

# CO adsorption energy on planar Au/TiO<sub>2</sub> model catalysts under catalytically relevant conditions

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## Abstract

The adsorption of CO on planar Au/TiO<sub>2</sub> model catalysts was studied by polarization-modulation infrared reflection–absorption spectroscopy (PM-IRAS) under catalytically relevant pressure (10–50 mbar) and temperature (30–120 °C) conditions, both in pure CO and in CO/O<sub>2</sub> reaction gas mixtures. The adsorption energy of CO on the Au particles was determined by a quantitative analysis of the temperature dependence of the CO absorption intensity in adsorption isobars. The data reveal considerable effects of the Au particle size when pure CO is used; the initial adsorption energy decreases from 74 kJ mol<sup>-1</sup> (2 nm mean Au particle diameter) to 62 kJ mol<sup>-1</sup> (4 nm). For CO/O<sub>2</sub> gas mixtures, the initial CO adsorption energy is, irrespective of the Au particle size, constant at 63 kJ mol<sup>-1</sup> (i.e., the CO adsorption energy is reduced for smaller Au particles), but this effect vanishes for larger Au particles.

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## 1. Introduction

Finely dispersed Au particles of <5 nm diameter supported on metal oxides show surprisingly high activity in a number of catalytic reactions, the most prominent one being the low-temperature CO oxidation [1–3]. Despite intense research efforts in recent, some basic aspects of the underlying reaction mechanism remain unresolved. Most important for the mechanistic understanding of the CO oxidation reaction, the activation of molecular oxygen and, closely related, the nature of the active site remain unclear for these catalysts, and it is questionable whether a single reaction pathway is sufficient to describe the reaction under different reaction conditions [4] and on Au catalysts supported by different oxides [5]. On the other hand, considering the weak interaction between bulk Au and CO [6–14], the adsorption of CO on these catalysts is highly important as well and, through the steady-state CO<sub>ad</sub> coverage, will affect the reaction rate.

IR spectroscopic studies on realistic Au/TiO<sub>2</sub> catalysts revealed that CO adsorbs under reaction conditions in a linear configuration on the Au nanoparticles [15,16]. From the position of the CO vibration, which is normally detected at around 2100 cm<sup>-1</sup>, it may be concluded that the Au nanoparticles are in a metallic state [17]. Similar results also were obtained on well-defined model catalysts [18,19], where, based on the preparation procedure, the presence of ionic Au species can be excluded. Recently, we demonstrated that for Au/TiO<sub>2</sub> model catalysts, interaction with CO at higher pressure (>20 mbar) leads to the emergence of a new IR signal at around 2060 cm<sup>-1</sup> [20]. We attributed this signal to the formation of negatively charged Au<sup>δ-</sup> particles generated through reduction of the substrate, by reaction of CO with surface oxygen. We observed a similar effect of CO on dispersed powder Au/TiO<sub>2</sub> catalysts at even lower CO pressure (1 mbar), leading in this case to the complete disappearance of the initial signal at 2100 cm<sup>-1</sup> [21].

The adsorption energy of CO on these catalysts has been the topic of a number of studies on both realistic catalysts [22] and planar model systems [18,19,23,24]. Based on a quantitative analysis of their IR results, Derrouiche et al. determined that the adsorption energy for CO on a Au/TiO<sub>2</sub> powder catalyst decreased with increasing CO coverage, from 74 to

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47 kJ mol<sup>-1</sup> [22]. Studies on planar Au/TiO<sub>2</sub> model catalysts revealed that the CO adsorption energy also depends on the Au particle size [18,19]. For smaller Au particles, an initial CO adsorption energy of 76 kJ mol<sup>-1</sup> was reported (adsorption energy in the limits of small CO<sub>ad</sub> coverages), in agreement with the results for powder catalysts. For samples with larger Au particle diameters, the initial CO adsorption energy decreased significantly [18], reaching values of around 50–60 kJ mol<sup>-1</sup>, which are typical for CO adsorption on smooth Au surfaces [6–14], indicating that CO adsorption on the Au particles of the model catalysts converges to a bulk-like character with increasing Au particle size. So far, however, IR spectroscopic studies of CO adsorption on model catalyst or single-crystal samples have been performed under ultra-high-vacuum (UHV) conditions at cryogenic temperatures only, leaving unanswered the pertinent question of whether the results from UHV studies can be extrapolated through the “pressure gap” and transferred to CO adsorption under reaction conditions at elevated pressures in the millibar regime and in the typical temperature range of room temperature to 100 °C.

Using different nominal Au coverages, we studied the influence of the Au particle size on the CO adsorption energy under the above reaction conditions. Possible effects caused by the presence of oxygen as second component in the CO oxidation reaction have not been investigated to date. For CO adsorption on various metal surfaces, it is well known that coadsorption of oxygen modifies the adsorption properties of CO considerably (for, e.g., CO/O coadsorption on Ru(0001) [25]), and similar effects also might occur on Au substrates. These questions are the topic of this paper, where we report results of an in situ IR spectroscopy study on the interaction of CO with a well-defined planar Au/TiO<sub>2</sub> model catalyst under temperature and pressure conditions relevant for catalytic reaction studies in both the presence and absence of O<sub>2</sub> in the gas phase. CO adsorption energies were derived from the IR intensities using a procedure described first by Bianchi and coworkers [26], which we describe in more detail below. Preliminary IR results obtained at room temperature were presented previously [27].

## 2. Experimental

The experiments were performed in a UHV system with facilities for surface preparation and characterization with an attached high-pressure cell. The design and function of the high-pressure cell has been described in detail previously [28]. Fully oxidized, smooth titania films were prepared by deposition of Ti onto a Ru(0001) substrate in an O<sub>2</sub> atmosphere and subsequent annealing steps in O<sub>2</sub> (more information in Ref. [19]). These TiO<sub>2</sub> films had a thickness of around 10 monolayer equivalents (MLEs), with 1 MLE defined as the amount needed to cover the Ru(0001) single crystal with a closed TiO<sub>x</sub> layer [29]. Subsequently, Au was deposited at room temperature on the titania films (deposition rate: 0.04 monolayers (ML) min<sup>-1</sup>). The Au coverage is given with respect to the atom density of the underlying Ru(0001) substrate of  $1.6 \times 10^{15}$  Au atoms cm<sup>-2</sup> as 1 ML.

For the high-pressure IR measurements, the samples were transferred from the UHV section to the high-pressure cell. Before the IR measurements, the samples were first treated in 50 mbar of a CO/O<sub>2</sub> gas mixture (2:1) for 30 min at 130 °C to ensure that the Au particles of the model catalyst remained stable throughout the experiment. The IR measurements were performed with a Bruker Tensor 27 spectrometer, using polarization-modulation (PM) techniques to remove the gas-phase CO contribution, which affects the IR measurements at higher pressure. The IR spectra displayed here were acquired by co-addition of 1024 scans with a spectral resolution of 4 cm<sup>-1</sup>.

## 3. Results and discussion

To study the influence of the Au particle size, we used samples with different nominal Au coverages for the IR measurements. Previous STM measurements with identically prepared samples had demonstrated that the deposited Au particles have a rather flat morphology [19,30]. The height of the particles increased from around two to six atomic layers in the Au coverage range covered by this study, from 0.15 to 1.6 ML. At the same time, the mean lateral diameter of the Au particles increased from 2 to 4 nm. A sequence of IR spectra collected in a CO atmosphere of 10 mbar on a sample with 0.21 ML Au at increasing temperatures from 30 to 120 °C is displayed in Fig. 1a. The characteristic feature at 30 °C is an IR band at 2108 cm<sup>-1</sup>, which, following previous assignments [31], is attributed to linearly adsorbed CO on the Au particles. The intensity of the IR peak decreased steadily with increasing temperature, pointing to a reduction of the CO coverage on the Au particles due to increasing desorption. Concurrently, the peak position shifted to slightly higher wave numbers, arriving at 2112 cm<sup>-1</sup> at 120 °C. After that, the temperature was stepped back to 30 °C to check for possible changes in the frequency or intensity of the peak during the isobaric measurement (Fig. 1a, lowest spectrum), which would indicate irreversible changes of the catalyst such as particle sintering or the pickup of surface contaminations during the IR experiment. Based on the identical appearance of the spectra, such changes can be excluded. In addition to this characteristic CO feature, no other absorption bands were detected [15,22,32].

Fig. 1b displays the development of the CO<sub>ad</sub> coverage with increasing temperature. It was derived from the integrated CO<sub>ad</sub> signal intensity, assuming that in the absence of different adsorption sites and for small interactions between adsorbed CO molecules, the cross-section is independent of the CO<sub>ad</sub> coverage, and thus IR intensity and CO<sub>ad</sub> coverage are linearly related. The saturation coverage was determined from higher pressure (50–100 mbar) IR measurements in a CO/O<sub>2</sub> (2:1) gas mixture. This calibration measurement had to be performed in a CO-rich CO/O<sub>2</sub> mixture rather than in pure CO, because at elevated CO pressures ( $\geq 20$  mbar), the interaction of pure CO with the catalyst leads to a modification of the model catalyst surface due to a partial reduction of the TiO<sub>2</sub> support and concomitant changes of the Au particle shape [20].

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