

1. Introduction

HISTORICAL APPROACH – Although there are a few examples of interest in surface phenomena as early as the 18th century B.C.¹, surfaces have had a bad reputation for a long time: they are – inherently – superficial, even diabolical²; they were considered deceptive and, therefore, morally suspicious. The greek philosopher Democritos of Abdera believed that the essence of a thing is hidden in its interior, while the (misleading) sensible qualities are caused by the surface.³ It was not before the middle of the 19th century that a cautious acknowledgement of surfaces began: in art, literature, and the sciences⁴ [Sc02a]. The intellectual prerequisite was to ascribe *positive* qualities to surfaces – in the widest sense. After this idea had been established, the progress of surface science, led by pioneers as J.W. Gibbs⁵ (surface thermodynamics) and I. Langmuir⁶ (adsorption and thin films), was rapid. From the beginning, practical questions influenced the development of surface science, especially due to its relevance to heterogeneous catalysis, which at that time had already attained immense technological importance for the production of chemicals.⁷ The need for a physico-chemical understanding of these catalytic processes prompted studies of the interactions between gases and solid surfaces. These studies required surface sensitive tools on the one hand and clean, well-defined surfaces on the other. Surface sensitive probing techniques were found in low-energy electrons,⁸ and to maintain clean surfaces over extended periods of time ultra-high vacuum (UHV) recipients were developed.

¹ Zangwill [Za88] mentions the spreading of oil on water, which was used in the time of Hammurabi (1795-1750 B.C.) to foretell the future. Much later, a similar phenomenon, the calming of water waves by an oil film, was studied by B. Franklin. Zangwill and other authors also place the early experiments with catalysts by Döbereiner, Faraday, and Berzelius into the ancestral line of surface science. However, all these examples have in common that the specific role of the surface had not been acknowledged. Sabatier was the first who proposed, in 1913, that heterogeneously catalysed reactions occur on the surface of the catalyst. In the following years, Langmuir could obtain experimental evidence for this idea. It took another ten years until this idea was generally accepted especially because three Nobel prize winners, Van't Hoff, Ostwald, and Arrhenius (had) propagated completely different approaches.

² As Wolfgang Pauli (1900-1958), a traditionalist, expressed it: "God made solids, but surfaces were the work of the Devil." This (very popular) quotation exists in a great variety of versions.

³ "In Wirklichkeit wissen wir nichts, denn in der Tiefe liegt die Wahrheit." After: H. Diels, W. Kranz, Fragmente der Vorsokratiker, Dublin-Zürich 1971, 68 B 117.

⁴ For a modern, interdisciplinary approach to surfaces see also: Plurale. Zeitschrift für Denkversionen. Heft 0: Oberflächen. Berlin 2001 (in German).

⁵ Josiah Willard Gibbs (1839-1903) studied several years in Paris, Berlin, and Heidelberg, was influenced by Kirchhoff and Helmholtz and "returned [to the United States] more a European than an American scientist in spirit – one of the reasons why general recognition in his native country came so slowly" (Encyclopaedia Britannica). Major work: *On the equilibrium of heterogeneous substances*, published 1876.

⁶ Irving Langmuir (1881-1957), a disciple of W. Nernst, had a very broad scientific interest ranging from electrical discharges in gases and electron emission over heterogeneous catalysis and molecular films on liquids and solids to the possibility of inducing rainfall by seeding clouds with silver iodide and solidified carbon dioxide. Nobel prize for chemistry in 1932.

⁷ Contact process for the production of sulphuric acid: invented 1879 (Cl. Winkler). Ostwald process (nitric acid): developed 1901-13. Haber-Bosch process (ammonia): developed 1903-1913.

⁸ See [Er85].

In this work, which is related to recent developments on the field of heterogeneous carbon monoxide oxidation catalysis, we employ these and further techniques in order to investigate the interaction of oxygen, carbon monoxide, and carbon dioxide, with a gold single-crystal surface.

CHEMICAL/CATALYTICAL APPROACH – As a noble metal with soft⁹ ions, gold has a low affinity towards oxygen. While the two group homologues, silver and copper, possess an extended oxide chemistry, only a small number of metastable gold-oxygen compounds exists. Despite this relative inertness, gold has remarkable chemical properties. Particularly surprising is the catalytic activity of gold clusters supported on various metal oxides. It has been known for more than 70 years that highly dispersed gold may catalyse oxidation reactions [Th20], but it was not until the 1980s that this observation was investigated further by Haruta and coworkers. In the past 15 years it has been shown that small gold particles supported on metal oxides can be highly active, low-temperature CO oxidation catalysts [Bo00, Bo99]. The numerous investigations, combined with the onset of practical applications of these catalysts has also revived the interest in the oxygen-gold interaction on Au single-crystal surfaces (see Saliba et al. [Sa98] and references therein). The crucial step of catalytic oxidation is the activation of the oxygen molecule, which is frequently achieved by a cleavage of the O-O bond resulting in the formation of chemisorbed oxygen atoms. However, this reaction step has not been observed on *extended* gold samples so far, suggesting a substantial activation barrier for the dissociative oxygen chemisorption on gold. In contrast, gold-based CO oxidation catalysts are active even below room temperature. This apparent difference in reactivity between supported gold clusters and gold single crystals limits the value of UHV model studies (as the present one) for the understanding of the catalytic process. Still, the second reaction step of a catalytic oxidation, the transfer of the oxygen atom to the reductand, can be studied if we succeed to induce oxygen chemisorption on Au surfaces.

We have proceeded to tackle the problem of CO oxidation on gold in the following manner: First, we studied the adsorption and condensation of dioxygen on Au(110)-(1×2) at a very low temperature of 28 K and focused on the question of whether dioxygen forms chemisorbed species on the gold surface at very high O₂ surface concentrations, despite the low temperature. Second, we developed a convenient, safe, and reproducible technique to produce chemisorbed oxygen, namely, by activation of physisorbed dioxygen at low temperatures, using either low-energy electron bombardment or irradiation with ultraviolet light (Chapter 5). An extensive discussion of the properties of chemisorbed oxygen will be presented in Chapter 6. Third, we found that the

⁹ Within the framework of Pearson's HSAB principle [Pe63, Pe68, Pa83, Pe88, Pe93].

simultaneous occupation of surface and bulk sites with oxygen can be achieved by bombardment of the surface with oxygen ions at room temperature (Chapter 7).

Furthermore, we studied the adsorption of the other participants in the CO oxidation, CO (Chapter 8) and CO₂ (Chapter 10), on the gold surface. Especially the CO/Au interaction is an appealing topic for a model study on a gold single-crystal surface, even more than O₂/Au, because there is strong evidence that, in the case of a real catalyst, CO adsorbs on the gold clusters, whereas oxygen is believed to (initially) occupy sites on the junction of Au cluster and support [Bo00]. Because of the remarkable similarities between the adsorbate systems CO/Au and C₂H₄/Au, suggesting a common bonding mechanism, we also studied ethylene adsorption (Chapter 9). As an additional motivation, ethylene epoxidation, among the most important processes in chemical industry, is catalysed by unsupported Ag. It may prove that gold in a suitable state can also – or even more efficiently – catalyse this reaction.

These studies provide the information necessary for a quantitative understanding of the CO oxidation reaction. In the final chapter, devoted to the kinetics of this reaction, we describe in detail the temperature and coverage dependence of the reaction rate and evaluate the activation energy of the CO oxidation on gold (Chapter 11).

THE (CATALYTIC) CO OXIDATION – The heterogeneously catalysed CO oxidation frequently requires adsorption of both reactants on the surface of the catalyst, i.e., it follows a Langmuir-Hinshelwood mechanism. A schematic energy diagram of this mechanism is displayed in Fig. 1.1, showing three activated steps: the dissociation of dioxygen O₂, the reaction between the adsorbed species CO(ad) and O(ad), and the desorption of the product, CO₂. The slowest step limits the overall reaction rate. On a perfect catalyst, all steps are fast, i.e., the activation energies E₂, E₅, and E₆ are small. However, no metal shows good performance in both the O₂ dissociation and the reaction of chemisorbed atomic oxygen with CO. A noble metal will be slow in cleaving O₂, but it will readily deliver O to CO, i.e., E₂ >> E₅. On a reactive metal, we find the reverse reactivity. For example, ruthenium is – under UHV conditions – a poor catalyst due to the high O-metal binding energy (≈ 4.5 eV). On the other hand, silver is also inefficient despite the relatively small O-Ag binding energy (≈ 1.6 eV), due to the high activation energy for the O₂ dissociation.¹⁰ Typical catalysts for oxidation reactions form bonds of medium strength with oxygen, e.g., Pt (≈ 2.2 eV) and Rh, which are widely used for automotive pollution abatement.

If silver is a poor CO oxidation catalyst because of a slow O₂ dissociation, one may suspect that gold is even less active, which is indeed true for extended gold samples.

¹⁰ An additional cause for the low catalytic activity of silver is the small CO-Ag binding energy, which leads to low equilibrium CO coverages on Ag.

However, gold is, as already mentioned, a very effective CO oxidation catalyst if it is highly dispersed on an oxidic support. Though the relation between material state and reactivity is a stimulating field, the focus of our work is the interaction of all relevant CO oxidation reactants, intermediates, and products with a well-defined, pure gold single-crystal surface. The question arises whether our studies may have any application in practical catalysis. We are certainly *not* on the way to a complete understanding of the real gold catalysts, since their outstanding reactivity is probably caused by the higher complexity, e.g., the influences of particle size or support. However, comparison of real catalysts with our idealised system may allow us to distinguish between these influences and additional factors, which are related to the chemical nature of gold.

The objective of this work is to investigate the energetics and kinetics of all steps displayed in Fig. 1.1, i.e., to determine the binding energies of all adsorbed species and the activation energies of all reaction steps. This information is obtained by quantitative thermal desorption and other kinetic measurements, or by determination of thermodynamic quantities such as the equilibrium heat of adsorption. Additionally, we acquired information about the adsorbed species by probing the occupied and unoccupied electronic states in the valence level range by means of UV photoelectron and near-edge x-ray absorption spectroscopy (UPS and NEXAFS). Structural information was obtained by low-energy electron diffraction (LEED). Surface potential measurements provided further information about the polarization of the adsorbate layer and were also employed to monitor equilibrium coverages, for example in isosteric heat measurements.

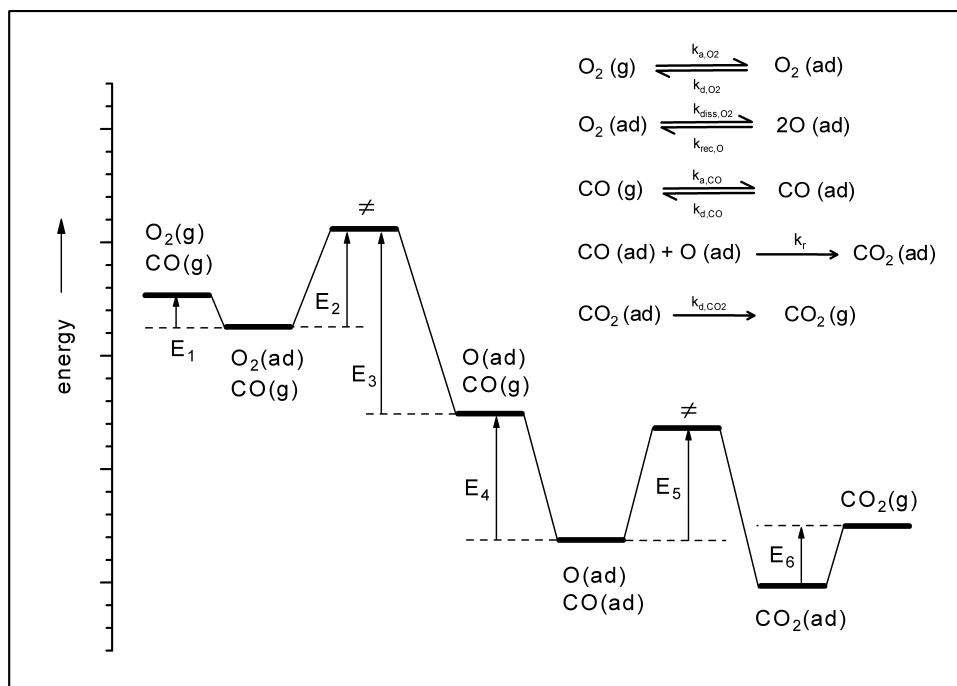


Fig. 1.1: Schematic energy diagram for a heterogeneously catalysed CO oxidation. Adsorption of both reactants is assumed (Langmuir-Hinshelwood reaction). This diagram is to be quantified.