



Spectroscopic insights into cobalt-catalyzed Fischer-Tropsch synthesis: A review of the carbon monoxide interaction with single crystalline surfaces of cobalt



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ABSTRACT

The present article summarizes experimental findings of the interaction of CO with single crystal surfaces of cobalt. We first provide a quantitative study of non-dissociative CO adsorption on Co(0001) and establish a quantitative correlation between θ_{CO} and adsorption site occupation. In light of these findings we revisit the structure of previously reported ordered CO/Co(0001) adsorbate layers. Measurements of the CO coverage at equilibrium conditions are used to derive a phase diagram for CO on Co(0001). For low temperature Fischer-Tropsch synthesis conditions the CO coverage is predicted to be ≈ 0.5 ML, a value that hardly changes with p_{CO} . The CO desorption temperature found in temperature programmed desorption is practically structure-independent, despite structure-dependent heats of adsorption reported in the literature. This mismatch is attributed to a structure-dependent pre-exponential factor for desorption. IR spectra reported throughout this study provide a reference point for IR studies on cobalt catalysts. Results for CO adsorbed on flat and defect-rich Co surfaces as well as particular, CO adsorbed on top sites, and in addition affect the distribution of CO_{ad} over the various possible adsorption sites.

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1. Introduction

Detailed knowledge about the interaction of CO with the surface of metals used as heterogeneous catalysts is of great importance for catalysis. Carbon monoxide is a reactant in a number of industrially important reactions, such as Fischer-Tropsch synthesis (FTS) and methanol synthesis. In addition to being a reactant for FTS, the mere presence of a large quantity of CO_{ad} on the catalytically active surface affects the reactions of C_xH_y adsorbates and thereby strongly affect the chemistry that leads to the growth of long hydrocarbon chains [1–3]. In other catalytic reactions CO is added to modify catalyst performance, e.g. in the selective hydrogenation of alkynes on Pd-based catalysts addition of small quantities of CO to the reactant gas improves the reaction selectivity [4]. The interaction of CO with metal surfaces has been studied in depth on a variety of metal surfaces, including those metals that show a high activity in the hydrogenation of CO, such as Ru, Ni, Fe and Co [5–9]. CO is also frequently used as a probe molecule in characterization of heterogeneous catalysts, for example in a

quantitative manner to determine the metal surface area, or in a more qualitative manner in (in-situ) infrared absorption spectroscopy studies to indirectly derive information about the catalyst surface [10–14].

Cobalt nanoparticles supported on an oxidic support are employed as catalysts in the low temperature Fischer-Tropsch synthesis (LT-FTS) [15]. For bulk cobalt, such as a single crystal, the hcp structure is favoured thermodynamically, but for Co crystallites < 20 nm, i.e. in the relevant size regime for Co FTS catalysts [16], the fcc structure is thermodynamically most favorable [17]. For fcc-Co nanoparticles, the majority of surface atoms form part of a close-packed (111) facet, which account for approximately 65% of all surface atoms [18,19]. Hence, in infrared studies of supported cobalt catalysts the close-packed facets are expected to contribute most to the measured signal.

The interaction of carbon monoxide with single crystal surfaces of cobalt, in particular the close-packed Co(0001) surface, has been studied previously. Early studies in the group of Lambert were performed at temperatures of 300 K and higher [9,20]. Papp performed extensive studies on several surface facets of hcp-cobalt, using a combination of LEED, UPS, EELS, AES and surface potential (work function) measurements to characterize CO adsorption at

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low surface temperatures and in an ultrahigh vacuum (UHV) environment [21–23]. Lahtinen et al. [8] performed a detailed study in which the interaction of CO with the Co(0001) surface was studied using a combination of temperature programmed desorption, work function measurements, X-ray photoemission spectroscopy (XPS) and low energy electron diffraction. Greuter et al. performed a detailed spectroscopic study regarding the structure and electronic properties of CO_{ad} on Co(0001) [24], whereas Ramsvik et al. focused in particular on the spectral shape of the C1s core level photoemission spectrum of CO adsorbed on the same surface [25]. IR absorption spectroscopy has been used by Toomes and King in combination with TPD and LEED in an in-depth study of CO_{ad} on Co(10 $\bar{1}$ 0) [26,27]. Beitel et al. [7,28] used phase-modulated reflection absorption infrared spectroscopy (PM-RAIRS) to study CO adsorption at room temperature, exploring the pressure regime from typical UHV-type pressures ($\sim 10^{-10}$ mbar) up to a pressure of 100 mbar. STM studies performed by Venvik et al. showed CO_{ad}-induced mobility of Co surface atoms on the Co(10 $\bar{1}$ 2) surface at room temperature already [29,30], and recently the group of Wintterlin applied this technique to reveal details of the CO dissociation reaction on the Co(0001) surface in the presence of a CO pressure in the mbar pressure range and at elevated temperature [31]. Lewis et al. also used STM, to study co-adsorption of CO and hydrogen on Cu-supported close-packed cobalt islands [32,33]. Faló et al. used a similar model system, 1–2 atomic layers of Co deposited onto a Cu(100) substrate [34], to study the interaction of CO with the fcc-(100) surface of cobalt. Liao et al. used single crystal adsorption calorimetry to study CO adsorption on the fcc-(110) cobalt surface [35]. The interaction of CO with polycrystalline cobalt surfaces was reported by Bardi et al. [36]. Finally, several authors looked into the co-adsorption of CO with hydrogen [32,33,37,38], carbon [39–41], oxygen [41,42], ammonia [43], magnesium [44] and potassium [27,45].

We aim to complement the previously published literature findings by a systematic study of the interaction of CO with the close-packed surface of cobalt, in particular looking at those aspects that are considered relevant for fundamental understanding of Fischer-Tropsch synthesis using cobalt-based catalysts. We employed a combination of five different experimental techniques to obtain detailed information on the interaction of carbon monoxide with the Co(0001) surface. We use high resolution X-ray photoemission spectroscopy (XPS) to obtain quantitative information on the occupation of the various adsorption sites. Work function (WF) measurements, temperature programmed desorption (TPD) spectroscopy as well as low energy electron diffraction (LEED) provide additional, quantitative information on the kinetics of CO adsorption and desorption and on the ordering of the CO_{ad} layer. Last but not least, reflection absorption Infrared Spectroscopy (RAIRS) was used to obtain qualitative information about the CO adsorption site.

The high resolution RAIRS spectra presented in this article provide useful reference material for IR studies on supported catalysts. In particular during in-situ studies [46], where infrared spectroscopy is one of the few experimental techniques compatible with the high reactant pressures used, the active surface will be covered by a mixture of reactants and products. With the currently limited quantity of reference data from well-defined Co surfaces, in particular regarding the question on how co-adsorbates such as H_{ad}, C_{ad}, O_{ad} and C_xH_y influence the CO vibrational frequency and the intensity, interpretation of such in-situ/operando data is challenging. With this application in mind, we discuss the pressure and temperature dependence of θ_{CO} , and furthermore explore co-adsorption of CO with adsorbates that are likely to be present during Fischer-Tropsch synthesis, in particular hydrogen and surface carbon, as well as hydrocarbonaceous surface intermediates. Taking into

account that metal nano-particles expose a significant number of under-coordinated sites we also explore the interaction of CO with a defective cobalt surface, generated by bombardment with 1 kV Ar⁺ ions at room temperature. In the co-adsorption studies infrared spectroscopy is the most important experimental technique, complemented in most cases by high resolution XPS for quantification purposes. The usefulness of this detailed, quantitative dataset is twofold: (i) it serves to understand infrared adsorption spectra measured under more realistic, but also less well-defined conditions; and (ii) the shift of the CO stretch vibration and relative quantities of adsorbates in co-adsorption systems provides a wealth of information for fundamental understanding of FTS on cobalt catalysts. Throughout the manuscript we also extract some of the information and put it into the context of other fundamental studies.

2. Experimental methods

In all studies the disk-shaped (diameter 10 mm) Co(0001) single crystal surface (Surface preparation laboratory, 4 N purity, cut and polished within 0.1 °C of the (0001) orientation) was cleaned by cycles of Ar⁺ ion bombardment (1–1.5 keV, 20 min.) followed by a 20 min. annealing in vacuum. The sample was held at 630 K during both steps. Sample cleanliness was checked either by XPS when available, or instead by TPD experiments, where both the shape of the H₂ desorption peak as well as the CO desorption spectrum can be used to check for common contaminants such as surface carbon [40] and surface oxygen [42], since the hydrogen desorption spectrum is particularly sensitive to the presence of surface defects [41,47]. Five different vacuum systems were used to obtain the data presented here. As measurement of the pressure in the UHV regime often has a large absolute error, in particular when comparing pressure readings in different vacuum systems, the pressure measurement in the instrument used to measure the work function data was taken as a reference, and pressure measurements in the other vacuum systems were corrected using a fixed multiplication factor for each system. Doses are reported in Langmuir (L), where 1 L equals 1×10^{-6} Torr s.

High-resolution photoemission measurements were performed at the SuperESCA beamline at ELETTRA (Trieste, Italy), I311 at Max-Lab (Lund, Sweden) and the MatLine beamline at ASTRID2 (Aarhus, Denmark). The C1s and O1s photoemission spectra were recorded in normal emission using a photon energy of 380 eV and 650 eV, respectively. The ($\sqrt{3} \times \sqrt{3}$) R30°-CO structure (1/3 ML, [48]), prepared by heating the CO saturated surface to 330 K, was used to quantify C1s and O1s signal intensities. Binding energies are reported with respect to the Fermi edge, which was measured after each change of the photon energy.

Reflection absorption infrared spectra (RAIRS) were obtained using a Fourier-transform infrared spectrometer equipped with a KRS-5 wire grid polarizer to selectively detect the p-polarized component of the light. A mercury cadmium telluride (MCT) detector was used with a spectral range of 4000–650 cm⁻¹. Outside of the vacuum system, the beam travels through an isolated compartment that is continuously flushed with dry N₂ to reduce the signals due to air. The RAIRS spectra shown here were obtained by averaging 256 scans and after subtraction of a stored background spectrum of the clean surface. For time-resolved measurements the number of scans was reduced down to 16 or 8 scans, to shorten the acquisition time. A resolution of 4 cm⁻¹ was used unless indicated otherwise.

Dynamic work function measurements were performed using a vacuum Kelvin probe (KP Technologies Ltd.), equipped with a stainless steel tip that is slightly smaller than the sample diameter (8 mm vs. 10 mm). The tip of the Kelvin probe remains at room

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