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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 \(^{13}\text{C}^{16}\text{O}/^{13}\text{C}^{18}\text{O}\) scrambling in the absence and presence of \(\text{H}_2\). The initial scrambling rate without \(\text{H}_2\) 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 \(\text{H}_2\) showed that CO dissociation was not affected by the presence of \(\text{H}_2\). The positive \(\text{H}_2\) 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 \(\text{N}_2\) 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 HCO\(^{[6]}\) or 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 surfaces.\(^{[7,8]}\) 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 \(^{13}\text{C}^{16}\text{O}/^{13}\text{C}^{18}\text{O}\) mixture provides a means of investigating C–O bond dissociation in the absence of \(\text{H}_2\).\(^{[10]}\) In our experiments, an equimolar mixture of \(^{13}\text{C}^{16}\text{O}\) 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 \(\text{H}_2\) chemisorption; see the Supporting Information for analysis details) at 220°C. This reaction leads to scrambled \(^{13}\text{C}^{16}\text{O}\) and \(^{13}\text{C}^{18}\text{O}\) products (Figure S3, Supporting Information), which demonstrates that CO dissociates and atomic C + O recombine in the absence of \(\text{H}_2\). In addition, CO\(_2\) is only 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 twice the CO 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 \(\text{Ar}\) flushing at

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**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: \(p(^{13}\text{C}^{16}\text{O}) = p(^{13}\text{C}^{18}\text{O}) = 45\text{ mbar}\). Lines correspond to MS measurements, and data points correspond to GC–MS measurements.

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\(^{[a]}\) W. Chen, B. Zijlstra, Dr. I. A. W. Filot, Dr. R. Pestman, Prof. Dr. E. J. M. Hensen
Schuit Institute of Catalysis, Department of Chemical Engineering and Chemistry
Eindhoven University of Technology
PO. Box 513, 5600 MB, Eindhoven (The Netherlands)
E-mail: e.j.m.hensen@tue.nl

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450 °C was initially empty, the C atoms that are deposited during the Boudouard reaction inhibit both CO$_2$ formation and CO scrambling.\cite{12} Owing to the chromatographic effect of CO, the first measurable scrambling rate was determined after 15 s. The TOF of $1.6 \times 10^{-4}$ s$^{-1}$ is five times higher than the rate of CO consumption in the presence of H$_2$ (H$_2$/CO ratio = 2, TOF = $3 \times 10^{-3}$ 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 H$_2$. We stress that CO dissociation can still control the overall rate at the higher CO coverage encountered under actual FT conditions.\cite{13}

As CO$_2$ 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,\cite{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 H$_2$ 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.\cite{15}

To study CO dissociation under conditions more relevant to the FT reaction, we also investigated CO scrambling in the presence of H$_2$ by co-feeding H$_2$ with $^{12}$C$^{16}$O/$^{13}$C$^{18}$O mixtures at 220 °C at different H$_2$/CO ratios. A typical result obtained at H$_2$/CO = 2 is shown in Figure 2 CO is mainly converted into hydrocarbons and only a small amount of CO$_2$ (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 ($0.95 \times 10^{-4}$) is slightly lower than that in experiment without H$_2$ ($1.4 \times 10^{-4}$). 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 H$_2$ 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 H$_2$ after 1 h on stream. The strong dependence of the CO consumption rate on the H$_2$ pressure (H$_2$ reaction order ≈ 0.7) is typically observed during CO hydrogenation on Co catalysts.\cite{16} On the other hand, the steady-state CO scrambling rate hardly changes with the partial pressure of H$_2$. Our steady-state isotopic transient kinetic analysis (SSITKA) results (Figure 4) reveal that the CO residence time ($\tau$) and CO coverage ($\theta$) are nearly independent of the partial pressure of H$_2$ (see the Supporting Information for details), which is consistent with previous work.\cite{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 H$_2$ pressure, a constant residence time implies that the reversible dissociation rate is practically independent of H$_2$ pressure. Below, we provide further evidence that H$_2$ 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 H$_2$. On the contrary, the residence time of CH$_4$ reaction inter-
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,[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 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 $\bar{\nu} = 2026 \text{ cm}^{-1}$, attributed to CO adsorbed on the top sites of metallic Co. [18] Upon increasing the temperature, this band undergoes a blueshift to $\bar{\nu} = 2060 \text{ cm}^{-1}$, which starts at 150 °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 CO₂ at $\bar{\nu} = 2360 \text{ cm}^{-1}$ (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. [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 predisposed. 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 C₂H₆ to C and H₂, a procedure taken from surface-science studies. [22] 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 $\bar{\nu} = 1996 \text{ cm}^{-1}$ at the lowest CO coverage, which shifts to $\bar{\nu} = 2018 \text{ cm}^{-1}$ with increasing coverage (final CO pressure: 10 mbar). On the basis of the IR results of CO adsorption on a Co(000 1) 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–¹³CO and ¹²CO–¹³CO switches, respectively, on the reduced Co catalyst at 35 °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
during the corresponding to 0.5 ML CO. It has been shown that the overall barrier for (EurisoTop, 99 % for aC Oc overage These results revealed that CO dissociation on a reduced Co catalyst. SSITKA experiments were performed by flowing an equalmolar CO/H₂ mixture (¹²C¹⁸O/¹³C¹⁶O, Cambridge Isotope Laboratories, ¹³C 99 %, ¹⁸O 95 %) over the reduced Co catalyst. SSITKA experiments were performed by switching from ¹²CO/H₂ to ¹¹CO/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 time.

Alternatively, CO intermediates involving H have been proposed to be relevant to CO dissociation on less-active terrace sites. 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. 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, ¹³C¹⁸O/¹³C¹⁶O 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 H 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 ¹²C¹⁸O/¹³C¹⁶O mixture (¹³C¹⁸O, Cambridge Isotope Laboratories, ¹³C 99 %, ¹⁸O 95 %) over the reduced Co catalyst. SSITKA experiments were performed by switching from ¹²CO/H₂ to ¹¹CO/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 C,H₄ or N₂O. Detailed experimental procedures, data analysis, and DFT methodology are given in the Supporting Information.

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**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.
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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