. The activation energy for the direct path was also calculated on a Ru\textsubscript{201} corner site as well as on a step-edge site that was formed by removing a row of Ru atoms at a (111) terrace edge to compare the reactivity of sites in low-coordination environments with terrace sites in highly-coordinated environments. Terrace sites represent the majority of exposed atoms (75-78\%) for clusters between 8-20 nm; in this size range, FTS turnover rates have been found to be essentially independent of cluster size for Ru [16, 27] and Co [14, 44] catalysts. Low-coordination sites, including step-edges, have been previously proposed as the sites required for direct CO dissociation on Co [19, 21] and Ru [18, 20] catalyst surfaces. Reactant and product states were calculated using the same methods and convergence criteria as for CO chemisorption on Ru\textsubscript{201}; transition state structures were isolated using the nudged elastic band (NEB) [45, 46] and dimer methods [47]. A linear interpolation between reactant and product states was used to generate the initial path (8 or 16 images) for all NEB calculations.
highest energy structure along the converged NEB path was used as the initial guess for the transition state structure, which was moved by the dimer method along the potential energy surface to a saddle point. Dimer convergence was achieved when the maximum force on any atom was < 0.05 eV/Å and the structure was at a saddle point, as determined by a negative curvature of the two-dimensional reaction coordinate.

2.2.2 Catalyst Synthesis Procedures

Silica-supported Ru catalysts (Ru/SiO₂) used in infrared studies of CO chemisorption were prepared using triethanolamine (TEA) ligands [48]. Ru(NO)(NO₃)₃ (0.756 g, Alfa-Aesar, 32 wt.% Ru) was dissolved in a solution of TEA (3.631 g Sigma Aldrich) in deionized H₂O (7.852 g) and added dropwise to SiO₂ gel (4.618 g, PQ Corp., CS-2133, 350 m² g⁻¹, 2.39 mL g⁻¹) to the point of incipient wetness. The SiO₂ was treated previously in flowing dry air (Praxair, extra-dry, 30 cm³ (STP) s⁻¹ g⁻¹) by heating to 773 K (at 0.083 K s⁻¹) and holding for 4 h. The resulting solids were treated in stagnant ambient air at 373 K for 10 h and then heated in flowing dry air (Praxair, extra-dry, 30 cm³ (STP) s⁻¹ g⁻¹) to 673 K (at 0.0167 K s⁻¹) and held for 3 h. These samples were then cooled to ambient temperature and heated in a flowing 10% H₂/He mixture (Praxair, UHP, 50 cm³ (STP) s⁻¹ g⁻¹) to 673 K (at 0.0167 K s⁻¹) and held for 3 h. Samples were passivated by contact with a flowing stream of 0.1% O₂/He (Praxair, UHP, 50 cm³ (STP) s⁻¹ g⁻¹) stream at 303 K for 0.25 h before exposure to ambient air.

2.2.3 Infrared Spectra of CO Chemisorbed on Ru/SiO₂

Catalyst samples were pressed into self-supporting wafers (30–50 mg cm⁻²) and held within an infrared flow cell [49]. Infrared spectra were acquired using a Thermo Nicolet 8700 infrared spectrometer equipped with a HgCdTe (MCT) detector cooled with liquid N₂. Passivated samples were treated by heating to 598 K (at 0.083 K s⁻¹) in 30% H₂/He flow (Praxair, 5.0 Grade, 20 cm³ (STP) s⁻¹ g⁻¹) and holding for 1 h. Samples were then cooled to ambient temperature in flowing He (Praxair, 5.0 Grade, 10 cm³ (STP) s⁻¹ g⁻¹) and exposed to a flowing stream of 0.75% CO/He (Praxair, Certified Standard, 40 cm³ (STP) s⁻¹ g⁻¹) at ambient pressure to prepare CO*-saturated catalyst surfaces; CO*-saturation was confirmed by the invariance of the CO adsorption spectra with CO pressure (0.2 – 0.75 kPa). Absorbance spectra (4000 – 400 cm⁻¹, 4 cm⁻¹ resolution) were obtained by averaging 16 scans per spectrum and subtracting a background spectrum (measured after the H₂/He treatments but before exposure to gaseous CO).

2.3 Results and Discussion

2.3.1 CO* coverage effects on CO binding energies on Ru(0001) surfaces

Figure 2.1 shows the effects of increasing fractional CO* coverages (adsorbed CO molecules per Ru surface atom, θ_CO) on differential CO adsorption energies estimated from DFT on 3x3 cells of Ru(0001) surfaces. The differential CO binding energy (ΔE_{CO,ads}) is defined as:
\[ \Delta E_{\text{CO,ads}} = E_{\text{Ru-CO}_n} - E_{\text{Ru-CO}_{n-1}} - E_{\text{CO}(g)} \]  

Here, \( E_{\text{Ru-CO}_n} \) is the energy of the Ru surface with \( n \) CO* molecules, \( E_{\text{Ru-CO}_{n-1}} \) is the energy of the Ru surface with \( n-1 \) CO* molecules, and \( E_{\text{CO}(g)} \) is the energy of one CO(g) molecule. CO adsorption energies (-158 ± 1 kJ mol\(^{-1}\)) did not vary within the accuracy of the methods used for these calculations for coverages between 0 and 0.33 monolayers (ML). Previous DFT simulations [50], as well as infrared [51] and low energy electron diffraction (LEED) [31, 51] data are consistent with a preference for atop CO* binding on Ru(0001). These binding energies are similar to previous DFT estimates (-164 kJ mol\(^{-1}\)) [50] and with CO adsorption energies measured from thermal desorption isolated CO* species on Ru(0001) surfaces (-160 ± 6 kJ mol\(^{-1}\)) of [30].

CO adsorption energies became less negative, indicative of weaker binding, at coverages above 0.33 ML, as a result of CO* binding on vicinal Ru atoms and of the concomitant repulsion within increasingly dense CO* adlayers on Ru(0001) surfaces. Our DFT estimates show that CO adsorption on Ru(0001) becomes endothermic (\( \Delta E_{\text{CO,ads}} > 0 \)) near 0.9 ML CO*, consistent with the sub-monolayer CO* saturation coverages measured on Ru(0001) [30], Co(0001) [29], and Fe(110) [52] single crystals. These sub-monolayer CO* saturation coverages on extended flat surfaces appear to reflect the rigid alignment of CO* adlayers, enforced over macroscopic distances by such extended flat geometries. Rigid adlayer arrangements exacerbate CO*-CO* repulsion and lead to surface restructuring as the sole means to achieve higher coverages [19, 32]; such restructuring becomes unnecessary on clusters because of facile lateral adsorbate relaxation and of the existence of low-coordination surface atoms that can form geminal di-carbonyls to accommodate multiple CO* species at one metal atom [33, 34, 35]. We extend our adsorption calculations to Ru\(_{201}\) clusters in the next section to investigate the effects of binding site coordination on CO binding modes and energies as a function of CO* coverage.

### 2.3.2 CO* coverage effects on CO binding energies on Ru\(_{201}\) clusters

Previous studies have shown that metal clusters allow lateral adlayer relaxations, which minimize repulsive CO*-CO* interactions even at near-saturation CO* coverages [4]. The fcc cuboctahedral Ru\(_{201}\) cluster surface (Figure 2.2) exposes atoms with four distinct coordination numbers (CN = 6, 7, 8, 9), associated with exposed corners, edges, (100) terraces, and (111) terraces, respectively. These distinct sites on Ru\(_{201}\) clusters are used here to probe CO* binding on surfaces with atoms in diverse coordination environments, as well as to probe the effects of coverage on CO* adlayer structures and energetics.

Figure 2.3 shows adsorption energies for isolated CO* species on essentially bare surfaces and for CO* species at 1 ML coverages on exposed metal atoms with different coordination number on Ru\(_{201}\) cluster surfaces. CO adsorption on bare Ru\(_{201}\) surfaces becomes weaker (\( \Delta E_{\text{CO}*} \) changes from -173 to -159 kJ mol\(^{-1}\)) as the coordination number of adsorption sites increases from six at corner sites to nine at (111) terraces; CO adsorption energies also become less negative (-148 to -107 kJ mol\(^{-1}\)) as the coordination
CO* molecules to share Ru atoms in (111) terraces and CO* binding coverage of one of the two CO* molecules bound at edge and corner Ru atoms and exothermic above 1 ML.

Taken together, surfaces, interpreted as curvature, and by Ru coverages is attenuated on Ru. Enforce rigid among significantly from the surface normal (closer to the surface normal (up to 25°)). These deviations increase distances among vicinal CO* species on Ru clusters, while flat extended Ru(0001) surfaces enforce rigid CO* alignments. Intermolecular CO*-CO* repulsion caused at high CO* coverages is attenuated on Ru clusters by interruptions caused by edges, loosely interpreted as curvature, and by Ru-Ru distances larger than in extended Ru(0001) surfaces.

CO adsorption on the (111) terraces of Ru clusters is significantly stronger (-108 kJ mol⁻¹) than on Ru(0001) surfaces (+16 kJ mol⁻¹) at 1 ML CO* coverages. The stronger binding of CO* on metal clusters (relative to extended flat surfaces) at high CO* coverages was previously reported and attributed to lateral adlayer relaxation and stronger M-CO bonding caused by an expansion of the M-M distances in surface and subsurface layers, which shifts the d-band center closer to the Fermi level and enhances back-donation [4]. These proposals are consistent with Ru-Ru distances in surface and subsurface layers on CO*-covered Ru clusters (0.271 to 0.28 nm), which are larger than Ru-Ru spacings in the bulk regions of large crystallites (0.2706 nm). Ru-Ru distances in surface layers increase only slightly (0.0015 nm) on CO*-covered Ru(0001) surfaces compared with bare Ru(0001) surfaces. The edges at the intersections of exposed facets of Ru clusters also allow CO* species at such edges to deviate significantly from the surface normal (up to 25°). These deviations increase distances among vicinal CO* species on Ru clusters, while flat extended Ru(0001) surfaces enforce rigid CO* alignments. Intermolecular CO*-CO* repulsion caused at high CO* coverages is attenuated on Ru clusters by interruptions caused by edges, loosely interpreted as curvature, and by Ru-Ru distances larger than in extended Ru(0001) surfaces.

The exothermic binding of CO* at all Ru surface sites at 1 ML CO* coverages, taken together with previous reports of supra-monolayer (> 1 ML) coverages on Ru/SiO₂ [34, 35], prompted us to calculate CO* binding energies on Ru surfaces at coverages above 1 ML. Figure 2.4 shows the CO* coverage effects on DFT-derived CO adsorption energies on both Ru(0001) and Ru surfaces. CO* binding on Ru surfaces remains exothermic above 1 ML; corner and edge atoms are able to adsorb more than one CO molecule and, in doing so, increase their overall coordination to values similar to those of exposed atoms in (111) terraces. Figure 2.5 shows the structure of the CO* adlayer on Ru surfaces at 1.5 ML; in this structure, geminal di-carbonyl species are present at edge and corner sites with calculated binding energies of -35 to -41 kJ mol⁻¹ for the removal of one of the two CO* molecules bound at edge and corner atoms, respectively. A CO* coverage of 1.5 ML on Ru represents the highest CO* coverage that maintains atop CO* binding at atoms in (111) terraces on Ru surfaces; CO* coverages above 1.5 ML require CO* molecules to share Ru atoms in (111) terraces and lead to Ru-CO-Ru...
bridging species. Infrared data has shown that bridging CO* represent minority species on Ru crystallites at near-saturation CO* coverages [12, 33]; therefore 1.5 ML appears to be the highest attainable coverage on Ru_{201} surfaces that remains consistent with predominant CO* binding in atop positions at high-coordination Ru atoms in terrace environments.

Previous kinetic studies of FTS at near CO*-saturation coverages on Fe, Co, and Ru have reported rate expressions consistent with quasi-equilibrated CO adsorption-desorption processes [8, 9, 10, 11]. CO adsorption-desorption is considered quasi-equilibrated when the adsorption and desorption rates are significantly larger than the net rates of FTS reactions: FTS turnover rates are \((10 – 40) \times 10^3 \text{ s}^{-1}\) on supported Ru/SiO\(_2\) catalysts, at conditions of significant chain growth \((\text{H}_2/\text{CO} = 1.5 – 4, 463 – 480 \text{ K}, 560 – 4000 \text{ kPa})\) [11, 27]. The rate of CO* desorption from the catalyst surface is given by Equation 2:

\[
\frac{r_{\text{des}}(\text{CO}^*)}{A_{\text{des}}} = k_{\text{des}}(\text{CO}^*) = A_{\text{des}} \exp\left(-\frac{E_{\text{des}}}{RT}\right) \tag{2.2}
\]

where \(r_{\text{des}}\) is the CO* desorption rate, \(k_{\text{des}}\) is the desorption rate constant, \((\text{CO}^*)\) is the fractional CO coverage on the catalyst surface, \(A_{\text{des}}\) is the pre-exponential factor for desorption, \(E_{\text{des}}\) is the desorption activation energy, \(R\) is the gas constant, and \(T\) is the temperature. Typical pre-exponential factors are on the order of \(10^{13} \text{ s}^{-1}\) [56] as a result of the large entropy gains associated with detachment of an adsorbed molecule from a surface into the gas phase. CO* desorption activation energies are essentially the same as the adsorption enthalpy (with opposite sign), because molecular adsorption processes are typically non-activated. Sub-monolayer CO* coverages on Ru_{201} surfaces lead to strong CO* binding \((E_{\text{des}} \sim 160 \text{ kJ mol}^{-1})\) that results in desorption rates of \(\sim 10^{-5} \text{ s}^{-1}\) in the 463-483 K temperature range. These desorption rates on Ru_{201} surfaces at sub-monolayer CO* coverages are smaller than FTS rates, and contradict the assumption of quasi-equilibrated CO adsorption-desorption during FTS reactions [8, 9, 10, 11]. CO* desorption energies at 1 ML CO* coverage on Ru_{201} clusters \((E_{\text{des}} = 104 \text{ kJ mol}^{-1}; \text{Figure } 2.4\) give desorption rates \(\sim 10 \text{ s}^{-1}\) consistent with CO adsorption-desorption equilibrium, but infrared spectroscopy on supported Ru catalysts detects supramonolayer coverages at CO*-saturation [34]. Electron paramagnetic resonance (EPR) spectroscopy later confirmed that Ru carbonyl species existed on CO*-saturated Ru clusters [35], consistent with supramonolayer CO* coverages. Supramonolayer (1.5 ML) CO* coverages lead to even smaller desorption barriers \((42 \text{ kJ mol}^{-1}; \text{Figure } 2.4\) on (111) terraces of Ru_{201} and to even faster CO* desorption rates \((2.7 \times 10^5 \text{ s}^{-1})\), also consistent with quasi-equilibrated CO adsorption-desorption during FTS reactions.

The CO* adlayer on Ru_{201} clusters at 1.5 ML CO* coverages contains geminal carbonyl species at low-coordination corner and edge sites. These CO* coverages contain CO* species bound much more weakly than CO* species at lower CO* coverages on these Ru_{201} surfaces. Previous studies have identified Ru(CO)_x \((x = 2-3)\) species using infrared [33, 34, 57, 58] and EPR [35] spectra of CO* species adsorbed on supported Ru catalysts. In the next section, we use infrared spectroscopy to probe CO* species adsorbed on Ru/SiO\(_2\) at near-saturation CO* coverages. DFT vibrational analysis
was not performed on nearly CO*-saturated Ru$_{201}$ surfaces due to the large (500+ atoms) system size, but high-frequency (> 2100 cm$^{-1}$) vibrations observed in infrared spectra are consistent with the strong C-O bonds associated with geminal Ru carbonyl species [33, 57, 58], which our DFT simulations show to be present at corner and edge atoms on Ru$_{201}$ surfaces at near-saturation coverages.

2.3.3 Infrared spectra of CO* on Ru/SiO$_2$ at saturation CO* coverages

The infrared spectra in Figure 2.6 show four absorption bands in the C-O stretching region (1700-2250 cm$^{-1}$) on a Ru/SiO$_2$ catalyst exposed to 0.75 kPa CO at 313 K. H$_2$, O$_2$, and CO chemisorption data showed that the fractional Ru dispersion for this Ru/SiO$_2$ catalyst was 0.12-0.14, which leads to a mean particle size of ~ 7 nm [59]. No changes in spectral features or intensities were detected as CO pressure increased from 0.2 to 0.75 kPa, indicating the presence of saturated CO* adlayers even at these low pressures. Isothermal CO adsorption spectra at 313 K did not change with time, but an increase in temperature from 313 to 363 K in the presence of 0.75 kPa CO decreased the intensity of the weak band at 2070 cm$^{-1}$ and strengthened, sharpened, and slightly shifted the most intense band (2042 cm$^{-1}$ to 2035 cm$^{-1}$; Figure 2.6, inset). The strengthening of the 2042 cm$^{-1}$ band is consistent with higher CO* coverages at 363 K than at 313 K; the narrowing of the 2042 cm$^{-1}$ band is consistent with a more effective dipole alignment of CO* species [4] caused by the annealing of the CO* adlayer into more densely-packed and stable structures at 363 K than at 313 K. Subsequent cooling to 313 K did not lead to detectable changes to the spectrum measured at 363 K. The increasing intensity of the 2042 cm$^{-1}$ band with increasing temperature (313-363 K) is unexpected for an exothermic adsorption process based on thermodynamic arguments. Also, isothermal CO adsorption spectra at 313 K did not change with time, leading us to conclude that CO exposure to Ru/SiO$_2$ at 313 K forms a metastable adlayer that is kinetically-trapped at these lower temperatures. Significant weakening of CO* binding at near-saturation CO* coverages, consistent with our DFT results for both Ru(0001) and Ru$_{201}$ surfaces, apparently allows the mobility required to restructure and densify CO* adlayers at temperatures slightly above ambient.

CO adlayer densification has also been detected on CO-covered Pt clusters during CO oxidation at 383 K; in this case, CO* bands became more intense during an initial induction period in which surfaces approached steady-state CO* coverages and turnover rates decreased to constant values [60]. FTS turnover rates also decrease with time and then reach constant values [61, 62, 63]. These transients appear to reflect surfaces that become less reactive as CO* species form a more stable adlayer; more stable CO* adlayers lead to stronger M-CO bonds and, as a result, less reactive CO* species.

Figure 2.6 shows bands at 2175, 2129, 2042 and 1790 cm$^{-1}$ (313 K, 0.75 kPa CO) in the C-O stretching region of the infrared spectrum. The band at the highest frequency disappeared when the CO-containing gas stream was replaced with pure He, suggesting that it arises from weakly-bound CO* species at frequencies shifted slightly from those for CO(g) (2142 cm$^{-1}$). The most intense band (2042 cm$^{-1}$ in Figure 2.6) has been previously assigned to linear CO* bound atop Ru atoms in the high-coordination environment of Ru(0001) surfaces [51] and to similar atop species on supported Ru
clusters [33, 57, 58]. Atoms at high-coordination terraces represent 73% of all exposed atoms in 7 nm fcc cubooctahedra [17], which is the most stable structure for Ru clusters with > 140 atoms [42]. Corner and edge sites in low-coordination environments account for only 9% of all surface atoms in such cubooctahedra, while atoms in (100) terraces account for the other 18%. Figure 2.6 shows that the 2042 cm\(^{-1}\) band is the most dominant feature in the CO* adsorption spectrum (313-363 K, 0.75 kPa CO) and is consistent with the majority of CO* species forming linear Ru-CO complexes on Ru atoms in high-coordination environments, which account for most of the exposed surface atoms for 7 nm Ru cubooctahedra. The weak broad shoulder at 1790 cm\(^{-1}\) (Figure 2.6) lies within the range of bridge-bound CO* species interacting with vicinal Ru atoms [33] and bridging CO* species exist as minority species only at very high CO* coverages, which cause repulsive CO*-CO* interactions that displace adsorbed CO species from their preferred atop binding sites [30, 51].

The infrared band at 2129 cm\(^{-1}\) (Figure 2.6) reflects the presence of CO* species with stronger C-O bonds than in linear Ru-CO species (2042 cm\(^{-1}\)). The C-O stretching frequency for gas-phase CO is 2142 cm\(^{-1}\) and decreases as CO binds to metal atoms to form linear Ru-CO species (2042 cm\(^{-1}\)). These lower frequencies reflect increasing back-donation of electron density from filled metal d-orbitals into the antibonding \(2\pi^*\) orbital of CO, which leads to weakening and elongation the C-O bonds and strengthening and contraction of M-C bonds [64]. The 2129 cm\(^{-1}\) band, therefore, represents CO* species with stronger C-O bonds (and presumably weaker binding) than linear CO* species in high-coordination environments (2042 cm\(^{-1}\)). Metal electron back-donation (\(\pi\)-bonding interaction) is not the only descriptor of metal-CO bonding, and X-ray emission spectroscopy has shown that \(\sigma\) (repulsive) and \(\pi\) (attractive) bonding contributions compensate one another during CO binding on Ni surfaces [54]. Such compensation effects preclude definitive inferences about the relations between M-C and C-O bond strengths from C-O vibrational spectra without additional theoretical evidence. Our simulations show stable geminal CO* species at low-coordination Ru sites for CO* coverages near saturation (1.5 ML); such species are bound slightly more weakly (by 5-10 kJ mol\(^{-1}\)) than linear atop CO* species. Others have observed infrared bands in the 2070 – 2150 cm\(^{-1}\) range for CO adsorbed on Ru surfaces and assigned them to geminal di-carbonyl and tri-carbonyl species (Ru(CO)_x, x = 2 or 3) on low-coordination Ru surface atoms [33, 57] because of similar frequencies observed for halogenated Ru_xCO_6 complexes. A Raman band at 2127 cm\(^{-1}\) has been reported for axial CO ligands in Ru_x(CO)_{12} crystals [65], for which each Ru atom interacts with four CO ligands; the reported CO* infrared bands at high frequencies (> 2040 cm\(^{-1}\)) lie within the range of C-O vibrations in known Ru carbonyls.

Small metal clusters expose a higher fraction of low-coordination atoms than larger metal clusters [17], and infrared bands for Ru carbonyls, if such species are indeed located preferentially at low-coordination Ru atoms, should become less intense (relative to atop CO* bands) with increasing Ru cluster size. A previous infrared study of CO adsorbed on supported Ru clusters of different size [33] reported a low-frequency band (2028 – 2050 cm\(^{-1}\)) on all Ru clusters, but higher frequency bands (2070 – 2148 cm\(^{-1}\)) were detectable only on Ru clusters smaller 6 nm. These latter bands were assigned to geminal CO* species at low-coordination Ru sites, while the bands at 2028 – 2050 cm\(^{-1}\)
were attributed to CO* at high-coordination binding sites [33]. The 2129 cm\(^{-1}\) band in the infrared spectra of Figure 2.6 is in the range of the high frequency (2070 – 2148 cm\(^{-1}\)) bands associated with geminal Ru carbonyl species. These infrared data, taken together with the DFT-derived CO* adlayer structures (Figure 2.5), are consistent with the presence of geminal CO* species at low-coordination atoms on CO*-covered Ru cluster surfaces.

Our DFT simulations of CO* adsorption on Ru\(_{201}\) surfaces show that CO* coverages above 1 ML are stable and evolve into more densely covered surfaces via the formation of geminal CO* species; these latter species reside at low-coordination corner and edge sites, consistent with the appearance of high frequency bands (2129 cm\(^{-1}\), Figure 2.6) on nearly CO*-saturated Ru/SiO\(_2\) samples. Geminal CO* species at such low-coordination sites were also detected on Rh [66, 67, 68] and Ir [68] clusters and appear to be general features of CO chemisorption on transition metals, which form stable carbonyl complexes as organometallic moieties. The binding of more than one CO* increases the overall coordination number (C.N.) of corner (C.N. = 6) and edge (C.N. = 7) atoms to values similar to those for atoms in high-coordination, close-packed surfaces (C.N. = 9). The tendency of surface metal atoms to maximize their coordination is reminiscent of bond-order conservation principles and of 18-electron configurations of stable organometallic complexes [64]. Repulsive adsorbate-adsorbate interactions become important, and available metal electron density becomes scarce, at the supramonolayer CO* coverages introduced by geminal CO* species at low-coordination Ru sites; these repulsive interactions and depleted electron densities weaken CO* binding (Figure 2.4), giving rise to metastable adlayers that reconstruct and densify at low temperatures (303 K) without requiring reconstruction of the underlying surface (Figure 2.6, inset).

Next, we explore CO activation processes on Ru\(_{201}\) surfaces at near-saturation CO* coverages; on such surfaces, weak CO* binding allows quasi-equilibrated CO adsorption processes [8, 9, 10, 11]. The energetics of elementary steps in CO activation processes are reported here using DFT methods for catalyst surfaces at near CO*-saturation, where CO* coverages strongly influence the binding and reactivity of adsorbed intermediates, for the first time.

2.3.4 \textit{CO* coverage effects on Fischer-Tropsch synthesis activation energies}

Equation 2.3 accurately describes FTS rates on Ru catalysts [8, 11]:

\[
 r_{CO} = \frac{\gamma P_{H_2} P_{CO}}{(1 + \sigma P_{CO})^2}
\]

(2.3)

Here, \( r_{CO} \) is the CO consumption rate, \( P_{H_2} \) and \( P_{CO} \) are the \( H_2 \) and CO pressures, respectively, and \( \gamma \) and \( \sigma \) are kinetic parameters. A set of elementary reaction steps consistent this equation is required to assign chemical meaning to its kinetic parameters and to define the relevant DFT simulations required for comparison with measured
activation energies. We first introduce the elementary steps for H-assisted CO activation paths consistent with Equation 2.3 and proposed previously on Fe and Co surfaces [9].

Scheme 2.1 depicts a sequence of elementary steps for H-assisted CO* activation paths; these steps are consistent with Equation 2.3 when CO adsorption, H$_2$ dissociation, and CO* hydrogenation to HCO* (Scheme 2.1, steps 1-3) are quasi-equilibrated, HCO* hydrogenation (Scheme 2.1, step 4) is irreversible, and CO* is the most abundant surface intermediate (MASI). Quasi-equilibrated CO* dissociation on a vacant surface atom and C* hydrogenation, followed by irreversible CH* hydrogenation would also lead to the form of Equation 2.3, but would require fast and equilibrated CO dissociation and C*-O* recombination. In-situ infrared spectra [12] and transient isotopic studies [13] have shown that FTS reactions occur on surfaces nearly saturated with CO*, consistent with the assumption of CO* being the MASI. CO binds very strongly on bare Ru$_{201}$ surfaces (-160 kJ mol$^{-1}$; Figure 2.4), making it unlikely that CO* will desorb from the catalyst surface in the time scale of a catalytic turnover; CO adsorption/desorption equilibrium, as a result, is not likely to be achieved on bare Ru$_{201}$ surfaces. We have shown here, however, that CO binds much more weakly (-42 kJ mol$^{-1}$) on Ru$_{201}$ surfaces near CO*-saturation than on bare Ru$_{201}$ surfaces (-160 kJ mol$^{-1}$); these near CO*-saturation coverages weaken CO* binding and result in desorption activation barriers that are consistent with quasi-equilibration of CO adsorption-desorption as required by the form of Equation 2.3.

The pseudo-steady state approximation for all reactive intermediates in Scheme 2.1, taken together with the assumptions about the quasi-equilibrium of steps 1-3 and CO* as the MASI gives Equation 2.4:

$$r_{CO} = \frac{K_1K_2K_3k_4P_{H_2}P_{CO}}{(1 + K_1P_{CO})^2}$$  \hspace{1cm} (2.4)

This equation shares the functional form of Equation 2.3, but assigns chemical meanings to the rate parameters ($\gamma = K_1K_2K_3k_4$; $\sigma = K_1$). For CO*-saturated surfaces ($K_1P_{CO} >> 1$), Equation 2.4 becomes:

$$r_{CO} \approx \frac{K_2K_3k_4P_{H_2}}{K_1P_{CO}} = \delta \frac{P_{H_2}}{P_{CO}}$$  \hspace{1cm} (2.5)

in which $\delta$ is a lumped ($K_2K_3k_4K_1^{-1}$) rate constant, with an Arrhenius form:

$$\delta = A \exp \left( \frac{-\Delta E_{app}}{RT} \right) = A \exp \left( \frac{-\left(\Delta H_2 + \Delta H_3 + \Delta E_4 - \Delta H_1\right)}{RT} \right)$$  \hspace{1cm} (2.6)
in which $A$ is the pre-exponential factor, $\Delta E_{\text{app}}$ is the apparent activation energy, $\Delta H_n$ is the enthalpy change for the $n$th elementary step in Scheme 2.1 and $\Delta E_i$ is the activation barrier for the H-assisted CO* dissociation step (step 4).

On these surfaces with saturated CO* adlayers ($K_pP_{\text{CO}} \gg 1$), apparent activation energies ($\Delta E_{\text{app}}$) depend on $-\Delta H_1$, the energy required to form a vacancy by desorbing one CO* molecule (Equation 2.6), which depends strongly on CO* coverage (Figure 2.4), making these activation energies also sensitive to CO* coverage. We have chosen a CO* coverage of 1.5 ML on Ru$_{201}$ clusters (with geminal carbonyl species at low-coordination sites and CO* species that can maintain equilibrium with the contacting CO(g)) as a reasonable representation of Ru cluster surfaces at near-saturation CO* coverages during FTS reactions.

The precise CO* coverages during FTS reactions remain experimentally inaccessible. Surfaces exhibit complex interactions within the adlayer at high CO* coverages; these include intermolecular repulsion and dipole coupling [4, 69, 70]. These interactions are non-additive and thus difficult to determine using current DFT methods. Rigorous determination of the CO* coverage that corresponds to near-CO* saturation, which would require ab-initio based kinetic simulations of CO adsorption, desorption, surface diffusion, as well as the incorporation of all lateral CO*-CO* interactions within the adlayer, is beyond the scope of this work.

These Ru$_{201}$ clusters with 1.5 ML CO* coverages are used next to obtain DFT-derived energies of reactants, products, and transition states for the elementary steps in the H-assisted CO activation path (Scheme 2.1), which is consistent with all rate data on Fe, Co, and Ru catalysts [8, 9, 10, 11]. These DFT-derived apparent activation energies are compared with those for routes involving CO* dissociation on a vicinal vacant Ru atom on both (111) terraces and low-coordination corner and step-edge atoms in these Ru clusters. Previous DFT studies have suggested that direct CO dissociation becomes facile when carried out on vacant metal atoms in low-coordination environments and low CO* coverages [18, 21, 22, 23]. This present study compares for the first time DFT-derived barriers for H-assisted paths on (111) terraces to direct paths on metal atoms with different coordination on Ru clusters at relevant near CO*-saturation coverages.

2.3.5 Contributions from hydrogen-assisted and direct CO dissociation paths in CO hydrogenation on CO*-covered Ru cluster surfaces

H*-assisted CO activation routes (Scheme 2.1) are consistent with the measured effects of $H_2$ and CO on FTS rates and on oxygen removal selectivities for Co-based and Fe-based catalysts and also with DFT estimates of activation energies at 0.5 ML CO* coverages on extended, low-index Fe and Co surfaces [9]. These previous studies are extended here to Ru$_{201}$ clusters saturated with CO* in order to reflect the size, shape, and CO* coverages in working FTS catalysts. In doing so, we examine more rigorously the relative contributions of H-assisted and direct CO dissociation paths on relevant surfaces at saturation CO* coverages.

The H-assisted CO activation path (Scheme 2.1) involves the quasi-equilibrated steps of molecular CO adsorption, $H_2$ dissociation, and CO* hydrogenation to formyl ($HCO^*$), followed by irreversible reactions of $HCO^*$ and H* to form hydroxymethylene...
(HCOH*). This sequence of elementary steps on surfaces near CO* saturation leads to a rate equation with an apparent activation energy that depends on the reaction enthalpies of the quasi-equilibrated steps and the forward barrier for the kinetically-relevant step (Equation 2.6). Figure 2.7 shows the concomitant DFT-derived reaction energy diagram for the H-assisted CO activation routes (Scheme 2.1). A vacant surface site forms first via desorption of CO* from the CO*-covered surface (-ΔH₁ = 42 kJ mol⁻¹). H* then forms by H₂ dissociation in a slightly exothermic step (ΔH₂ = -15 kJ mol⁻¹) before H* reacts with CO* and HCO* in steps 3 and 4, respectively. Figures 2.8 and 9 show the DFT-derived reactant, transition state, and product structures for HCO* and HCOH* formation, respectively, on Ru₂₀₁ (111) terraces at 1.5 ML CO* coverages. CO* reacts with H* via hydrogen insertion into Ru-CO bonds to form the three-center H*-Ru-CO* transition states (Figure 2.8b) that then form stable formyl species (ΔH₃ = 50 kJ mol⁻¹). Hydroxymethylene (HCOH*) forms as HCO* reacts with H* (Figure 2.9) with a barrier (ΔE₄) of 88 kJ mol⁻¹. Figure 2.7 shows that the DFT-derived activation energy for H-assisted CO activation on (111) terraces of Ru₂₀₁ clusters at 1.5 ML CO* coverages is 165 kJ mol⁻¹. These values are much smaller than for unassisted (direct) CO dissociation (322 kJ mol⁻¹), a route that we examine in more detail below; overall H-assisted barriers (165 kJ mol⁻¹) also resemble measured FTS activation barriers (90 – 120 kJ mol⁻¹) on Ru catalysts [11, 27] more closely than those for the direct path. The DFT-derived activation energy for the H-assisted path suggests that CO can be activated with the assistance of H* atoms on low-index planes. Direct CO activation paths, which in any case cannot account for the measured effects of reactant pressures on FTS rates and oxygen removal selectivities, are in fact unnecessary for CO* activation at the near CO*-saturation coverages that prevail during FTS reactions.

The rate equation for the H-assisted CO activation path is predicated on the assumptions that CO and H₂ adsorption, as well as CO* hydrogenation (to HCO*), are quasi-equilibrated. H₂-D₂ isotope scrambling occurs rapidly in H₂/D₂/CO reactant streams on supported Ru [71] and Co [72] catalysts, suggesting that H₂ and D₂ adsorb dissociatively and recombine much faster that forward reactions of H* that lead to CO and H₂ consumption during FTS. The reversibility of CO* hydrogenation to HCO* can be inferred from the forward rate of HCO* hydrogenation (step 4; Scheme 2.1) relative to that of HCO* decomposition to CO* and H* (reverse of step 3; Scheme 2.1). HCO* formation is considered to be in quasi-equilibrium when its reverse (HCO* decomposition) occurs much faster than its forward reaction (HCO* hydrogenation). Both HCO* hydrogenation and HCO* decomposition are surface-catalyzed reactions and, as a result, are likely to have similar pre-exponential factors: therefore, activation barriers for HCO* hydrogenation and HCO* decomposition determine their relative rates. Our DFT calculations show that HCO* decomposition barriers (31 kJ mol⁻¹; Figure 2.7) are much smaller than for HCO* hydrogenation (88 kJ mol⁻¹, Figure 2.7); therefore, we conclude that HCO* decomposition occurs much faster than HCO* hydrogenation, consistent with quasi-equilibrated formation of HCO* intermediates.

The form of Equation 2.4 requires HCO* hydrogenation (step 4; Scheme 2.1) to be the first irreversible step in the H-assisted CO activation mechanism. The irreversible nature of HCO* hydrogenation to HCOH* is determined by the relative rates of its reverse reaction (HCOH* decomposition to HCO* and H*) and of HCOH*
decomposition to CH* and OH* (step 5, Scheme 2.1). Both forward and reverse HCOH* reactions are unimolecular and expected to have similar pre-exponential factors. Figure 2.7 shows that the calculated barrier for HCOH* decomposition (to HCO* and H*) is 21 kJ mol\(^{-1}\) larger than for HCOH* decomposition to CH* and OH*. This barrier difference makes HCOH* decomposition to CH* and OH* faster than HCOH* decomposition to HCO* and H* and the step that forms HCOH* formation (step 4, Scheme 2.1) essentially irreversible. The DFT-derived energies of the intermediates and transition states in the H-assisted CO activation path (Scheme 2.1) are consistent with the quasi-equilibrium assumptions for steps 1-3 and with the kinetic relevance of step 4.

Next, we explore proposals about the relevance of direct CO* dissociation paths and the requirements for special surface sites with low coordination to catalyze such reactions during FTS. CO* activation during FTS may also occur via CO* dissociation on vicinal vacant sites [12, 18, 71, 73, 74]. Scheme 2.2 shows a sequence of elementary steps for such paths in which each step is reversible; we comment later on the kinetic relevance of each step after presenting our DFT-derived energy profile for the direct paths.

Unassisted CO* activation paths involve C-O bond dissociation on a vicinal vacant Ru atom. Figure 2.10 shows the reactant, transition, and product state structures for direct CO* dissociation on (111) terraces of Ru\(_{201}\) clusters (Scheme 2.2, step 6). The DFT-derived activation and reaction energies for direct CO* dissociation steps are 280 kJ mol\(^{-1}\) and 113 kJ mol\(^{-1}\), respectively. The direct path involves the migration of a CO* molecule towards a vacancy and the subsequent tilting of this CO* molecule toward the (111) terrace of the Ru\(_{201}\) surface. The insertion of an exposed Ru atom into the C-O bond activates CO* in the transition state, as shown in Figure 2.10b. The resulting C* and O* fragments then relax into stable bound species at three-fold hollow sites in the product state (Figure 2.10c). The direct CO* dissociation reaction is endothermic (+113 kJ mol\(^{-1}\)) because of the repulsive interactions from metal atom sharing and the through-space interactions of C* and O* between them and with vicinal CO* species. The intrinsic barrier for this reaction (\(\Delta E_b = 280\) kJ mol\(^{-1}\)) is actually larger than that reported for direct CO dissociation on Ru(0001) surfaces (227 kJ mol\(^{-1}\)) at low CO* coverages (<0.25 ML) [20]. The near-saturation CO* coverages on the Ru\(_{201}\) cluster exacerbate the repulsive interactions between the C* and O* species and vicinal CO* species at transition states and lead to higher barriers than those reported on bare Ru(0001) surfaces.

CO* dissociation must be reversible for any direct CO* dissociation path to be consistent with FTS rate equations (Equation 2.3) [8, 9, 10, 11]. The assumption regarding the reversibility of CO* dissociation (step 3, Scheme 2.2) can be probed by comparing the reverse barriers of such steps to the forward barriers of C* hydrogenation to CH* (step 4, Scheme 2.2) on the (111) terraces of CO*-saturated (1.5 ML) Ru\(_{201}\) cluster surfaces. The reversal of direct CO* dissociation steps (C* and O* recombination) has a DFT-derived barrier of 164 kJ mol\(^{-1}\); the calculated activation barrier for C* hydrogenation to CH* is 45 kJ mol\(^{-1}\), suggesting that if C* species formed, they would preferentially react with H* (to form CH*) instead of with O* (to form CO). Thus, any direct CO* dissociation steps on (111) terraces on Ru\(_{201}\) at 1.5 ML CO* coverages would occur irreversibly (and with large activation energies); these simulations suggest that such steps, ubiquitously proposed as the underlying basis for Equation 2.3 on
Co [75], Fe [76, 77], and Ru [12, 71] catalysts, are implausible on the active low-index planes of Ru clusters.

Irreversible CO* dissociation steps, taken along with CO* as the MASi leads to the rate equation:

\[ r_{CO}^{\text{direct}} = \frac{K_1k_6P_{CO}}{(1 + K_1P_{CO})^2} \]  \hspace{1cm} (2.7)

On surfaces nearly saturated with CO* (\( K_1P_{CO} >> 1 \)), Equation 2.7 becomes:

\[ r_{CO}^{\text{direct}} = \frac{k_6}{K_1P_{CO}} = \varepsilon \left( \frac{1}{P_{CO}} \right) \]  \hspace{1cm} (2.8)

in which the effective rate constant \( \varepsilon \) is given by:

\[ \varepsilon = A_{\text{direct}} \exp \left( \frac{-\Delta E_{\text{app}}^{\text{direct}}}{RT} \right) = A_{\text{direct}} \exp \left( \frac{-(\Delta E_6 - \Delta H_1)}{RT} \right) \]  \hspace{1cm} (2.9)

Here, \( A_{\text{direct}} \) is the apparent pre-exponential factor for the direct path and \( \Delta E_6 \) and \( \Delta H_1 \) are the activation energy and reaction enthalpy of step 6 and step 1 in Scheme 2.2, respectively.

Figure 2.11 shows the DFT-derived energy diagram for irreversible, unassisted CO* dissociation on the (111) terraces of Ru\(_{201}\) surfaces at 1.5 ML CO*; the apparent activation energy (-\( \Delta H_1 + \Delta E_6 \)) for this path is 322 kJ mol\(^{-1}\). Enthalpies of quasi-equilibrated elementary steps, as well as activation energies of the kinetically-relevant steps for both the direct and H-assisted CO* activation paths, are shown for comparison in Table 2.1. The apparent activation energy for the direct CO activation path is 157 kJ mol\(^{-1}\) larger than H-assisted CO* activation on (111) terraces of Ru\(_{201}\) clusters at near-saturation CO* coverages (1.5 ML), making direct CO activation unlikely during FTS on Ru catalysts. The irreversible nature of CO* dissociation and its high activation barrier require that active FTS surfaces use more facile bimolecular CO* activation routes to achieve observed reaction rates. Any sequence of elementary steps involving unassisted CO* dissociation must equilibrate this step and the first H* addition to its C* products and require that CH* + H* reactions be the first irreversible step for agreement with measured rate equations (Equation 2.3) [8, 9, 10, 11]. DFT results show that CH* decomposition to C* and H*, the microscopic reverse of C* hydrogenation (Scheme 2.2; step 7), has a higher barrier (150 kJ mol\(^{-1}\)) than CH* hydrogenation to CH\(_2\)* (40 kJ mol\(^{-1}\)), a result that is inconsistent with CH* hydrogenation (Scheme 2.2; step 8) as the first irreversible step in direct CO* activation paths on nearly CO* -saturated (111) terraces of Ru\(_{201}\) clusters. Our DFT-derived reaction energies indicate that CO* dissociation on (111) terraces of CO*-saturated Ru\(_{201}\) clusters is irreversible and involves activation
energies that render such steps unproductive in FTS reactions; as a result, CO* dissociation must occur with H-assistance.

Previous studies have proposed that direct CO dissociation becomes facile (and perhaps reversible) only on low-coordination step-edge or corner sites, thus avoiding the high CO* dissociation barriers prevalent on high-coordination atoms on Ru [18, 20], Co [19, 21], Rh [22], and Fe [23] surfaces at low CO* coverages. These proposals seem to find support in scanning tunneling microscopy (STM) studies by Shell that detect roughening of extended Co(0001) surfaces upon exposure to synthesis gas (4 bar, H₂/CO = 2.523 K) to form monoatomic step-edge sites claimed to act as direct CO* dissociation sites in FTS reactions [19]. DFT studies have concluded also that direct CO* dissociation occurs preferentially at step-edge sites [22]. Next, we calculate activation energies for direct CO* dissociation on low-coordination atoms at Ru₃₀₁ cluster surfaces saturated with CO* and compare them to those for direct and H-assisted CO* activation paths on high-coordination atoms at similar CO* coverages.

2.3.6 CO* dissociation on low-coordination Ru atoms and cluster size effects on FTS rates

DFT-derived reactant, transition state, and product structures for direct CO activation on the Ru₂₀₁ corner site are shown in Figure 2.12. The activation energy (-ΔH_d + ΔE_a; Equation 2.9) for direct CO activation on the Ru₂₀₁ corner site is 356 kJ mol⁻¹, which is actually 34 kJ mol⁻¹ higher than for the same reaction on the (111) terraces of these clusters at the same CO* coverage (1.5 ML). CO* activation at these corner sites involves a transition state in which the incipiently formed C* and O* species interact repulsively with each other and with the vicinal CO* species residing at the low-coordination corner and edge Ru atoms at 1.5 ML CO* coverages (Figure 2.12). These repulsive interactions lead to a larger intrinsic barrier for direct C-O dissociation at corner atoms than at atoms in (111) terraces, because CO* species in (111) terraces are packed less densely than geminal CO* carbonyls at corner and edge sites. At these CO* coverages, Ru atoms in low-coordination environments are even less reactive than those in low-index planes for direct C-O bond dissociation, a conclusion that differs markedly from those derived from DFT simulations of CO* dissociation on bare, extended stepped Ru [18, 20] and Co [21] surfaces.

We have used the (111) terraces of Ru₃₀₁ surfaces at near CO*-saturation coverages as a surrogate for the working catalyst during FTS reactions; these (111) terraces feature highly-coordinated Ru atoms that account for > 75% of surface atoms for Ru clusters > 9 nm [17]. CO consumption turnover rates for clusters in this size range are independent of cluster size and rates are higher than on smaller clusters [16]. FTS turnover rates decrease strongly with decreasing cluster size (clusters smaller than 10 nm) on Ru and Co catalysts [11, 14, 16]. The fraction of surface sites in low-coordination environments increases with decreasing particle size [17]; as a result, the observation that small clusters are less reactive than large clusters is inconsistent with CO activation reactions preferentially occurring on low-coordination corner and edge atoms, irrespective of whether CO activation occurs directly or with H-assistance.
The unreactive nature of corner and edge atoms reflect the requirement for vacant sites at such locations; these vacancies are required for both direct and H-assisted CO activation paths and are unlikely to exist at corner or edge atoms, which tend to maximize their overall coordination number by forming geminal di-carbonyl species (Figure 2.5 and 2129 cm\(^{-1}\) band in Figure 2.6) at the near-saturation CO* coverages. Our DFT-derived activation barriers show that, even in the unlikely event of a vacant Ru corner atom at high CO* coverages, direct CO activation has an effective barrier that is 34 kJ mol\(^{-1}\) larger than the activation energy for direct CO activation on vacant Ru atoms in (111) terraces of Ru\(_{201}\) clusters. CO dissociation reactions on vacant Ru atoms, irrespective of coordination, must overcome activation barriers that are larger than H-assisted CO dissociation on (111) terraces by 157 kJ mol\(^{-1}\) than on vacancies in (111) terraces and by 191 kJ mol\(^{-1}\) on corner vacancies. Low-coordination atoms are therefore not required for CO dissociation during FTS reactions; CO* activation on these sites lead to inconsistencies with both measured rate equations and with DFT-derived activation barriers on CO*-saturated Ru cluster surfaces and cannot be supported by either experiment or theory.

Recent theoretical studies [18, 22, 23] suggest that direct CO* activation occurs preferentially at special B5 step-edge sites (Figure 2.13) on bare Co [21], Ru [18], and Rh [22] surfaces. These sites consist of five metal atoms, two of which are metal atoms (with C.N. of 7) in the upper (111) terrace at the step-edge (Figure 2.13). The remaining three metal atoms that compose the B5 site include two atoms at the base of the step-edge (C.N. = 11) and one remaining metal atom in the exposed lower (111) terrace (C.N. = 9). The DFT-derived reactant, transition state, and product structures for direct CO activation at the uniquely positioned B5 step-edge sites on Ru\(_{201}\) surfaces at 1 ML CO* coverages are shown in Figure 2.13. The intrinsic barrier for direct CO activation at the B5 step-edge site is 125 kJ mol\(^{-1}\); the CO* adsorption energy (\(\Delta H_a\); Equation 2.6), which is required to form a vacant Ru atom on the step-edge site during FTS at saturation coverages, is -119 kJ mol\(^{-1}\). This leads to an effective activation energy (-\(\Delta H^*_a + \Delta E_a\)) of 244 kJ mol\(^{-1}\) for direct CO dissociation at such step-edge sites. The intrinsic direct CO activation barrier (\(\Delta E_a\)) reported here is larger than barriers reported for CO activation on the low-coordination B5 sites and 4F-bridge sites by 36 and 60 kJ mol\(^{-1}\), respectively, on bare extended Ru surfaces [18]. These high barriers on B5 sites of Ru\(_{201}\) surfaces reflect strong repulsive interactions at the required transition states at these high CO* coverages (Figure 2.13). The effective activation energy for direct CO* dissociation at B5 sites is still 91 kJ mol\(^{-1}\) larger than the H-assisted CO* activation path on (111) terraces of CO*-saturated Ru\(_{201}\) cluster surfaces. Such special low-coordination sites are unlikely, in any case, to prevail at relative abundances independent of cluster size and seem more likely to exist, in fact, on small clusters where measured turnover rates are much lower than on larger Ru [16] and Co [14] clusters. Moreover, such sites would have to give not only low activation barriers for CO* dissociation, but also for C* and O* recombination; the latter must be significantly smaller than barriers for C* and CH* reactions with H* for consistency with measured FTS rate equations. Our DFT calculations, however, show that direct CO dissociation at the step-edge site is exothermic (-53 kJ mol\(^{-1}\)), so any forward CO* dissociation barrier would lead to a reverse barrier that is higher than C* hydrogenation barriers (45 kJ mol\(^{-1}\)).
Our DFT estimates of apparent activation energies on Ru$_{201}$ cluster surfaces saturated with CO* are consistent with CO* occurring predominantly on low-index planes via H-assisted paths that involve CO* reacting with co-adsorbed H* atoms, instead of vicinal vacant Ru sites that are scarce at high CO* coverages. These H-assisted paths have been previously proposed to occur on Co [9, 26, 78, 79] and Fe [9, 80] surfaces, and are consistent with measured FTS rates and oxygen removal selectivities for FTS on Ru catalysts [8, 11]. DFT-derived activation energies have shown that direct CO dissociation on vacant Ru atoms, irrespective of coordination, is essentially irreversible and inconsistent with FTS rate equations. We have also shown that CO adsorption becomes weaker with increasing CO* coverage, and that this destabilization of adsorbed CO* species at near-saturation CO* coverages allows the equilibration of CO adsorption-desorption processes during FTS reactions. DFT simulations of chemical reactions on surfaces with relevant adsorbate coverages are necessary because coverages affect adsorbate binding and reactivity. Surface adsorbate coverage also determines the identity of the kinetically-relevant step in heterogeneous catalytic reactions, which makes the use of relevant surface coverages in DFT modeling vital for verifying catalytic mechanisms and predicting catalyst reactivity.

2.4 Conclusions

Fischer-Tropsch synthesis (FTS) occurs on Ru surfaces near CO*-saturation, conditions that can be simulated by CO* coverages above one monolayer on Ru$_{201}$ cluster surfaces. DFT simulations show that supramonolayer coverages on Ru$_{201}$ cluster surfaces evolve via formation of geminal CO* species, consistent with infrared spectra of CO* at saturation coverages on Ru/SiO$_2$, that exist at low-coordination corner and edge atoms. Surface metal atoms tend to increase their coordination number by interacting with multiple adsorbed species at high coverages instead of by surface reconstruction. CO* coverage affects adsorption energies, heats of reaction, and activation energies that contribute to effective activation barriers for CO* activation paths in FTS reactions. DFT simulations show that CO* is activated predominantly via H-assisted paths on high-coordination Ru atoms in (111) terrace environments on CO*-saturated Ru$_{201}$ cluster surfaces, consistent with measured FTS rate equations, oxygen rejection selectivities, and particle size effects on FTS rates. CO* dissociation is essentially irreversible on both high-coordination and low-coordination Ru atoms and, as a result, inconsistent with measured FTS rate expressions. This study shows that high adsorbate coverages control adsorption behavior and reactivity of catalyst surfaces; as a result, the usage of relevant surface coverages is of paramount importance when using theoretical models to simulate heterogeneous catalytic reactions.

2.5 Acknowledgements

The author gratefully acknowledges Professor Matthew Neurock and Dr. Corneliu Buda (both of the University of Virginia) for assistance performing and interpreting some of the DFT simulations reported here, as well as for critical reviewing of this work. The BP Conversion Consortium (BP-XC$^2$) provided financial support for this work. The
author also kindly acknowledges the computational resources provided by the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy, Office of Biological and Environmental Research at the Pacific Northwest National Laboratory. The author also wishes to thank Dr. David Flaherty and Mr. Robert Carr (both of UC-Berkeley) for useful discussions and for manuscript proofreading.
2.6 Figures, Schemes, and Tables

2.6.1 Figures

Figure 2.1 Effect of fractional CO* coverage (adsorbed CO molecules per surface Ru atom) on calculated differential CO adsorption energies for the 3x3 Ru(0001) surface.
Figure 2.2  Idealized structural model of the 201-atom cubooctahedral Ru cluster (Ru$_{201}$) with four distinct surface sites labeled by their nearest-neighbor coordination number. Dashed lines emphasize the exposed (111) and (100) planes by their hexagonal and cubic symmetry, respectively.
Figure 2.3  Site coordination number effects on calculated differential adsorption energies for isolated CO* species (♦) and CO* species at one monolayer (CO*/Ru_{surf}, or $\theta_{CO} = 1$) coverage (■) on Ru$_{201}$ clusters.
Figure 2.4  Comparison of CO* coverage effects on CO adsorption energies on the flat, extended 3x3 Ru(0001) surface (filled symbols) and the cubo-octahedral Ru$_{201}$ nanocluster (open symbols). Adsorption energies are reported for corner sites (□) for 1 ML < $\theta_{CO}$ < 1.5 ML on Ru$_{201}$ because they form geminal di-carbonyl species in this CO* coverage range before subsequent filling of (111) terraces at $\theta_{CO}$ > 1.5; all other reported adsorption energies are for terrace sites on Ru(0001) (▲) and Ru$_{201}$ (△).
Figure 2.5  DFT-calculated structures of geminal CO* species (highlighted with ovals) formed at low-coordination corner and edge sites of Ru$_{201}$ (CO* fractional coverage = 1.5 ML). Under-coordinated Ru atoms bind multiple CO species in order to increase their coordination to resemble Ru atoms in close-packed (111) terraces (enclosed by dashed line). (Carbon = black, oxygen = red, ruthenium = teal)
Figure 2.6  Infrared spectra of a CO*-saturated Ru/SiO$_2$ catalyst (7 nm Ru particles, 0.75 kPa CO, 313 K). CO* saturation was indicated by no observable changes in the IR spectra with increases in CO pressure. Inset: Intensity increase and band sharpening of the 2042 cm$^{-1}$ absorption band as a function of temperature (0.75 kPa, 313 – 363 K)
Figure 2.7  DFT-calculated energy diagram for the elementary steps (Scheme 2.1) involved in the H-assisted CO* activation path on the (111) terrace of Ru$_{201}$ (1.5 ML CO*). The apparent activation energy for the H*-assisted path is a sum of the energy required to generate a vacancy (-ΔH$_1$) from a CO*-covered surface (a), the enthalpy of H$_2$ adsorption (ΔH$_2$; (b) to (c)), the enthalpy of H* addition to CO* (ΔH$_3$; (c) to (d)), and the activation barrier for H* addition to HCO* (ΔE$_4$, (d) to (e)). The barrier for the dissociation reaction of HCOH* to CH* + OH* ((e) to (f)) is shown to justify the irreversibility of HCO* hydrogenation. Transition state energies are denoted by double daggers.
Figure 2.8  DFT-calculated reactant (a), transition (b), and product (c) states for quasi-equilibrated H* addition to CO* to form formyl (HCO*) on (111) terraces of Ru$_{201}$ at 1.5 ML CO* coverage. The reader is referred to Scheme 2.1 for the complete set of elementary steps for the H*-assisted path. (Hydrogen = white, carbon = black, oxygen = red, ruthenium = teal)
Figure 2.9 DFT-calculated reactant (a), transition (b), and product (c) states for irreversible H* addition to HCO* to form hydroxymethylene (HCOH*) on (111) terraces of Ru_{201} at 1.5 ML CO* coverage. The reader is referred to Scheme 2.1 for the complete set of elementary steps for the H*-assisted path. (Hydrogen = white, carbon = black, oxygen = red, ruthenium = teal)
Figure 2.10  DFT-derived reactant (a), transition (b), and product (c) state structures for direct C-O bond activation (Scheme 2.2, step 6) on the (111) terraces of Ru$_{201}$ at 1.5 ML CO$^*$ coverage. The reader is referred to Scheme 2.2 for the complete set of elementary steps for the direct path. (Carbon = black, oxygen = red, ruthenium = teal)
Figure 2.11 DFT-derived energy diagram for vacancy generation and direct CO* activation on (111) terraces of Ru201 (1.5 ML CO*). The apparent activation energy ($\Delta E_{\text{app}}$) for the direct path is a sum of the energy required to generate a vacancy ($-\Delta H_1$) from a CO*-covered surface (a) and the intrinsic activation energy ($\Delta E_6$) for direct activation of CO* by a surface vacancy (b) to form chemisorbed C* and O* species (c); see Scheme 2.2 for a complete description of the elementary steps involved in the direct path. Transition state energies are denoted by double daggers.
Figure 2.12  DFT-derived reactant (a), transition (b), and product (c) state structures for direct C-O bond activation (Scheme 2.2, step 6) on the corner sites of Ru\textsubscript{201} at 1.5 ML CO\textsuperscript{*} coverage. The reader is referred to Scheme 2.2 for the complete set of elementary steps for the direct path. (Carbon = black, oxygen = red, ruthenium = teal)
Figure 2.13  DFT-derived reactant (a), transition (b), and product (c) state structures for direct CO* activation (Scheme 2.2, step 6) on the B5 step-edge site (broken pentagon outline in white) of Ru$_{201}$ at 1 ML CO* coverage. The reader is referred to Scheme 2.2 for the complete set of elementary steps for the direct path. (Carbon = black, oxygen = red, ruthenium = teal)
2.6.2 Schemes

Scheme 2.1 Elementary steps and their associated thermodynamic ($K_n$) and kinetic ($k_n$) constants for H*-assisted CO* activation on Ru surfaces. Quasi-equilibrated steps are denoted by $\equiv$, with $\rightarrow$ denoting the kinetically-relevant step.
**Scheme 2.2** Elementary steps and their associated kinetic ($k_n$) constants for direct CO* activation on Ru surfaces. *Quasi*-equilibrated steps are denoted by $\xrightarrow{\text{chain growth}}$, with $\xrightarrow{\text{kinetically-relevant step}}$ denoting the kinetically-relevant step.
### Table 2.1
Elementary steps and their DFT-calculated reaction enthalpies and activation energies for H*-assisted and direct CO* activation paths on the (111) terrace of Ru$_{201}$ (1.55 ML CO*). *Quasi*-equilibrated steps are denoted by $\leftrightarrow$, with $\leftrightharpoons$ denoting the kinetically-relevant step.

<table>
<thead>
<tr>
<th>CO Activation Path</th>
<th>Step</th>
<th>Energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H*-assisted</td>
<td>1. CO*(g) + * $\rightleftharpoons$ CO*</td>
<td>$\Delta H_1$</td>
</tr>
<tr>
<td></td>
<td>2. H$_2$(g) + * $\rightleftharpoons$ 2H*</td>
<td>$\Delta H_2$</td>
</tr>
<tr>
<td></td>
<td>3. CO* + H* $\rightleftharpoons$ HCO* + *</td>
<td>$\Delta H_3$</td>
</tr>
<tr>
<td></td>
<td>4. HCO* + H* $\leftrightharpoons$ HCOH* + *</td>
<td>$E_4$</td>
</tr>
</tbody>
</table>

$E_{app} = \Delta H_2 + \Delta H_3 + E_4 - \Delta H_1$  \hspace{1cm} 185

<table>
<thead>
<tr>
<th>Step</th>
<th>Energy (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>1. CO*(g) + * $\rightleftharpoons$ CO*</td>
</tr>
<tr>
<td></td>
<td>6. CO* + * $\leftrightharpoons$ C* + O*</td>
</tr>
</tbody>
</table>

$E_{app} = E_6 - \Delta H_1$  \hspace{1cm} 322
2.7 References

Chapter 3
Catalytic CO Hydrogenation on Ru clusters: Kinetics, oxygen rejection selectivities, and CO activation paths

Abstract

We present here CO consumption rates, oxygen-rejection selectivities (H₂O/CO₂ product ratios), and CO conversion activation energies to investigate the nature of CO activation paths during Fischer-Tropsch synthesis (FTS) on supported Ru catalysts. FTS rates and oxygen-rejection selectivities are consistent with H-assisted CO* activation paths on both small (1 nm) and large (7 nm) Ru clusters. Measured activation energies are independent of Ru cluster size and consistent with density functional theory (DFT) estimates of barriers for H-assisted CO* activation on high-coordination Ru atoms in (111) terraces of CO*-saturated Ru clusters. CO adsorption equilibrium constants measured during FTS reactions are similar on large and small Ru clusters, suggesting that CO activation occurs on sites with similar CO binding behavior on both large and small Ru clusters. FTS turnover rates are 3-4 times larger on large Ru clusters than on small clusters. Turnover rates become independent of cluster size when rates are normalized by the number of exposed high-coordination terrace sites; these data suggest that CO activation reactions occur on low-index planes of Ru cluster surfaces. H₂O, whether formed in-situ as a reaction product or co-fed with H₂/CO reactant mixtures, increases CO turnover rates and C₅⁺ selectivities with a concomitant decrease in CH₄ selectivities; DFT-estimated activation barriers for H₂O-assisted HCO* activation reactions are lower than those for direct H* addition to HCO* species. H₂O may act as a co-catalyst by shuttling H* species from the catalyst surface to vicinal HCO* species.

3.1 Introduction

CO hydrogenation, or the Fischer-Tropsch synthesis (FTS), on supported metal catalysts is a useful process for converting synthesis gas derived from biomass or natural gas to chemicals and transportation fuels [1]. FTS has been studied extensively, but many essential details about the C-O bond activation paths remain unclear, including whether chemisorbed CO species (CO*) dissociate on catalyst surfaces before or after such species are hydrogenated [2, 3]. Infrared spectroscopic [4] and transient isotopic data [5] have shown that FTS occurs on catalyst surfaces nearly saturated with CO*; these CO* species can be activated either directly on vicinal vacant metal atoms (*) or via reactions with chemisorbed hydrogen atoms (H*). Measured rates, oxygen-rejection selectivities, and density functional theory (DFT) calculations are consistent with unassisted and H-assisted CO* activation paths occurring in parallel during FTS on Fe catalysts at relevant CO* coverages [6]. Reported FTS rates on Co-based catalysts [7, 8], H₂O/CO₂ product ratios [9], and DFT-estimated activation energies on bare [10, 11] and moderately (0.5 ML CO*) covered Co(0001) surfaces [6] are consistent CO* activation occurring predominantly via H*-assisted paths; unassisted CO* activation paths must include quasi-equilibrated CO* dissociation and C* hydrogenation steps, followed by an
irreversible hydrogenation of CH* species (to CH₃*) [12], for such routes to be consistent with the observed effects of CO and H₂ pressures on FTS rates. DFT-derived activation barriers for C* + O* reactions on Co(0001) surfaces (115 to 167 kJ mol⁻¹) [6, 10] are much larger than those for C* + H* reactions (82 kJ mol⁻¹) [13], making direct CO* dissociation an irreversible step, a conclusion inconsistent with reported effects of H₂ and CO pressures on FTS rates.

Co-based and Ru-based catalysts show similar FTS rate equations [7, 14, 15], large H₂O/CO₂ product ratios [9, 16], and similar chain termination probabilities [15], suggesting that CO* activation proceeds via similar paths on Co and Ru catalysts. DFT-derived activation barriers on CO*-saturated Ru₃₀₁ cluster surfaces, consistent with calculations on Co(0001) surfaces, show that CO* dissociation is essentially irreversible and has a much larger activation barrier than CO* activation via H-assisted paths on high-coordination metal atoms [12]. We present here FTS rate data, oxygen rejection selectivities, and activation energies on small (~ 1 nm) and large (~ 7 nm) Ru clusters consistent with all theoretical evidence [12] and showing that CO* dissociation occurs primarily with H-assistance on low-index planes exposed at Ru cluster surfaces.

DFT studies on bare Fe [17], Co [18, 19, 20], Ru [21, 22], and Rh [23] surfaces have led to proposals that direct CO* dissociation steps, which are irreversible and must overcome large activation barriers on low-index planes, become facile on metal atoms with low-coordination. Such low-coordination atoms can exist either at corner or edge sites on small clusters or can be formed as a result of surface reconstruction of low-index planes. FTS turnover rates on Fe [24], Co [25], and Ru [26] surfaces decrease strongly with decreasing cluster size, suggesting that smaller clusters, in spite of their tendency to preferentially expose low-coordination atoms [27], are less reactive than larger clusters. Recent DFT simulations of CO* dissociation on CO*-saturated Ru₃₀₁ cluster surfaces showed that low-coordination corner and step-edge sites do not in fact provide more facile paths than those on high-coordination sites [12]. Activation barriers for direct CO* dissociation on low-coordination sites are actually higher than those on high-coordination sites, because the relevant near-saturation CO* coverages lead to repulsive interactions between CO* dissociation transition states and geminal Ru carbonyl species at low-coordination sites. Mechanistic studies of CO* activation have not been performed on Ru clusters of different sizes, so it remains ambiguous as to whether decreased reactivity of small clusters is a consequence of their surface structure or a consequence of CO* activation paths on small clusters that differ from paths on large clusters.

This study reports FTS rate data and activation energies on small (~ 1 nm) and large (~ 7 nm) Ru clusters at conditions of significant hydrocarbon chain growth (C₅⁺ carbon selectivity > 75%); oxygen rejection selectivities (H₂O/CO₂ formation rate ratios), which reflect the relative contributions of the direct and H-assisted CO activation paths [6], are also reported. These rate data, activation energies, and oxygen rejection selectivities on small and large Ru clusters are consistent with CO* activation occurring via H-assisted paths, and also with DFT simulations of CO* activation at near-saturation CO* coverages on Ru₃₀₁ cluster surfaces, which show H-assisted paths are much more facile than unassisted CO dissociation [12]. CO conversion turnover rates (per surface Ru atom) are lower on small (~ 1 nm) than on large (~ 7 nm) Ru clusters, even though measured CO adsorption equilibrium constants during FTS are similar on both cluster
sizes; reactivity differences between small and large Ru clusters become attenuated when CO conversion rates are normalized by the number of surface Ru atoms at low-index planes of large and small clusters, consistent with preferential activation of CO* on metal atoms in high-coordination environments.

3.2 Experimental Methods

3.2.1 Catalyst synthesis and characterization

SiO$_2$-supported Ru catalysts were synthesized using triethanolamine (TEA) [28] and incipient wetness methods [12]. A 0.5 wt. % Ru/SiO$_2$ catalyst was prepared by dissolving Ru(NO)(NO$_3$)$_3$ powder (0.161 g, Alfa Aesar, 32% by mass) in deionized H$_2$O (11.3 g) to form a reddish-brown clear solution (pH = 2). TEA (0.767 g, Sigma-Aldrich) was added to the aqueous Ru(NO)(NO$_3$)$_3$ solution; this led to a pH increase (from 2 to 8) and to a loss in solution transparency. Subsequent addition of HNO$_3$ (0.56 g, Fisher Scientific, 16 mol L$^{-1}$) decreased the pH to 2 and led to the redissolution of the colloidal particles. This clear liquid was added dropwise to SiO$_2$ (10 g, Davisil 646, Sigma Aldrich, 300 m$^2$ g$^{-1}$, 1.15 cm$^3$ g$^{-1}$ pore volume) to the point of incipient wetness.

Impregnated powders were treated in flowing dry air (Praxair, extra-dry, 20 cm$^3$ g$^{-1}$ s$^{-1}$) by heating to 393 K at 0.0167 K s$^{-1}$ and holding for 6 h and then heating to 578 K at 0.0167 K s$^{-1}$ and holding for 1 h. The samples were then cooled to ambient temperature overnight and treated in flowing H$_2$ (Praxair, 99.995%, 20 cm$^3$ g$^{-1}$ s$^{-1}$) by heating to 673 K at 0.05 K s$^{-1}$ and holding for 3 h. Catalyst synthesis was completed by treatment at ambient temperature in flowing 0.1% O$_2$/He (Praxair, UHP, 20 cm$^3$ g$^{-1}$ s$^{-1}$) for 1 h. A 5 wt. % Ru/SiO$_2$ catalyst was also prepared, using methods reported previously [12]; these samples were treated in flowing dry air to higher temperatures (673 K) than the 0.5 wt. % Ru/SiO$_2$ samples (598 K) in order to vary Ru dispersion [28].

Ru dispersions were measured from O$_2$-H$_2$ titrations [29] and CO adsorption uptakes. Samples (0.4 g) were loaded into a glass cell and treated in flowing H$_2$ (Praxair, 99.995%; 0.4 cm$^3$ g$^{-1}$ s$^{-1}$) by heating to 598 K at 0.083 K s$^{-1}$ and holding for 1 h. The cell was then evacuated at 598 K, and cooled to ambient temperature in vacuum (< 10$^{-3}$ Pa). Oxygen (Praxair 99.99%) adsorption isotherms (1 – 8 kPa O$_2$) were measured at ambient temperature, followed by evacuation of the cell and treatment of the samples by heating to 373 K under vacuum. Hydrogen (Praxair 99.995%) titration-adsorption isotherms (1 – 11 kPa) were then measured, using the stoichiometry [29]:

$$Ru_s - O + 1.5 H_2 \rightarrow Ru_s - H + H_2 O$$  \hspace{1cm} (3.1)

where Ru$_s$ is defined as a surface Ru atom.

CO adsorption uptakes for the 5 wt. % Ru/SiO$_2$ sample were measured at ambient temperature and 1 – 9 kPa CO (Praxair, 99.9%) after the treatment protocol described above. Isotherms were extrapolated to zero pressure to remove adsorption contributions from weakly-adsorbed species. O$_2$-H$_2$ titration cycles and CO adsorption (assuming 1 CO molecule per surface Ru atom) [29] resulted in fractional Ru dispersions of 0.11 – 0.13, showing excellent agreement between O$_2$-H$_2$ titrations and CO uptake methods; these
dispersions correspond to a mean Ru cluster size of ~ 7 nm when assuming a spherical particle shape [30]. H2 adsorption isotherms for the 0.5 wt. % Ru/SiO2 sample were measured at 373 K and 1 – 7 kPa H2. Total H2 uptakes were determined by extrapolating the linear portion of the adsorption isotherm to zero pressure and corresponded to a Ru dispersion of 0.98 (~ 1 nm Ru clusters) [30].

### 3.2.2 Steady-state Fischer-Tropsch synthesis rates and selectivities

FTS rates and selectivities were measured in an isothermal (± 2 K), fixed-bed stainless steel reactor (I.D. = 1 cm). Catalyst samples (0.9 to 2.5 g) were crushed and sieved to retain 105-177 μm aggregates, and were diluted with SiO2 (1.6 to 3.5 g, Davisil 62, 105-177 μm aggregates, 1.15 cm3 g−1, 300 m2 g−1) to avoid temperature gradients caused by exothermic FTS reactions. Catalyst-diluent mixtures were treated in flowing H2 (Praxair, 99.995%, 1.67 cm3 (STP) g cat−1 s−1) at ambient pressures by heating to 673 K at 0.033 K s−1 and holding for 8-10 h. Samples were then cooled to 453 K and exposed to synthesis gas (Praxair, certified standard, H2/CO = 2, 0.44 cm3 (STP) g cat−1 s−1) at ambient pressure before slowly increasing the catalyst temperature to 463 K and the total system pressure to 2.1 MPa using a dome-loaded back-pressure regulator (Mity-Mite, stainless steel). All gas streams were purified upstream of the catalyst bed by contact with hydrocarbon and H2O traps (Matheson type 451); synthesis gas mixtures were also exposed to activated carbon (Matheson type 450B) to trap any hydrocarbon or carbonyl impurities. All CO consumption turnover rates (g-mol CO g-mol surface Ru−1 s−1) and selectivities are reported after catalysts reached steady-state (~ 24 h); turnover rates generally decreased (by 20-30%) while CH4 carbon selectivities decreased (by 5-10%) and C₅+ selectivities increased (5-10%) during the initial 24 h after contact with synthesis gas.

The effects of H2 and CO pressures on CO turnover rates and selectivities were measured by varying H2 and CO molar rates and the system pressure, while maintaining differential CO conversions (< 10%). The effects of H2O pressures on rate and selectivities were measured by adding water to synthesis gas streams using a high-pressure pump (ISCO Model 500D). A trap at 393 K and at reactor pressure was used to collect C12+ hydrocarbons for GC analysis; all other process lines were kept above 423 K to prevent condensation of water and hydrocarbon products. The reactor effluent was analyzed by on-line gas chromatography (Agilent 6890N) equipped with a methyl silicone capillary column (HP-1, Agilent, 50 m x 0.320 mm x 0.15 μm film) and flame ionization detector for C1-C12 hydrocarbons and a packed column (Porapak Q, Supelco, 12 ft x 0.125 in) with a thermal conductivity detector for analysis of light (CO, Ar, CO2, CH4) gases. Hydrocarbon wax samples (C12+) were analyzed by dissolving samples (~ 0.1 g) in n-hexane (3 g, Sigma-Aldrich, 99%) at ambient temperature. A small aliquot (1 μL) of the resulting solution was analyzed via gas chromatography using a non-polar, capillary column (J&W Scientific, DB-1HT, 15 m x 0.320 mm O.D. x 0.10 μm film thickness).
3.3 Results and Discussion

3.3.1 \textit{H}_2 and CO pressure effects on Fischer-Tropsch synthesis turnover rates

Figures 3.1 and 3.2 show the effects of \textit{H}_2 and CO pressures, respectively, on CO consumption turnover rates during FTS on small (~1 nm) and large (~7 nm) Ru clusters; measured rates on large Ru clusters (~23 s\(^{-1}\), \textit{H}_2/CO = 2; Figure 3.1) agree with those reported previously (11 – 16 s\(^{-1}\)) on clusters in a similar size range (4 – 11 nm) and slightly lower total pressures (~0.5 MPa) [15]. FTS turnover rates on 1 nm Ru clusters are smaller than those on 7 nm Ru clusters at all conditions (Figures 3.1 and 3.2), consistent with reports of lower CO consumption turnover rates on smaller Ru clusters (below ~10 nm) [25, 26]. CO conversion turnover rates depend linearly on \textit{H}_2 pressure (Figure 3.1) and decrease with increasing CO pressure (Figure 3.2), consistent with reported effects of \textit{H}_2 and CO pressures on FTS rates for Fe [6], Co [7, 31], and other Ru [14, 32] catalysts.

The effects of \textit{H}_2 and CO pressures on FTS rates on Co [7, 8] and Ru [14] catalysts, as well as the data presented here, are consistent with Equation 3.2:

$$\frac{r_{CO}}{[L]} = \frac{\gamma P_{H_2} P_{CO}}{(1 + \sigma P_{CO})^2}$$

(3.2)

in which \(r_{CO}\) is the molar CO conversion rate, \([L]\) is the total number of exposed Ru atoms, \(\gamma\) and \(\sigma\) are rate parameters, and \(P_{H_2}\) and \(P_{CO}\) are \textit{H}_2 and CO pressures, respectively. The rearranged form of Equation 3.2:

$$\left(\frac{[L]P_{CO}P_{H_2}}{r_{CO}}\right)^{0.5} = \left(\frac{1}{\gamma^{0.5}}\right)(1 + \sigma P_{CO})$$

(3.3)

plotted as a function of CO pressure in Figure 3.3, shows the predicted linear dependence on both small (1 nm) and large (7 nm) Ru clusters. These equations provide empirical descriptions of measured rates and parameters (\(\gamma, \sigma\)) of uncertain chemical significance, which can be resolved by deriving the functional forms of these equations from plausible sequences of elementary steps for the activation of CO and \textit{H}_2 and for the formation of the relevant C\(_1\) monomers. Both unassisted and H-assisted CO* activation paths, taken together with a set of assumptions about the nature of the most abundant surface intermediates (MASI) and the the reversibility of their respective elementary steps, can lead to functional forms of Equation 3.2, but with different chemical significance of rate parameters. In the next section, we examine the contributions from these different mechanisms to FTS turnovers and specifically the role of H-assistance in CO* dissociation on Ru cluster surfaces.
3.3.2 Unassisted CO* dissociation paths and corresponding FTS rate equations

Scheme 3.1 is a set of elementary steps for CO* dissociation on a vicinal vacant metal atom that is consistent with the functional form of Equation 3.2 for the specific case of quasi-equilibrated molecular CO adsorption, H₂ dissociation, CO* dissociation on a vacant surface site (*), and hydrogenation of chemisorbed C atoms (C*) to CH* species on surfaces that are predominantly covered by vacant sites (*) and CO* species:

\[
\frac{r_{CO}}{[L]} = \frac{K_1 K_2 K_3 K_4 k_5 P_{H2} P_{CO}}{(1 + K_1 P_{CO})^2}
\]

(3.4)

Here, \( K_n \) is the equilibrium constant for the \( n \)th elementary step in Scheme 3.1 and \( k_5 \) is the forward rate constant for CH* hydrogenation by H* (step 5, Scheme 3.1). Scheme 3.1 provides specific chemical meaning to \( \gamma (K_1 K_2 K_3 K_4 k_5) \) and \( \sigma (K_1) \) in Equation 3.2.

Steps 1-4 in Scheme 3.1 must be quasi-equilibrated for unassisted CO* dissociation paths to give Equation 3.2, which accurately describes the measured effects of H₂ and CO pressures on FTS rates [7, 8, 14]. CO* is present at coverages near saturation during FTS, which causes intermolecular repulsion and metal-atom sharing that destabilizes metal-CO bonds; weakly-bound CO* species, as a result, desorb rapidly relative to forward C* reactions that lead to FTS turnovers [12], as required by the quasi-equilibrium assumption for CO adsorption-desorption steps. H₂/D₂/CO reactants form equilibrated hydrogen isotopologues on Co [9] and Ru [33] catalysts, consistent with quasi-equilibrated dihydrogen dissociation. Unassisted CO* dissociation (step 3, Scheme 3.1), however, involves large activation barriers on both low-coordination sites (356 kJ mol⁻¹) and high-coordination sites (322 kJ mol⁻¹) on Ru\(_{201}\) clusters saturated with CO* [12]. Also, activation barriers for reactions of C* with O* are much larger (164 kJ mol⁻¹) than for reactions of C* with H* (45 kJ mol⁻¹; step 4, Scheme 3.1) on high-coordination sites in (111) terraces of Ru\(_{201}\) clusters at CO*-saturation [12]. Therefore, C* species react with H* species much faster than with O* species, making CO* dissociation, as a result, an irreversible process and, as we show next, the kinetically-relevant step in a rate equation that is inconsistent with measured kinetic effects of H₂ and CO. The unassisted CO* dissociation steps in Scheme 3.1, although consistent with the observed dependences of FTS rates on H₂ and CO pressures (Equation 3.4), are still inconsistent with oxygen-removal selectivities measured on Fe catalysts [6] and with DFT studies of CO* activation on Fe(111) and Co(0001) surfaces at moderate CO* coverages (0.5 ML) [6].

Irreversible unassisted CO* dissociation steps in Scheme 3.1 lead to the equation:

\[
\frac{r_{CO}}{[L]} = \frac{K_1 k_3 P_{CO}}{(1 + K_1 P_{CO})^2}
\]

(3.5)
which predicts rates to be independent of \( \text{H}_2 \) pressure, as a result of the absence of \( \text{H}^* \) in the first irreversible step (\( \text{CO}^* \) dissociation). Thus, any scheme with irreversible \( \text{CO}^* \) dissociation steps cannot account for the observed effects of \( \text{H}_2 \) on FTS rates (Figure 3.1; Equation 3.2). Instead, \( \text{CO}^* \) dissociation must be assisted by \( \text{H}^* \) species, a conclusion suggested previously from isotopic tracer studies on Fe [34, 35] and Co [36] catalysts. More recent isotopic transients [37, 38], kinetic studies [6], and density functional theory [6, 10, 11, 12, 19] have probed the involvement of \( \text{H} \)-assisted \( \text{CO}^* \) activation paths in FTS reactions on Co and Fe catalysts as we also do next by examining a sequence of elementary steps for \( \text{H} \)-assisted \( \text{CO}^* \) dissociation that is consistent with measured FTS rates (Equation 3.2). We also show that oxygen-rejection selectivities for Ru catalysts are consistent with \( \text{H} \)-assisted \( \text{CO}^* \) activation paths in FTS.

### 3.3.3 \( \text{H} \)-assisted \( \text{CO}^* \) activation paths in FTS and corresponding rate equations

Scheme 3.2 shows a sequence of elementary steps that includes \( \text{H} \)-assisted \( \text{CO}^* \) dissociation steps and in which molecular \( \text{CO} \) adsorption, \( \text{H}_2 \) dissociation, and \( \text{CO}^* \) hydrogenation to surface formyl species (\( \text{HCO}^* \)) steps are assumed to be quasi-equilibrated; when \( \text{CO}^* \) and \( * \) species are the MASI, this sequence leads to the rate equation:

\[
\frac{r_{\text{CO}}}{[L]} = \frac{K_1 K_2 K_6 k_\gamma P_{\text{H}_2} P_{\text{CO}}}{\left(1 + K_1 P_{\text{CO}}\right)^2} \quad (3.6)
\]

In this equation, the lumped rate constant \( \gamma \) in Equation 3.2 \( (K_1 K_2 K_6 k_\gamma) \) differs in chemical interpretation from that for unassisted \( \text{CO}^* \) dissociation paths \( (\gamma = K_1 K_2 K_3 K_4 k_5, \text{Scheme 3.1}) \). C-O bond cleavage in \( \text{H} \)-assisted paths occurs after reactions of \( \text{CO}^* \) with \( \text{H}^* \); this reaction must be quasi-equilibrated (followed by an irreversible hydrogenation of \( \text{HCO}^* \) species) for \( \text{H} \)-assisted paths to be consistent with Equation 3.2. DFT-derived activation barriers for \( \text{HCO}^* \) decomposition (31 kJ mol\(^{-1}\)) are much smaller than those for \( \text{HCO}^* \) hydrogenation (88 kJ mol\(^{-1}\); step 7, Scheme 3.2) on \( \text{CO}^* \)-saturated Ru\(_{20}\) cluster surfaces [12]; as a result, \( \text{HCO}^* \) species likely decompose much faster than \( \text{HCOH}^* \) species form, and \( \text{CO}^* \) hydrogenation to \( \text{HCO}^* \) is a quasi-equilibrated step. DFT-derived activation barriers also suggest \( \text{HCOH}^* \) formation is irreversible on \( \text{CO}^* \)-saturated Ru cluster surfaces [12], which is consistent with Equation 3.6 and supports the proposal that \( \text{CO}^* \) species are activated with \( \text{H} \)-assistance during FTS on Ru catalysts.

Rate measurements alone cannot distinguish between unassisted and \( \text{H} \)-assisted \( \text{CO}^* \) activation paths because both paths can lead to rate equations (Equation 3.2) that describe FTS rate data. A recent kinetic study of FTS reactions on supported Fe catalysts showed that the effects of \( \text{CO} \) and \( \text{H}_2 \) pressures on \( \text{H}_2\text{O}/\text{CO}_2 \) product rate ratios reflect the predominance of unassisted and \( \text{H} \)-assisted \( \text{CO}^* \) activation paths [6]. We use the dependences of \( \text{H}_2\text{O}/\text{CO}_2 \) product rate ratios on \( \text{CO} \) and \( \text{H}_2 \) pressures in the following section to probe the relative contributions of unassisted and \( \text{H} \)-assisted \( \text{CO}^* \) activation paths in FTS on small (~1 nm) and large (~7 nm) Ru clusters.
3.3.4 Oxygen removal selectivities in Fischer-Tropsch synthesis on Ru clusters

The effects of H₂ and CO pressures on the oxygen removal selectivities (H₂O/CO₂ product rate ratios) in FTS on small (1 nm) and large (7 nm) Ru clusters are shown in Figures 3.4 and 3.5, respectively. H₂O/CO₂ product ratios are proportional to H₂ pressures (at constant CO pressure) and independent of CO pressures (at constant H₂ pressure) for both Ru cluster sizes. H₂O formation rates are between 20 and 60 times larger than CO₂ formation rates in the range of CO and H₂ pressures studied (Figures 3.4 and 5), consistent with previous reports of H₂O as the predominant oxygen-containing product of FTS reactions on Ru catalysts [14, 39].

DFT studies have suggested that OH* species formed in H-assisted CO activation paths on Co(0001) surfaces at moderate CO* coverages (0.5 ML) react with H* to form H₂O, while chemisorbed oxygen (O*) atoms, formed in unassisted CO activation paths (step 3, Scheme 3.1), react with CO* to form CO₂ [6]. The similarities in FTS rates, oxygen rejection selectivities, and chain termination parameters for Ru and Co catalysts suggest that H₂O and CO₂ are formed on Ru catalysts via similar paths as on Co catalysts. Since H₂O and CO₂ are formed exclusively via H-assisted (Equation 3.6) and unassisted (Equation 3.5) CO* activation paths, respectively, the ratio of the rate equations for each path leads to the (H₂O/CO₂) rate ratios for FTS:

\[
\frac{r_{H_2O}}{r_{CO_2}} = \left( \frac{K_2 K_6 k_7}{k_3} \right) P_{H_2} \tag{3.7}
\]

which is proportional to H₂ pressures and consistent with the effects of H₂ and Co pressures on measured H₂O/CO₂ rate ratios for both Ru cluster sizes (Figures 3.4 and 3.5).

The large (H₂O/CO₂) rate ratios (~20 to 60) in Figures 3.4 and 3.5 reflect the preferential formation of OH* species derived from H-assisted CO* activation paths (Scheme 3.2); these OH* species react with H* species to form H₂O. These large H₂O/CO₂ ratios are consistent with CO* activation occurring predominantly via H-assisted paths on supported Ru catalysts, as suggested previously by DFT studies on CO*-saturated Ru₂₀₀₁ cluster surfaces [12]. The very low primary CO₂ selectivities (between 2-6% at all conditions) on both small and large Ru clusters reflect a dearth of O* species, which form via unassisted CO* dissociation and are removed from the catalyst surface via reactions with CO*. These low CO₂ selectivities also suggest that O* species are not formed from H₂O-derived intermediates, consistent with the large activation barriers (151 kJ mol⁻¹) calculated for OH* dehydrogenation on Co(0001) surfaces at 0.5 ML CO* coverages [6].

Small (1 nm) Ru clusters are less reactive than large (7 nm) clusters (Figures 3.1 and 3.2) in FTS reactions [26], but rate and oxygen selectivity data are consistent with CO* activation occurring through similar H-assisted paths on both samples. In the next section, we present measured FTS activation energies on small and large Ru clusters and
compare those energies to DFT-derived barriers for H-assisted paths previously reported on relevant CO*-saturated Ru$_{201}$ cluster surfaces [12].

### 3.3.5 Comparison of activation energies and DFT-derived barriers for CO* activation on CO*-saturated Ru clusters

DFT-estimated activation barriers for H-assisted CO activation paths have been reported previously (165 kJ mol$^{-1}$) for Ru$_{201}$ clusters at near CO*-saturation coverages (1.55 ML) [12]; the chemical interpretation of such barriers was elucidated by considering FTS rates in the limit of CO*-saturated surfaces ($K_1 P_{CO} \gg 1$):

$$r_{CO} = \frac{K_2 K_6 k_7}{K_1} \left( \frac{P_{H_2}}{P_{CO}} \right) = \delta \left( \frac{P_{H_2}}{P_{CO}} \right)$$  \hspace{1cm} (3.8)

where $\delta$ is a lumped rate constant ($K_2 K_6 k_7$) and can be expressed in its Arrhenius form:

$$\delta = A \exp \left( -\frac{\Delta E_{app}}{RT} \right) = A \exp \left( -\frac{(\Delta H_2 + \Delta H_6 + \Delta E_7 - \Delta H_1)}{RT} \right)$$  \hspace{1cm} (3.9)

where $A$ is the pre-exponential factor, $\Delta E_{app}$ is the apparent activation energy, $R$ is the gas constant, $T$ is the temperature, $\Delta H_n$ is the enthalpy change for elementary step $n$ (Scheme 3.2), and $\Delta E_7$ is the activation energy for HCO* hydrogenation (step 7, Scheme 3.2). The temperature dependence of the lumped rate constant $\delta$ (and the apparent activation energy, as a result) cannot be measured rigorously because the denominator in FTS rate equations contains a term that corresponds to the concentration of vacant metal sites (Equation 3.2); the effects of temperature on FTS rates, as a result, are a combination of temperature effects on the kinetic parameters $\gamma$ and $\sigma$ (Equation 3.2). Equation 3.6 shows that the kinetic parameter $\sigma$ is the equilibrium constant for CO adsorption (Scheme 3.2, $K_1$); the temperature dependence of $\sigma$, then, can be modeled by the van’t Hoff equation with an appropriate value for the heat of CO adsorption during FTS, which we chose to be $-40$ kJ mol$^{-1}$ as predicted by DFT simulations of CO adsorption on Ru$_{201}$ cluster surfaces nearly saturated with CO* [12]. The value of the rate parameter $\gamma$ at each temperature can then be calculated by utilizing the corresponding turnover rates and the values of $\sigma$ (Equation 3.2).

The relative concentration of CO* species ($\sigma P_{CO}$, Equation 3.2) was larger ($2 - 3.7$) than the relative concentration of vacant surface sites ($1$) at all temperatures in this study; we can recast Equation 3.2, as a result, to approximate a CO*-covered surface:

$$r_{CO} = \frac{\gamma P_{H_2} P_{CO}}{(1 + \sigma P_{CO})^2} \approx \frac{\gamma P_{H_2} P_{CO}}{\sigma^2 P_{CO}^2} = \delta \left( \frac{P_{H_2}}{P_{CO}} \right)$$  \hspace{1cm} (3.10)
where the apparent rate constant $\delta$ is now a ratio of the measured rate constants ($\gamma \sigma^2$). Figure 3.6 shows the Arrhenius plot of the apparent rate constant $\delta$ for both the small (~1 nm) and large (~7 nm) Ru clusters. The measured apparent activation energies, given by the slopes of the lines in Figure 3.6, are similar for the small ($110 \pm 15 \text{ kJ mol}^{-1}$) and large ($100 \pm 20 \text{ kJ mol}^{-1}$) Ru clusters, and consistent with values reported previously ($90 – 120 \text{ kJ mol}^{-1}$) for FTS on supported Ru catalysts [15].

The activation energies reported here (95 – 125 kJ mol$^{-1}$; Figure 3.6) for FTS on Ru catalysts are much closer to DFT-derived barriers for H-assisted CO* activation paths (165 kJ mol$^{-1}$) than to those for unassisted paths (322 kJ mol$^{-1}$) on CO*-covered (111) terraces of Ru$_{201}$ cluster surfaces [12]. The resemblances in activation energies, FTS rate dependences on H$_2$ and CO pressures, and oxygen-rejection selectivities between small (~1 nm) and large (~7 nm) Ru clusters suggest that CO* species can be activated on Ru surfaces via identical H-assisted paths, irrespective of Ru cluster size. The identity of the active site for CO* activation in FTS, however, remains unclear. In the next section, we utilize CO adsorption equilibrium constants ($K_1$, Scheme 3.2) measured during FTS reactions, as well as relations between average coordination of surface atoms and metal cluster size, to determine the local environment in which CO* activation occurs on both small and large Ru clusters.

### 3.3.6 Ru cluster size effects on FTS turnover rates, CO adsorption equilibrium constants, and product selectivities

Figures 3.1 and 3.2 show that CO consumption turnover rates on large (~7 nm) Ru clusters are 3-4 times larger than on small (~1 nm) Ru clusters, when turnover rates are obtained by normalization to the total number of surface Ru atoms measured via chemisorption uptakes before FTS reactions. This increase in turnover rates with increasing Ru cluster size (Figures 3.1 and 3.2) is consistent with the three-fold increase in the fraction of surface atoms in high-coordination (111) terrace environments for fcc cubo-octahedra (0.8 nm – 7 nm) [27]; such structures are the most stable configurations for Ru clusters with more than 140 atoms, according to DFT-estimated formation energies [40]. This correspondence between turnover rate increases and the increase of exposed high-coordination Ru atoms suggests that H-assisted CO* activation occurs on Ru atoms in low-index terraces, consistent with DFT studies of unassisted and H-assisted CO* activation paths on CO*-saturated Ru$_{201}$ clusters [12].

Table 3.1 shows the best-fit values of $\gamma$ and $\sigma$ ($K_1$) for both small (~1 nm) and large (~7 nm) Ru clusters obtained from regression of measured rate data to the functional form of Equation 3.6. CO adsorption equilibrium constants ($K_1$, Scheme 3.2) on small ($6.2 \pm 0.7 \text{ MPa}^{-1}$) and large ($5.6 \pm 0.6 \text{ MPa}^{-1}$) Ru clusters at 463 K are very similar; these data, along with FTS rates that scale with the fraction of Ru atoms in low-index terraces, are consistent with H-assisted CO activation occurring on high-coordination Ru atoms that bind CO species similarly on small and large clusters nearly saturated with CO* species. Low-coordination Ru atoms appear unable to activate CO* species at the same rate as those on low-index planes at the CO*-saturation coverages that prevail during FTS; suppressed rates at low-coordination atoms is likely due to
repulsive steric interactions between CO activation transition states and vicinal di-carbonyl structures at corner and edge atoms [12].

FTS turnover rates on small and large Ru clusters are different because their implicit normalization is premised on the similar reactivity of all exposed Ru atoms. As a result, they do not reflect the intrinsic reactivity of those surface atoms that contribute to the formation of the detected reaction products. In fact, not all exposed atoms activate CO* at similar rates and those at low-index planes are responsible for most of the hydrocarbon chains formed in FTS reactions. Our results, combined with previous reports of increasing rates with increasing cluster size on Fe [17], Co [25], and Ru [26] catalysts, indicate that CO* activation occurs preferentially on metal atoms exposed in the high coordination environment of low-index planes; turnover rates are higher on large clusters than small clusters because large clusters expose more high-coordination atoms that mediate more facile kinetically-relevant CO* dissociation steps.

Figures 3.7 and 3.8 show the effects of H2 pressure on the CH4 and C5+ product selectivities, respectively, for both the small (~1 nm) and large (~7 nm) Ru catalyst samples. CH4 selectivities increase and C5+ selectivities decrease with increasing H2 pressures for both catalyst samples (Figures 3.7 and 3.8). Surface-bound hydrocarbon chains are terminated irreversibly to alkanes via hydrogenation reactions [41], so increasing H2 pressures apparently leads to increased availability of H* species and, as a result, decreased hydrocarbon chain growth. CH4 selectivities for small Ru clusters (4-8%) are larger than those for large Ru clusters (2-3%) at all H2 pressures (Figure 3.7). Small Ru clusters expose a higher fraction of low-coordination atoms than large Ru clusters, and such atoms, in rare instances, may catalyze unassisted C-O bond dissociation reactions that result in chemisorbed carbon (C*) and chemisorbed oxygen (O*) species bound strongly at low-coordination sites. C* residues are likely removed from these sites exclusively as CH4 via hydrogenation reactions because chain growth reactions, which invariably involve C-C coupling steps, incur entropic penalties at corner and edge sites that form geminal di-carbonyls at near-saturation CO* coverages [12].

The effects of CO pressure on CH4 and C5+ selectivities are shown in Figures 3.9 and 3.10, respectively, for both catalyst samples. Increasing CO pressure decreases CH4 selectivities (Figure 3.9) and increases C5+ selectivities (Figure 3.10), suggesting that chain growth reactions involve species that are derived from CO*; chain growth paths and the identity of the chain growth monomer in FTS will be discussed further in Chapter 4 of this work. C5+ selectivities are slightly larger on small Ru clusters (82-86%, Figure 3.10) than on large Ru clusters (75-81%, Figure 3.10); such differences are likely due to diffusion-enhanced re-adsorption and growth of 1-alkenes [15] in the pores of the 0.5 wt.% Ru samples (~1 nm Ru clusters), which contain a higher density of Ru clusters than that of the 5 wt.% Ru catalyst samples (~7 nm Ru clusters).

Tables 3.2 and 3.3 show the effects of H2 and CO pressures on CH4 selectivities, C5+ selectivities, and 1-alkene to n-alkane (olefin to paraffin, O/P) product ratios for the small and large Ru samples, respectively. O/P ratios decrease with increasing H2 pressure and increase with increasing CO pressure for both samples. High H2/CO ratios lead to relatively high H*/CO* ratios and, as a result, preferential termination of surface hydrocarbon chains to alkanes for all carbon numbers (Tables 3.2 and 3.3). Low H2/CO ratios, on the other hand, result in hydrogen-poor surfaces and high O/P ratios. The
effects of H₂ and CO pressures on CH₄ selectivities (Figures 3.7 and 3.9), Cₛₛ selectivities (Figures 3.8 and 3.10), and O/P ratios (Tables 3.2 and 3.3) are all consistent with H* and CO* concentrations that reflect H₂/CO reactant ratios; such correspondence between adsorbate concentrations and the gas phase also indicate that there exist no reactant transport restrictions in the catalyst particles (104 – 177 μm aggregates) used in this study.

Many studies have shown that H₂O, which is the predominant oxygen-containing product in FTS reaction on Co [9, 41] and Ru [15] catalysts, can increase CO conversion turnover rates, suppress CH₄ formation, and enhance chain growth [9, 42]. Very few studies, however, have considered the direct involvement of surface H₂O (H₂O*) species in the elementary steps of FTS reactions to explain the observed effects of H₂O on FTS rates and selectivities. We report the effects of H₂O pressure on CO turnover rates, CH₄ selectivities, and Cₛₛ selectivities in the next section, and present preliminary DFT-estimated activation barriers for H₂O-assisted H* shuttling reactions that may catalyze CO* activation reactions more effectively than direct H* addition to vicinal CO* species.

3.3.7 Effects of H₂O on CO conversion rates and hydrocarbon product selectivities

Figures 3.11 and 3.12 show the effects of H₂O pressure on CO conversion turnover rates and on hydrocarbon (CH₄, Cₛₛ) selectivities, respectively, for the large (~ 7 nm) Ru clusters. CO conversion turnover rates increase monotonically with increasing H₂O pressures, irrespective of whether H₂O is formed indigenously or added externally (Figure 3.11). Increasing H₂O pressures also increases Cₛₛ selectivities with concomitant decreases in CH₄ selectivities (Figure 3.12); both rates and selectivities reach asymptotic limits at high H₂O pressures (0.6 MPa), and all H₂O effects shown in Figures 3.11 and 3.12 are completely reversible.

Previous studies have reported that H₂O, whether formed indigenously or added externally, increases CO conversion rates and Cₛₛ selectivities, while decreasing CH₄ selectivities on Co [9, 41, 42, 43, 44] and Ru [42, 45] catalysts; such rate and selectivity enhancements, however, depend strongly on variables such as H₂O/CO ratios and the mean pore size and volume of the catalyst support [46]. H₂O could increase CO conversion rates and Cₛₛ selectivities by relieving CO transport restrictions within catalyst particles [41], although infrared studies at FTS conditions have shown that H₂O does not detectably influence the structure or coverage of chemisorbed CO* on Co-based catalysts [9].

The observed increase in CO conversion rates with increasing H₂O pressures may reflect the direct intervention of H₂O (or H₂O-derived species) in the kinetically-relevant CO* activation steps, leading to H₂O-assisted CO* activation paths that are even more facile than H-assisted steps. Figure 3.13 shows DFT-calculated reactant, transition, and product states for H₂O-assisted, kinetically-relevant HCO* hydrogenation reactions on (111) terraces of Rulobber cluster surfaces at near CO*-saturation coverages (1.55 ML). H₂O-assisted HCO* hydrogenation reactions occur via abstraction of surface H* species by H₂O to form H₂O* species, which rapidly transfer a proton to vicinal HCO* species to form HCOH* and H₂O (Figure 3.13). H₂O-assisted CO* activation paths have activation barriers (139 kJ mol⁻¹) that are lower than those for H-assisted (165 kJ mol⁻¹) paths [12]; these barriers suggest that H₂O can act directly as a co-catalyst in H-assisted CO*
activation steps. Increases in H$_2$O pressures may reflect a higher concentration of H$_2$O species near the catalyst surface that can activate HCO* species via proton shuttling faster than reactions of HCO* and H*.

The concurrent increase in turnover rates and increasing C$_5^+$ selectivities (and formation rates [9]) with increasing H$_2$O pressures (Figure 3.11) implies that H$_2$O also promotes chain propagation reactions, which involve the stepwise addition of C$_1$ monomers to growing hydrocarbon chains [5]. The chain growth mechanism in FTS is still widely debated [47]; a chain growth mechanism that involves CO* species as monomers [48, 49], however, is consistent with isotopic transient data that shows chain growth is very rapid on surfaces nearly saturated with CO* [5]. Preliminary DFT calculations suggest that H$_2$O molecules do not facilitate chain propagation via reactions of surface alkyl species (C$_n$H$_{2n+1}$*) and CO*; the kinetically relevant step for chain propagation, however, could be reactions of acyl species (C$_n$H$_{2n+1}$CO*) with H*, analogous to the kinetic relevance of HCO* + H* reactions in H-assisted CO activation paths. Chain growth reactions (RCO* + H*) via H$_2$O-assisted proton shuttling, as a result, could be a reasonable explanation for increasing chain propagation rates with increasing H$_2$O pressures.

We are currently investigating the effects of H$_2$O on catalyst samples with small Ru clusters; such effects should be analogous to those on large Ru cluster samples if H$_2$O in fact does intervene directly in CO* activation and C-C bond formation processes. A more complete understanding of chain growth reactions in FTS is also needed in order to supplement rate and selectivity data with DFT simulations of relevant C-C bond formation reactions and the associated effects of vicinal H$_2$O (or H$_2$O*) species.

### 3.4. Conclusions

Rate data and oxygen-rejection selectivities are consistent with CO* activation in Fischer-Tropsch synthesis (FTS) occurring predominantly via H-assisted paths on both small (~1 nm) and large (~7 nm) supported Ru clusters. Measured apparent activation energies were similar for both catalyst samples, and comparable to density functional theory (DFT) estimates of activation energies for H-assisted CO* activation paths on high-coordination Ru atoms in CO*-saturated (111) terraces of Ru clusters. FTS turnover rates were 3-4 fold larger on large (7 nm) Ru clusters than on small (1 nm) clusters, consistent with H-assisted CO* activation events occurring on Ru sites in high-coordination environments, which compose a higher fraction of exposed surface atoms on large clusters than on small clusters. CO adsorption equilibrium constants, measured during reaction and obtained from fitting rate data to H-assisted CO* activation rate equations, were independent of Ru cluster size and suggest CO* activation occurs on catalyst sites that bind CO* similarly on both small and large Ru clusters. H$_2$/CO ratios determine the relative concentrations of H* and CO* species on catalyst surfaces; high H$_2$/CO ratios lead to more CH$_4$ and other alkanes, whereas low H$_2$/CO ratios lead to larger C$_5^+$ selectivities and a more olefinic product distribution. CO conversion rates increase with increasing H$_2$O pressures on large Ru clusters, consistent with DFT results that show H$_2$O can facilitate H-transfer reactions to HCO* species in the kinetically-relevant step for CO activation (R = H); chain propagation rates also increase with
increasing H$_2$O pressures, although further investigations on the kinetic relevance of RCO + H reactions for chain growth (R = C$_n$H$_{2n+1}$) are needed.

3.5 Acknowledgements

The author gratefully acknowledges Professor Matthew Neurock and Dr. David Hibbitts (University of Virginia) for assistance with the DFT calculations presented in this work. BP, p.l.c. is acknowledged for financial support through the XC$^2$. Drs. Jay Labinger (California Institute of Technology) and Glenn Sunley (BP) are gratefully acknowledged for helpful technical discussions.
3.6 Figures, Tables, and Schemes

3.6.1 Figures

**Figure 3.1** CO consumption turnover rates as a function of H$_2$ pressure for supported 7 nm Ru (●) and 1 nm Ru (○) clusters (463 K, 0.65 MPa CO, fractional CO conversion < 0.1).
Figure 3.2  CO consumption turnover rates as a function of CO pressure for supported 7 nm Ru (●, 1.1 MPa H₂) and 1 nm Ru (○, 1.3 MPa H₂) clusters (463 K, fractional CO conversion < 0.1).
Figure 3.3  Effects of CO pressure on the linearized CO consumption rates (see text, Equation 3.3) for 7 nm (●) and 1 nm (○) Ru clusters (463 K, fractional CO conversion < 0.1).
Figure 3.4  Molar (H₂O/CO₂) product ratios as a function of CO pressure (Ο, 1.1 MPa H₂) and H₂ pressure (●, 0.65 MPa CO) for 7 nm Ru clusters (463 K, fractional CO conversion < 0.1).
Figure 3.5 Molar (H₂O/CO₂) product ratios as a function of CO pressure (●, 1.3 MPa H₂) and H₂ pressure (○, 0.65 MPa CO) for 1 nm Ru clusters (463 K, fractional CO conversion < 0.1).
Figure 3.6  Arrhenius plot for the apparent rate constant $\delta$ on CO*-saturated surfaces (see text, Equation 3.10) for 7 nm (●) and 1 nm (○) Ru clusters (1.3 MPa $H_2$, 0.65 MPa CO, fractional CO conversion < 0.1).
Figure 3.7  Effects of H₂ pressure on CH₄ selectivities (carbon basis) for 7 nm (●) and 1 nm (○) Ru clusters (463 K, 0.65 MPa CO, fractional CO conversion < 0.1).
Figure 3.8  Effects of H$_2$ pressure on C$_{5+}$ selectivities (carbon basis) for 7 nm (●) and 1 nm (○) Ru clusters (463 K, 0.65 MPa CO, fractional CO conversion < 0.1).
Figure 3.9  Effects of CO pressure on CH₄ selectivities (carbon basis) for 7 nm (●, 1.1 MPa CO) and 1 nm (○, 1.3 MPa CO) Ru clusters (463 K, fractional CO conversion < 0.1).
Figure 3.10  Effects of CO pressure on $C_{5\#}$ selectivities (carbon basis) for 7 nm (●, 1.1 MPa CO) and 1 nm (Ο, 1.3 MPa CO) Ru clusters (463 K, fractional CO conversion < 0.1).
Figure 3.11  Effects of average H₂O pressure on CO conversion turnover rates (463 K, Ru/SiO₂ (7 nm), 2.2 MPa H₂, 0.5 MPa CO, fractional CO conversion 0.05 – 0.3). H₂O pressures were varied by changing reactant space velocity (□) or by adding H₂O via a high-pressure pump (■).
Figure 3.12  Effects of average H$_2$O pressure on CH$_4$ (□,■) and C$_{5+}$ (○,●) carbon selectivities (463 K, Ru/SiO$_2$ (7 nm), 2.2 MPa H$_2$, 0.5 MPa CO, fractional CO conversion 0.05 – 0.3). H$_2$O pressures were varied by changing reactant space velocity (open symbols) or by adding H$_2$O via a high-pressure pump (filled symbols).
**Figure 3.13**  DFT-calculated reactant (a), transition state (b), and product (c) structures for \( \text{H}_2\text{O} \)-assisted hydrogenation reactions of \( \text{HCO}^* \) species on (111) terraces of \( \text{Ru}_{201} \) cluster surfaces at 1.55 ML CO* (oxygen – red, carbon – grey, ruthenium – teal, hydrogen – white).

### 3.6.2 Schemes

**Scheme 3.1**  Sequence of elementary steps for unassisted CO activation. Quasi-equilibrated (\( \rightleftharpoons \)) and kinetically-relevant steps (\( \rightarrow \)) are denoted by their equilibrium (\( K_n \)) and kinetic (\( k_n \)) constants, respectively.
Scheme 3.2  Sequence of elementary steps for H-assisted CO* activation. Quasi-equilibrated (\(\text{\LARGE \rightarrow} \)) and kinetically-relevant steps (\(\text{\LARGE \Rightarrow} \)) are denoted by their equilibrium (\(K_n\)) and kinetic (\(k_n\)) constants, respectively.

3.6.3 Tables

Table 3.1  Best-fit values of the lumped rate constant \(\gamma\) and the CO adsorption equilibrium constant \(K_1\) (see text, Equation 3.10) for FTS on supported Ru clusters at 463 K.

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<th>Ru cluster size / nm</th>
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Table 3.2  Effects of H\textsubscript{2} and CO pressures on CH\textsubscript{4} selectivities, C\textsubscript{5+} selectivities, and 1-olefin to n-paraffin product ratios for a 0.5 wt.% Ru/SiO\textsubscript{2} catalyst sample (average Ru cluster size ~ 1 nm) at 463 K (fractional CO conversion 0.05 – 0.1).

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Table 3.3  Effects of H\textsubscript{2} and CO pressures on CH\textsubscript{4} selectivities, C\textsubscript{5+} selectivities, and 1-olefin to n-paraffin product ratios for a 5 wt.% Ru/SiO\textsubscript{2} catalyst sample (average Ru cluster size ~ 7 nm) at 463 K (fractional CO conversion 0.02 – 0.07).

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3.7 References

Chapter 4

C-C Bond Formation Paths in Catalytic CO Hydrogenation

Abstract

C-C bond formation paths in Fischer-Tropsch synthesis are investigated by measuring the effects of H₂ and CO pressure on CH₄ and C₅+ product selectivities, 1-alkene to n-alkane ratios in products, and chain termination parameters. Ratios of H₂/CO reactants determine the ratios of chemisorbed hydrogen (H*) and chemisorbed CO (CO*) on catalyst surfaces; chain termination and propagation reactions, as a result, are preferred at high and low H₂/CO reactant ratios, respectively. Alkane chain termination parameters for C₁ species are nearly ten-fold larger than such parameters for C₂ and C₃ species, indicating that chains terminate preferentially to CH₄ before growing. Chain termination parameters are related to differences in activation barriers for propagation and termination reactions; density functional theory (DFT) estimates of such activation barrier differences are consistent with measured chain termination parameters when chain termination and chain propagation are modeled by reactions of surface alkyl species with H* and CO* species, respectively, on Ru cluster surfaces at relevant CO* coverages. DFT-estimated activation barriers for chain termination reactions are independent of chain length because such reactions are highly exothermic and proceed via early transition states. Chain propagation reactions via alkyl migration to vicinal CO* species, however, occur via late transition states in which the metal-alkyl bond is broken completely; C₁ alkyl migration reactions must overcome larger barriers than C₂ and C₃ migrations because C₁ species form the strongest metal-alkyl bonds. Total CO consumption rates are discussed for the first time in the context of both CO activation and consumption of CO* monomers in chain growth reactions.

4.1 Introduction

Fischer-Tropsch synthesis (FTS) is an established industrial process that converts synthesis gas (CO + H₂) to long-chain hydrocarbons via C-O bond activation and subsequent C-C bond formation reactions on Group VIIIB metals. Controversies remain, however, about how C-O bonds are activated and C-C bonds are formed during FTS; our previous studies have shown that measured rates, oxygen rejection selectivities, and density functional theory (DFT) estimates of activation barriers are consistent with C-O bond activation occurring via H-assisted paths on low-index planes of Ru catalysts saturated with chemisorbed CO (CO*) [1, 2]. C-C bond formation paths in FTS have been studied extensively by co-feeding labeled probe molecules [3, 4, 5, 6, 7], by using transient isotopic kinetic methods [8, 9], and by calculating activation barriers for various chain growth mechanisms using DFT methods [10, 11, 12, 13]. Significant chain growth occurs at high pressures (> 1 MPa) and moderate temperatures (463-483 K), which result in nearly CO*-saturated catalyst surfaces during FTS [8, 14, 15, 16]; such surface coverages differ markedly from those present in many experimental and DFT studies of
chain growth paths. CO* coverages affect CO adsorption energies and CO* activation barriers [2]; investigation of chain growth paths at relevant CO* coverages, as a result, may lead to different conclusions regarding C-C bond formation reactions than investigations of such processes at low CO* coverages.

C-C bond formation paths first proposed by Fischer and Tropsch [17] involve C-C bond formation via CH₂-CH₃ coupling reactions (e.g., carbene mechanism, x=2). The carbene mechanism gained support after reports that contacting Ru, Co, and Fe catalysts with CH₃N₂-H₂ mixtures at ambient pressures led to product distributions similar to those obtained with CO and H₂ reactant mixtures [18]; other studies have proposed similar CH₂-CH₃ coupling chain growth mechanisms based on isotopic transient results on a Ni catalyst [9], as well as on kinetic and selectivity measurements [19] and infrared results [20] on supported Ru catalysts. DFT studies of CH₃-CH₃ coupling reactions on bare flat extended Co(0001) [10, 11] and Ru(0001) [12] surfaces showed that such reactions can occur with modest activation barriers (70 - 100 kJ mol⁻¹); these barriers are lower on stepped and defect surfaces at low adsorbate coverages [11], but such surfaces do not necessarily reflect the catalyst surfaces that exist during FTS reactions. These calculated activation barriers, as a result, do not necessarily reflect measured barriers on CO*-covered surfaces in FTS [2].

A myriad of other chain growth mechanisms have been proposed, including alkenyl mechanisms, in which vinylic species (CH₂CH*) react with methylene (CH₂) species to propagate chains [6, 7]. Condensation-type reactions of oxygen-containing chain growth intermediates (H₂CO*) were proposed, initially without significant experimental support [21]; later results showed that isotopically-labeled alcohols and aldehydes were incorporated into larger hydrocarbon species [3, 4, 5], possibly via their initial conversion to alkenes followed by subsequent re-adsorption and growth. Chain growth reactions in FTS involve reactions of vicinal surface intermediates, irrespective of the identity of the monomer or the structure of the growing chain; one requirement of any such mechanism, as a result, is that the growth monomer be vicinal to the growing chain. Results from isotopic transient experiments on supported Co and Fe catalysts have shown that CO* is the most abundant surface intermediate during FTS, that growing chains occupy less than 1% of the catalyst surface area, and that the lifetime of a growing hydrocarbon chain during FTS is ~ 40 times shorter than that of the monomer involved in chain growth [8]. Such rapid chain growth on catalyst surfaces covered in CO* species is consistent with CO* species as the relevant monomer for chain growth.

A chain growth mechanism involving CO* insertion into a metal-alkyl bond was proposed to explain the product distributions from FTS, which include small amounts of alkanols and alkanals [22, 23]; such CO* insertions (or alkyl migrations) are ubiquitous in organometallic systems [24, 25] and occur during homogeneous hydroformylation reactions on Ru [26] and Co [27] carbonyl complexes. Heterogeneous reactions of CO* with CH₂* on bare Co(0001) surfaces were recently examined by DFT and CO* insertion into a M-CH₂ bond was found to have a lower activation barrier (80 kJ mol⁻¹) than CO* insertion into M-CH (107 kJ mol⁻¹) or M-CH₃ (185 kJ mol⁻¹) bonds [13]. The M-CH₂ bond is fully cleaved in such transition states [13]; thus, the large reported activation barriers for such reactions on bare Co(0001) surfaces (185 kJ mol⁻¹) reflect the strength of the M-CH₃ bond. High adsorbate coverages destabilize surface-adsorbate bonds [1, 2, 28,
however, making these reactions possible on surfaces saturated with CO* and relevant to FTS catalysis.

C1 chain termination probabilities (to form CH4) are 5-10 times higher than those for larger surface alkyls (to the corresponding alkane) on supported Ru and Co catalysts at the high pressures required for significant chain growth [30, 31]; any proposed C-C bond formation mechanism in FTS, as a result, must be consistent with the apparent difficulty in forming the first C-C bond in such reactions. Synthesis gas is generally produced via steam reforming of CH4, an expensive and energy-intensive process. Any CH4 formed during FTS, as a result, must be recycled to an upstream reformer and CH4 formation is thus an unproductive reaction; a fundamental understanding of why C1 chains terminate preferentially, however, remains unavailable.

This work reports the effects of CO conversion (residence time) and reactant (H2 and CO) pressures on measured hydrocarbon product selectivities and chain termination parameters on Ru/SiO2 catalysts at pressures and temperatures relevant for significant chain growth. We propose a chain growth scheme that involves reactions of CO* monomers with surface alkyl (CnH2n+1*) species, consistent with CO* as the most abundant surface intermediate (MASI) in FTS [8, 14, 15, 16]. We also report here DFT-derived activation barriers for CO* + CnH2n+1* reactions on 201-atom Ru cluster surfaces at near-saturation CO* coverages and show that such alkyl migration activation barriers are consistent with chain termination probabilities measured during FTS. Finally, we present a modified CO consumption rate equation that is required to account for CO consumption via both CO* activation to CHx species and CO* incorporation into growing alkyl chains.

4.2 Experimental and Theoretical Methods

4.2.1 Steady-state rate and selectivity measurements

FTS turnover rates (per surface Ru atom) and product selectivities were measured in an isothermal (± 2 K), stainless-steel packed-bed reactor; the packed-bed contained a 5 wt. % Ru/SiO2 catalyst (1-2 g, average aggregate particle diameter 105 – 177 μm, average Ru cluster size ~ 7 nm as determined by H2, O2, and CO chemisorption) diluted with SiO2 (1-3 g, Davisil 62, 105 – 177 μm, 1.15 cm3 g-1, 300 m2 g-1) to maintain isothermal reaction conditions. Catalyst samples were synthesized using incipient wetness impregnation methods and were characterized using volumetric adsorption methods described previously [2]. The reactor temperature was measured by a thermocouple (K-type, Omega) that provided feedback to a three-zone furnace (Carbolite TVS 12/600) for temperature control. The catalyst bed was treated in flowing H2 (Praxair, 5.0 grade, 75 cm3 (STP) g-1 s-1) to 673 K at 0.017 K s-1 and held for 8 – 10 h prior to synthesis gas (CO/ H2) exposure. The catalyst samples were then cooled to 443 K before exposure to a CO/H2 stream (Praxair, Certified Standard, H2/CO = 2, 0.5 cm3 (STP) g-1 s-1) with Ar as an internal standard. The system pressure was then increased slowly using a back-pressure regulator (Mity-Mite, stainless-steel) to 2.1 MPa, followed by a slow increase in reactor temperature (0.0083 K s-1) to 463 K. All reported rate and selectivity
measurements were steady-state values obtained from catalyst samples after at least 24 h on-stream.

Reaction products were analyzed via on-line gas chromatography (Agilent 6890N) equipped with a methyl silicone capillary column (Agilent, HP-1, 50 m x 0.320 mm x 0.15 μm film thickness) and flame ionization detector for C₁-C₈ hydrocarbons and a packed-column (Porapak Q, Supelco, 12 ft x 0.125 in) with a thermal conductivity detector for analysis of light gases (CO, Ar, H₂, CH₄, CO₂). All transfer lines were kept above 423 K to avoid condensation of large hydrocarbons, which were collected in a hot trap (393 K) at reactor pressure for offline analysis using high-temperature gas chromatography. A cold trap at ambient temperature and pressure was used to collect water and any liquid organic products that were not collected in the hot trap.

4.2.2 Offline hydrocarbon wax analysis using high-temperature gas chromatography

Large hydrocarbons were collected from the hot trap, sealed in a glass vial, and cooled to ambient temperature before analysis. A wax sample (~ 0.1 g) was dissolved in n-hexane (~ 30 mL) by stirring at ambient temperature until the resulting mixture was transparent. A small amount (~ 1 μL) of the dissolved wax solution was injected manually into the inlet of a gas chromatograph (Agilent 6890N) with a high-temperature capillary column (J&W Scientific, DB-1HT, 15 m x 0.320 mm x 0.10 μm film thickness) and flame ionization detector. C₈ – C₃₅ products were separated and identified via boiling point; offline quantitative analysis of C₈⁺ products was combined with the online analysis of C₁-C₇ products to close the carbon balance (based on total CO consumption) within ±10%.

4.2.3 Computational procedures

Periodic plane-wave, gradient-corrected density functional theory (DFT) calculations were performed using the Vienna Ab-Initio Software Package [32, 33, 34]; the revised Perdew-Becke-Ernzerhof (RPBE) density functional [35] and Vanderbilt ultrasoft pseudo-potentials [36] were used in all calculations. Calculations were performed on the low-index (111) terraces of 201-atom fcc cubo-octahedral Ru clusters (Ru₂₀₁, average diameter ~ 1.8 nm); the details of the structure and geometry of the Ru₂₀₁ clusters have been described elsewhere [2]. A single gamma-centered k-point was used to sample the first Brillouin zone for the Ru₂₀₁ cluster, while a 0.25 x 0.25 x 0.25 nm³ unit cell was used to provide ample vacuum space between cluster images to minimize their interactions. Calculations were assumed to converge when the electronic energy changed by less than 10⁻⁵ eV between energy iterations and the forces on all atoms were less than 0.05 eV Å⁻¹; our previous work has shown that these criteria are adequate for modeling CO adsorption and CO activation reactions on Ru₂₀₁ cluster surfaces [2].

Reactant, transition state, and product structures and energies were calculated for CO* + CₙH₂ₙ₊₁* (n = 1 – 3) reactions on the low-index (111) terraces of Ru₂₀₁ particles at 1 monolayer (ML) CO* coverage. The reaction paths for all systems were generated initially by a linear interpolation of images between converged reactant and product structures; this initial path was further refined by the nudged elastic band (NEB) method.
[37, 38] until the forces on all atoms were less than 0.3 eV Å⁻¹. The highest energy point along the resulting path was used as input to a dimer calculation [39], which located the transition state by moving the initial structure to a saddle point along the reaction energy surface where the forces on all atoms were less than 0.05 eV Å⁻¹.

4.3 Results and Discussion

4.3.1 Effects of CO conversion, H₂ pressures, and CO pressures on Fischer-Tropsch synthesis product selectivities

Figure 4.1 shows the effects of CO conversion, changed by adjusting the CO space velocity, on CH₄ and C₅₆ selectivities (carbon basis) during FTS on a 5 wt. % Ru/SiO₂ catalyst. CH₄ selectivities decreased, while C₅₆ selectivities increased as CO conversion (and the residence time of CO reactants) increased; similar trends were reported previously on supported Ru [30], Co [31, 40], and Fe [41] catalysts and show that hydrocarbon chain growth is favored at long residence times and high CO conversions. FTS hydrocarbon products are predominantly 1-alkenes and n-alkanes, which form via β-hydrogen abstraction and hydrogen addition reactions of surface alkyl groups, respectively [9]. Longer residence times for product alkenes lead to a higher probability of re-adsorption to the catalyst surface and to re-incorporation of alkenes into growing hydrocarbon chains [30, 42]; as a result, product distributions are shifted to larger hydrocarbon chains as residence times and CO conversions increase. We show later that alkene re-adsorption and growth occurs slowly on our catalyst sample and that alkenes instead undergo secondary hydrogenation to the corresponding alkane; the observed increases in C₅₆ selectivity with increasing CO conversion (Figure 4.1), however, suggest that alkene re-adsorption and growth still occurs on Ru catalysts.

Figure 4.2 shows the effects of CO conversion on 1-alkene to n-alkane ratios (χ) for C₅-C₆ hydrocarbons. 1-Alkene to n-alkane ratios decreased slightly with increasing CO conversion for all carbon numbers; such decreases reflect a higher probability of irreversible hydrogenation of alkenes to alkanes as residence time increases and alkenes re-visit the catalyst surface. These results suggest that alkenes can apparently re-adsorb also on catalyst sites that cannot catalyze chain propagation reactions. 1-Alkene to n-alkane ratios decreased with increasing carbon number at all CO conversions, except for C₅ species, which exhibit low ratios because of the high reactivity of ethene [43]. Larger alkenes diffuse more slowly than smaller alkenes in liquid-filled catalyst pores [44]; 1-alkene to n-alkane ratios decrease with carbon number, as a result, because larger alkenes are more likely to be hydrogenated to the corresponding alkane before escaping the catalyst pores.

Higher CO conversions also lead to higher H₂O product concentrations [16, 45]; effects of CO conversion (residence time) and H₂O pressures on product selectivities, as a result, cannot be separated from these measurements. CH₄ selectivities decreased and C₅₆ selectivities increased with increasing inlet H₂O pressures on Ru [45] and Co [40] catalysts; these trends parallel those observed with increasing CO conversion (Figure 4.1). A competitive adsorption between H₂O and H₂ that decreases the availability of surface hydrogen atoms (H*) may explain the observed suppression of secondary
hydrogenation reactions. H$_2$O can also increase CO consumption rates on Ru [45] and Co [40, 46] catalysts; H$_2$O species, as a result, may not only suppress hydrogenation reactions, but also intervene directly in CO* activation reactions.

Figures 4.3 shows the effects of H$_2$ pressure (at constant CO pressure) on CH$_4$ and C$_5$+ selectivities; CO conversion was maintained between 4 and 8% to minimize effects of secondary reactions and of H$_2$O on product selectivities. CH$_4$ selectivities increased and C$_5$+ selectivities decreased with increasing H$_2$ pressure. Figure 4.4 shows the effects of H$_2$ pressure on 1-alkene to n-alkane ratios for C$_2$-C$_6$ species; these $\chi$ values decreased for all carbon numbers with increasing H$_2$ pressure. The data shown in Figures 4.3 and 4.4 suggest that chain termination increases with increasing H$_2$ pressure because H* species become increasingly available on catalyst surfaces. Our results suggest that liquid phase fugacities of CO and H$_2$ (and thus surface concentrations of CO* and H*) reflect the CO and H$_2$ pressures in the contacting gas phase. Larger catalyst particles (~ 1 mm) can lead to intrapellet H$_2$ and CO concentration gradients, which cause, in turn, CO depletion at active sites, large chain termination probabilities, and even secondary alkane hydrogenolysis on Ru catalysts [42].

Figures 4.5 and 4.6 show the effects of CO pressure (at constant H$_2$ pressure) on CH$_4$ and C$_5$+ selectivities (Figure 4.5) and $\chi$ ratios for C$_2$-C$_6$ species (Figure 4.6). Increasing CO pressure led to lower CH$_4$ selectivities and higher C$_5$+ selectivities (Figure 4.5), while $\chi$ ratios increased with increasing CO pressure for all carbon numbers (Figure 4.6). These data, taken together with those in Figures 4.3 and 4.4, suggest that gas phase H$_2$/CO ratios set the relative CO* and H* concentrations on catalyst surfaces, which determine, in turn, the relative concentrations of monomers for chain growth reactions and of H* species for irreversible chain termination.

We have shown here that H$_2$/CO gas phase ratios determine the relative abundance of H* and CO* species on the catalyst surface in the absence of transport restrictions that lead to concentration gradients within catalyst particles. We also illustrate how secondary reactions during FTS depend on the residence time of primary products, especially 1-alkenes, which can re-adsorb to the catalyst surface and participate in further chain growth; measured chain termination parameters reported next, however, suggest that secondary hydrogenation reactions are favored on Ru catalysts. Product selectivities on a carbon basis, however, are not the most appropriate descriptor of inherent termination and propagation rates in FTS, because they cannot be expressed in terms of elementary steps for chain growth and termination. The mole fractions of each hydrocarbon product in FTS, which are related to chain termination parameters for each carbon number in the product spectrum, can be used to describe termination and propagation rates on the catalyst surface. We describe in the next section a chain growth scheme for surface hydrocarbon intermediates and present data that probe the effects of chain length, H$_2$, and CO pressures on chain termination parameters measured on Ru/SiO$_2$ catalysts under conditions of significant chain growth.

4.3.2 Chain growth pathways and termination parameters in Fischer-Tropsch synthesis

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Scheme 4.1 shows chain propagation and termination reactions, as well as secondary reactions (alkene re-adsorption) occurring during FTS. CO(g) species adsorb to the catalyst surface and form CO-derived activated species I₁*, which then enter the chain growth pool as C₁* intermediates (Scheme 4.1). The C₁* intermediate can react with chemisorbed hydrogen (H*) and leave the catalyst surface irreversibly (r₁,1) as CH₄ or with a chain growth monomer (r₁,1) to form a C₂* hydrocarbon. The total chain termination rate (r₁,n) for any carbon number n is the sum of the Cₙ 1-alkene and the Cₙ n-alkane formation rates. The chain propagation rate for each carbon number n (rₚ,n) is the rate at which Cₙ species add a monomer to form Cₙ₊₁* species and ultimately appear as any of the chains with more than n-carbons. FTS product distributions can then be described by individual chain termination parameters βₙ[30, 47]:

\[
βₙ = \frac{r_{t,n}}{r_{p,n}} = \frac{φₙ}{\sum_{i=n+1}^{∞} φᵢ}
\]  

(4.1)

where φₙ is the mole fraction of the n-hydrocarbon product. The chain termination parameter βₙ can be expressed as the sum of those for each termination route:

\[
βₙ = β_{H,n} + β_{O,n} - β_{R,n}
\]  

(4.2)

where β_{H,n} is the termination parameter to n-alkanes (via hydrogenation), β_{O,n} is the termination parameter to 1-alkenes, and β_{R,n} is the 1-alkene re-adsorption parameter [30]. The individual parameters in Equation 4.2 can be calculated by substituting the mole fraction of each species (alkane or alkene) in the numerator of Equation 4.1. The chain termination parameter βₙ is also related to the chain growth parameter αₙ for each chain with n-carbons by:

\[
αₙ = \frac{r_{p,n}}{r_{p,n} + r_{t,n}} = \frac{1}{1 + \sum_{i=n+1}^{∞} φᵢ} = \frac{\sum_{i=n}^{∞} φᵢ}{\sum_{i=n}^{∞} φᵢ}
\]  

(4.3)

The net chain growth parameter (αₙ) was first proposed to describe FTS product distributions in which chain propagation rates were independent of chain length [48]. FTS product distributions, however, can deviate from such Anderson-Schulz-Flory (ASF) kinetic as FTS chain growth probabilities that increase with increasing chain length are often reported [30, 31, 49]. The non-ASF product distributions can be described accurately using chain termination parameters (βₙ) that can vary with chain length. Deviations from ASF kinetics reflect re-adsorption of large alkenes that are subject to transport restrictions in the liquid-filled catalyst pores during FTS; such deviations can be
modeled quite well by alkene readsorption and CO/H$_2$ reaction-diffusion models reported previously [50].

Figure 4.7 shows the total chain termination parameters ($\beta_n$), the termination parameters to alkanes ($\beta_H$), and the termination parameters to alkenes ($\beta_O$) as a function of chain length. The total chain termination parameter ($\beta_n$) is much larger for C$_1$ species (0.43) than for larger chains; it becomes nearly independent of carbon number for C$_2$-C$_{30}$ hydrocarbons (0.15 – 0.2), consistent with previously reported chain termination parameters on Ru and Co catalysts [30]. Chain termination parameters to alkenes decrease with increasing carbon number until alkenes are no longer detected in the product distribution. The disappearance of alkenes with increasing carbon number reflects higher hydrogenation and chain re-initiation rates for larger alkenes, which exacerbates transport restrictions within catalyst pellets [42]. The chain termination parameter to alkanes ($\beta_H$) equals the total chain termination parameter (Equation 4.2) when alkenes disappear from the product distribution. The sum of the alkane ($\beta_H$) and alkene ($\beta_O$) termination parameters is nearly equal to the total chain termination parameter ($\beta_n$) for C$_2$+ species, indicating that the alkene re-adsorption (Equation 4.2) is slow and does not contribute significantly to chain growth.

The chain termination parameter for C$_1$ species to CH$_4$ (0.43) is nearly ten-fold larger than for C$_2$-C$_{15}$ alkanes (0.01 – 0.07) and still more than two-fold larger than $\beta_H$ (and $\beta_O$) at large carbon numbers (C$_{25+}$). A C$_1$ chain termination parameter of 0.43 implies that about one-third of all C$_1$* species terminate as CH$_4$, before chain growth; similar C$_1$ termination parameters (0.50 – 0.55) and discrepancies between C$_1$ termination parameters and those for larger alkyls have been reported previously for FTS on Ru catalysts [30]. Relatively large C$_1$ termination parameters suggest that the relative rates for termination and growth for C$_1$ species differ from those for larger species (Figure 4.7).

The chemical significance of the chain termination parameters is provided by the elementary steps involved in chain termination and chain propagation. Here we propose that chain termination and propagation occur via reactions of surface alkyl species with H* and C$_1$* monomer species, respectively. The chain termination parameter to alkanes ($\beta_H$) is then given by:

$$\beta_{H,n} = \frac{r_{H,n}}{k_{p,n}} \frac{k_{H,n} \left( C_n H_{2n+1}^* \right) \left( H^* \right)}{k_{p,n} \left( C_n H_{2n+1}^* \right) \left( C_1^* \right)} = \frac{k_{H,n} \left( H^* \right)}{k_{p,n} \left( C_1^* \right)}$$  \hspace{1cm} (4.4)

where $r_{H,n}$ is the alkane termination rate for carbon number n, $k_{H,n}$ is the alkane termination rate constant for carbon number n, $k_{p,n}$ is the propagation rate constant for carbon number n, $(C_n H_{2n+1}^*)$ is the surface concentration of n carbon alkyl species, $(H^*)$ is the surface concentration of hydrogen atoms, and $(C_1^*)$ is the surface concentration of chain growth monomers. The rate constants in Equation 4.4 can be restated in their Arrhenius form:
\[ \beta_{H,n} = A \exp \left( \frac{-(E_{H,n} - E_{p,n})}{RT} \right) \frac{H^*}{C_1^*} \]  

(4.5)

where \( A \) is the pre-exponential factor, \( E_{H,n} \) is the activation barrier for the termination of an \( n \)-carbon alkyl species, and \( E_{p,n} \) is the activation barrier for the propagation of an \( n \)-carbon alkyl species. Equation 4.5 shows that the chain termination parameter to alkanes is related to the difference in activation barriers of the elementary steps for chain termination and chain propagation.

We have used a generic designation for the monomer (\( C_1^* \)) thus far to describe chain propagation reactions. The identity of the \( C_1 \) monomer species, however, is still debated in the literature and critical for any more detailed analysis of chain growth – although the rapid chain growth measured by isotopic transient methods on supported Co catalysts [8] suggests that the reactive monomer species must be a readily available and possibly the predominant surface species during FTS. Kinetic [1, 15, 16], infrared [14], and transient isotopic measurements [8] are consistent with CO* as the most abundant surface intermediate (MASI) during FTS; therefore, rapid chain growth in FTS would be consistent with a mechanism involving CO* as the chain growth monomer. Other chain growth mechanisms, involving CH\(_x\)-CH\(_x\) coupling or condensation reactions of H\(_x\)CO species, as a result, are unlikely to contribute to chain growth paths. In the next section, we apply density functional theory (DFT) methods to estimate activation barriers for chain termination via alkyl hydrogenation to the corresponding alkane, as well as to calculate such barriers for chain propagation via alkyl migration to vicinal CO* species to reconcile the abrupt changes in chain termination probabilities after chains form the first C-C bond.

4.3.3 DFT-derived chain termination and chain propagation barriers on Ru clusters at high CO* coverages

Figure 4.8 shows DFT-derived reactant, transition state, and product structures for \( C_1 \) chain termination (CH\(_3^*\) + H*) reactions on the (111) terraces of Ru\(_{201}\) cluster surfaces at 1 ML CO* coverages. Chain termination and chain propagation reactions were modeled on (111) terraces of Ru\(_{201}\) clusters because cluster size effects on rate data for Ru [51] and Co [52] catalysts are consistent with FTS reactions occurring predominantly on high-coordination exposed metal atoms; recent DFT studies of CO* activation at relevant CO* coverages have also shown that activation barriers for CO* dissociation on high-coordination sites are lower than those for low-coordination sites [2].

Surface methyl species react with co-adsorbed H* species via a three-center (H-Ru-CH\(_3\)) transition state (Figure 4.8, panel b) to form CH\(_4\), which does not interact with the Ru surface in the product state (Figure 4.8, panel c). Methane formation is exothermic (-150 kJ mol\(^{-1}\)), and proceeds via early transition states, in which the H-CH\(_3\) bond is not yet formed (H-CH\(_3\) = 1.97 Å; Figure 4.8, panel b); the calculated activation energy for CH\(_4\) formation is 30 kJ mol\(^{-1}\).
DFT-derived reactant, transition state, and product structures for C₂ and C₃ alkyl termination reactions are shown in Figures 4.9 and 4.10, respectively. C₂ and C₃ alkyl termination reactions, as in the case of C₁ termination, are strongly exothermic (-172 kJ mol⁻¹ and -166 kJ mol⁻¹, respectively) and proceed via early transition states, in which H-C₂H₆₃ bonds have not yet formed. The activation energies for C₄H₁₀ and C₅H₁₂ formation are 27 kJ mol⁻¹ and 30 kJ mol⁻¹, respectively. Activation energies for alkyl termination reactions are essentially independent of alkyl size, because such reactions occur via early transition states. Early transition states for alkyl hydrogenation reactions are consistent with previous studies showing that C-H bond activation in alkanes (the microscopic reverse of alkyl hydrogenation) proceeds via late transition states in which C-H bonds are completely broken [53]. The difference in chain termination parameters between C₁ and C₃ species (Figure 4.7), therefore, must arise from effects of alkyl size in chain propagation activation energies, in light of the size independence of termination rate constants (Equation 4.5, Eₜₐₙ).

Figure 4.11 shows the DFT-derived reactant, transition state, and product structures for C₁ chain propagation (CH₃* + CO*) reactions on CO*-covered (1 ML) Ru₂₀₁ cluster (111) surfaces. Surface methyl species react with vicinal CO* species via late transition states, in which Ru-CH₃ bonds are fully cleaved (Figure 4.11, panel b), suggesting that activation barriers will “sense” the strength of such M-C bonds; such propagation reactions are slightly endothermic (+8 kJ mol⁻¹) and form C₂ acyl species (CH₃CO*) in the product state. The calculated activation energy for C₁ propagation reactions is 70 kJ mol⁻¹, which reflects, in part, the energy required to cleave Ru-CH₃ bonds before the incipient formation of the new C-C bond as a result of the reaction between CH₃* and CO* species.

Figures 4.12 and 4.13 show reactant, transition state, and product structures for C₂ and C₃ propagation reactions, respectively. These alkyl migrations also proceed through late transition states analogous to those for CH₃* migration reactions and again, Ru-alkyl bonds are fully cleaved at the transition state (Panel b in Figures 4.12 and 4.13). C₂ and C₃ propagation reactions are exothermic (-30 kJ mol⁻¹ and -25 kJ mol⁻¹, respectively) with calculated activation barriers of 40 kJ mol⁻¹ and 48 kJ mol⁻¹, which are significantly lower than those for the formation of the first C-C bond via CH₃* reactions with CO*.

Table 4.1 shows the calculated activation barriers and reaction energies for C₁-C₃ chain termination and propagation steps on (111) facets of Ru₂₀₁ clusters with 1 ML CO* coverages; saturation coverages are larger (~ 1.55 ML) on Ru₂₀₁ clusters [2], but we expect the trends in DFT-derived barriers at 1 ML are similar to those at CO*-saturation. All chain termination reactions, irrespective of chain length, are strongly exothermic (-150 kJ mol⁻¹ to -172 kJ mol⁻¹) with modest activation barriers (27 kJ mol⁻¹ to 30 kJ mol⁻¹). C₁ chain propagation activation energies (70 kJ mol⁻¹) are larger than those for C₂ (40 kJ mol⁻¹) and C₃ species (48 kJ mol⁻¹). The differences between propagation and termination barriers, which are reflected in the chain termination parameters (Equation 4.5), are larger for C₁ species (40 kJ mol⁻¹) than for C₂ (13 kJ mol⁻¹) or C₃ (18 kJ mol⁻¹) species. These differences in barriers are consistent with the preferential termination of C₁ species (to CH₄) reported here (Figure 4.7), and also previously on Ru [30] and Co [31] catalysts.

Alkyl migration reactions proceed through late transition states in which metal–alkyl (M-alkyl) bonds are fully cleaved; the apparent difficulty in forming the first C-C
bond reflects M-CH₃ bonds that are significantly stronger than M-C₂H₅ or M-C₃H₇ bonds in the reactants involved in alkyl migration (chain propagation). Earlier molecular orbital treatments of alkyl migration reactions on Mn carbonyls reported similar chain length effects on such reactions [25]; these studies related weaker M-alkyl bonds to smaller σ orbital overlap between the alkyl ligands and metal centers in the alkyl reactants involved in these steps. Strong M-CH₃ bonds lead to large CH₃* propagation barriers and, as a result, preferential CH₄ formation (termination). Differences in barriers for propagation and termination of C₂ and C₃ alkyl species, however, are much smaller than those for C₁ species and thus the chain termination probability for larger alkyls is controlled by the relative concentrations of CO* and H* species. Chain propagation for C₂⁺ alkyls occurs more readily than C₁ propagation because chain termination requires desorption of a CO* molecule (from the CO*-saturated surface) to accommodate the H* species that is used ultimately to termination the surface alkyl. CO* desorption requires ~ 40 kJ mol⁻¹ at CO*-saturation coverages [2]; this energy is not compensated by H* adsorption because such steps are nearly thermoneutral at saturation coverages and the apparent activation energy for termination, as a result, is essentially 40 kJ mol⁻¹ larger than the corresponding propagation barrier.

Equation 4.5 shows that when the chain growth monomer (C₁*) is CO*, measured alkane chain termination parameters should be inversely proportional to CO* concentrations (CO pressures) and first-order in H* concentrations (half-order in H₂ pressures). We report the measured effects of H₂ and CO pressures on alkane termination parameters in the next section.

4.3.4 Effects of H₂ and CO pressures on alkane chain termination parameters

Figure 4.14 shows the C₁ alkane termination parameter (β₁) and the Cₙ (n > 25) alkane termination parameter as a function of the P₁²⁻⁰·⁵. Both C₁ and Cₙ alkane chain termination parameters are proportional to the P₁²⁻⁰·⁵, consistent with chain termination to alkanes proportional to (H*) coverages (Equation 4.5). Increasing H₂ pressures has a greater effect on C₁ alkane chain termination parameters than on Cₙ chain termination parameters (Figure 4.14), suggesting that the termination to propagation rate constant ratios for C₁ species (Equation 4.5) are greater than such ratios for large (Cₙ, n > 25) alkyl chains. The slopes of the lines in Figure 4.14 are consistent with the DFT results reported here, which show larger differences in propagation and termination barriers (and thus larger differences in the rate constants for such reactions) for reactions of C₁ alkyl species than for such reactions of larger alkyls (Table 4.1).

Figure 4.15 shows the C₁ and Cₙ alkane termination parameters as a function of the inverse CO pressure. Both C₁ and Cₙ alkane termination parameters are proportional to the inverse of CO pressure, consistent with increased chain propagation rates with increasing CO* concentrations (Equation 4.5); decreasing CO pressures (and thus increasing the inverse of CO pressures) has a greater effect on C₁ termination parameters than on Cₙ termination parameters (Figure 4.15), indicating that differences in termination and propagation rate constants for C₁ species are larger than those for Cₙ species (Equation 4.5). The slopes of the lines in Figure 4.15 are also consistent with the DFT-predicted differences in activation energies (and thus rate constants) for chain
propagation and chain termination reactions as a function of alkyl chain size. These results show that experiment and theory are consistent with hydrocarbon chain propagation in FTS occurring via reactions of alkyl species with vicinal CO* species.

Chain growth mechanisms that involve CO* as monomers result in two possible routes for consuming CO* – via CO* activation reactions (to CH,* ) and via CO* addition to growing chains. Thus, measured CO conversion rates must contain both contributions; reported CO consumption rates in FTS, however, obey a simple Langmuir-Hinshelwood rate equation [1, 2, 14, 15, 16, 30], which ostensibly includes only CO* activation paths as the mechanism for CO* consumption. In the next section, we consider CO* as the monomer in chain propagation reactions (Scheme 4.1) to derive a complete CO* consumption rate equation with contributions from both CO* activation paths and from steps that insert CO* into hydrocarbon chains.

4.3.5 Consequences of CO* as the chain growth monomer on total CO conversion rate equations in Fischer-Tropsch synthesis

Scheme 4.1 shows that CO species can enter chain growth paths (r,), Scheme 4.1) in FTS as an activated C* intermediate (I,* ); we will refer to this CO* consumption route as CO* activation, which is described on Co [15] and Ru [16] catalysts by the following rate equation:

\[
 r_{CO,act} = \frac{k_{act} P_{H_2} P_{CO}}{(1 + K_{CO} P_{CO})^2}
\]  

(4.6)

In this equation, \( r_{CO,act} \) is the rate of CO consumption via CO* activation, \( k_{act} \) is a lumped rate constant, \( P_{H_2} \) and \( P_{CO} \) are the H\(_2\) and CO pressures, respectively, and \( K_{CO} \) is the equilibrium constant for CO adsorption. CO* species may also act as chain growth monomers in FTS; CO* species, as a result, are consumed in C\(_1\) propagation reactions at rates given by:

\[
 r_1 = r_i \left( \frac{r_{p,1}}{r_{p,1} + r_{r,1}} \right) = r_i \alpha_1
\]

(4.7)

where \( r_i \) is the molar entry rate of activated C\(_1\)* species into the chain growth pool (Scheme 4.1). CO* species are consumed similarly in C\(_n\) propagation reactions at the following rates:
The total CO consumption rate is then given by:

$$r_{CO, total} = r_i + r_i \alpha_1 + r_i \alpha_1 \alpha_2 + r_i \alpha_1 \alpha_2 \alpha_3 + ...$$  \hspace{1cm} (4.9)$$

This expression can be related to CO* activation rates and CO* consumption rates via chain growth by:

$$r_{CO, total} = r_{CO, act} + r_{CO, prop} = r_i \left[ 1 + \sum_{j=1}^{\infty} \prod_{i=1}^{j} \alpha_i \right] = r_i \left( 1 + \zeta \right)$$  \hspace{1cm} (4.10)$$

Equation 4.10 shows that, if CO* species are consumed directly in chain propagation reactions, total CO consumption rates depend on how often chains are initiated ($r_i$) and on the probability that a growing chain adds a CO* monomer, for a given average product chain length ($\zeta$). Previous mechanistic interpretations of total CO consumption rates were based on the premise that all CO species were consumed via CO* activation reactions and that species derived from activated CO acted as both the initiator and the propagating monomer; the observed H$_2$ and CO dependences of CO consumption rates (Equation 4.6), as a result, were justified by a set of elementary steps for CO* activation in which hydrogenation of surface formyl (HCO*) species is the kinetically-relevant step [1, 2]. The probability of CO consumption via chain growth ($\zeta$, Equation 4.10) may also be a function of H$_2$ and CO pressures; in such cases, the identity of the kinetically-relevant step in CO* activation reactions must change in order to reflect the overall dependences of the total CO consumption rates on H$_2$ and CO pressures (Equation 4.10).

Figure 4.16 shows the effects of H$_2$ and CO pressures on the chain propagation part of the total CO consumption rate expression ($\zeta$, Equation 4.10). The $\zeta$ term increases slightly with CO pressures, and decreases slightly with H$_2$ pressures, indicating that chain growth (via CO* addition) probabilities are determined by the H*/CO* ratios prevalent at catalyst surfaces. Three-fold and four-fold changes in H$_2$ and CO pressures lead to only slight changes in $\zeta$ (Figure 4.16). Selectivities to C$_5+$ hydrocarbons (76-82%) were also fairly insensitive to changes in H$_2$ and CO pressures in this range, indicating that the “average” hydrocarbon chain length was similar for all conditions and that the probability of monomer addition to growing chains, as a result, was also similar.

The total CO consumption rate in FTS is first-order in H$_2$ pressure [1, 15, 16, 30]. Chain propagation processes ($\zeta$, Equation 4.10) that are inversely proportional to H$_2$ pressure (Figure 4.16), as a result, requires a second-order dependence of CO activation rates on H$_2$ pressure. A plausible set of elementary steps in which dissociative H$_2$...
adsorption and three successive CO* hydrogenation steps are in quasi-equilibrium results in a second-order H2 dependence of (H-assisted) CO* activation. H2 adsorption-desorption processes are indeed in quasi-equilibrium during FTS reactions [19]; recent DFT-estimated activation barriers for reactions of CO* and H*, however, showed that HCO* hydrogenation is irreversible on Ru201 cluster surfaces at saturation CO* coverages (1.55 ML) [2]. Barriers for the hydrogenation of HCOH* and H2COH* species on Ru surfaces at relevant CO* coverages have not been performed, so no unequivocal comments on the irreversibility of H2COH hydrogenation steps can be made currently. It is unlikely, however, that H2COH hydrogenation reactions are the first irreversible steps in CO activation sequences because such sequences must overcome, at the very least, HCO* hydrogenation barriers (162 kJ mol\(^{-1}\)) that are already larger than measured FTS consumption activation barriers on supported Ru catalysts (90-110 kJ mol\(^{-1}\)) [30].

The effects of H2 and CO pressures on CO consumption via chain growth (\(\zeta\), Equation 4.10) are still inconclusive because of the somewhat narrow H2 and CO pressure ranges studied. Rigorous measurements of chain termination parameters, which require quantification of all FTS products, must be made over a broader range of H2 and CO pressures in order to accumulate enough data to make conclusions regarding chain growth mechanisms in FTS. The form of the total CO consumption rate when CO* is a chain monomer (Equation 4.10), however, is a rigorous descriptor of CO consumption and warrants further investigation to determine whether chain propagation proceeds via reactions of CO* species with surface hydrocarbon chains.

### 4.4 Conclusions

The effects of H2 and CO pressures on product selectivities and chain termination parameters in Fischer-Tropsch synthesis (FTS) on supported Ru catalysts suggest that growing alkyl hydrocarbon chains are terminated to alkanes via reactions with chemisorbed hydrogen (H*) and are propagated to larger species via reactions with monomers derived from chemisorbed CO (CO*). FTS products are predominantly primary alkenes and linear alkanes; increases in C\(\text{5+}\) selectivities with increasing CO conversions (and residence times) are consistent with the re-adsorption and growth of primary alkenes as a chain propagation mechanism. CO* is the most abundant surface intermediate (MASI) during FTS, and, as a result, previous reports of rapid chain growth in FTS is consistent only with CO* functioning as the monomer for chain propagation.

Chain propagation reactions via the migration of surface alkyl species (C\(\text{nH}_{2n+1}\)*) to vicinal CO* species, according to density functional theory (DFT) estimates of activation barriers for such reactions, proceed via late transition states in which the surface-alkyl bonds are broken completely; the lateness of such transition states results in chain propagation barriers that depend on the chain length, viz., the binding energy, of the migrating alkyl species. Chain termination reactions between alkyl species and H* species, according to DFT, are highly exothermic, proceed via early transition states and, as a result, are independent of the identity of the surface alkyl species. Chain termination parameters, which are a rigorous measure of chain propagation and chain termination rates in FTS, are large for C1 species and small and nearly independent of carbon number for C\(\text{2+}\) species; such chain termination parameters are related to differences in activation
barriers between propagation and termination reactions for each carbon number. Differences in alkyl migration (propagation) and alkyl hydrogenation (termination) activation barriers, calculated by DFT, are consistent with measured chain termination barriers that suggest the initial C-C bond formation step in FTS is difficult and that C\textsubscript{1} species terminate preferentially as CH\textsubscript{4}. C\textsubscript{1} alkyl (CH\textsubscript{3}* ) migration to a vicinal CO* species is relatively difficult because CH\textsubscript{3}* species form much stronger surface bonds than do C\textsubscript{2+} alkyls.

Total CO consumption rates include CO activation reactions and chain propagation reactions when CO* species are monomers for chain growth; the kinetic dependences of total CO consumption rates, as a result, reflect contributions from both CO activation and CO consumption via chain propagation. Mechanistic interpretations of CO activation have been made, historically, to justify the observed dependences of CO consumption rates on H\textsubscript{2} and CO pressures; such interpretations must change if H\textsubscript{2} and CO pressures also affect chain propagation reactions. Our data suggest that H\textsubscript{2} and CO pressures weakly affect chain propagation, although larger data sets comprising a broader range of H\textsubscript{2} and CO pressures are needed for further interpretation.

4.5 Acknowledgements

The author gratefully acknowledges Professor Matthew Neurock, Drs. Corneliu Buda and David Hibbitts, and Tom Lawlor (all of the University of Virginia) for assistance with performing and interpreting the density functional theory calculations reported in this work. The BP Conversion Consortium (BP-XC\textsuperscript{2}) provided financial support for this work.
4.6 Figures, Schemes, and Tables

4.6.1 Figures

**Figure 4.1** Effects of fractional CO conversion on CH$_4$ (●) and C$_5$+ (□) carbon selectivities for a 5 wt% Ru/SiO$_2$ catalyst (1.1 MPa H$_2$, 0.55 MPa CO, 463 K).
Figure 4.2. Effects of fractional CO conversion on 1-alkene to n-alkane product ratios for C$_2$ (◆), C$_3$ (■), C$_4$ (▲), C$_5$ (★), and C$_6$ (●) species (5 wt% Ru/SiO$_2$, 1.1 MPa H$_2$, 0.55 MPa CO, 463 K).
Figure 4.3  Effects of H₂ pressure on CH₄ (●) and C₅⁺ (□) carbon selectivities for a 5 wt% Ru/SiO₂ catalyst (0.55 MPa CO, 463 K, CO conversion < 10%).
Figure 4.4  Effects of H$_2$ pressure on 1-alkene to n-alkane product ratios for C$_2$ (♦), C$_3$ (■), C$_4$ (▲), C$_5$ (×), and C$_6$ (●) species (5 wt% Ru/SiO$_2$, 0.55 MPa CO, 463 K, CO conversion < 10%).
Figure 4.5  Effects of CO pressure on CH₄ (●) and C₅⁺ (□) carbon selectivities for a 5 wt% Ru/SiO₂ catalyst (1.1 MPa H₂, 463 K, CO conversion < 10%).
Figure 4.6  Effects of CO pressure on 1-alkene to n-alkane product ratios for C₂ (◆), C₃ (■), C₄ (▲), C₅ (◆), and C₆ (●) species (5 wt% Ru/SiO₂, 1.1 MPa H₂, 463 K, CO conversion < 10%).
Figure 4.7  Effects of chain length on total ($\beta_n$, ▲), alkene ($\beta_o$, ⬤), and alkane ($\beta_H$, ■) chain termination parameters (5 wt% Ru/SiO$_2$, 1.3 MPa H$_2$, 0.65 MPa CO, 463 K, CO conversion = 14%).
Figure 4.8  DFT-calculated reactant (a), transition state (b), and product (c) structures for C\textsubscript{1} alkyl (CH\textsubscript{3}* ) reactions with chemisorbed hydrogen (H*) to form methane (CH\textsubscript{4}) on (111) terraces of Ru\textsubscript{201} cluster surfaces at 1 ML CO* coverage. Color coding is as follows: oxygen (red), carbon (grey), hydrogen (white), ruthenium (teal).

Figure 4.9  DFT-calculated reactant (a), transition state (b), and product (c) structures for C\textsubscript{2} alkyl (C\textsubscript{2}H\textsubscript{5}* ) reactions with chemisorbed hydrogen (H*) to form ethane (C\textsubscript{2}H\textsubscript{6}) on (111) terraces of Ru\textsubscript{201} cluster surfaces at 1 ML CO* coverage. Color coding is as follows: oxygen (red), carbon (grey), hydrogen (white), ruthenium (teal).

Figure 4.10  DFT-calculated reactant (a), transition state (b), and product (c) structures for C\textsubscript{3} alkyl (C\textsubscript{3}H\textsubscript{7}* ) reactions with chemisorbed hydrogen (H*) to form propane (C\textsubscript{3}H\textsubscript{8}) on (111) terraces of Ru\textsubscript{201} cluster surfaces at 1 ML CO* coverage. Color coding is as follows: oxygen (red), carbon (grey), hydrogen (white), ruthenium (teal).
Figure 4.11  DFT-calculated reactant (a), transition state (b), and product (c) structures for $C_1$ alkyl (CH$_3^*$) reactions with chemisorbed carbon monoxide (CO*) to form $C_2$ acyl species (CH$_3$CO*) on (111) terraces of Ru$_{201}$ cluster surfaces at 1 ML CO* coverage. Color coding is as follows: oxygen (red), carbon (grey), hydrogen (white), ruthenium (teal).

Figure 4.12  DFT-calculated reactant (a), transition state (b), and product (c) structures for $C_2$ alkyl (C$_2$H$_5^*$) reactions with chemisorbed carbon monoxide (CO*) to form $C_3$ acyl species (C$_2$H$_5$CO*) on (111) terraces of Ru$_{201}$ cluster surfaces at 1 ML CO* coverage. Color coding is as follows: oxygen (red), carbon (grey), hydrogen (white), ruthenium (teal).

Figure 4.13  DFT-calculated reactant (a), transition state (b), and product (c) structures for $C_3$ alkyl (C$_3$H$_7^*$) reactions with chemisorbed carbon monoxide (CO*) to form $C_4$ acyl species (C$_3$H$_7$CO*) on (111) terraces of Ru$_{201}$ cluster surfaces at 1 ML CO* coverage. Color coding is as follows: oxygen (red), carbon (grey), hydrogen (white), ruthenium (teal).
Figure 4.14  Effects of the square root of H$_2$ pressure on C$_1$ (■) and C$_n$ (n > 25) (●) alkane chain termination parameters (5 wt% Ru/SiO$_2$, 0.65 MPa CO, 463 K, CO conversion 10-11%).
Figure 4.15  Effects of the inverse CO pressure on $C_1$ (■) and $C_n$ (n > 25) (●) alkane chain termination parameters (5 wt% Ru/SiO$_2$, 1.3 MPa H$_2$, 463 K, CO conversion 10-11%).
Figure 4.16  Effects of H₂ pressure (■, 0.65 MPa CO) and CO pressure (●, 1.3 MPa H₂) on CO consumption via chain propagation parameters (see Equation 4.11 in text) (5 wt% Ru/SiO₂, 463 K, CO conversion 10-11%).
4.6.2 Schemes

![Diagram of Scheme 4.1]

Scheme 4.1 Chain growth scheme for surface hydrocarbon intermediates \((C_n^*)_\). Activated CO* species \((I_1^*)\) enter the chain growth path \((r_i)\) to form \(C_1^*\) intermediates; n-carbon surface chains are terminated \((r_{t,n})\) as either the corresponding 1-alkene or n-alkane, while n-carbon surface chains are propagated by reacting with \(C_1\) monomers \((r_{p,n})\).

4.6.3 Tables

Table 4.1 DFT-calculated activation energies for reactions of surface alkyl groups \((R)\) with CO (chain propagation) and for reactions of R groups with H (chain termination) on the (111) planes of \(Ru_{201}\) cluster surfaces at 1 ML CO* coverage.

<table>
<thead>
<tr>
<th>Alkyl (R) species</th>
<th>(R + CO) (propagation) barrier / kJ mol(^{-1})</th>
<th>(R + H) (termination) barrier / kJ mol(^{-1})</th>
<th>Barrier difference / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>70</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>C(_2)H(_5)</td>
<td>40</td>
<td>27</td>
<td>13</td>
</tr>
<tr>
<td>C(_3)H(_7)</td>
<td>48</td>
<td>30</td>
<td>18</td>
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4.7 References

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