

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

David D. Hibbitts, Brett T. Loveless, Matthew Neurock,* and Enrique Iglesia*

Ru and Co catalyze Fischer–Tropsch synthesis (FTS) with high rates and C_{5+} 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 H_2O ,^[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 C_{5+} and alkene selectivities on Co and Ru.^[2,4,5]

H_2O can inhibit rates by increasing O^* coverages on Co;^[6] such coverages require higher H_2O/H_2 ratios on Ru catalysts, rendering Ru catalysts stable even in aqueous media during FTS.^[8] H_2O promotion of FTS rates may reflect faster CO transport within H_2O -rich intrapore liquids when CO diffusion limits rates,^[2] but H_2O effects are observed even under conditions of strict kinetic control. H_2O -mediated rate enhancements may arise from higher densities of exposed metal atoms during FTS catalysis, possibly because chemisorbed carbon (C^*) reacts with H_2O -derived species. Such a loss of binding sites, however, is inconsistent with CO^* coverages (from infrared spectra) that do not depend on H_2O 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 H_2O pressures for intrapore condensation than small-pore supports, suggesting that a condensed H_2O 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 SiO_2 are used to measure rate and selectivity enhancements by H_2O , and

density functional theory (DFT) calculations are used to examine the role of H_2O as a co-catalyst in O–H formation steps in kinetically-relevant CO activation steps.

H_2O pressures were varied by changing residence time (and CO conversion) or adding H_2O to H_2 –CO reactants.^[5] CO consumption rates increased monotonically with increasing H_2O pressure (up to 0.3 MPa H_2O ; Figure 1), suggesting

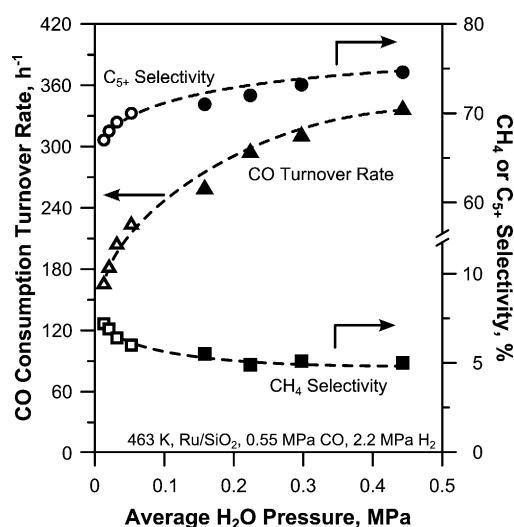


Figure 1. CO consumption rate (Δ or $\blacktriangle$), CH_4 selectivity ($\square$ or $\blacksquare$), and C_{5+} selectivity ($\circ$ or $\bullet$) as a function of H_2O partial pressure on 5 wt% Ru/ SiO_2 (463 K, 2.9 MPa, $H_2/CO = 4.5$). Open symbols: space velocity changes; closed symbols: H_2O -addition.

that H_2O influences kinetically-relevant CO activation steps.^[10] The weaker effects above 0.3 MPa H_2O reflect co-adsorption of H_2O -derived species with CO^* , H^* , and their products. H_2O decreased CH_4 selectivity and increased C_{5+} selectivity (Figure 1), suggesting that H_2O -derived species increase monomer concentrations and/or their propagation rate constants.

Equation (1) describes the effects of H_2 and CO pressure on FTS rates at low and nearly constant H_2O pressures on Co and Ru.^[2,3,5,7,10,11]

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

where (CO) and (H_2) 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

[*] Dr. M. Neurock
Departments of Chemical Engineering and Chemistry
University of Virginia, Charlottesville, Virginia, 22904 (USA)
E-mail: neurock@virginia.edu
Homepage: <http://www.che.virginia.edu/people/faculty/neurock.html>

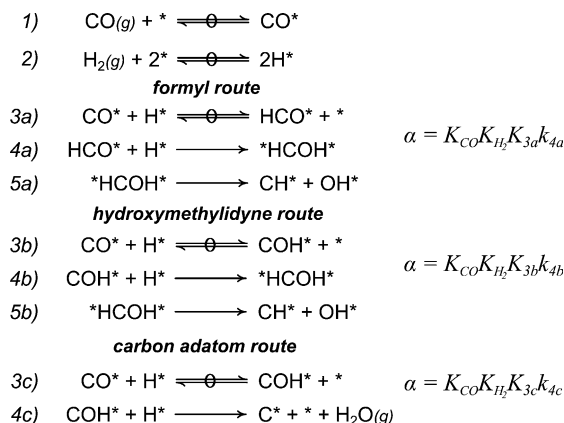
Dr. D. D. Hibbitts, Dr. B. T. Loveless, Dr. E. Iglesia
Department of Chemical and Biomolecular Engineering
University of California at Berkeley
Berkeley, California, 94720 (USA)
E-mail: iglesiasia@berkeley.edu
Homepage: <http://iglesias.cchem.berkeley.edu/>

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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



Scheme 1. Hydrogen-assisted CO* activation during FTS. Quasi-equilibrated steps are denoted by reaction arrows overlaid with a circle.

constants (α). 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* (step 4a) (formyl route, Scheme 1),^[10] as also found on Co and Fe surfaces.^[3,11,12] Another route adds H* at the O-atom in CO* to form COH* (step 3b) in a quasi-equilibrated step that is followed by irreversible H* addition at the C-atom to form *HCOH* (step 4b) (hydroxymethylidyne route, Scheme 1).

The coverage dependence of CO* binding energies shows that Ru₂₀₁ clusters become saturated at 1.5 CO* per exposed Ru atom with supra-stoichiometric CO* species residing at corners and edges, and all CO* remaining in atop positions.^[10] DFT-derived CO* binding energies (−42 kJ mol^{−1}) and CO* entropies from Volmer gas 2-D models at these coverages give an adsorption free energy ($\Delta G_{\text{ads}} = 7.8$ kJ mol^{−1}) similar to measured values (2.2 kJ mol^{−1}).^[10] These coverages and Ru₂₀₁ (111) terraces are used in all energy calculations (see Experimental Section)^[10] and reflect the active sites involved in FTS.^[10,13]

At high CO* coverages, Equation (1) becomes:

$$r_{\text{CO}} = \frac{K_{\text{H}_2} K_3 k_4 (\text{H}_2)}{K_{\text{CO}} (\text{CO})} \quad (2)$$

and effective barriers reflect energy differences between kinetically-relevant transition states (TS) and reactant states:

$$\Delta H_{\text{eff}} = -Q_{\text{CO}} + Q_{\text{H}_2} + \Delta H_{\text{Rxn},3} + \Delta H_{\text{Act},4} \quad (3)$$

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)]:

$$\Delta H_{\text{eff}} = H_{\text{TS}_i^*} - (H_{\text{CO}^*} - H_{\text{CO(g)}}) - H_{\text{CO}^*} - \frac{n}{2} H_{\text{H}_2(\text{g})} \quad (4)$$

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},^[10] 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*

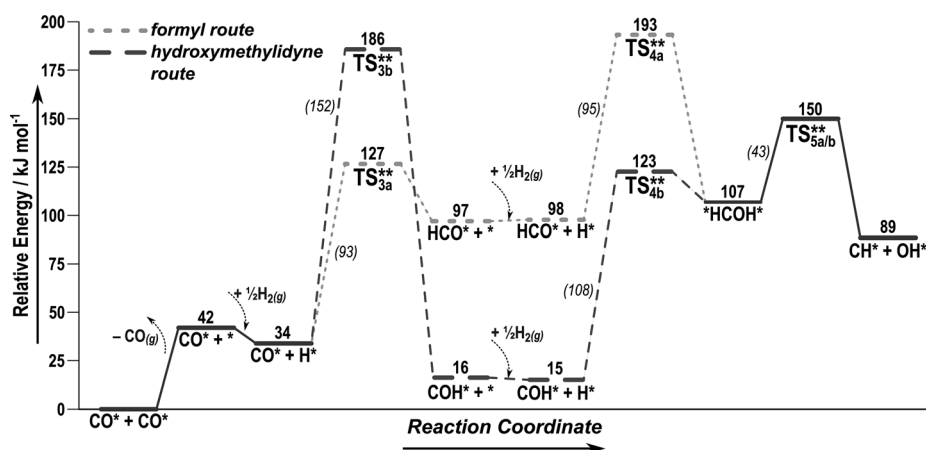


Figure 2. Reaction coordinate diagrams for the two H*-assisted CO activation mechanisms in Scheme 1. Intrinsic activation barriers are in italics and effective barriers (with respect to CO*-covered Ru₂₀₁ particles; [Eq. (4)]) are in bold.

(43 kJ mol^{−1}), indicating that *HCOH* formation is irreversible. It forms CH* and OH* species that react in subsequent kinetically-irrelevant steps to form the hydrocarbon and H₂O products of FTS. The effective barrier for this formyl route is 193 kJ mol^{−1} [Eq. (4)], which is much smaller than those for routes involving unassisted CO* dissociation (322 kJ mol^{−1}).^[10]

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

becomes the kinetically-relevant step, leading to the rate equation:

$$r_{\text{CO}} = \frac{k_{3b} K_{\text{CO}} K_{\text{H}_2}^{0.5} (\text{CO})(\text{H}_2)^{0.5}}{[1 + K_{\text{CO}}(\text{CO})]^2} \quad (5)$$

inconsistent with the measured first-order H_2 dependence of FTS rates, as also found on Co surfaces.^[3]

H_2O -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_2O molecules involved. Measured effects of H_2O 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_2O and denominator terms for co-adsorption of H_2O -derived species formed in quasi-equilibrated steps [H_2O^* , OH^* , O^* , Eqs. (7)–(9)].

$$r_{\text{CO}} = \frac{\alpha(\text{CO})(\text{H}_2) + \beta(\text{CO})(\text{H}_2)(\text{H}_2\text{O})}{[1 + K_{\text{CO}}(\text{CO}) + K_{\text{H}_2\text{O}}(\text{H}_2\text{O}) + K_{\text{OH}}(\text{H}_2\text{O})(\text{H}_2)^{-0.5} + K_{\text{O}}(\text{H}_2\text{O})(\text{H}_2)^{-1}]^2} \quad (6)$$



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^* , OH^* and H_2O^* 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)

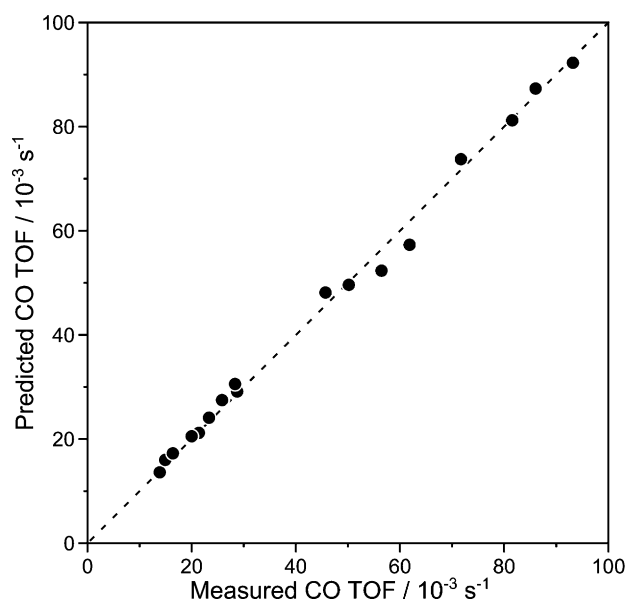


Figure 3. Measured and predicted CO consumption turnover rates (predictions from Equation (9) and parameters in Table 1.)

Table 1: Fitted lumped rate constants α and β , and CO and H_2O adsorption constants (K_{CO} and $K_{\text{H}_2\text{O}}$) for FTS on SiO_2 -supported 7 nm Ru clusters (463 K).

	α [mol s ⁻¹ mol Ru ⁻¹ MPa ⁻²]	β [mol s ⁻¹ mol Ru ⁻¹ MPa ⁻³]	K_{CO} [MPa ⁻¹]	$K_{\text{H}_2\text{O}}$ [MPa ⁻¹]	K_{OH} [MPa ^{-0.5}]	K_{O}
Ref. [10a] also on 7 nm Ru	0.58 ± 0.08	–	5.6 ± 0.6	–	–	–
This work	0.66 ± 0.11	4.72 ± 1.1	6.2 ± 0.7	0–3.1	0–3.9	0–5.1

show that H_2O^* is the preferred H_2O -derived adsorbate on Ru. The values of α (0.66 ± 0.11) and K_{CO} (6.2 ± 0.7) shown in Table 1 agree with values reported previously^[10] at low H_2O pressures (0.58 ± 0.08 and 5.6 ± 0.6 , respectively).

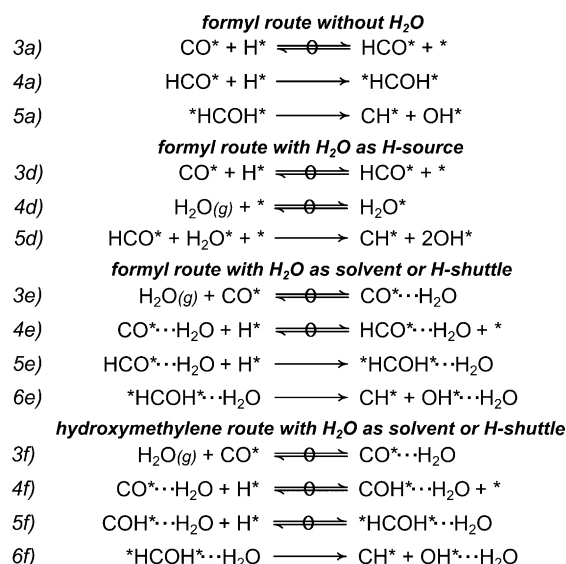
The H_2O enhancement factor (χ):

$$\chi = \frac{\beta(\text{H}_2\text{O})}{\alpha} = \exp\left(\frac{-\Delta(\Delta G_{\text{eff}})}{RT}\right) \quad (10)$$

is defined as the ratio of the two numerator terms from Equation (6). The fitted values of α and β (Table 1) gives a χ of 7 ± 3 at 1 bar H_2O and 463 K, which corresponds to a difference in free energy barriers ($\Delta(\Delta G_{\text{eff}})$) between H_2O -mediated and anhydrous routes of -8 ± 2 kJ mol⁻¹.

H_2O may influence formyl routes 1) as a H-source (H_2O^* reaction with HCO^* to form $^*\text{HCOH}^*$ and OH^*), 2) as a “solvent” to stabilize the TS for H-addition at the O-atom in HCO^* (through H-bonding with incipient O–H bonds), or 3) as a H-shuttling agent (as a H_2O molecule or extended phase) for H^* transfer to the O-atom in HCO^* , as shown in Scheme 2.

Figure 4 shows DFT-derived energies for H_2O -mediated hydroxymethylidyne route, for which the effective barriers are:



Scheme 2. H_2O -mediated $^*\text{HCOH}^*$ formation via formyl or hydroxymethylidyne intermediates. Quasi-equilibrated steps are denoted by reaction arrows overlaid with a circle.

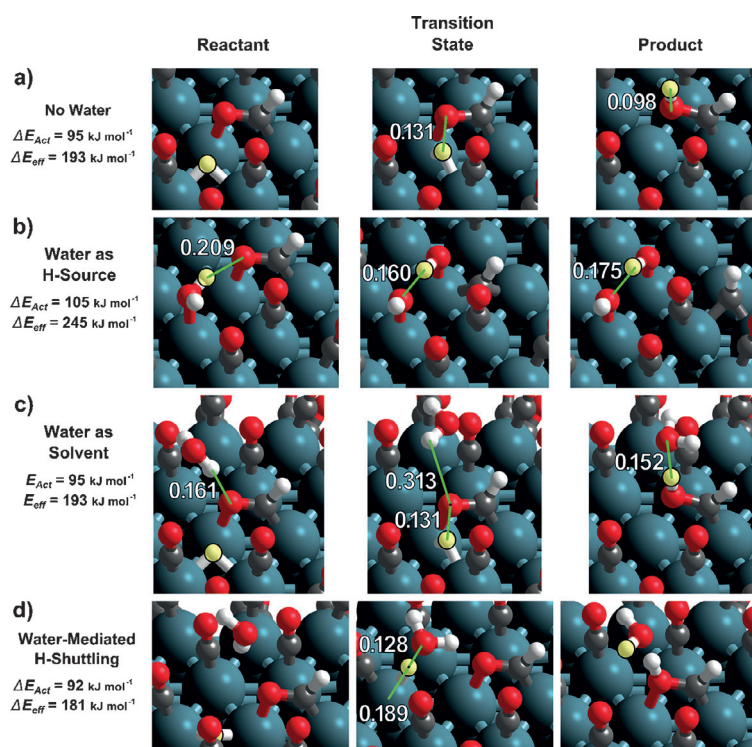


Figure 4. DFT-derived reactant, TS, and product structures in $^*\text{HCOH}^*$ formation of the formyl route a) direct H^* -addition, b) H_2O as a H-source, c) H_2O as a solvent, and d) H_2O as a H-shuttle (the transferred H-atom is highlighted and distances are in nm).

$$\Delta H_{\text{eff}} = H_{\text{TS}_i^*} - (H_{\text{CO}^*} - H_{\text{CO(g)}}) - H_{\text{CO}^*} - \frac{n}{2} H_{\text{H}_2(\text{g})} - H_{\text{H}_2\text{O(g)}} \quad (11)$$

These barriers include, in contrast with those for the anhydrous case [Eq. (5)], energies for the H_2O -containing transition state and its $\text{H}_2\text{O(g)}$ precursor (Scheme 2, Steps 3e/f). H_2O 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 H_2O (Figure 4). Concomitant entropy losses upon H_2O fixation, however, make activation free energies larger than for anhydrous routes, even for H-shuttling. We conclude that these H_2O 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. H_2O -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 H_2O [186 kJ mol^{-1} , Figure 2, Eq. (4)]. H-shuttling involves electron transfer from H^* to Ru as H^* interacts with H_2O to form $\text{H}_3\text{O}^{\delta+}$ species, which protonates CO^* in a manner reminiscent of proton coupled electron transfer steps in aqueous media^[14] and in H_2O -aided H-diffusion.^[15] Bader charges^[16] indicate that δ is $+0.87$. $^*\text{HCOH}^*$ dissociation barriers (129 kJ mol^{-1}) are larger than for COH^* dissociation (111 kJ mol^{-1}), consistent with quasi-equilibrated COH^* formation through H_2O -assisted H-shuttling [Eq. (S26), SI]. The effective barrier for H_2O -mediated hydroxymethylidyne routes (129 kJ mol^{-1}) is much smaller than for H_2O -mediated formyl routes (181 kJ mol^{-1}), indicating that H_2O mediation opens a C–O activation route absent at low H_2O concentrations. In this route, the kinetically-relevant activation of C–O bonds in $^*\text{HCOH}^*$ (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 α and β values for the full FTS rate equation [Eq. (6)] gives:

$$\alpha = K_{\text{CO}} K_{\text{H}_2} K_{3a} K_{4a} k_{5a} \quad (12)$$

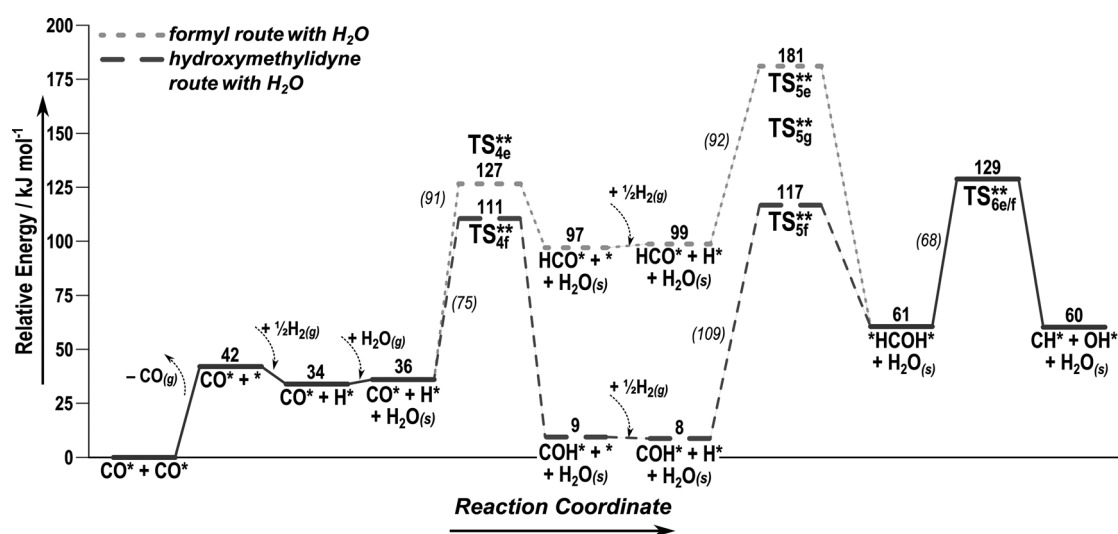


Figure 5. Reaction coordinate diagrams for H_2O -mediated formyl and hydroxymethylidyne routes in the presence of H_2O . Intrinsic activation barriers are in italics and effective barriers (with respect to CO^* -covered Ru_{201} particles; [Eq. (11)]) are in bold.

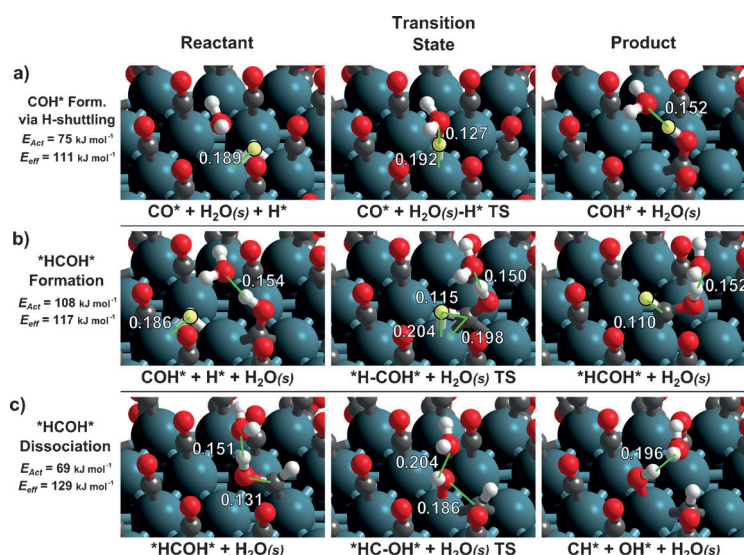


Figure 6. DFT-derived reactant, TS and product structures for the H_2O -mediated hydroxymethylidyne route (the transferred H-atom is highlighted and distances are in nm).

$$\beta = K_{\text{CO}} K_{\text{H}_2} K_{3\text{f}} K_{4\text{f}} K_{5\text{f}} k_{6\text{f}} \quad (13)$$

$$\chi = \frac{K_{3\text{f}} K_{4\text{f}} K_{5\text{f}} k_{6\text{f}} (\text{H}_2\text{O})}{K_{3\text{a}} K_{4\text{a}} k_{5\text{a}}} = \exp\left(\frac{-\Delta(\Delta G_{\text{eff}})}{RT}\right) \quad (14)$$

The measured free energy difference between the anhydrous and H_2O -mediated terms in Equation 10 ($\Delta(\Delta G_{\text{eff}}) = -8 \pm 2 \text{ kJ mol}^{-1}$) is related to their respective differences in enthalpy ($\Delta(\Delta H_{\text{eff}})$) and entropy ($\Delta(\Delta S_{\text{eff}})$):

$$\Delta(\Delta G_{\text{eff}}) = \Delta(\Delta H_{\text{eff}}) - T(\Delta(\Delta S_{\text{eff}})) \quad (15)$$

The $\Delta(\Delta H_{\text{eff}})$ between the H_2O -mediated hydroxymethylidyne route ($\Delta H_{\text{eff}} = 129 \text{ kJ mol}^{-1}$, Figure 4) and the anhydrous formyl route ($\Delta H_{\text{eff}} = 193 \text{ kJ mol}^{-1}$, Figure 2) is -64 kJ mol^{-1} , and is related to the difference in enthalpy of the H_2O -mediated kinetically-relevant transition state ($H_{\text{H}_2\text{O-med.}}^\ddagger$) and the anhydrous kinetically relevant transition state ($H_{\text{Anh.}}^\ddagger$) and gas-phase water.

$$\Delta(\Delta H_{\text{eff}}) = H_{\text{H}_2\text{O-med.}}^\ddagger - H_{\text{Anh.}}^\ddagger - H_{\text{H}_2\text{O(g)}} \quad (16)$$

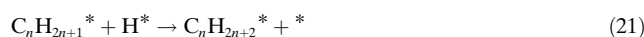
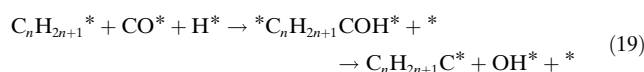
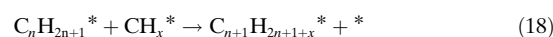
The value of $\Delta(\Delta S_{\text{eff}})$ reflects the entropy loss caused by the “fixation” of a H_2O molecule at the hydroxymethylene TS. Assuming that the vibrational entropy of the two transition states are similar, the majority of this loss can be estimated as the ΔS upon H_2O physisorption which has been estimated from adsorption isotherms [Eq. (S27)–(S30)] as $134 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$.^[17]

$$\Delta(\Delta S_{\text{eff}}) = S_{\text{H}_2\text{O-med.}}^\ddagger - S_{\text{Anh.}}^\ddagger - S_{\text{H}_2\text{O(g)}} \approx S_{\text{H}_2\text{O,Phys.}} \quad (17)$$

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

H_2O 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_2O on chain growth, based on the experimental and theoretical evidence presented above for H_2O 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^* and H^* to form hydroxyalkylidenes that dissociate to form alkylidynes and OH^* [Eq. (19)]. CO^* may also react with alkylidynes and alkylidenes,^[18] which hydrogenate to form hydroxyalkylidenes; our simulations^[19] show, however, that CH^* and CH_2^* hydrogenation barriers are much smaller than for their reactions with CO^* , 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^* -addition to form n -alkanes [Eq. (21)].^[3]



H_2O 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^* reacts with an alkyl chain and H^* [Eq. (19)] are analogous to CO^* activation in which CO^* reacts with two H^* as the chemical nature of an alkyl species is similar to that of H^* indicating that H_2O 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_2O , whether indigenous or co-fed, increases CO activation rates on Ru-based catalysts in a manner consistent with the involvement of H_2O -mediated H-transfer routes and competitive adsorption of H_2O -derived intermediates [Eq. (9)]. DFT-derived reaction and activation energies indicate that H_2O mediates the kinetically-relevant H-transfer required for O–H bond formation in pathways involving $^*\text{HCOH}^*$ 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^* is the monomer. H_2O 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_2O -mediated routes

apply to FTS catalysis on Co, on which FTS rates and product chain length also increase with increasing H₂O pressure.^[2,4,5]

Experimental Section

A 5 wt % Ru/SiO₂ catalyst was prepared as reported elsewhere.^[10,21] The Ru particle size was found to be 7 nm^[10] and the SiO₂ support (PQ Corp. CS-2133, 350 m² g⁻¹) has an average pore diameter of 13 nm.^[5] 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 at 2 K min⁻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 reported^[10] 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]

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