

Dynamic characterization of surfaces of Co/TiO₂ Fischer-Tropsch catalysts with infrared spectroscopy and DFT calculations

Jie Gao¹, Emiel de Smit², George Fitzgerald³, Bert M. Weckhuysen², Simon G. Podkolzin¹

¹Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, Hoboken, NJ 07030 USA. Simon.Podkolzin@Stevens.edu

²Department of Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Sorbonnelaan 16, 3584CA Utrecht, The Netherlands.

³Accelrys Software, Inc, 10188 Telesis Court, San Diego, CA 92121 USA.

Although Fischer-Tropsch (F-T) technology has been known for more than 80 years, the information on the fundamentals of the catalytic chemistry is limited, hindering improvements in process development. With respect to the reaction mechanism, most publications generally consider the same limited number of reaction pathways but reach different, often mutually exclusive, conclusions. Specifically for cobalt-based catalysts, traditional reaction models assume static metallic Co as the only active catalytic sites. Our studies, however, suggest that it is important to take into account changes not only in the concentrations of active and spectator surface species, but also in the composition and structure of the catalyst bulk, subsurface and surface. By tightly integrating reaction measurements, catalyst characterization, spectroscopic studies and DFT calculations with vibrational analyses, we are developing new methodologies for detection and description of dynamic changes in the composition and structure of catalytic surfaces under reaction conditions.

As an initial step in the methodology development, adsorption of carbon monoxide on several samples of Co/TiO₂ under static conditions was analyzed and compared to that under reaction conditions with hydrogen (not shown). Contrary to traditional F-T reaction models,

our results show that the surface changes dynamically between oxide CoO and metallic Co as a layer over an oxide CoO bulk.

Two Co/TiO₂ catalysts were prepared by (1) incipient wetness impregnation (IWI) and (2) homogeneous deposition precipitation (HDP). These samples were calcined and then reduced at either 300 or 350°C, generating a total of 4 samples differentiated by two preparation methods and two reduction temperatures. TPR results indicate that not all of Co is fully reduced at our chosen temperatures of 300 and 350°C and during F-T reaction testing

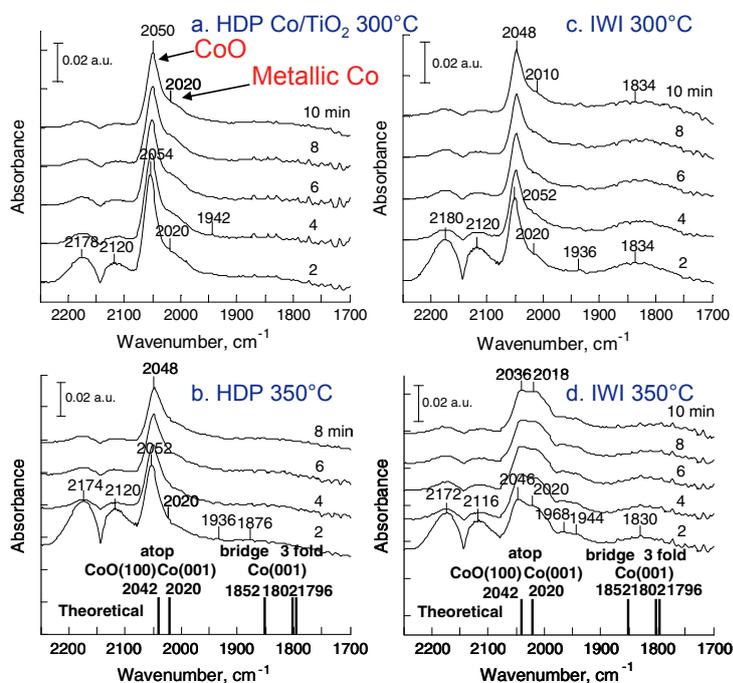


Figure 1. IR spectra of CO adsorption at room temperature on Co/TiO₂ prepared by homogeneous deposition precipitation (HDP) and by incipient wetness impregnation (IWI) and reduced at either 300 or 350°C. Time evolution with He purge is shown. DFT calculated frequencies, shown as bars, suggest that 2 atop-bonded CO peaks can be assigned to CoO and metallic Co.

at 220°C and that some Co is present in the form of oxide CoO. The ratios of Co present as a metal and as CoO were

estimated with XANES measurements.

IR spectra for CO adsorption at room temperature on the four Co/TiO₂ samples were collected as a function of He purging time (Figure 1) and also with syngas at 220°C as a function of time on stream. In the CO adsorption spectra in Figure 1, the broad band between 1800 and 1900 cm⁻¹ corresponds to bridge-bonded and three-fold adsorbed CO. The band for atop-bonded (linear) CO is located at about 2010-2060 cm⁻¹. Interestingly, there are two distinct atop CO peaks, one centered at 2020 and the other one at 2050 cm⁻¹. Our IR spectra for syngas under reaction conditions contain the same 2 atop-bonded CO peaks.

Cobalt surfaces in Figure 2 were used in DFT calculations in order to explain the origin of the two atop-bonded CO species and to analyze other features of our IR spectra. First, CO adsorption on a flat Co(001) (Figure 2a) surface was compared to that on step sites of Co(102) (Figure 2b) and Co(001) with 2 top atom rows removed (Figure 2c). The calculations suggest that the frequency for CO on step sites is only higher by several wavenumbers. In addition, higher adsorption energies for CO on step sites compared to that on the flat Co(001) are inconsistent with a more rapid decrease of the peak at 2050 cm⁻¹ on He

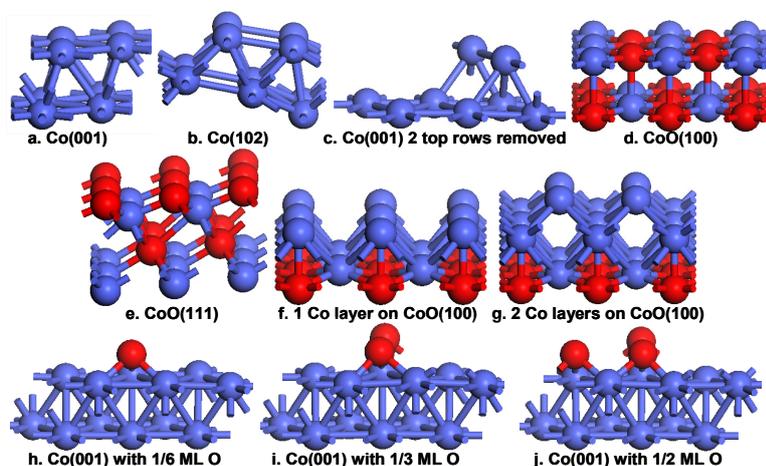


Figure 2. Models of metallic and Co oxide surfaces used in DFT calculations for interpretation of IR spectra for CO adsorption on Co/TiO₂ in Figure 1. Only 2 top layers are shown for each model for clarity.

purging. Surface models with 1 and then with 2 layers of metallic Co on top of CoO shown in Figure 2f-g were evaluated as representations of materials with a metallic surface shell over an oxide core. The results for these metallic shell structures indicate that even a single layer of metallic Co on a top of an oxide structure would adsorb CO similarly to purely metallic Co. In addition, a shell metal model by itself would not be able to explain the experimentally observed

decrease in the concentration of bridge-bonded CO associated with the dominance of the atop-bonded peak at 2050 cm⁻¹.

This decrease in bridged-bonded CO coverage could be explained if the atop-bonded CO at 2050 cm⁻¹ were associated with Co atoms surrounded by oxygen atoms on the surface. Accordingly, cobalt oxide surfaces – CoO(100) and CoO(111) in Figure 2d-e – and metallic Co surfaces with different concentrations of oxygen atoms on the surface in Figure 2h-j were evaluated. The CO frequency on CoO(100) is calculated to be at 2042 cm⁻¹ in line with the experimental peak at 2050 cm⁻¹. In addition, the calculated adsorption energy for CO on CoO is lower than that on metallic Co by about 10 kJ/mol and, therefore, the former can be expected to desorb preferentially on He purge, again in line with the experimental observations. Furthermore, our XANES results and the IR spectra in Figure 1 suggest that the intensity of the CO peak at 2050 cm⁻¹ correlates with the concentration of a CoO phase. We, therefore, conclude that, as indicated in Figure 1, the peaks at 2020 and 2050 cm⁻¹ in our spectra can be assigned to atop-bonded CO on, respectively, metallic Co and CoO.

Our results for the cobalt metal-oxide surface transition in F-T synthesis illustrate importance and general methodology for detection, analysis and description of dynamic changes in the composition and structure of catalytic surfaces under reaction conditions on molecular level.