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## Introduction

**OBJECTIVE AND STRUCTURE OF THIS THESIS** This thesis focuses on the elucidation of structural and electronic parameters of gold/oxygen species prepared with electrochemical methods and plasma oxidation. The main points of interest were

- to analyse the structure of electrochemically grown gold oxide films by using X-ray absorption spectroscopy (XAS),
- to design a recipient which is capable of transferring electrochemically prepared samples under inert gas atmosphere into UHV conditions,
- to elucidate the electronic and thermodynamic properties of the mentioned gold oxide samples by means of analysing data obtained from XPS and TPD experiments.

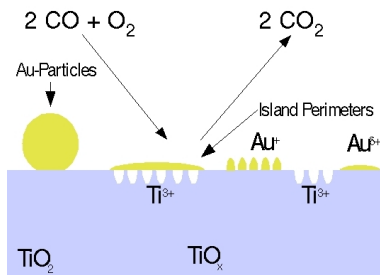
The main motivation of this thesis was to contribute more detailed information about the structure and composition of anodic oxide layers on gold. A second objective was to provide a link between the information known on gold/oxygen phases and the catalytic experiments done in our group on promoted gold catalysts. As these studies mainly rely on XAS, reference studies on well defined systems were needed.

The work comprises five chapters which are organised as follows. This first chapter gives an introduction to the gold/oxygen system. It also focuses on the role of gold in electrochemistry and catalysis. In the second chapter, the experimental methods are introduced. Details on the electrochemical sample preparation, X-ray absorption spectroscopy, photoelectron spectroscopy and thermal desorption spectroscopy are given. Chapter three focuses on the experimental results, chapter four on their discussion. The last chapter summarises the work and relates it to a wider context.

**GOLD AND CATALYSIS** Because of its noble character, metallic gold exhibits only low activity in catalytic processes such as CO oxidation. However, in 1987 Haruta *et al.* [29] found that gold particles supported on cer-

tain oxides show activity in the CO oxidation process even below room temperature. Since then, chemists and engineers have become more interested in these systems. Recent studies focused also on catalysts for  $\text{NO}_x$  conversion [88]. Gold shows good activity for the reduction of  $\text{NO}_x$  with hydrocarbons, which are present in fuel to ppm levels. The reason for this activity is still under investigation. It is well known that particle sizes in the nanometer range exhibit strong catalytic activity [32, 67, 85]. Figure 1.1 shows some discussed active sites in the catalysis of the CO oxidation by Au/ $\text{TiO}_x$  systems. The roles of particle size, oxidation state of support and metal, island perimeters and defect sites appear to be critical.

Figure 1.1: Active sites in an Au/ $\text{TiO}_x$  catalyst.



**NOTES ABOUT GOLD** The physical properties of gold are strongly influenced by the *relativistic effect*. It has to be taken into consideration for all elements with a high nuclear charge  $Z$ . It accounts for two important aspects. First, the 6s electrons are more tightly bound to the nucleus while the d and f electrons become less strongly bound. Comparing the influence of the relativistic effect on the 6s orbital radii, gold exhibits the strongest relativistic effect of all elements [5]. Comparing gold with silver, this effect explains why (i) gold is more resistant to oxidation than silver and (ii) why higher oxidation states are more stable in gold than in silver. The typical yellowish colour can also be attributed to the relativistic effect.

Gold is chemically inert. It is unaffected by moisture, oxygen, or ordinary acids but is attacked by halogens. Despite its chemical inertness gold chemistry has made remarkable advances over the last years. Gold is very ductile and is the most malleable metal, it can be rolled into extremely thin sheets of gold leaf. Only the other group Ib metals - silver and copper - are

better electric conductors. A relatively soft metal, gold is usually hardened by alloying with copper, silver, or other metals. White gold, a substitute for platinum, is an alloy of gold with platinum, palladium, nickel, or nickel and zinc. Green gold, also used by jewellers, is usually an alloy of gold with silver. Alloys of gold with copper are a reddish yellow and are used for coinage and jewelry. Gold is widely distributed on earth. Although large amounts are present also in seawater, the cost of current methods for recovering it exceeds its value. Most gold is found in the metallic state in the form of dust, grains, flakes, or nuggets. It occurs usually in association with silver or other metals, in quartz veins or lodes so finely disseminated that it is not visible. Gold is extracted from its ores by mechanical means and separated from other metals by chemical processes, notably the cyanide process, the amalgamation process, and the chlorination process. It also occurs in compounds, notably telluride minerals. Gold has been known from prehistoric times and was possibly the first metal used by humans. Table 1.1(a) summarises some important properties of gold.

Table 1.1: Some selected physical data on gold and oxygen

natural isotopes	$^{197}_{79}\text{Au}$ (100 %)	[31]		$^{16}_8\text{O}$ (99.76 %)	
atomic mass	196.966	[31]			
melting point	1337.6 K	[31]	isotopes	$^{17}_8\text{O}$ (0.04 %)	[31]
boiling point	2933 K	[31]		$^{18}_8\text{O}$ (0.20 %)	
atomic radius	1.442 Å	[31]	atomic mass	15.9994	[31]
covalent radius	1.34 Å	[31]	1. IP	13.618 eV	[31]
ionic radii	0.68 Å(+3, c.n.=4)	[31]	2. IP	35.114 eV	[31]
	1.37 Å(+1, c.n.=6)	[31]	electron affinity	1.465 eV	[31]
work function	5.1 eV ( $Au_{poly}$ )	[33]	covalent radius	0.66 Å	[31]
	5.37 eV ( $Au(110)$ )		atomic radius	0.604 Å	[31]
	5.31 eV ( $Au(111)$ )		ion radius $O^{2-}$	1.38 Å	[31]
EN (Allred & Rochow)	1.4	[31]	EN (Allred & Rochow)	3.5	[31]
			$O_2$ bond length	1.207 Å	[31]
			$O_2$ $E_{diss}$	498.67 kJ/mol	[31]

(a) Gold

(b) Oxygen

THE SYSTEM GOLD/OXYGEN Although oxygen is a very reactive substance, the affinity of gold towards this element is quite low. Adsorption studies of the system oxygen / gold (110)-(1x2) have been carried out, which show that molecular adsorption occurs below 50 K. Physisorbed oxygen can be converted to chemisorbed atomic oxygen by irradiating physisorbed oxy-

gen with electrons or UV light [20]. As these single crystal studies show, the affinity of gold towards oxygen is low. Therefore it is not surprising that gold exhibits a very limited oxide chemistry, which has been comparatively little investigated. The Au-O bond strength is considerably lower than the general trend in gold chalcogenides would suggest. The application of the HSAB (hard/soft acid/base) principle to gold oxide chemistry suggests a low bond strength between the soft gold ions and the hard oxygen ion. The only known and well defined binary gold/oxygen phase is gold(III) oxide -  $\text{Au}_2\text{O}_3$ . Different preparation methods have been explored, the most popular being hydrothermal synthesis and anodic oxidation of gold in aqueous solution. The most viable access to crystalline  $\text{Au}_2\text{O}_3$  is the dehydration of aqueous  $\text{Au}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  under hydrothermal conditions [35].

This method yields a highly crystalline material which has been analysed by X-ray diffraction.  $\text{Au}_2\text{O}_3$  exhibits a distorted square planar geometry of oxygen atoms around the gold atom [17, 35, 37]. These units are connected *via* common vertices and form a complex and very open crystal structure.  $\text{Au}_2\text{O}_3$  is isostructural with  $\text{Ag}_2\text{O}_3$  [80]. In the crystal, one of the four oxygen neighbours is nearer than the other three atoms. The electrochemical preparation often yields complex materials consisting of a highly hydrated form of  $\text{Au}_2\text{O}_3$ . An advantage compared to the hydrothermal route is the ease of application of this method. While hydrothermal synthesis requires conditions which can only be fulfilled by a few laboratories in the world, the electrochemical route is straightforward and gives gold(III) oxide with modest yields.

**ELECTROCHEMISTRY OF GOLD** Comparing the standard electrode potentials for the group 11 metals copper, silver and gold one remarks some anomalies which have to be discussed. In fig. 1.2, the *Latimer* diagrams are given for the three coinage metals. Despite its low reactivity, only gold shows a remarkable chemistry of the oxidation states -I and V. While for gold the most important oxidation state is +III, for silver it is +I and for copper +II. For copper, only the oxidation state +II is really stable. Most  $\text{Cu}^+$  compounds disproportionate while  $\text{Cu}^{3+}$  compounds are strong oxidants. However, peptide complexation can lower the oxidation potential of  $\text{Cu}^{3+}$  significantly making this oxidation state available to biological systems [34]. Silver compounds with positive oxidation states are all strong oxidants. Therefore, most of them are not stable and can only be observed *in situ* or under very special circumstances. Even the most common oxidation state +I still shows

a high oxidation potential.

For gold chemistry, most oxidation states are unstable. Even the only known oxide -  $\text{Au}_2\text{O}_3$  is still quite sensitive to thermal decomposition.  $\text{Au}^+$  and  $\text{Au}^{2+}$  compounds tend to disproportionate into  $\text{Au}^{3+}$  and  $\text{Au}^0$ . Recent studies have revealed the role of gold in electrocatalysis [8]. Electrocatalytic substances either increase the rate of a certain reaction at given overpotentials or reduce the overpotential for this reaction without being consumed. Two important models deal with the interpretation of electrocatalytic materials, the first being the IHOAM (incipient hydrous oxide/adatom mediator) model, the second being the concept of activated chemisorption.

Figure 1.2: Latimer Diagram for the coinage metals

