



Mechanism of Carbon Monoxide Dissociation on a Cobalt Fischer–Tropsch Catalyst

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The way in which the triple bond in CO dissociates, a key reaction step in the Fischer–Tropsch (FT) reaction, is a subject of intense debate. Direct CO dissociation on a Co catalyst was probed by $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{18}\text{O}$ scrambling in the absence and presence of H_2 . The initial scrambling rate without H_2 was significantly higher than the rate of CO consumption under CO hydrogenation conditions, which indicated that the surface contained sites sufficiently reactive to dissociate CO without the assistance of H atoms. Only a small fraction of the surface was involved in CO scrambling. The minor influence of CO scrambling and CO residence time on the partial pressure of H_2 showed that CO dissociation was not affected by the presence of H_2 . The positive H_2 reaction order was correlated to the fact that the hydrogenation of adsorbed C and O atoms was slower than CO dissociation. Temperature-programmed in situ IR spectroscopy underpinned the conclusion that CO dissociation does not require H atoms.

CO bond dissociation is the initiating step of the Fischer–Tropsch (FT) reaction, which is at the heart of rapidly growing industrial gas-to-liquids technology to convert synthesis gas into clean transportation fuels.^[1] There has been considerable debate on the mechanism of CO dissociation. Density functional theory (DFT) calculations have demonstrated that step-edge sites of sufficiently reactive metals such as Co^[2] and Ru^[3] can directly dissociate CO with much lower activation barriers than terrace sites. This mechanism is similar to the well-accepted mechanism of N_2 dissociation on step-edge sites of Ru nanoparticles relevant to NH_3 synthesis.^[4] However, whether these coordinatively unsaturated sites are active during the FT reaction has been questioned, as they are vulnerable to poisoning by strongly adsorbed CO or reaction intermediates.^[5] H-assisted CO dissociation on terrace sites is therefore considered as an alternative pathway in which CO is hydrogenated to $\text{HCO}^{[6]}$

or $\text{HCOH}^{[7]}$ intermediates prior to C–O bond cleavage. This CO dissociation pathway has been invoked in mechanisms that take place on highly CO-covered terraces.^[7,8] Besides, the way in which CO dissociates also depends on the crystallographic structure of the catalyst nanoparticles.^[9] So far, convincing experimental evidence for either of these two pathways is still lacking.

Following the isotopic scrambling of a $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{18}\text{O}$ mixture provides a means of investigating C–O bond dissociation in the absence of H_2 .^[10] In our experiments, an equimolar mixture of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ was passed over a reduced SiO_2 -supported Co catalyst (17 wt% Co, 0.04 wt% Pt as a reduction promoter, and 7% dispersion based on H_2 chemisorption; see the Supporting Information for details) at 220 °C. This reaction leads to scrambled $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ products (Figure S3, Supporting Information), which demonstrates that CO dissociates and atomic C + O recombine in the absence of H_2 . In addition, CO_2 is obtained as a result of the recombination of CO with O, which is usually termed the Boudouard reaction. Both scrambling and CO_2 formation require CO dissociation. These two reactions may share the same type of active site.^[11] These reactions lead to a Co surface covered with C and to a lesser extent with O atoms.

The CO consumption rate (equal to two times the CO_2 formation rate) and the scrambling rate expressed as the turnover frequency (TOF) are displayed in Figure 1 (see the Supporting Information for analysis details). The results show that both rates decrease rapidly with time. As the surface of the reduced Co catalyst (reduction at 450 °C followed by Ar flushing at

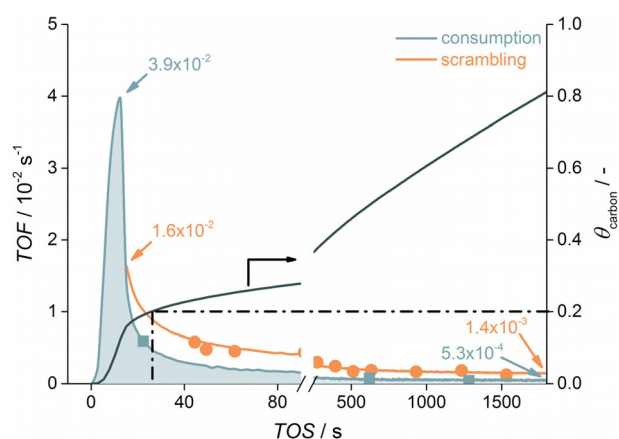


Figure 1. Dependence of CO consumption, CO scrambling rate [expressed as turnover frequency (TOF), left axis], and carbon coverage (right axis) on time-on-stream (TOS) at 220 °C [conditions: $p(^{12}\text{C}^{16}\text{O}) = p(^{13}\text{C}^{18}\text{O}) = 45$ mbar]. Lines correspond to MS measurements, and data points correspond to GC–MS measurements.

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450 °C) was initially empty, the C atoms that are deposited during the Boudouard reaction inhibit both CO₂ formation and CO scrambling.^[12] Owing to the chromatographic effect of CO, the first measurable scrambling rate was determined after 15 s. The TOF of $1.6 \times 10^{-2} \text{ s}^{-1}$ is five times higher than the rate of CO consumption in the presence of H₂ (H₂/CO ratio = 2, TOF = $3 \times 10^{-3} \text{ s}^{-1}$, see Figure 2). The significantly higher scrambling rate implies that the intrinsic rate of direct CO dissociation is sufficiently high to provide the C monomers for hydrocarbon formation during CO hydrogenation in the presence of H₂. We stress that CO dissociation can still control the overall rate at the higher CO coverage encountered under actual FT conditions.^[13]

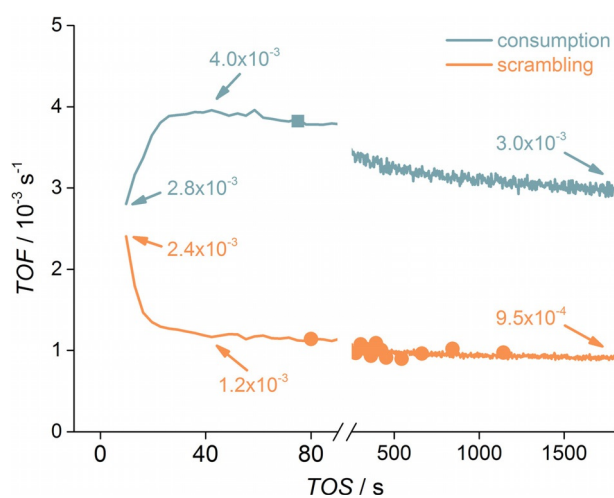


Figure 2. Dependence of CO consumption and scrambling rate in the presence of H₂ on time-on-stream at 220 °C [conditions: $p(^{12}\text{C}^{16}\text{O}) = p(^{13}\text{C}^{18}\text{O}) = 45 \text{ mbar}$, $p(\text{H}_2) = 180 \text{ mbar}$].

As CO₂ and C are formed in equimolar amounts, it becomes possible to quantify the amount of C atoms deposited as a function of time-on-stream. Approximately 90% of the activity for CO dissociation is lost when less than one-fifth of the Co metal surface is covered by C atoms. On the basis of statistical analysis,^[14] 15 nm face-centered cubic particles comprise approximately 20% coordinatively unsaturated atoms. Considering the size of the particles, step-edge sites will dominate over edge and corner sites. This result indicates that not terrace sites but a minority site is involved in C–O bond dissociation and that the observed rapid deactivation of CO bond dissociation in the absence of H₂ results from the blocking of step-edge sites by adsorbed C atoms. Considering that a large part of the rate stems from a small fraction of surface sites, it can be inferred that step-edge sites are responsible for CO activation. This is in line with the microkinetic simulations results.^[15]

To study CO dissociation under conditions more relevant to the FT reaction, we also investigated CO scrambling in the presence of H₂ by co-feeding H₂ with ¹²C¹⁶O/¹³C¹⁸O mixtures at 220 °C at different H₂/CO ratios. A typical result obtained at H₂/CO = 2 is shown in Figure 2. CO is mainly converted into hydrocarbons and only a small amount of CO₂ (Table S1). The

scrambling rate is initially comparable to that of CO consumption but rapidly decreases because of the build-up of reaction intermediates. The scrambling rate at steady state (0.95×10^{-3}) is slightly lower than that in experiment without H₂ (1.4×10^{-3}). This small decrease in the CO scrambling rate can be explained by the fact that the hydrogenation lowers the coverage of C and O. The presence of H₂ therefore only slightly affects the recombination rate. Notably, the CO dissociation rate equals the sum of the CO consumption rate and the scrambling rate and that the scrambling rate relates to the recombination rate.

Figure 3 presents the CO scrambling and consumption rates as a function of the partial pressure of H₂ after 1 h on stream. The strong dependence of the CO consumption rate on the H₂ pressure (H₂ reaction order ≈ 0.7) is typically observed during CO hydrogenation on Co catalysts.^[16] On the other hand, the

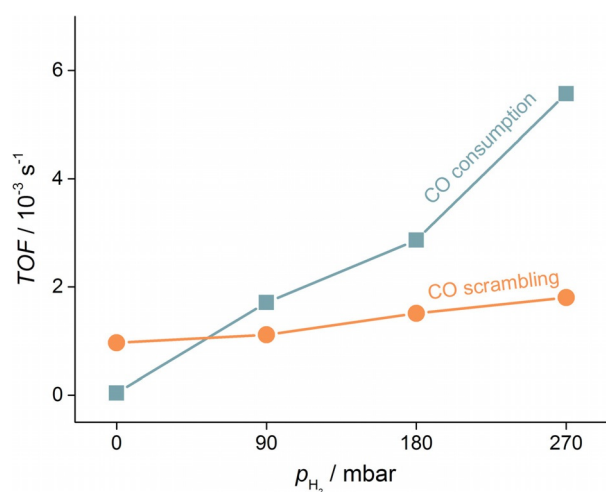


Figure 3. CO consumption (squares) and scrambling (circles) rates as a function of H₂ partial pressure at 220 °C [conditions: $p(^{12}\text{C}^{16}\text{O}) = p(^{13}\text{C}^{18}\text{O}) = 45 \text{ mbar}$].

steady-state CO scrambling rate hardly changes with the partial pressure of H₂. Our steady-state isotopic transient kinetic analysis (SSITKA) results (Figure 4) reveal that the CO residence time (τ) and CO coverage (θ) are nearly independent of the partial pressure of H₂ (see the Supporting Information for details), which is consistent with previous work.^[16] Taking into account the observation that C and O atoms can recombine, the measured residence time of CO not only depends on the reversible adsorption of CO but also on CO dissociation and recombination reactions. As reversible CO adsorption is not expected to be dependent on the H₂ pressure, a constant residence time implies that the reversible dissociation rate is practically independent of H₂ pressure. Below, we provide further evidence that H₂ is not involved in CO dissociation, although on the basis of Figure 3 alone, a parallel mechanism involving H atoms cannot be excluded.

The findings described above lead to the conclusion that the overall process of CO adsorption/desorption accompanied by reversible CO dissociation is independent of the presence of H₂. On the contrary, the residence time of CH_x reaction inter-

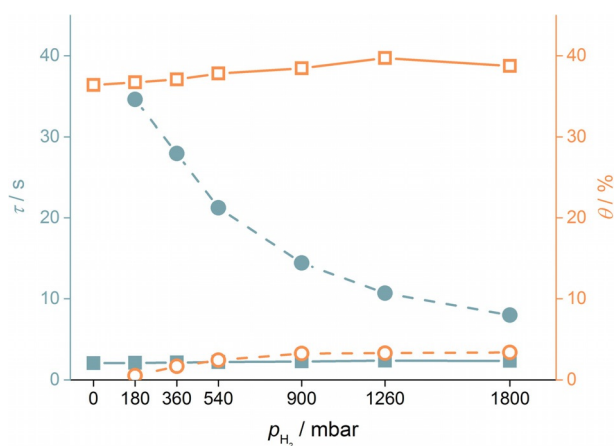


Figure 4. Residence times (solid symbols, left axis) and surface coverages (open symbols, right axis) of CO (squares) and CH_x (circles) as a function of H_2 partial pressure [SSITKA, $p(CO) = 180$ mbar, $220^\circ C$].

mediates strongly depends on the partial pressure of H_2 , which demonstrates that not CO dissociation but hydrogenation of adsorbed C causes the positive H_2 reaction order. In view of the literature,^[17] O hydrogenation also controls the overall reaction rate. In this sense, the increase in the CO dissociation rate (consumption + scrambling) with the partial pressure of H_2 is interpreted in terms of increasing rate of C and O removal. The relatively minor increase in the scrambling rate with the partial pressure of H_2 is also likely owing to more rapid removal of surface species. Separate experiments clearly show that the total amount of C deposited, which is not explicitly involved in CO hydrogenation and not measurable by SSITKA, increases with decreasing H_2 partial pressure (Figure S6). This further underpins the strong dependence of C removal on the partial pressure of H_2 . The major kinetic implications of these results is that direct CO dissociation is sufficiently fast and that the H_2 pressure only affects the overall rate of CO consumption, as adsorbed H atoms increase the hydrogenation rate of adsorbed C and O, which regenerates surface vacancies that are needed for CO dissociation and hydrogen adsorption.

Additional proof for the possibility of direct CO dissociation on Co was obtained by in situ IR spectroscopy in transmission mode. We followed the IR absorption bands of CO chemisorbed on the reduced Co catalyst, which was extensively evacuated at an elevated temperature prior to CO adsorption (details are given in the Supporting Information). The catalyst was exposed to CO at $35^\circ C$, which was followed by heating at $5^\circ C min^{-1}$ to $300^\circ C$. Figure 5 shows the evolution of the IR spectra for three cases: one, without H_2 ; two, in the presence of 5 mbar H_2 ; three, in the presence of 10 mbar H_2 . After exposure to CO, a prominent band appears at $\tilde{\nu} = 2026$ cm^{-1} , attributed to CO adsorbed on the top sites of metallic Co.^[18] Upon increasing the temperature, this band undergoes a blueshift to $\tilde{\nu} = 2060$ cm^{-1} , which starts at $150^\circ C$.^[19] At high temperatures, the intensity of this band decreases, presumably as a result of the desorption of CO.^[20] The observation of the asymmetric stretching vibration of gaseous CO_2 at $\tilde{\nu} = 2360$ cm^{-1} (Figure S8b) accompanied by the blueshift in adsorbed CO sug-

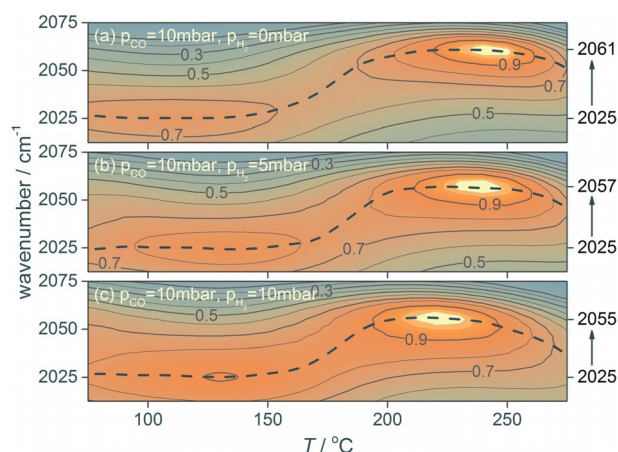


Figure 5. IR spectra of the CO adsorption band on the cobalt-based FT catalyst as a function of temperature a) in the absence of H_2 and in the presence of b) 5 mbar and c) 10 mbar H_2 . The normalized signal intensity is presented by contour labels.

gests that these two changes are correlated. The formation of CO_2 implies that CO dissociates and C atoms remain on the surface. In a reference experiment involving the use of a SiO_2 -supported Pt catalyst, we did not observe a blueshift as observed for Co (Figure S9), and this is consistent with the notion that Pt cannot dissociate CO under these conditions.^[21] Accordingly, we speculate that the blueshift for the Co catalyst can be attributed to lateral interactions of CO with adsorbed C and, possibly, O atoms released from CO dissociation.

To verify that lateral CO–C and CO–O interactions cause the CO frequency shift, we recorded the IR spectra of CO adsorption on Co surfaces for which either C or O atoms were pre-deposited. We also used DFT calculations to determine the influence of co-adsorbates on the stretching frequency of top-adsorbed CO (computational details are given in the Supporting Information). Carbon atoms were deposited on the surface by exposure to 0.05 mbar C_2H_2 at $50^\circ C$, and this was followed by evacuation at $130^\circ C$ to decompose adsorbed C_2H_2 to C and H_2 , a procedure taken from surface-science studies.^[22] The O atoms were adsorbed by exposing the reduced catalyst to 0.5 mbar N_2O at $50^\circ C$, followed by evacuation at the same temperature. The coverages of the C and O atom obtained in this way could not be quantified in these experiments in the IR cell. The effect of co-adsorbates is, however, clear.

The reference spectra depicted in Figure 6a relate to an initially clean Co surface. Without co-adsorbates, the CO band appears at $\tilde{\nu} = 1996$ cm^{-1} at the lowest CO coverage, which shifts to $\tilde{\nu} = 2018$ cm^{-1} with increasing coverage (final CO pressure: 10 mbar). On the basis of the IR results of CO adsorption on a Co(0001) single crystal by Weststrate et al.,^[23] we estimate the CO coverage to be 0.35 ML. In good agreement with this, we determined the total CO coverage and the reversibly adsorbed CO coverage of 0.38 and 0.31 ML at a CO partial pressure of 15 mbar by $Ne \rightarrow ^{12}CO$ and $^{12}CO \rightarrow ^{13}CO$ switches, respectively, on the reduced Co catalyst at $35^\circ C$ (Figure S5). These experimental data are in good agreement with DFT calculations of CO adsorbed on a Co(0001) terrace (Tables S2 and S3); the CO

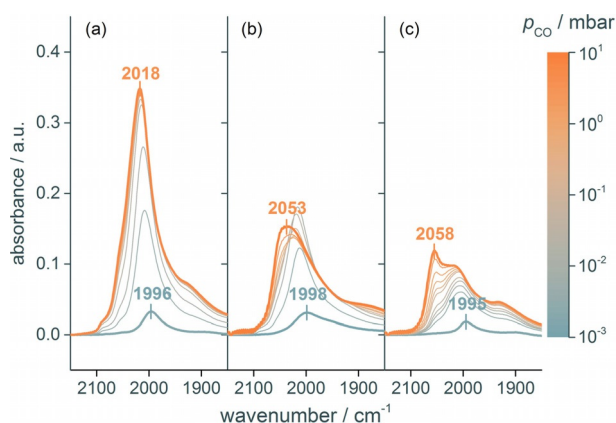


Figure 6. IR spectra of the CO adsorption band on a cobalt-based FT catalyst at 35 °C: a) reduced at 450 °C, b) precoverage by C atoms following acetylene adsorption on the clean Co surface and decomposition at 130 °C, c) precoverage by O atoms following nitrous oxide adsorption on the clean Co surface and decomposition at 50 °C.

stretch frequency occurs at $\tilde{\nu}=1988\text{ cm}^{-1}$ for a CO coverage of 0.11 ML. This band will shift to $\tilde{\nu}=2007$ and 2026 cm^{-1} at CO coverages of 0.22 and 0.33 ML, respectively. At a slightly higher CO coverage of 0.67 ML, the frequency shifts to $\tilde{\nu}=2109\text{ cm}^{-1}$. Saeys and co-workers reported that the maximum CO coverage was limited to 7/12 ML under practical FT conditions.^[24]

The experimental IR spectra at low CO coverage for the Co catalyst, partially precovered with atomic C and O species, show similar bands at $\tilde{\nu}=1998$ and 1995 cm^{-1} , respectively. Upon increasing the CO coverage, the blueshift is, however, much stronger for the precovered surfaces ($\tilde{\nu}=2053$ and 2058 cm^{-1} for partially C- and O-covered surfaces, respectively) than for the initially clean surface ($\tilde{\nu}=2018\text{ cm}^{-1}$). Qualitatively, these data are in agreement with the CO IR data for Co(0001) with frequency shifts of $\tilde{\nu}=47$ and 42 cm^{-1} for 0.5 ML C and 0.2 ML O, respectively, with respect to an initial CO frequency of $\tilde{\nu}=2026\text{ cm}^{-1}$ corresponding to 0.5 ML CO.^[25] These results demonstrate that C and O atoms exert larger lateral repulsions on adsorbed CO than CO itself. DFT calculations (Table S4) confirm that co-adsorbed C and O atoms can cause the strong blueshift. The results show that CO stretches at $\tilde{\nu}=2011\text{ cm}^{-1}$ for a unit cell containing 0.25 ML CO in the absence of co-adsorbates. The frequency shifts to $\tilde{\nu}=2052$ and 2058 cm^{-1} after adding 0.50 ML C and 0.25 ML O, respectively.

Taken together, these findings show that the shift observed during temperature-programmed CO dissociation can be explained by lateral interactions with C and O atoms. Accordingly, we interpret the onset of the CO frequency shift at 150 °C in Figure 5a as the start of C–O bond dissociation on the clean Co surface. Figure 5b,c depicts similar data recorded in the presence of 5 and 10 mbar H₂. Clearly, the onset of CO dissociation occurs at nearly the same temperature irrespective of whether H₂ is present. On the basis of these data, we infer that CO dissociation does not involve H₂.

Theoretical studies indicate that step-edge B5-type sites provide a unique low-barrier pathway for direct CO dissocia-

tion.^[25,26] Alternatively, CO intermediates involving H have been proposed to be relevant to CO dissociation on less-active terrace sites.^[6–8,16] It has been shown that the overall barrier for direct CO dissociation on step edges is lower than those for the H-assisted pathways on step-edge and terrace sites.^[26] The IR and kinetic results discussed above demonstrate that H atoms need not be involved in the CO dissociation reaction. Accordingly, it is likely that step-edge sites are the sites at which CO dissociation occurs. This is in keeping with the finding that during CO scrambling in the absence of H₂, most of the activity is lost by covering the surface with a small number of C atoms. These C atoms migrate to the terrace and exert lateral interactions on co-adsorbed CO, as demonstrated by IR spectroscopy. Under actual CO hydrogenation conditions, these C atoms will be hydrogenated; this results in hydrocarbon formation, which thereby regenerates the active sites for CO dissociation. We point out that the data of the present work do not exclude the parallel path of CO dissociation.

In summary, ¹²C¹⁶O/¹³C¹⁸O scrambling experiments in the absence of H₂ revealed that CO dissociation on a reduced Co catalyst was intrinsically fast and reversible. Only a minor fraction of the metallic Co surface, likely coordinatively unsaturated sites, were involved in direct CO dissociation. In the presence of H₂, the scrambling rate was slightly lower, as slow C and O hydrogenation lowered the coverage of C and O. The CO scrambling rate and CO residence time depended only weakly on the partial pressure of H₂, which implied that reversible CO adsorption and CO dissociation were only weakly affected by H₂. In situ IR spectroscopy confirmed that CO dissociation was not affected by H₂. These findings indicate that the explanation for the near-unity reaction order with respect to H₂ during the Fischer–Tropsch reaction need not involve H atoms in the assumed rate-limiting CO dissociation step. Instead, we propose that the removal of C and O species from the surface by hydrogenation controls the CO consumption rate. Removing these atoms from the surface regenerates the vacancies required for the Fischer–Tropsch reaction.

Experimental Section

The SiO₂-supported catalyst containing 17.1 wt% Co and 0.04 wt% Pt was prepared by the incipient wetness impregnation method. The amount of Co surface atoms was determined by H₂ chemisorption. The Co particle size of the reduced Co samples was estimated by transmission electron microscopy (FEI Tecnai 20) and in situ X-ray diffraction (Rigaku, D/max-2600). CO scrambling experiments were performed by flowing an equalmolar ¹²C¹⁶O/¹³C¹⁸O mixture (¹³C¹⁸O, Cambridge Isotope Laboratories, ¹³C 99%, ¹⁸O 95%) over the reduced Co catalyst. SSITKA experiments were performed by switching from ¹²CO/H₂ to ¹³CO/H₂ (EurisoTop, 99% ¹³C). Online MS (ESS, GeneSys), GC (VARIAN CP-3800), and GC–MS (Shimadzu GCMS-QP 2010) were used to analyze the effluent products and their isotopic compositions. In situ Fourier-transform infrared spectroscopy data (Bruker Vertex V70v) were recorded as a function of CO pressure at 35 °C, followed by heating to 300 °C in the absence and presence of H₂. In some experiments, the Co catalyst was first exposed to C₂H₂ or N₂O. Detailed experimental procedures, data analysis, and DFT methodology are given in the Supporting Information.

Conflict of interest

The authors declare no conflict of interest.

Keywords: Fischer–Tropsch · in-situ characterization · IR spectroscopy · isotopic labeling · reaction mechanisms

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