Mechanistic Role of Water on the Rate and Selectivity of Fischer–Tropsch Synthesis on Ruthenium Catalysts

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Ru and Co catalyze Fischer–Tropsch synthesis (FTS) with high rates and C₅+ selectivities using stoichiometric synthesis gas and provide the preferred route to liquid fuels and petrochemicals.[1–3] O-atoms in CO are predominantly removed as H₂O,[2,3] a product that has been shown to increase,[2,4,5] decrease,[6] or not affect[3,7] turnover rates on Co-based catalysts, but which in all cases increases C₅+ and alkene selectivities on Co and Ru.[2,4,5]

H₂O can inhibit rates by increasing O* coverages on Co,[6] such coverages require higher H₂O/H₂ ratios on Ru catalysts, rendering Ru catalysts stable even in aqueous media during FTS.[9] H₂O promotion of FTS rates may reflect faster CO transport within H₂O-rich intrapore liquids when CO diffusion limits rates,[2] but H₂O effects are observed even under conditions of strict kinetic control. H₂O-mediated rate enhancements may arise from higher densities of exposed metal atoms during FTS catalysis, possibly because chemisorbed carbon (C*) reacts with H₂O-derived species. Such a loss of binding sites, however, is inconsistent with CO* coverages (from infrared spectra) that do not depend on H₂O pressure at levels that increased FTS rates by ca. 30%.[5]

Stronger rate enhancements were reported for Co on large-pore supports, which require higher H₂O pressures for intrapore condensation than small-pore supports, suggesting that a condensed H₂O phase, which may exist within small-pore supports at very low CO conversions, may be required.[2,5,9] Here, Ru clusters on large-pore SiO₂ are used to measure rate and selectivity enhancements by H₂O, and that H₂O influences kinetically-relevant CO activation steps.[10] The weaker effects above 0.3 MPa H₂O reflect co-adsorption of H₂O-derived species with CO*, H*, and their products. H₂O decreased CH₄ selectivity and increased C₅+ selectivity (Figure 1), suggesting that H₂O-derived species increase monomer concentrations and/or their propagation rate constants.

Figure 1. CO consumption rate (△ or ●), CH₄ selectivity (□ or ▪), and C₅+ selectivity (○ or ♦) as a function of H₂O partial pressure on 5 wt% Ru/SiO₂ (463 K, 2.9 MPa, H₂/CO = 4.5). Open symbols: space velocity changes; closed symbols: H₂O-addition.

Equation (1) describes the effects of H₂ and CO pressure on FTS rates. 

\[
\dot{r}_{CO} = \frac{a(CO)(H₂)}{(1 + b(CO))}
\]

where (CO) and (H₂) are pressures. This equation indicates that kinetically-relevant transition states (TS) are bound at two vicinal Ru atoms and contain one CO and two H atoms. Direct CO* dissociation is irreversible and exhibits very high
activation barriers, and the resulting rate equation is inconsistent with measured FTS rates, rendering such alternate routes implausible, as previously shown.[10]

Scheme 1 depicts three H-assisted CO activation routes consistent with Equation (1) and their respective lumped rate constants (\(a\)). DFT-derived energies on CO*-covered Ru201 clusters show that CO* and H* react to form HCO* in quasi-equilibrated steps (Step 3a), which then reacts irreversibly with H* to form *HCOH* (95 kJ mol\(^{-1}\)), indicating that HCO* formation is quasi-equilibrated. HCO* dissociation to form CH* and O* has a barrier of 155 kJ mol\(^{-1}\), which is much larger than H*-addition to HCO* to form *HCOH* (95 kJ mol\(^{-1}\)). *HCOH* decomposes to HCO* and H* with a much larger barrier (86 kJ mol\(^{-1}\)) than to CH* and OH*.

Figure 2 shows DFT-derived reaction and activation energies for the formyl and hydroxymethylidyne routes. The HCO* formation barrier is 93 kJ mol\(^{-1}\), while its reverse barrier (30 kJ mol\(^{-1}\)) is much smaller than for its reaction with H* to form *HCOH* (95 kJ mol\(^{-1}\)), indicating that HCO* formation is quasi-equilibrated. HCO* dissociation to form CH* and O* has a barrier of 155 kJ mol\(^{-1}\), which is much larger than H*-addition to HCO* to form *HCOH* (95 kJ mol\(^{-1}\)). *HCOH* decomposes to HCO* and H* with a much larger barrier (86 kJ mol\(^{-1}\)) than to CH* and OH*.

The barrier for H* addition to the O-atom in CO* (to form COH*; 152 kJ mol\(^{-1}\)) is larger than for the addition at the C-atom (93 kJ mol\(^{-1}\)). COH* undergoes subsequent H*-addition to form *HCOH*, which forms CH* and OH*, as in the formyl route. In this route, COH* formation has the largest effective barrier (186 kJ mol\(^{-1}\), Figure 2, Eq. (4)) and effective barriers reflect energy differences between kinetically-relevant transition states (TS) and reactant states:

\[
\Delta H_{\text{eff}} = -Q_{\text{CO}} + Q_{\text{H1}} + \Delta H_{\text{Rxn,1}} + \Delta H_{\text{A1,4}}
\]

Here, steps 3 and 4 refer to those in Scheme 1 for each H-assisted CO activation sequence. In terms of the energies of the species involved, Equation (3) becomes [derivation in Supporting Information (SI), Eqs. (S3)–(S5)]:

\[
\Delta H_{\text{eff}} = H_{\text{TS}} - (H_{\text{TS}} - H_{\text{CO}}) - H_{\text{CO}} - \frac{n}{2} \Delta H_{\text{TS}}
\]

where \(n\) is the number of H-atoms in the TS of step \(i\).

Figure 2 shows DFT-derived reaction and activation energies for the formyl and hydroxymethylidyne routes. The HCO* formation barrier is 93 kJ mol\(^{-1}\), while its reverse barrier (30 kJ mol\(^{-1}\)) is much smaller than for its reaction with H* to form *HCOH* (95 kJ mol\(^{-1}\)), indicating that HCO* formation is quasi-equilibrated. HCO* dissociation to form CH* and O* has a barrier of 155 kJ mol\(^{-1}\), which is much larger than H*-addition to HCO* to form *HCOH* (95 kJ mol\(^{-1}\)). *HCOH* decomposes to HCO* and H* with a much larger barrier (86 kJ mol\(^{-1}\)) than to CH* and OH*.
becomes the kinetically-relevant step, leading to the rate equation:

\[
r_{\text{CO}} = \frac{k_0 K_{\text{CO}} (\text{CO})^5 (\text{H}_2)^3}{[1 + K_{\text{CO}} (\text{CO})]^2}
\]  

(5)

inconsistent with the measured first-order H\textsubscript{2} dependence of FTS rates, as also found on Co surfaces.[3]

H\textsubscript{2}O-mediated rate enhancements require changes in the dynamics or identity of kinetically-relevant steps. Any enthalpic stabilization of relevant transition states must overcome concomitant entropy losses from hindered mobility of any H\textsubscript{2}O molecules involved. Measured effects of H\textsubscript{2}O on FTS rates can be described by Equation (6), a modified version of Equation (1). This equation contains a numerator term that accounts for the promotion of FTS rates by H\textsubscript{2}O and denominator terms for co-adsorption of H\textsubscript{2}O-derived species formed in quasi-equilibrated steps [H\textsubscript{2}O\textsuperscript{*}, OH\textsuperscript{*}, O\textsuperscript{*}, Eqs. (7)–(9)].

\[
r_{\text{CO}} = \alpha (\text{CO} + \beta (\text{CO}) (\text{H}_2) (\text{H}_2 \text{O}))
\]

(6)

The parity plot in Figure 3 shows that Equation (6) accurately describes all rate data in Figure 1, as well as previously reported data.[10] The relative contributions from O\textsuperscript{*}, OH\textsuperscript{*} and H\textsubscript{2}O\textsuperscript{*} coverages cannot be inferred from these data as determined by a sensitivity analysis (Table S2, Figure S10, SI), but DFT-derived free energies (Figure S12, SI) show that H\textsubscript{2}O\textsuperscript{*} is the preferred H\textsubscript{2}O-derived adsorbate on Ru. The values of (0.66 ± 0.11) and K\textsubscript{CO} (6.2 ± 0.7) shown in Table 1 agree with values reported previously[10] at low H\textsubscript{2}O pressures (0.58 ± 0.08 and 5.6 ± 0.6, respectively).

The H\textsubscript{2}O enhancement factor (χ): 

\[
\chi = \frac{\beta (\text{H}_2 \text{O})}{\alpha} = \frac{\exp \left(-\Delta \Delta G_{\text{eff}} \right)}{RT}
\]

(10)
is defined as the ratio of the two numerator terms from Equation (6). The fitted values of \(\alpha\) and \(\beta\) (Table 1) gives a \(\chi\) of 7 ± 3 at 1 bar H\textsubscript{2}O and 463 K, which corresponds to a difference in free energy barriers (\(\Delta \Delta G_{\text{eff}}\)) between H\textsubscript{2}O-mediated and anhydrous routes of \(-8 \pm 2\) kJmol\textsuperscript{-1}.

H\textsubscript{2}O may influence formyl routes 1) as a H-source (H\textsubscript{2}O\textsuperscript{*} reaction with HCO\textsuperscript{*} to form *HCOH* and OH\textsuperscript{*}), 2) as a “solvent” to stabilize the TS for H-addition at the O-atom in HCO\textsuperscript{*} (through H-bonding with incipient O–H bonds), or 3) as a H-shuttling agent (as a H\textsubscript{2}O molecule or extended phase) for H\textsuperscript{*} transfer to the O-atom in HCO\textsuperscript{*}, as shown in Scheme 2.

Figure 4 shows DFT-derived energies for H\textsubscript{2}O-mediated hydroxymethylidyne route, for which the effective barriers are:

\[
\begin{align*}
3a) & \quad \text{CO}^* + \text{H}^* \quad \Leftrightarrow \quad \text{HCO}^* + \star \\
4a) & \quad \text{HCO}^* + \text{H}^* \quad \rightarrow \quad \text{H}^* + \text{OH}^* \\
5a) & \quad *\text{HCOH}^* \quad \rightarrow \quad \text{CH}^* + \text{OH}^* \\
3b) & \quad \text{H}_2\text{O}(g) + \star \quad \rightarrow \quad \text{CO}^* \cdot \cdot \cdot \text{H}_2\text{O} \\
4b) & \quad \text{CO}^* \cdot \cdot \cdot \text{H}_2\text{O} + \text{H}^* \quad \rightarrow \quad \text{HCO}^* \cdot \cdot \cdot \text{H}_2\text{O} + \star \\
5b) & \quad \text{HCO}^* \cdot \cdot \cdot \text{H}_2\text{O} + \text{H}^* \quad \rightarrow \quad *\text{HCOH}^* \cdot \cdot \cdot \text{H}_2\text{O} \\
6b) & \quad *\text{HCOH}^* \cdot \cdot \cdot \text{H}_2\text{O} \quad \rightarrow \quad \text{CH}^* + \text{OH}^* \cdot \cdot \cdot \text{H}_2\text{O} \\
3f) & \quad \text{H}_2\text{O}(g) + \star \quad \rightarrow \quad \text{CO}^* + \text{H}_2\text{O} \\
4f) & \quad \text{CO}^* \cdot \cdot \cdot \text{H}_2\text{O} + \text{H}^* \quad \rightarrow \quad \text{COH}^* \cdot \cdot \cdot \text{H}_2\text{O} + \star \\
5f) & \quad \text{COH}^* \cdot \cdot \cdot \text{H}_2\text{O} + \text{H}^* \quad \rightarrow \quad *\text{HCOH}^* \cdot \cdot \cdot \text{H}_2\text{O} \\
6f) & \quad *\text{HCOH}^* \cdot \cdot \cdot \text{H}_2\text{O} \quad \rightarrow \quad \text{CH}^* + \text{OH}^* \cdot \cdot \cdot \text{H}_2\text{O} \\
\end{align*}
\]

Scheme 2. H\textsubscript{2}O-mediated *HCOH* formation via formyl or hydroxymethylidyne intermediates. Quasi-equilibrated steps are denoted by reaction arrows overlaid with a circle.

Table 1: Fitted lumped rate constants \(\alpha\) and \(\beta\), and CO and H\textsubscript{2}O adsorption constants (K\textsubscript{CO} and K\textsubscript{H2O}) for FTS on SiO\textsubscript{2}-supported 7 nm Ru clusters (463 K).

<table>
<thead>
<tr>
<th></th>
<th>(\alpha) [mol s\textsuperscript{-1} mol \textsuperscript{-1} Ru MPa\textsuperscript{-1}]</th>
<th>(\beta) [mol s\textsuperscript{-1} mol \textsuperscript{-1} Ru MPa\textsuperscript{-1}]</th>
<th>K\textsubscript{CO} [MPa\textsuperscript{-1}]</th>
<th>K\textsubscript{H2O} [MPa\textsuperscript{-1}]</th>
<th>K\textsubscript{OH} [MPa\textsuperscript{-1}]</th>
<th>K\textsubscript{O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. [10a] also on 7 nm Ru</td>
<td>0.58 ± 0.08</td>
<td>–</td>
<td>5.6 ± 0.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>This work</td>
<td>0.66 ± 0.11</td>
<td>4.72 ± 1.1</td>
<td>6.2 ± 0.7</td>
<td>0–3.1</td>
<td>0–3.9</td>
<td>0–5.1</td>
</tr>
</tbody>
</table>

Figure 3. Measured and predicted CO consumption turnover rates (predictions from Equation (9) and parameters in Table 1.)
These barriers include, in contrast with those for the anhydrous case [Eq. (5)], energies for the H2O-containing transition state and its H2O(g) precursor (Scheme 2, Steps 3e/f). H2O as a H-source, solvent, or H-shuttle can increase (by 52 kJ mol$^{-1}$), have no effect, or slightly decrease (by 12 kJ mol$^{-1}$), respectively, the effective barriers in the formyl route that prevails in the absence of H2O (Figure 4). Concomitant entropy losses upon H2O fixation, however, make activation free energies larger than for anhydrous routes, even for H-shutting. We conclude that these H2O mediated routes do not account for the measured rate enhancements.

Hydroxymethylidyne routes are disfavored in the absence of water, but may become the preferred path through the influence of water. H2O-mediated H-shuttling leads to COH* formation activation energies [111 kJ mol$^{-1}$, Figure 5, Figure 6a, Eq. (11)] much smaller than for H* addition without H2O [186 kJ mol$^{-1}$, Figure 2, Eq. (4)]. H-shuttling involves electron transfer from H* to Ru as H* interacts with H2O to form H3O$^{+}$ species, which protonates CO* in a manner reminiscent of proton coupled electron transfer steps in aqueous media$^{[14]}$ and in H2O-aided H-diffusion.$^{[15]}$ Bader charges$^{[16]}$ indicate that $\delta = 0.87$. *HCOH* dissociation barriers (129 kJ mol$^{-1}$) are larger than for COH* dissociation (111 kJ mol$^{-1}$), consistent with quasi-equilibrated COH* formation through H2O-assisted H-shuttling [Eq. (S26), SI]. The effective barrier for H2O-mediated hydroxymethylidyne routes (129 kJ mol$^{-1}$) is much smaller than for H2O-mediated formyl routes (181 kJ mol$^{-1}$), indicating that H2O mediation opens a C–O activation route absent at low H2O concentrations. In this route, the kinetically-relevant activation of C–O bonds in *HCOH* (to form CH* and OH*) proceeds through a TS that involves two H atoms and a CO-derived species, which is consistent with reported FTS rate equations on Co and Ru catalysts$^{[2,3,5,7,10,11]}$ [Eq. (1)].

Rearranging Equation (10) with the $a$ and $b$ values for the full FTS rate equation [Eq. (6)] gives:

$$
\alpha = K_{CO}K_{H_2}K_{a}K_{b}K_{m}
$$

Figure 4. DFT-derived reactant, TS, and product structures in *HCOH* formation of the formyl route a) direct H*-addition, b) H2O as a H-source, c) H2O as a solvent, and d) H2O as a H-shuttle (the transferred H-atom is highlighted and distances are in nm).

Figure 5. Reaction coordinate diagrams for H2O-mediated formyl and hydroxymethylidyne routes in the presence of H2O. Intrinsic activation barriers are in italics and effective barriers (with respect to CO*-covered Ru201 particles; [Eq. (11)]) are in bold.
the “fixation” of a H$_2$O molecule at the hydroxymethylene transition states are similar, the majority of this loss can be estimated from adsorption isotherms [Eq. (S27)–(S30)] as 134 ± 10 J mol$^{-1}$ K$^{-1}$.[17]

Substituting $\Delta(\Delta H_{ts})$ and $\Delta(\Delta S_{ts})$ values into Equation (15) gives a $\Delta(\Delta G_{ts})$ estimate of $-2.8 \pm 5$ kJ mol$^{-1}$ at 463 K and 1 bar, which lie within the uncertainty range of the measured enhancement factor ($-8 \pm 2$ kJ mol$^{-1}$).

H$_2$O also increases the chain length of FTS products (Figure 1 and Ref. [2,4]), indicating that it promotes chain growth without commensurate effects on chain termination. The precise nature of chain growth pathways and the monomers involved remains controversial, a subject that we address in a later study.[2,3] We illustrate here two plausible effects of H$_2$O on chain growth, based on the experimental and theoretical evidence presented above for H$_2$O mediation of H-assisted C–O bond cleavage.

C–C bonds may form by alkyl chain reactions with “activated” C$_1$ species [Eq. (18)] or by sequential reactions of such alkyls with CO$^\ast$ and H$^\ast$ to form hydroxalkylidenes that dissociate to form alkylidyne and OH$^\ast$ [Eq. (19)]. CO$^\ast$ may also react with alkylidyne and alkylidynes,[14] which hydrogenate to form hydroxalkylidenes; our simulations[19] show, however, that CH$^\ast$ and CH$_2$= hydrogenation barriers are much smaller than for their reactions with CO$^\ast$, indicating that they would convert to alkyls before further chain growth. Termination occurs either by β-H elimination to form terminal alkenes [Eq. (20)] or H$^\ast$-addition to form n-alkanes [Eq. (21)].[7]

$$\begin{align*}
C\text{H}_{2n+1}^\ast + \text{CH}_2^\ast &\rightarrow C_{n+1}\text{H}_{2n+1}^\ast + \ast \quad (18) \\
C\text{H}_{2n+1}^\ast + \text{CO}^\ast + \text{H}^\ast &\rightarrow C_n\text{H}_{2n+1}^\ast\text{CO}^\ast + \ast \\
&\rightarrow C_n\text{H}_{2n+1}^\ast\text{C}^\ast + \text{OH}^\ast + \ast \\
C\text{H}_{2n+1}^\ast + \text{C}^\ast &\rightarrow C_{n+1}\text{H}_{2n+1}^\ast + \text{H}^\ast \\
C\text{H}_{2n+1}^\ast + \text{H}^\ast &\rightarrow C_n\text{H}_{2n+2}^\ast + \ast
\end{align*}$$

H$_2$O increases the rate of formation of activated C$_1$ species and, in doing so, the steady-state CH$_x$* coverages and the chain growth rate [through Eq. (18)], without concomitant effects on termination rates.[20] C–C bond formations by reactions in which CO$^\ast$ reacts with an alkyl chain and H$^\ast$ [Eq. (19)] are analogous to CO$^\ast$ activation in which CO$^\ast$ reacts with two H$^\ast$ as the chemical nature of an alkyl species is similar to that of H$^\ast$ indicating that H$_2$O would decrease activation barriers for chain growth via Equation (19) by similar H-shuttling mediation, leading to heavier products and higher C$_5$ selectivities, as found experimentally.

We conclude that H$_2$O, whether indigenous or co-fed, increases CO activation rates on Ru-based catalysts in a manner consistent with the involvement of H$_2$O-mediated H-transfer routes and competitive adsorption of H$_2$O-derived intermediates [Eq. (9)]. DFT-derived reaction and activation energies indicate that H$_2$O mediates the kinetically-relevant H-transfer required for O–H bond formation in pathways involving *HCOH$^\ast$ intermediates and increases chain growth probabilities by increasing the rate of monomer formation when growth occurs via CH$_x$* or the rate constant for chain growth when CO$^\ast$ is the monomer. H$_2$O can act as a co-catalyst in FTS reactions in doing so, as previously observed in metal-catalyzed hydrogenations in protic media.[14,15] The kinetic resemblance among Ru and Co catalysts[2,3,5,6,10] suggest that similar conclusions about H$_2$O-mediated routes...
apply to FTS catalysis on Co, on which FTS rates and product chain length also increase with increasing H₂O pressure.²,³

**Experimental Section**

A 5 wt% Ru/SiO₂ catalyst was prepared as reported elsewhere.¹⁰,¹² The Ru particle size was found to be 7 nm¹⁰ and the SiO₂ support (PO Corp. CS-2133, 350 m² g⁻¹) has an average pore diameter of 13 nm.¹² FTS rates and selectivities were measured in an isothermal (±2 K) fixed bed stainless steel reactor (I.D. = 1 cm) with a catalyst bed (15 cm) consisting of 5 wt% Ru/SiO₂ (0.9 g) catalyst and SiO₂ diluent (3.5 g). The catalyst and diluent mixture was heated to 673 K (2 Kmin⁻¹) in flowing H₂ and holding for 10 h at ambient pressures prior to exposure of the catalyst to reactants. Reported rates and selectivities, determined via analysis of the reaction effluent by online gas chromatography as reported elsewhere,¹⁰ correspond to steady-state values obtained after 24 h on-stream. DFT calculations were performed as previously reported¹⁰ on a 201-atom Ru nanoparticle at a CO* coverage of 1.55 ML using the VASP software package with ultra-soft pseudopotentials and the Perdew-Wang 91 form of the generalized gradient approximation.²²

Received: May 28, 2013  
Revised: August 5, 2013  
Published online: October 2, 2013

**Keywords:** density functional calculations - Fischer-Tropsch synthesis - heterogeneous catalysis - hydrogenation - kinetics


