

# Dynamic characterization of Co/TiO<sub>2</sub> Fischer-Tropsch catalysts with infrared spectroscopy and DFT calculations

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## Introduction

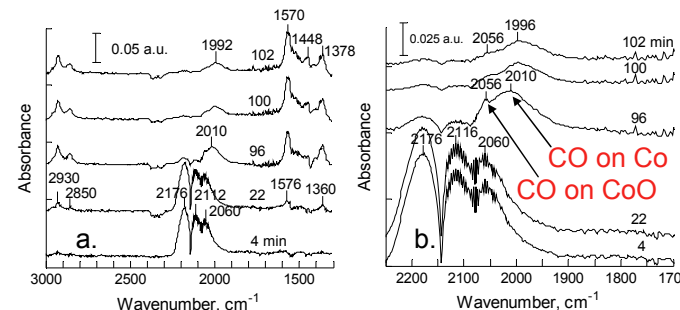
Although Fischer-Tropsch (F-T) technology has been known for more than 80 years, the information on the fundamentals of this catalytic chemistry is limited, hindering improvements in catalyst and process development [1-3]. In the current study, multiple catalyst characterization techniques, in-situ IR spectroscopic measurements and DFT calculations with vibrational analyses were synergistically combined in order to develop molecular surface models for cobalt-based catalysts and to establish a methodology for describing the dynamics of catalyst surface changes under reaction conditions.

## Materials and Methods

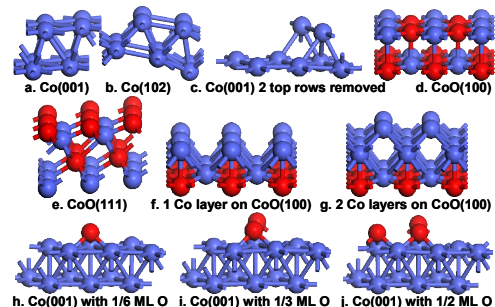
Two Co/TiO<sub>2</sub> catalysts were prepared by (1) incipient wetness and (2) deposition precipitation [3]. These samples were calcined and then reduced at either 300 or 350°C for 2 h, generating a total of 4 samples differentiated by two preparation methods and two reduction temperatures. IR spectra in DRIFT mode were collected (1) *at the reaction conditions* with syngas (CO + H<sub>2</sub>) at 220°C as a function of time on stream, (2) for CO adsorption as a function of He purging time and also (3) for formic acid HCOOH adsorption at 100-400°C. Gradient-corrected periodic DFT calculations were performed with the DMol3 code in Materials Studio by Accelrys using the double numerical with polarization (DNP) basis set and the generalized gradient-corrected revised Perdew-Burke-Ernzerhof (GGA RPBE) functional.

## Results and Discussion

The in-situ IR spectra in Figure 1 exhibit two distinct atop CO peaks: at 2010 and 2056 cm<sup>-1</sup>. Cobalt surfaces in Figure 2 were used in DFT calculations in order to explain the origin of these two atop-bonded CO species and to analyze other features of the IR spectra. First, CO adsorption on a flat Co(001) surface (Figure 2a) was compared to that on step sites of Co(102) and Co(001) with 2 top atom rows removed (Figures 2b-c). DFT calculations suggest that atop-bonded CO on the flat and step sites should be spectroscopically indistinguishable and, thus, the two CO peaks in Figure 1 cannot be explained by the morphology of Co nanoparticles. Surface models with layers of metallic Co on top of CoO in Figures 2f-g were evaluated as representations of materials with a metallic surface shell over an oxide core. The results indicate that even a single layer of metallic Co on top of an oxide would adsorb CO similarly to purely metallic Co. In contrast, the CO frequency on CoO(100) in Figure 2d is



**Figure 1.** IR spectra of 9.5 wt % Co/TiO<sub>2</sub> catalyst (pre-reduced at 350°C) under reaction conditions as a function of time on stream. Feed GHSV 3010 h<sup>-1</sup>, CO/H<sub>2</sub> mol feed ratio of 0.5, 1 atm, 220°C. (a) Full spectrum and (b) enlarged CO adsorption region.



**Figure 2.** Models of metallic and oxide Co surfaces used in DFT calculations for interpretation of IR spectra.

calculated to be in line with the experimental peak at 2056 cm<sup>-1</sup>. The peaks at 2010 and 2056 cm<sup>-1</sup> can, therefore, be assigned to atop-bonded CO on, respectively, metallic Co and CoO oxide. The coexistence of metallic Co and Co(II) oxide was confirmed with H<sub>2</sub> TPR measurements. Furthermore, our EXAFS results suggest that the intensity of the CO peak at 2056 cm<sup>-1</sup> correlates with the concentration of the CoO phase. The IR bands in the 1370-1570 cm<sup>-1</sup> range are assigned to formate species Co-O-CH-O-Co on Co and CoO based on an agreement with formic acid adsorption spectra and vibrational modes from DFT calculations.

## Significance

Our results suggest that the catalytic surface changes dynamically between oxide CoO and metallic Co as an overlayer on the oxide CoO bulk with formates as the dominant hydrocarbon species. The dynamic surface changes dramatically influence the catalyst activity and selectivity. A new methodology has been developed for monitoring the extent of surface oxidation and for selection of appropriate surface models for understanding reaction mechanisms at the molecular level.

## References

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