

# Models for oxidation catalyst: Characterization and reaction at the atomic level

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## Abstract

Three case studies to demonstrate the ability to characterize oxidation model catalysts and reactions of these systems at the atomic level are reviewed. Firstly, results on small Au aggregates on a clean MgO(1 0 0) surface which are interesting model systems for low temperature oxidation are considered. Secondly, oxidative dehydrogenation of methanol on alumina-supported Pd is addressed. The problem of oxygen storage in and on the Pd particles is studied for nanoparticles on Fe<sub>3</sub>O<sub>4</sub>(1 1 1). Finally, morphology–spectroscopy relations for oxide-supported so-called monolayer vanadia catalysts are investigated.

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## 1. Introduction

Creating model catalysts has come quite a way over the last decade [1–5]. Nanoparticles have been grown on well defined substrates, i.e. oxide surfaces on bulk single crystals or thin films [6]. Its nucleation has been studied in an attempt to prepare model systems with narrow size distribution of nanoparticles [7]. In fact, gas phase size selected clusters and nanoparticles have been deposited in order to create monodisperse model systems [8] but so far, experimental proof that these systems fulfill the promise is scarce [9]. In the present paper we will briefly discuss three different examples from our laboratory in order to document current progress with respect to oxidation model catalysts. The first one demonstrates how to engineer defects, such as color center, on a model MgO(1 0 0) surface [10] and use them as nucleation centers for Au aggregates in an attempt to calibrate circumstantial experimental evidence [9,11] for charge transfer from the substrate to the Au aggregate, thought to be important in low temperature CO oxidation [12]. The second example involves oxidative methanol dehydrogenation on Pd nanoparticles in the 4 nm size range in order to show the influence of defects, such as edges and corners, on the selectivity of the reaction [13,14].

The third example discusses structure–morphology-to-spectroscopy correlations on nanoparticles of vanadium oxide on different oxide substrates, in particular with respect to generally accepted assignments in vibrational spectroscopy [15–17].

## 2. Experimental

Experiments have been carried out in a number of ultrahigh vacuum systems located at the Fritz Haber Institute in Berlin. The experimental details have been reported in the literature and we refer to these papers for a detailed description [13,15,18].

## 3. Results and discussion

### 3.1. MgO(1 0 0) and Au/MgO(1 0 0): engineering defects

By depositing Mg in an oxygen ambient on Ag(1 0 0) and Mo(1 0 0) one may grow ordered MgO(1 0 0) films [19,20] as imaged in Fig. 1a. The surface exposes terraces and steps and in particular terraces which correspond to regions of the film of varying thickness [21]. This allows us to study the electronic structure of the support as a function of thickness by performing scanning tunneling spectroscopy (STS) experiments. Fig. 1b shows a scanning tunneling spectrum of a MgO film [22] of four monolayer thickness. At this coverage one observes a band gap very similar to the bulk material, while for thinner layers

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## 4ML MgO(001)/Ag(001)

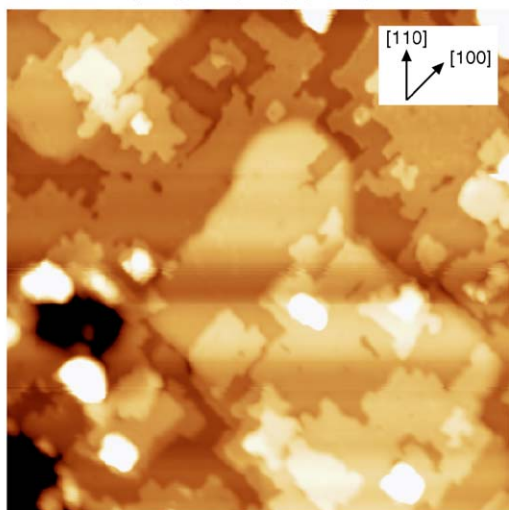
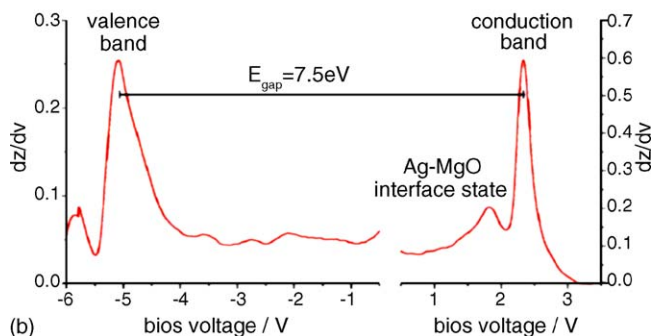
(a) 100x100nm<sup>2</sup>

Fig. 1. (a) Scanning tunneling microscopy (STM) of an MgO(1 0 0) film grown on Ag(1 0 0) and imaged at 4 K and (b) scanning tunneling spectroscopy (STS) taken on the MgO(1 0 0)/Ag(1 0 0) film at a spot with nominal thickness of four monolayers MgO.

variations indicating the influence of the metallic substrate are observed.

Obviously, the film, also, exposes a considerable number of defects, including step and edge sites but the number of terrace defects and in particular the number of oxygen vacancies (so called F centers), is very small. The absence of paramagnetic color centers has independently been proven via ESR spectroscopy on the same films [10]. Color centers, however, can be created by electron bombardment and then spectroscopically identified via STS [22] as shown in Fig. 2 or via ESR spectroscopy [10] as recently demonstrated. Correlation between experiment and theory indicates that we are dealing with two different types of color centers, in particular the neutral  $F_s^0$  centers characterized by states below and above the Fermi energy, and  $F_s^+$  centers characterized by an occupied state whose energy depends strongly on its location at the surface, i.e. its coordination [22].

Depositing metal atoms onto such surfaces allows us to differentiate metal aggregates located on non-defect sites and defect sites using the above information. Fig. 3 shows Au atoms and small Au clusters deposited onto a MgO surface [23]. The left panel represents Au atoms on flat MgO terraces, the middle panel images Au aggregate sitting at step sites and in the right panel one Au atom is localized at defects. It is possible to prepare surfaces with dominant coverage of each of the different Au adsorbates indicated in Fig. 3. This allows us to take IRAS spectra of carbon-monoxide adsorbed onto Au atoms and aggregates in different environments [24].

Fig. 4a shows IRAS spectra of CO/Au/MgO(1 0 0). The left panel summarizes data for Au aggregates on regular terrace sites giving rise to a CO stretching frequency near  $2121\text{ cm}^{-1}$  while for CO molecules residing on Au aggregates located on color centers a stretching frequency in the range of  $2010\text{--}2080\text{ cm}^{-1}$  is observed. The characteristic width in the latter case is due to the heterogeneity of Au aggregates adsorbate

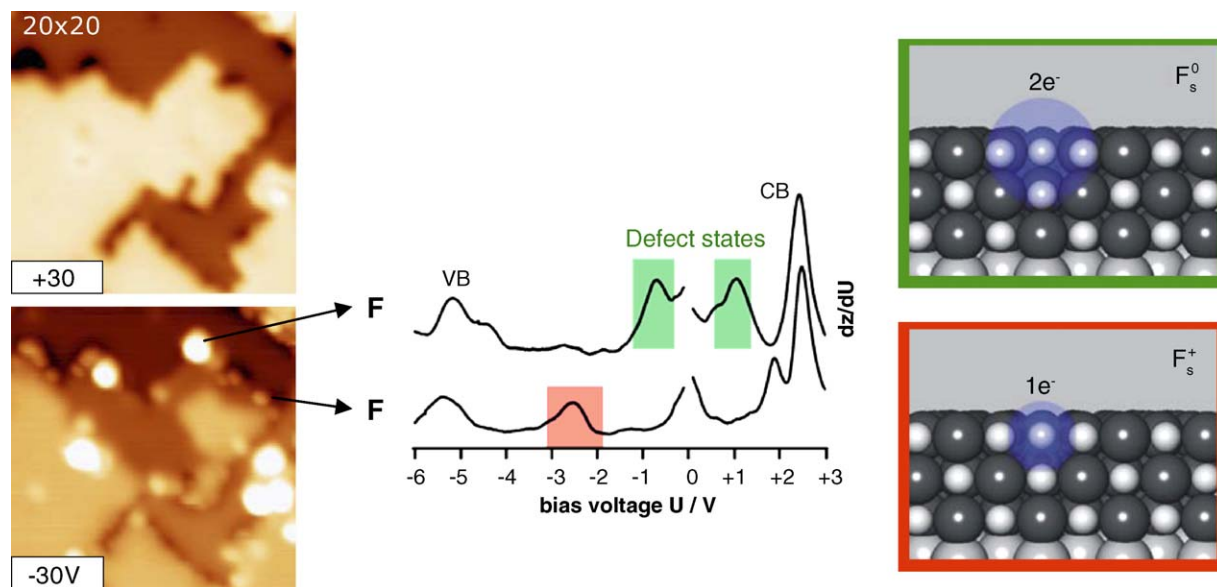


Fig. 2. STM images and STS spectra of color centers on MgO(1 0 0) after irradiation of the sample with electrons. On the right hand side a schematic representation of the color centers within the MgO(1 0 0) surface is shown.

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