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

Wei Chen, Bart Zijlstra, Ivo A. W. Filot, Robert Pestman, and Emiel J. M. Hensen

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 $^{13}$C$^{16}$O/$^{13}$C$^{18}$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. There has been considerable debate on the mechanism of CO dissociation. Density functional theory (DFT) calculations have demonstrated that step-edge sites of Ru nanoparticles relevant to NH$_3$ synthesis can directly dissociate CO with much lower activation barriers than terrace sites. This mechanism is similar to the well-accepted dissociation pathway has been invoked in mechanisms that involve CO dissociation on terrace sites. This mechanism is similar to the well-accepted mechanism of NH$_3$ dissociation on step-edge sites of Ru nanoparticles relevant to NH$_3$ synthesis. 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. H-assisted CO dissociation on terrace sites is therefore considered as an alternative pathway in which CO is hydrogenated to HCO or HCOH intermediates prior to C–O bond cleavage. This CO dissociation pathway has been invoked in mechanisms that take place on highly CO-covered terraces. Besides, the way in which CO dissociates also depends on the crystallographic structure of the catalyst nanoparticles. So far, convincing experimental evidence for either of these two pathways is still lacking.

Following the isotopic scrambling of a $^{13}$C$^{16}$O/$^{13}$C$^{18}$O mixture provides a means of investigating C–O bond dissociation in the absence of H$_2$. In our experiments, an equimolar mixture of $^{13}$C$^{16}$O and $^{13}$C$^{18}$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 $^{13}$C$^{16}$O and $^{13}$C$^{18}$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. 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 scrambling 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: $p(^{13}$C$^{16}$O) = $p(^{13}$C$^{18}$O) = 45 mbar). Lines correspond to MS measurements, and data points correspond to GC–MS measurements.](https://doi.org/10.1002/cctc.201701203)
450 °C was initially empty, the C atoms that are deposited during the Boudouard reaction inhibit both CO₂ formation and CO scrambling.⁻ Owing to the chromatographic effect of CO, the first measurable scrambling rate was determined after 15 s. The TOF of 1.6 × 10⁻⁵ s⁻¹ is five times higher than the rate of CO consumption in the presence of H₂ (H₂/CO ratio = 2, TOF = 3 × 10⁻⁵ 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.¹²

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,¹³ 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.¹⁴

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 steady-state CO scrambling rate hardly changes with the partial pressure of H₂. Our steady-state isotopic transient kinetic analysis (SITKINA) 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.¹⁵ 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 CH₄ reaction inter-

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**Figure 2.** Dependence of CO consumption and scrambling rate in the presence of H₂ on time-on-stream at 220 °C (conditions: \( p(¹²C¹⁶O) = p(¹³C¹⁸O) = 45 \text{ mbar}, p(H₂) = 180 \text{ mbar} \)).

**Figure 3.** CO consumption (squares) and scrambling (circles) rates as a function of H₂ partial pressure at 220 °C (conditions: \( p(¹²C¹⁶O) = p(¹³C¹⁸O) = 45 \text{ mbar} \)).
mediates strongly depends on the partial pressure of H₂, which demonstrates that not CO dissociation but hydrogenation of adsorbed C causes the positive H₂ reaction order. In view of the literature, oxidative 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 H₂ 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 H₂ 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 H₂ partial pressure (Figure S6). This further underpins the strong dependence of C removal on the partial pressure of H₂. The major kinetic implications of these results is that direct CO dissociation is sufficiently fast and that the H₂ 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 °C, which was followed by heating at 5 °C min⁻¹ to 300 °C. Figure 5 shows the evolution of the IR spectra for three cases: one, without H₂, two, in the presence of 5 mbar H₂; three, in the presence of 10 mbar H₂. After exposure to CO, a prominent band appears at ̃ν = 2026 cm⁻¹, attributed to CO adsorbed on the top sites of metallic Co. Upon increasing the temperature, this band undergoes a blueshift to ̃ν = 2060 cm⁻¹, which starts at 150 °C. At high temperatures, the intensity of this band decreases, presumably as a result of the desorption of CO. The observation of the asymmetric stretching vibration of gaseous CO₂ at ̃ν = 2360 cm⁻¹ (Figure S8b) accompanied by the blueshift in adsorbed CO suggests that these two changes are correlated. The formation of CO₂ implies that CO dissociates and C atoms remain on the surface. In a reference experiment involving the use of a SiO₂-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. 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 predeposited. 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 C₂H₆ at 50 °C, and this was followed by evacuation at 130 °C to decompose adsorbed C₂H₂ to C and H₂, a procedure taken from surface-science studies. The O atoms were adsorbed by exposing the reduced catalyst to 0.5 mbar N₂O at 50 °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 ̃ν = 1996 cm⁻¹ at the lowest CO coverage, which shifts to ̃ν = 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., 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→¹⁴CO and ¹²CO→¹⁴CO switches, respectively, on the reduced Co catalyst at 35 °C (Figure S5). These experimental data are in good agreement with DFT calculations of CO adsorption on a Co(0001) terrace (Tables S2 and S3); the CO...
stretch frequency occurs at $\tilde{\nu} = 1988$ 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 $\tilde{\nu} = 2109$ cm$^{-1}$. Saeyes 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 ($\tilde{\nu} = 2018$ 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 $\tilde{\nu} = 2026$ 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 $\tilde{\nu} = 2011$ 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.

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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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Manuscript received: July 24, 2017
Revised manuscript received: August 16, 2017
Accepted manuscript online: August 17, 2017
Version of record online: November 23, 2017