# Effect of $CO_2$-Rich Syngas on the Chemical State of Fe(110) During Fischer-Tropsch Synthesis

*David Degerman*[a*], *Mikhail Shipilin*[a], *Patrick Lömker*[a], *Markus Soldemo*[a], *Christopher M. Goodwin*[a†], *Michael Wagstaffe*[b], *Mia Börner*[a], *Christoph Schlueter*[c], *Peter Amann*[a‡] and *Anders Nilsson*[a*]

AUTHOR ADDRESS

[a] Stockholm University, Department of Physics
AlbaNova University Center
Roslagstullsbacken 21
114 21 Stockholm
Sweden

[b] Centre for X-ray and Nanoscience (CXNS), DESY
Notkestraße 85
226 07 Hamburg
Germany

[c] Deutsches Elektronen-Synchrotron DESY
Notkestraße 85
226 07 Hamburg
Germany

[*] email: david.degerman@fysik.su.se

[*] email: andersn@fysik.su.se

## Table of contents

Beam Damage Test ........................................................................................................S2
Dependency of Experimental Order ...........................................................................................S3
Additional Spectra: Fitted $CO_2$ Hydrogenation Spectra ........................................................S5
Additional Spectra: Gas Phase Peaks Included ..........................................................................S6
Online Mass Spectrometry ..........................................................................................................S7

## Beam Damage Test

The experiment in the main text was performed with full beam, and the beam damage test was performed in order to elucideate potential effects of the beam. The main mechanism for beam induced effects is secondary electrons weakening the bonds of the gas phase molecules, facilitating their bond dissociation. When the reaction itself turns over rapidly the contribution of the beam to the dissociation of the atoms is not visible in the spectra. Consequently, the spectra are most affected at reaction conditions where the turnover is slow. At, i.e. with low temperatures and inert reactants. Thus, we performed the beam damage tests in a 1:4 $CO_2$:$H_2$ reaction mixture at 200 mbar, 152 °C and a 0.4° incidence angle of the x-rays. See Figure S1 for a comparison between the C 1*s* spectra using full photon flux reduced by a factor 8. Inspection of Figure S1 shows that the full beam experiment had a slight increase in carbide coverage, as shown by the increased intensity around 283 eV, and a slightly decreased coverage of $CH_x$, as indicated by a lower intensity around 284.4 eV. Otherwise, the spectra are very similar indicating a low sensitivity of the reaction to beam induced effects.

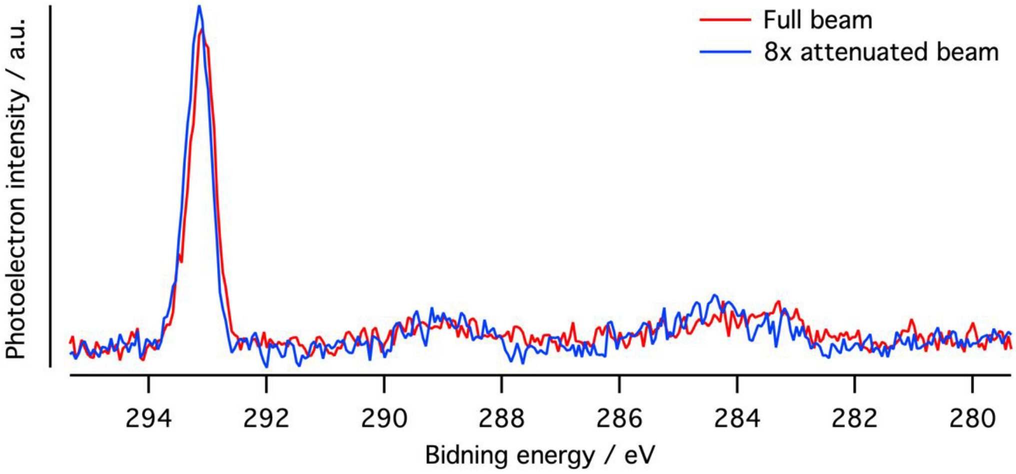

**Figure S1.** Comparison of XP spectra of the C 1s region at identical $CO_2$ hydrogenation reaction condistions with full and reduced photon flux.

## Dependency of Experimental Order

The experiemental order affects the spectra as demonstrated by the Figure S2 below. Both green spectra are acquired at 192°C, but the uppermost spectrum had experienced the lower temperature of 115 °C before acquisition. The sample was initially mainly metallic, and expressed a small amount of carbidic and hydrocarbon-related compounds in the C 1s. Upon cooling to 115 °C, spectrum features related to oxide and carbonate speices appear, whereas th rate between hydrocarbon and carbide changes. When the temperature was reverted to 192 °C newly formed oxide and carbonate features remain (and seemingly grow larger), whereas the hydrocarbon and carbidic part of the spectra changed back to a similar shape as in the initial 192 °C spectrum. This example illsutrates how the experimental order matters for the spectra and serves to motivate the acquisition order of the $CO_2$ hydrogenation spectra in the main text.

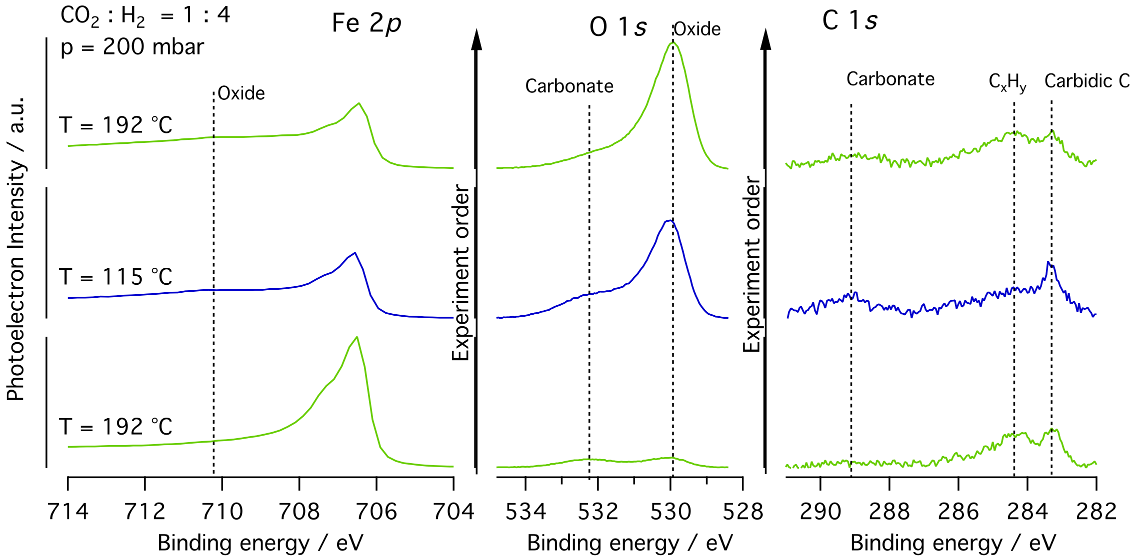

**Figure S2.** X-ray photoelectron (XP) spectra of the Fe $2p_{3/2}$, O 1*s* and C 1*s* region. All spectra are normalized to the lower binding energy side of the spectrum, and acquired at a 200 mbar pressure of 1:4 $CO_2$ and $H_2$.

Similarly in Figure S3 we can see the influence of experiment order for the CO hydrogenation reaction where the carbide formed 363 °C remains in the spectra at 152 °C even though it was not quite present in the initial 152°C spectrum.

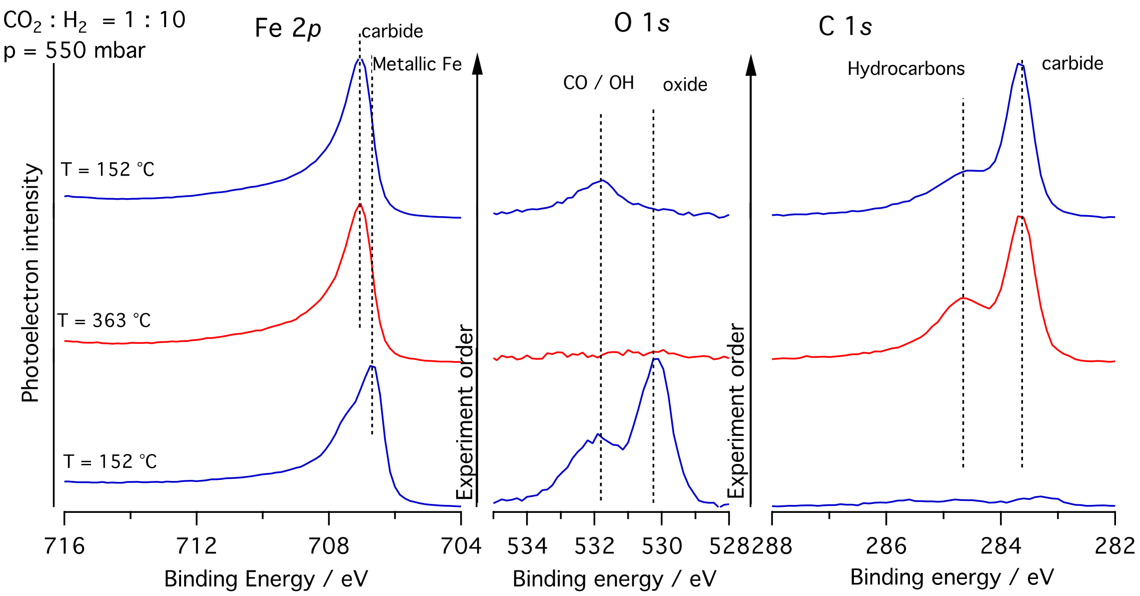

**Figure S3.** X-ray photoelectron (XP) spectra of the Fe $2p_{3/2}$, O 1*s* and C 1*s* region. All spectra are normalized to the area of the Fe $2p_{3/2}$ region, and acquired at a 500 mbar pressure of 1:10 $CO_2$ and $H_2$.

## Additional Spectra: Fitted $CO_2$ Hydrogenation Spectra

Spectra for the measurement at 500 mbar, presented in Figure 1 of the main text are complemented with fits in Figure S4. At the higher pressure a lower sensitivity towards temperature-related changes are observed, as hydrocarbons and CO-related features are observed, but the ratio between CO and hydrocarbons change slightly with temperature.

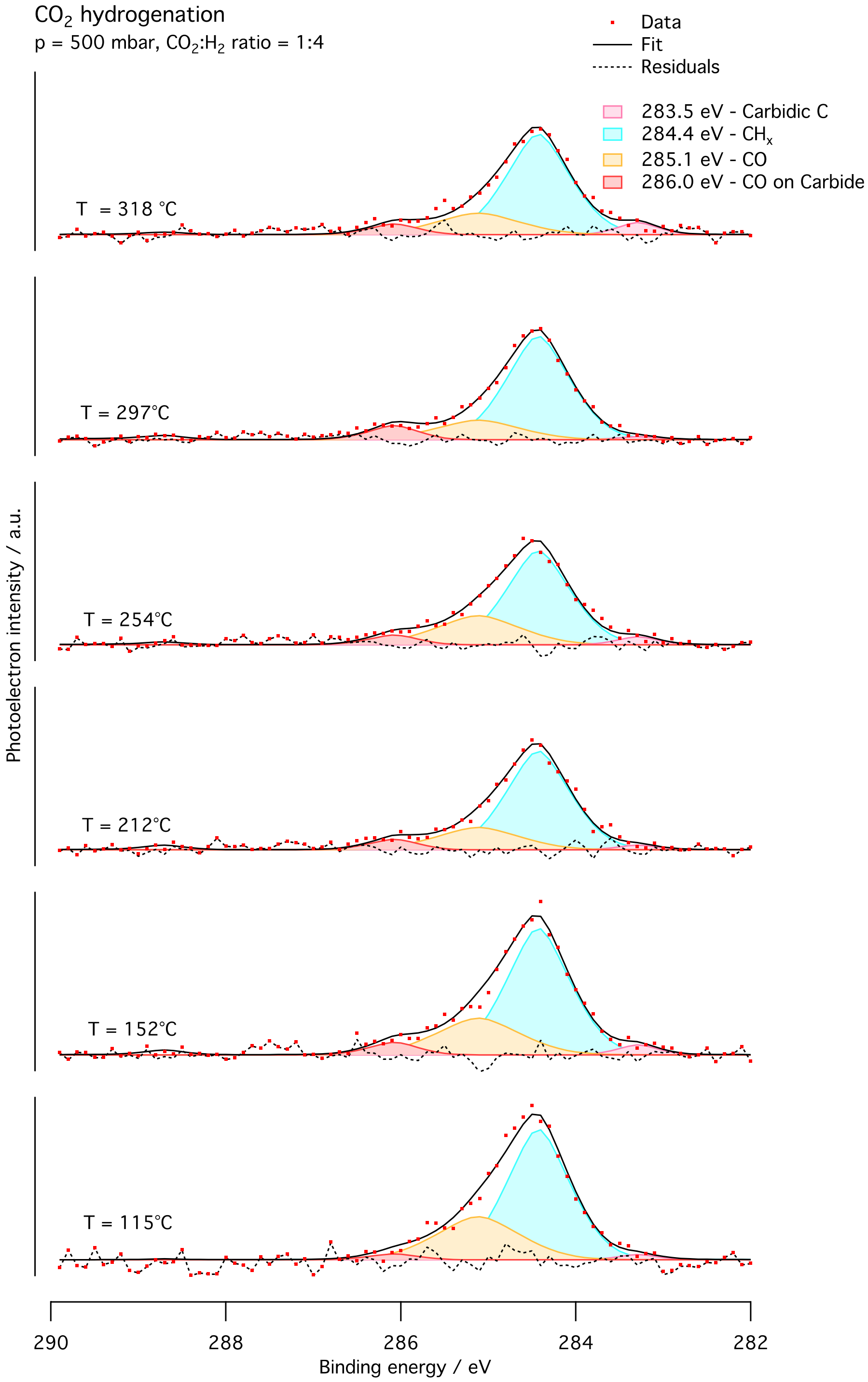

Figure S4. Fits of the C 1*s* spectra, using the same components as in Figure 6 of the man text, applied to the same data set as in Figure 1 of the main text. The gas flow ratio was 1:4 $CO_2$:$H_2$.

## Additional Spectra: Gas Phase Peaks Included

Gas phase peaks binding energies are referenced to the vacuum level, but the spectrum is referenced to the fermi level. This causes apparent binding energy shifts in the gas phase peaks whenever a process happens on the surface that alters the work function, such as oxidation, carbuization or build up of hydrocarbon coverage. The main text focuses on the adsorbate region of the C 1*s* and O 1*s* spectra, but a set of spectra are displayed in Figure S5 which also includes the O 1*s* gas phase peaks.

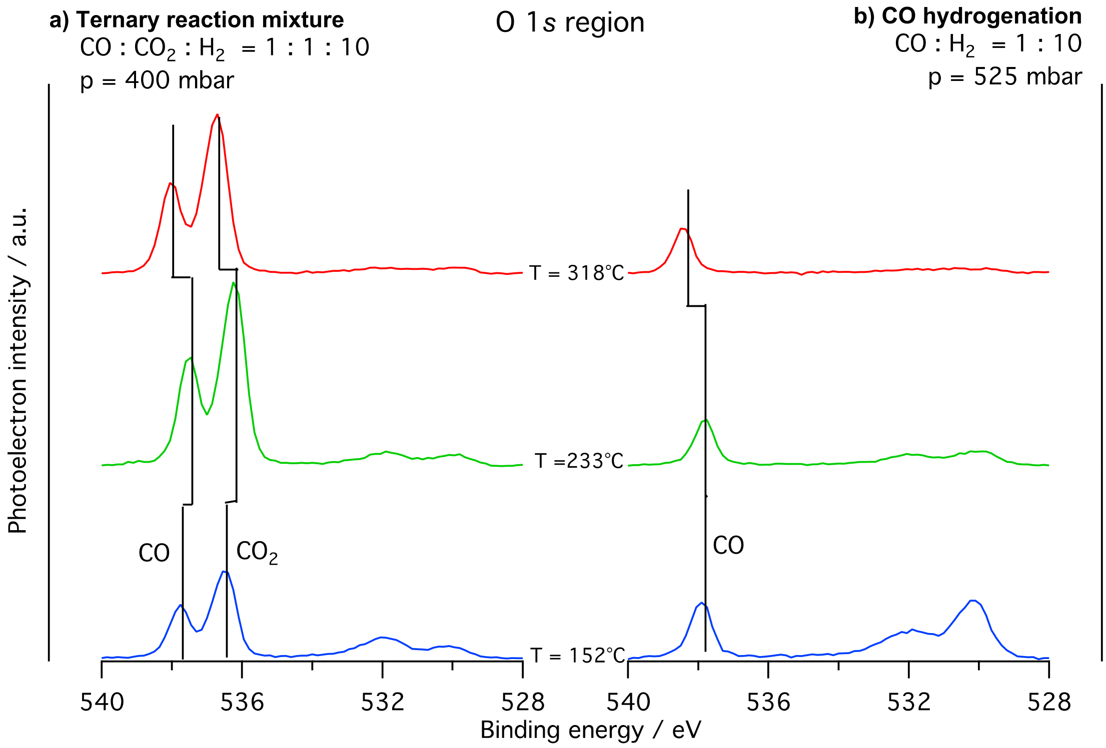

Figure S5. XP spectra of the O 1*s* region during $CO_x$ hydrogenation using a) a ternary reaction mixture of $CO:CO_2:H_2$ = 1:1:10 and b) a pure CO hydrogenation reaction mixture with $CO:H_2$ = 1:10. The data is from the same acquisition as in Figure 1 of the main text, but extended to include the gas phase peaks. The shifts of the gas phase peaks are indiacted with a solid line.

## Online Mass Spectrometry

The working principle of the instrumental set-up in this work is a virtual pressure cell which requires high flow rates (0.5-4 $L_N$/min) and a small reaction volume (< 0.03 $mm^3$). As a consequence, the exchange rate of the gas volume surpasses 1000 $s^{-1}$. Thus, the quantification of reaction products requires a higher conversion than what is achieved in these measurements. The online mass spectrometry (MS) data reported herein can thus be taken as an indicator that the catalyst is active at all, but should not be used for determination of turnover frequencies. A Hiden (HAL/3F RC 301 PIC system) mass spectrometer was sampling from the first differntial pumping stage of the electron analyzer pre-lens. A needle valve was adjusted to set the pressure in the MS volume to less than $4.5*10^{-6}$ mbar, limited by the secondary electron multiplier detection mode. Example data from two of the measurements following the m/z = 15 signal is shown in Figure S6. The m/z = 15 correspond to the methyl group ($CH_3$) which is a common fragment in the mass spcectra of all alkenes. The data is normalized to the CO signal at m/z=28 to enable comparison between the different total pressures and to reduce the influence of drifts due to sample motion, i.e. thermal expansion. The steeper slope of the pure CO hydrogenation reaction data (red color in Figure S6), and the generally higher intensity of the methyl signal indicate that the pure CO hydrogenation activity is generally higher. During the the very initial stage, a period of <30 minutes do the MS data indicate a higher activity in the ternary reaction mixture.

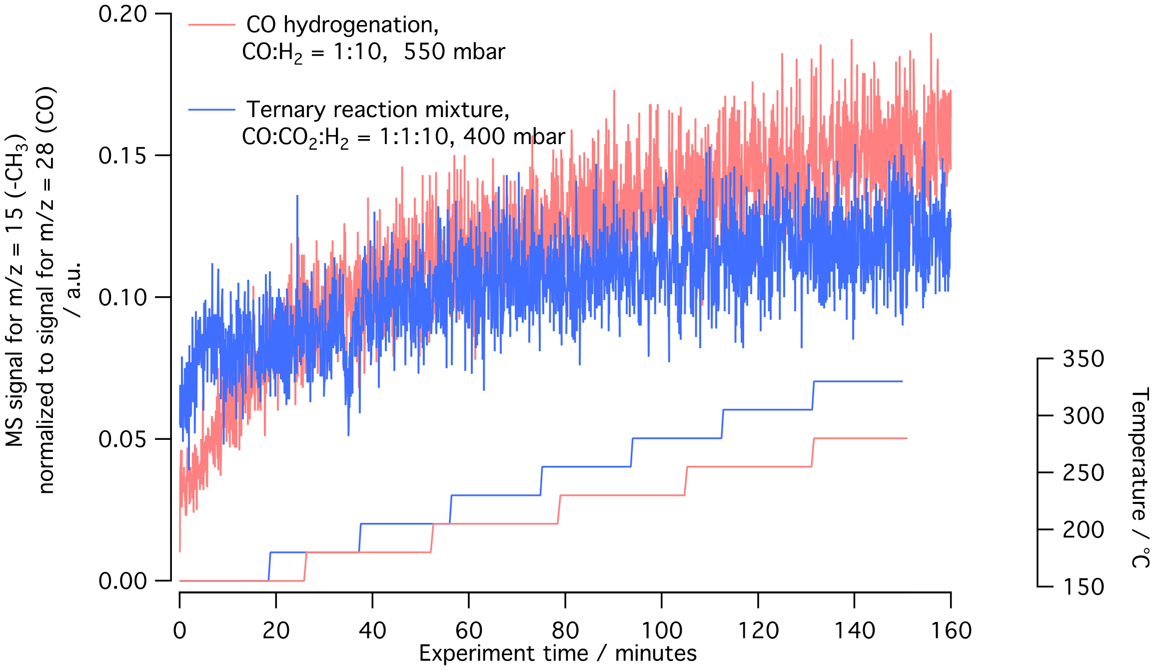

Figure S6. Online mass spectrometry data acquired during the hydtogenation reactions. The data in blue was acquired while the photemission spectra in Figure 1b of the main text was acquiring, while the data in red correspond to Figure 1c) in the main text.