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Preferential activation of CO near hydrocarbon chains during Fischer–Tropsch synthesis on Ru

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ABSTRACT

We report here theoretical evidence for an enhancement in CO activation to form C_1 monomers at locations near growing hydrocarbon chains as a result of their ability to disrupt the dense monolayers of chemisorbed CO* present during Fischer–Tropsch synthesis (FTS). These previously unrecognized routes become favored at the high CO* coverages that prevail on curved cluster surfaces at conditions of FTS practice and account for the rapid growth of chains, which requires a source of vicinal monomers. CO activation initially requires a vacant site (and consequently CO* desorption) and proceeds via CO* reactions with H* to form hydroxymethylene (CH*OH*), which then dissociates to form OH* and CH*; CH_x* species can subsequently act as monomers and insert into chains, a process denoted as the 'carbene' mechanism. These CH*, and their larger alkylidyne ($C_nH_{2n-1}^*$) homologs, disrupt the dense CO* adlayers and in doing so allow the facile formation of vicinal CH*OH* intermediates that mediate CO activation, without requiring, in this case, CO* desorption. This causes CO* activation effective enthalpy and free energy barriers to be ~100 and ~15 kJ mol^{-1} lower, respectively, near growing chains than within unperturbed monolayers. These effects are observed near alkylidyne ($C_nH_{2n-1}^*$) but not alkylidene (C_nH_{2n}*) or alkyl ($C_nH_{2n+1}^*$) chains. These phenomena cause monomers to form preferentially near growing alkylidyne chains, instead of forming at undisrupted regions of CO* monolayers, causing chain growth (via CH_x*-insertion) to occur much more rapidly than chain initiation, a requirement to form long chains. Such routes resolve the seemingly contradictory proposals that CH_x* species act as monomers (instead of CO*) and chain initiators, but their formation and diffusion on dense CO* adlayers must occur much faster than chain initiation for such chains to grow fast and reach large average lengths. Chains disrupt surrounding molecules in the adlayer, causing faster monomer formation precisely at locations where they can readily react with growing chains. This work illustrates how interactions between transition states and co-adsorbates can dramatically affect predicted rates and selectivities at the high coverages relevant to practical catalysis.

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1. Introduction

Fischer–Tropsch synthesis (FTS) converts synthesis gas mixtures (CO and H_2) to hydrocarbons on Fe, Co, and Ru catalysts [1–3]; it is a process critical to the success of many strategies for the conversion of natural gas, biomass, and CO_2 to fuels, energy carriers, and chemicals. Hydrocarbon chains are initiated by CO activation on metal surfaces; these chains propagate by adding CO-derived monomers and terminate via desorption as alkenes, alkanes, and mixtures of oxygenates [2–4]. Kinetic [5–7], infrared [8,9], isotopic switch [4], and theoretical studies [8] indicate that these reactions occur on surfaces nearly saturated with chemisorbed CO (CO*).

Recent studies have confirmed that CO activation occurs via H-assisted routes that form hydroxymethylene (CH*OH*) species before the cleavage of the C–O bond on Co and Ru [6,8,10,11]. CH*OH* dissociates to form CH* species that hydrogenate to form CH_x* (and ultimately CH_4) or react with a CO*-derived monomer (C_1^*, CO* or CH_x*) to form C–C bonds; the OH* formed via CH*OH* dissociation results in H_2O co-products [6,8,10–12]. Such

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mechanistic consensus is not apparent for C–C bond formation routes. $^{12}CO/^{13}CO$ isotopic switch data have shown that alkenes form with similar isotopic content at each location along the backbone, indicating that all of its C-atoms are added within a period of time much shorter than the time required to replace CO* reactant with a given carbon isotope [4]. These data indicate that a small number of chains grow rapidly on surfaces during FTS, via a process that appears to require the rapid formation of monomers within diffusion distances from growing chains.

Hydrocarbon chains can react with vicinal CO* in CO-insertion routes that form C–C bonds and CH_xCO^* species; the latter may desorb after H-addition to form alkanals and alkanols or cleave its C–O bond to form precursors to alkenes and alkanes [13–18]. The rapid chain growth processes discussed above could plausibly occur via CO*-insertion because of readily available vicinal CO* when chains grow on CO*-saturated surfaces; theoretical treatments of such routes will be reported in a separate manuscript at a later time.

CH_x^* addition to growing chains can also form C–C bonds, as inferred from the incorporation of CH_2^* species derived from CH_2N_2 into the hydrocarbons formed from H_2–CO reactants [19,20], via a process that has been denoted as the carbene route [21–26]. These CH_x^* species form from CO* via the same H*-assisted CO cleavage that initiates chains. For fast chain growth [4], such CH_x-insertion propagation routes would require that CO activation steps be much faster than the corresponding steps that initiate chains and that CH_x^* species, some with multiple covalent surface attachments, diffuse very rapidly on CO*-saturated surfaces.

Here, we provide theoretical evidence for an alternate route that involves the preferential H-assisted activation of CO* molecules that reside next to a growing chain. Such processes are made possible through a disruption of dense CO* monolayers by such growing chains, which lead to an “activation space”; this space avoids the need to desorb an additional CO*, which carries a significant enthalpic penalty, to ameliorate the repulsive forces that destabilize transition states at high CO* coverages. These first-principles density functional theory (DFT) calculations show that enthalpy and free energy barriers for H*-assisted CO* activation on Ru surfaces are lower for activating CO* vicinal to hydrocarbon chains, via monolayer disruption phenomena that are likely to prevail at the CO* coverages required for significant chain growth from H_2–CO reactants on other FTS catalysts. These seemingly unrecognized processes allow fast CH_x^* mediated chain propagation to readily occur via preferential monomer formation near growing chains and thus account for the rapid chain growth observed experimentally but inconsistent with the carbene route. More generally, the results presented herein indicate that dense adlayers, ubiquitous in the practice of catalysis, significantly influence the steric and electronic properties of sites and intermediates and thus the reactivity of adsorbates, an essential feature often ignored in fundamental studies carried out on model surfaces at low surface coverages.

2. Methods

Periodic plane-wave DFT methods implemented in the Vienna *ab initio* simulation package (VASP) [27–30] were used to calculate adsorption and reaction energies and activation barriers for elementary steps involved in CO* activation and CH_x^* formation. Plane-waves were constructed using projector augmented-wave (PAW) potentials with an energy cutoff of 400 eV [31,32]. The revised Perdew–Burke–Ernzerhof (RPBE) form of the generalized gradient approximation (GGA) was used to determine exchange and correlation energies [33–35]. Furthermore, calculations were carried out using optB86b-vdW [36] and vdw-DF2 [37] GGA functionals to describe dispersion forces among atoms. Similar dispersive interactions were incorporated into RPBE calculations using DFT-D3 with Becke and Johnson (BJ) damping [38,39]. DFT-D3 was also used to determine interactions among non-metal atoms (C, O, and H) to correct for dispersive interactions only between co-adsorbates, as the parameters for the DFT-D3 method were primarily based on interactions of gas-phase species [38,39]. Wavefunctions were converged to within 10^{-6} eV and forces were computed using a fast Fourier transform (FFT) grid with a cutoff of twice the planewave cutoff. A $1 \times 1 \times 1$ Monkhorst–Pack sampling of the first Brillouin zone (k-point mesh) was used [40] and structures were relaxed until forces on unconstrained atoms were <0.05 eV/Å.

A 586-atom Ru cubo-octahedral particle (~2.5 nm in diameter) was used in the calculations at 1.044 CO*/Ru coverages (284 CO* on 272 surface Ru atoms) to account for sites with different coordinations and relevant CO* coverages. Edge and corner atoms of low coordination (96 atoms) on Ru_{586} stabilized bridge-bound CO* species (108 CO* species) that lead to supramonolayer coverages (Fig. 1) through the formation of geminal dicarbonyl species as observed with infrared experiments [8]. The high saturation coverages found here are fully consistent with in situ infrared studies [8,9,41], isotopic switch experiments [4], transient kinetic studies [6] and previous FTS kinetic studies [5–7] that all indicate that the Co and Ru surfaces are fully covered in CO* at FTS conditions. CO* peak intensities measured on Ru with in situ infrared spectroscopy no longer increase with increasing CO pressures above ~0.5 kPa CO even at higher temperatures (548–598 K) than those associated with FTS (~500 K), indicating that surfaces are saturated at such pressures [41]. Furthermore CO hydrogenation rates on Ru obtained at near-methanation conditions (548–598 K and 0.01–10 kPa CO) show that hydrogenation becomes inhibited by CO (indicating CO* coverages exceed 0.5 ML) at less than 0.1 kPa CO [41]. This is consistent with high-vacuum studies that indicate saturation coverages of ~0.9 ML CO* are reached at 10^{-2} Torr [42]. Rigorous FTS kinetic studies on Ru [8] and Co [6] also show that the rates of FTS are inhibited by increasing CO pressure which is a direct result of the dominance of the $K_{CO}(CO)$ term in the denominator of the rate equation:

$$r = \frac{\alpha(H_2)(CO)}{[1 + K_{CO}(CO)]^2}$$

At conditions typical of FTS, the surface is fully covered in CO* and thus $K_{CO}(CO)$ is $\gg$1, leading to rates inversely proportional to CO pressure:

$$r = \frac{\alpha'(H_2)}{K_{CO}(CO)}$$

The bottom six layers of the Ru_{586} cluster were removed along the (1 1 1) surface and the bottom two layers of this structure and their CO* species were not allowed to relax during the calculations in order to decrease the computational demands and thus be able to explore a wider range of plausible intermediates and routes (Fig. 1). This Ru_{218} polycrystalline model was used for all calculations reported.

Transition state structures obtained for elementary steps were explored using nudged elastic band (NEB) methods [43,44] and then refined using dimer methods [45]. NEB methods used 16 images and wavefunctions converged to 10^{-4} eV with a FFT grid 1.5 times the size of the plane-wave cutoff. Maximum forces on each atom were converged to <0.3 eV/Å. The dimer algorithm was then used with wavefunctions converged to <10^{-6} eV and a FFT grid size twice the planewave cutoff and converged to a maximum force of <0.05 eV/Å on each atom.