Real-Time Elucidation of Catalytic Pathways in CO Hydrogenation on Ru

J. LaRue‡§∥* O. Krejčí,‡⊥# L. Yu,∇ M. Beye,⋄ M. L. Ng,† H. Öberg,‡ H. Xin,∇ G. Mercurio,◆ S. Moeller,§ J. J. Turner,§ D. Nordlund,◊ R. Coffee,§ M. P. Miniti,§ W. Wurth,◆† L. G. M. Pettersson,‡ H. Öström,‡ A. Nilsson,‡ F. Abild-Pedersen,† H. Ogasawara*†

†SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA

‡Department of Physics, AlbaNova University Center, Stockholm University, SE-10691 Stockholm, Sweden

§Schmid College of Science and Technology, Chapman University, One University Drive, Orange, California 92866, USA

∥Fritz-Haber Institute of the Max-Planck-Society, Faradayweg 4-6, D-14195 Berlin, Germany

⊥Charles University in Prague, Faculty of Mathematics and Physics, Department of Surface and Plasma Science, V Holešovičkách 2, 180 00, Prague, Czech Republic
AUTHOR INFORMATION

Corresponding Authors

J. L. LaRue (larue@chapman.edu) and H. Ogasawara (hirohito@slac.stanford.edu).
ABSTRACT

The direct elucidation of the reaction pathways in heterogeneous catalysis has been challenging due the short-lived nature of reaction intermediates. Here, we directly measured on ultrafast timescales the initial hydrogenation steps of adsorbed CO on a Ru catalyst surface, which is known as the bottleneck reaction in syngas and CO$_2$ reforming processes. We initiated the hydrogenation of CO with an ultrafast laser temperature jump and probed transient changes in the electronic structure using real-time x-ray spectroscopy. In combination with theoretical simulations, we verified the formation of CHO during CO hydrogenation.

TOC GRAPHICS
Hydrogenation of CO is a pivotal step in forming fuels and base chemicals using Fischer-Tropsch synthesis in syngas utilization and artificial photosynthesis CO$_2$ reduction.(1-12) Ru is one of the best Fischer-Tropsch catalysts to convert CO and hydrogen into hydrocarbon chains with a high selectivity. Although the breaking of the C-O bond to produce C$_1$ species has been realized as being the important step to initiate the hydrocarbon chain growth,(13) the specific pathway by which CO dissociates has been under debate for almost a century.(13-18) The proposed mechanisms have involved the direct dissociation of the C-O bond followed by hydrogenation of atomic C and O,(13) or hydrogenation of CO before dissociation,(14) but no direct experimental verification of hydrogen attachment has been reported.

In this study, we aim for the direct verification of adsorbed CHO species as a consequence of CO hydrogenation that is considered as an important intermediate in thermal and electrocatalytic reactions. In a steady-state catalytic condition, the reaction occurs completely stochastically, and only the few molecules in the far tail of the Maxwell-Boltzmann distribution can cross the barrier and form the product. This fraction of transient species, e.g. of the order 10$^{-11}$ under Fischer-Tropsch reaction at 500 K, is clearly too small to detect spectroscopically (Supporting Information: Arrhenius Expression and Fraction of Reacting Molecules).

To detect the transient species in CO hydrogenation, we employed a pump-probe approach. We first produce a monolayer of the reactants as adsorbed H and CO on Ru(0001) and then, secondly, initiate the reaction with a transient temperature jump induced by a femtosecond optical laser pulse. We selectively probed the species formed during the hydrogenation of CO by probing changes in the electronic structure of the reactant in real time using an x-ray free-electron laser to measure x-ray absorption and x-ray emission spectra. The ultrashort pulse-
lengths of the x-ray free-electron laser and the femtosecond optical laser are the key elements that enabled following the reaction on the femtosecond timescale.

The optical laser pulse excites electrons in the metal to high electronic temperatures, reaching around 5600 K within a few 100 femtoseconds. The system subsequently thermalizes on a picosecond timescale to around 2000 K with the nuclear vibrational motions, such as phonon modes in the substrate and vibrations and frustrated translations and rotations of adsorbed species (Figure S1).(19) Before the thermalization completes, the adsorbate vibrational motions can be excited through ballistic transfer of hot electrons,(20) which thus increases the fraction of molecules which can cross the reaction barrier in the CO hydrogenation reaction in the first few picoseconds (Supporting Information: Arrhenius Expression and Fraction of Reacting Molecules).

The hydrogenation of CO on Ru(0001) upon the femtosecond laser excitation of the Ru(0001) surface covered with CO (CO(ads)), and H (H(ads)) was confirmed by probing the formation of singly (m/e=29) and doubly (m/e=30) hydrogenated CO in gas phase (CH\textsubscript{2}O(g)). Figure 1a shows desorption yields for singly and doubly hydrogenated CO for multiple laser shots. The m/e=30 formaldehyde (CH\textsubscript{2}O) mass spectroscopy peak is accompanied by a fragmentation peak at m/e=29 of known ratio to that at m/e=30. This ratio is strongly exceeded due to dominating contributions from singly hydrogenated CO desorbing from the surface due to the high temperature induced by the optical laser. The highest desorption yield for hydrogenated CO was detected on the first laser shot. The yield on the first shot towards singly hydrogenated CO is an order of magnitude higher than for doubly hydrogenated CO. These hydrogenation pathways compete with the desorption of H\textsubscript{2} and CO.(21) As a result, the amount of CO(ads) and H(ads)
covering Ru(0001) is diminished, which decreases the total yield of CH$_2$O(g) on subsequent laser shots.
Figure 1. O K-edge XAS and XES data for CO hydrogenation. Solid or dotted lines represent the smoothed curve, and points represent true measured values from experiments. (a) The laser-induced desorption signal of m/e=29 (CHO) and m/e=30 (CH₂O) from a (CO + H) / Ru(0001)
surface. (b) O K-edge XAS at negative delay for the unpumped system and at 1.5-2.0 ps after laser excitation, and simulated spectra for CO(ads) (black, solid), CHO(ads) (red, dot) and the transition state from CO(ads) to CHO(ads) (TS, blue, dash-dot). Vertical bars represent the standard deviation of error depending on incoming photon energy. The inset shows a schematic illustration of the excitation process from the O1s level to the unoccupied 2π* resonance in XAS. (c) O K-edge XES excited with x-rays in the range between 530.2 and 533.0 eV at negative delay for the unpumped system (black) and at 0.0-3.0 ps after laser excitation (red). The inset shows a schematic illustration of the core hole decay process from occupied molecular orbitals back to the O1s in XES. (d) The intensity contrast in the x-ray absorption spectra integrated between 530.2 and 533.0 eV versus time delay. The constant error bar indicates the confidence limit of 1.5%, which corresponds to the standard deviation of peak-to-peak fluctuations of contrast at negative delay, in which x-ray measurements were conducted without the laser excitation. Dashed line added as a guide to the eye.
We investigated the hydrogenation of CO on the first laser shot with femtosecond time-resolved x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) by continuously replenishing the sample for each laser and x-ray shots. Figure 1b shows O1s XAS for unreacted CO(ads), measured at delays where the probe pulse arrives before the pump pulse (t < 0 ps), and for reacting CO(ads) probed at 1.5 – 2.0 ps delay time after the reaction is initiated. The intense peak at 533.8 eV is assigned to the O 1s → 2π* electronic excitation of CO(ads) (CO 2π*), which is seen in both unreacted CO(ads) and reacting CO(ads). Most interestingly, we clearly see additional intensity appearing at lower photon energies as a broad feature around 531.6 eV for reacting CO(ads).

To distinguish the various species formed during CO(ads) reduction, we identified the transition states during the formation of CHO(ads) and COH(ads) from CO(ads) and H(ads) using the minimum energy reaction paths and computed the O1s XAS at selected points (Figure 1b, Figure S7, Supporting Information: Spectrum calculations and Supporting Information: Free-energy calculations). We will focus on the spectral regions to which the different species contribute. The addition of hydrogen to C in CO shifts the π* resonance down in energy (Figure 1b) while the addition to the O atom leads to a significant upwards shift (Figure 1b, Figure S7); CH₂O(ads) and COH(ads) do not contribute to the change in intensity as shown in Figure S7(b).

Computed spectral signatures of intermediate species along the reaction coordinate towards CHO(ads) reveal that the resonance shifts down in energy as the reaction proceeds towards CHO(ads). Considering these trends, the observed transient features in the low-energy region of O1s XAS indicate that the reaction is directed towards formation of CHO(ads) or more generally CHₓO(ads) species. This interpretation is further confirmed by considering XES.
We can enhance features of particular species in XES by tuning the excitation energy to specific absorption features of XAS. Figure 1c shows O1s XES selectively excited with x-rays in the range between 530.2 and 533.0 eV corresponding to the lower-energy part of the XAS spectrum for unreacted CO(ads) recorded before the pump pulse (t < 0 ps) and reacting CO(ads) recorded at 0.0 – 3.0 ps after the reaction is initiated. The integrated spectral intensity of XES in Figure 1c corresponds to the XAS intensity integrated over the x-ray energy range 530.2 to 533.0 eV. In the XES spectrum for reacting CO(ads), there is an increase in intensity between 525 eV and 530 eV. The spectral difference (Figure 1c, Figure S6 and Supporting Information: XES Difference Spectra), reacting CO(ads) minus unreacted CO(ads), contains increased XES intensity due to reacting CO(ads) and reduced intensity due to the decrease in the population of unreacted CO(ads). Figure 1c also shows the calculated O1s XES of CO(ads), CHO(ads), and the CHO(ads) transition state; CH2O(ads) and COH(ads) are shown in Figure S7(a). For COH(ads) the intensity between 515 and 520 eV should be considerably enhanced, while the increase of the intensity between 525 and 530 eV is small. On the other hand, for the CHxO(ads) species almost no changes in the intensity below 520 eV are observed but the increase for energies higher than 525 eV is significant, analogous to what is observed in the experimental data. Thus, the appearance of the low-energy peak in XAS and the high-energy peak in XES is fully consistent with the formation of CHxO(ads) species.

It was previously shown for CO on Ru(0001) that excitation of lateral translational motion of CO(ads) parallel to the surface, hot CO, induced by an optical laser pulse gives rise to shifts towards lower energies of the CO 2 $\pi^*$ peak in the XAS spectra and a shift in the CO 5 $\sigma$ peak in the XES spectra towards lower energy that persists on time scales beyond 10 ps upon selective excitation.(22) These spectral changes are due to shifts in the core level as the CO(ads) moves
from on-top position towards higher coordination sites. (23-25) In the current data for CO and H on Ru(0001), there is clearly no shift in the position of the CO 2π* peak in the XAS spectra within the experimental resolution, indicating that CO(ads) mobility is reduced in the high coverage of hydrogen. The additional intensity in XAS and XES is instead related to new species due to interactions with the rapidly moving hydrogen atoms, which we interpret as the onset of CO reduction during the reaction between CO(ads) and H(ads).

Figure 1d displays the time evolution of the O1s XAS signal integrated over the energy range 530.2 - 533.0 eV. This corresponds to the intensity of CH₃O(ads) species plotted as a function of delay between laser pump and x-ray probe; the assignment is corroborated by the spectroscopic fingerprints in XES (Figure 1c and Figure S7). The evolution of transient CH₃O(ads) species is seen only at short time scales, t < 3 ps. On a longer timescale, CO(ads) enters the weakly adsorbed precursor state prior to desorption (Figure S2). (22,26,27) The amount of transient CH₃O(ads) species reaches a maximum around 1.5 ps after the laser pulse and from that point it decays on a time-scale of 1.5 - 2 ps. The rapid rise at t = 0 - 2 ps and the sudden drop at t = 2 – 3 ps suggest that CH₃O(ads) is formed during the relaxation period of electronic temperature, where the electron bath in the substrate couples strongly to the lateral motions of H(ads) (21) and the frustrated rotation of CO(ads). (19) It is well established from two-pulse correlation measurements and an observed nonlinear dependence of desorption yield with laser fluence that desorption of H₂ is also initiated on this time scale. (21) This puts desorption of H₂ in competition with CH₃O(ads) formation, potentially depleting the system of atomic hydrogen on the surface available to react with CO(ads).

For metals, the quenching time of electronically excited states is of the order of 0.1 to 10 fs. In the case of CO on Ru(0001), an extremely fast quenching time of 0.6 fs has been experimentally
determined. This time scale is short compared with the vibrational motions of CO on Ru(0001), therefore the nuclei do not move much before the quenching of the electronically excited states. In this case, the resulting free energy distribution in nuclear motions can have the Boltzmann distribution form. We will show that the free-energy surfaces at the high temperature determine how these products are formed by laser induced reaction.

Figure 2 shows the calculated free-energy surfaces at 0 K, 1500 K, and 2500 K for desorption of H₂, and the subsequent desorption of CHO and CH₂O. Entropic contributions to the free energy are included using either a harmonic approximation or a potential of mean force approach, in which we integrate over all degrees of freedom perpendicular to the pathway (for more details see Supporting Information: Free energy calculations). The entropic contribution to the free energy is largest for the desorption processes, followed by transition state structures. It hardly affects the strongly bound intermediates on the surface and we have thus neglected their temperature dependence. Without entropic contribution, i.e. at 0 K, the formation of CHO(g), CH₂O(g) (Figure 2a) and H₂(g) (Figure 2b) are uphill in energy by 3.6 eV, 2.0 eV and 0.9 eV, respectively, relative to the initial configuration. At 2500 K, the activation barrier for the formation of CHO(ads) and CH₂O(ads) increases by 0.42 eV and 0.56 eV, respectively, due to entropic contributions originating from the thermally activated vibrational motion in the initial states. The desorption of CHO(ads) and CH₂O(ads) to the gas phase become more favored with increasing temperature and the barrier drops dramatically at 2500 K. The desorption of CHO(ads) is kinetically favored by 0.4 eV more than the formation and desorption of CH₂O(ads) and this disparity grows with increasing temperature.
Figure 2. The free-energy profiles of the reaction pathways for the formation (solid lines) and desorption (dashed lines) of (a) CH$_3$O and (b) H$_2$ at 1500 K, and 2500 K. To indicate the situation without entropic contribution, the free-energy profiles at 0 K are also shown. For desorption of CHO, CH$_2$O, and H$_2$, the free-energy profile was calculated as a function of the distance between the center of mass and the Ru surface plane. The insets illustrate the structures at each step of the reaction.
To further address the energy transfer channel associated with the coupling between the hot electron bath in the substrate and the vibrational motion of the adsorbates, we applied an *ab initio* electronic friction model. Using the hot electron temperature profile associated with our experimental conditions, combined with calculated friction parameters for atomic hydrogen on Ru(0001) ($\eta_{el}^H = 1.3$ ps$^{-1}$ for lateral motion), we can estimate the adsorbate temperature $T_{ads}^H$ for H from the electronic temperature ($T_{el}$) using the friction model:

$$\frac{dT_{ads}^H}{dt} = \eta_{el}(T_{el} - T_{ads}^H)$$

(1)

where $\frac{dT_{ads}^H}{dt}$ is the rate of change in the temperature of atomic hydrogen. The average energy gain for atomic hydrogen associated with the sudden temperature increase is of the order 0.2 - 0.25 eV at its maximum and we calculate the barrier for hydrogen diffusion on Ru(0001) as 0.14 eV. The available excess energy results in extremely mobile atomic hydrogen on the surface on a short timescale, leading to an increased probability of H(ads) and CO(ads) interaction. The frustrated rotation of CO(ads) is also initiated through a strong coupling to the electron bath,(22,31,32) which excites the CO molecules and causes them to tilt, exposing the C atoms and leading to an increased probability of interaction with hydrogen.(33)

To gain further insight into the reaction dynamics in the transient temperature jump process, we have performed *ab initio* Molecular Dynamics (AIMD) simulations on a 2H-4CO/Ru(0001) system in three different temperature regimes; ($T_H = T_{CO} = T_{Ru} = 300$ K), ($T_H = T_{Ru} = 2500$ K, $T_{CO} = 500$ K) and ($T_H = T_{CO} = 300$ K, $T_{Ru} = 2500$ K). These regimes represent $t < 0$ ps (before laser pump), $t \sim 1.5$ ps assuming the substrate has not yet thermalized and there is significant coupling between the substrate electrons and adsorbate vibrational modes, and $t \sim 1.5$ ps where insignificant coupling between substrate electrons and adsorbate vibrational modes is assumed, respectively. The H-CO distance distributions reveal a significant dependence on the adsorbate
temperature (Figure S3). We see increases in the H-CO distance distribution between 1.6 Å and 1.8 Å, which corresponds to population of a pre-transition state (pre-TS) region along the reaction coordinate. We identify the features that develop in the region between 530 – 533.8 eV after the laser excitation in Figure 1b as the evolution of peaks assignable to the transition state (TS) and pre-TS along the reaction coordinate to form CHO. We performed additional MD simulations on systems with a higher coverage of hydrogen, 4H-3CO/Ru(0001), and in all simulations H$_2$(g) is formed through H-H collisions on a time-scale less than 1 ps, suggesting that desorption of H$_2$ is dominant immediately after the initiation. On a longer timescale (1 ps < t < 1.5 ps), the probability of H(ads) and CO(ads) collisions gradually increases due to the removal and high mobility of atomic surface hydrogen (Figure. S4), resulting in the observed increase in intensity in Figure 1d. By explicitly inducing excited translational motion of H and frustrated rotation of CO in the MD simulations, the formation of gas-phase CHO(g) is observed on very short time-scales, in agreement with our experimental observations of CHO desorption (see Figure S5).
Figure 3. Schematic of different reaction pathways in the CO/H/Ru(0001) coadsorption system following laser irradiation. From left to right: Laser pump, H + H recombinative desorption and CHO and CH$_3$O species formation and desorption occur at early timescales (< 1 ps), while CO desorption through the precursor state occurs at longer timescales.
Figure 3 shows the reaction pathways induced by laser irradiation. On the short time scale, while the temperature of the system is high, desorption of CHO(ads) dominates over formation and desorption of CH₂O(ads). As the energy gradually dissipates to the bulk, decreasing the temperature at the surface, the CHO desorption channel closes and the reaction is directed to either decomposition back to CO(ads) and H(ads) or formation and desorption of CH₂O. After 3 ps, the surface concentration of any transient CHO(ads) drops to near zero. This is likely due to a combination of factors. First, the temperature, $T_{ads}^H$, of the hot H(ads) decreases on the picosecond time scale, leading to weaker interactions with CO(ads) and a much reduced probability to form any CH₃O(ads) species. Second, the surface will have a lower H concentration due to the formation and desorption of either H₂(g) or CH₃O(g). Lastly, the CH₃O(ads) on the surface are thermodynamically unstable, as seen from Figure 2, and prefer to decompose back to CO(ads) and H(ads). This will occur as the surface thermalizes and there are fewer collisions between CO and H. On a longer timescale, a fraction of the CO molecules transition from the chemisorbed state to weakly adsorbed CO in the precursor state with elongated distance to the surface.(26) This leads to fewer collisions between adsorbed CO and H, which limits further H-CO bond formation with transient H that may remain on the surface.

The present “pump-probe” approach has identified the hydrogenation mechanism of CO. We have shown that, on the Ru(0001) surface, the collision of H and CO in the chemisorbed state leads to adsorbed CHO as a metastable intermediate species produced only during the first few picoseconds. The H-CO bond formation is clearly favored over H-OC bond formation. In the case of laser induced reaction, the formation of CHO(ads) is kinetically competing with other reaction pathways: the desorption of H₂ and CO. Here it is important to note that accompanying DFT calculations, which account for the entropic contributions in the transient temperature jump
process, substantiate the observations from spectral measurements of the surface species, as well as mass spectrometry measurements of desorption products.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Experimental. The (CO + H) / Ru(0001) surface was prepared by exposing the clean Ru(0001) surface to CO and H\textsubscript{2} gas. Reference O1s XAS and XES spectra of the prepared (CO + H) / Ru(0001) surface were recorded at beamline 13-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory. The time-resolved O1s XAS and XES were recorded at the Soft X-Ray (SXR) instrument at the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory. The reaction was initiated with a 400 nm, 70 fs laser pulse. O K-edge XAS spectra were recorded in fluorescence yield, i.e. the total integrated intensity of O K-edge XES measured at a particular photon energy. This gave less noise in XAS than XES, allowing for quantitative analysis. The spectra were normalized to the incoming x-ray photon flux. The laser-induced desorption mass spectrometry studies were performed at Stockholm University. The laser-induced desorption product yield was measured using an ion-counting quadrupole mass spectrometer. See Supporting Information: Laser pump x-ray probe experiments for more information.

Computational. The simulated XAS and XES spectra were computed using the real-space-grid GPAW code.(34,35) Structures along the transition state path were calculated using the nudged elastic band (NEB) technique.(36,37) Ab Initio molecular dynamics (AIMD) simulations of (CO + H) / Ru(0001) were carried out in the NVT ensemble using Langevin dynamics implemented
in the Atomic Simulation Environment (ASE). More details are given in the Supporting Information: Spectrum and Free energy calculations.

ASSOCIATED CONTENT

Supporting Information

Experimental details, theoretical background, additional data from both theory and experiment, and analysis (PDF)

AUTHOR INFORMATION

The authors declare no competing financial interests.

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