

A surface science approach to ambient pressure catalytic reactions

Günther Rupprechter*

Institute of Materials Chemistry, Vienna University of Technology, Veterinärplatz 1, A-1210 Vienna, Austria

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Abstract

Recent advances in the preparation and characterization of planar model catalysts and in ambient pressure surface spectroscopy enable us to investigate well-defined supported metal nanoparticles under working conditions, approaching the conditions of applied catalysis. The reactivity of Pd–Al₂O₃/NiAl(1 1 0) model catalysts for CO hydrogenation and methanol partial oxidation were examined by sum frequency generation (SFG) vibrational spectroscopy and by polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) at pressures ranging from ultrahigh vacuum to ~1 bar. Kinetic measurements were performed by on-line gas chromatography. A comparison with Pd(1 1 1) revealed the inherent differences between Pd nanoparticles and Pd single crystals. Apart from differences in surface structure, the small volume (or finite size) of Pd nanoparticles strongly affected their properties, in particular for hydrogen absorption. Methanol oxidation proceeded via dehydrogenation to formaldehyde CH₂O, which either desorbed or further dehydrogenated to CO, which was subsequently oxidized to CO₂. Carbonaceous overlayers that were present during the reaction were shown to favourably affect the selectivity towards CH₂O. During methanol oxidation Pd particles were more easily oxidized than Pd(1 1 1), which reduced their activity. Deactivation of Pd nanoparticles supported on Nb₂O₅/Cu₃Au(1 0 0), a support less inert than alumina, originated from the formation of mixed “Pd–NbOx” sites. 1,3-butadiene hydrogenation is known to be particle size dependent but when a realistic structural model of Pd nanoparticles on alumina was used for rate normalization, the reaction turned out to be particle size independent, even though the reaction is structure-sensitive, as corroborated by reactivity studies on Pd single crystals.

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1. Introduction

Model Catalysis has come a long way. For many years surface science studies of catalytic processes have been nearly exclusively performed on transition and noble metal single crystals ([1–4] and references therein). Although these studies have elucidated many elementary steps of catalytic reactions, the single crystal approach carries inherent deficiencies. For instance, the absence of nano-sized (metal) particles or of an oxide support makes it difficult to extrapolate surface science results to technological supported metal catalysts. First attempts to overcome this so called “materials gap” involved the growth of oxide islands on metal substrates (“inverse catalysts” [1,5,6]) but significant advances were based on the development of planar nanoparticle model catalysts, consisting

of well-defined metal particles supported on thin oxide films or on oxide single crystals [7–15]. The preparation of planar model systems under ultrahigh vacuum (UHV) using ultra pure materials guarantees the absence of undesired elements that are sometimes difficult to avoid (and detect) for conventional catalysts. The mean particle size (~1–10 nm) as well as the particle morphology and defect structure can be accurately controlled (cf. Fig. 1) and the planarity and electrical and thermal conductivity of the model systems allows applying a wide range of surface sensitive imaging (e.g. scanning tunneling microscopy, STM) and spectroscopic (e.g. X-ray photoelectron spectroscopy, XPS; infrared reflection absorption spectroscopy, IRAS; sum frequency generation, SFG; temperature programmed desorption, TPD, etc.) techniques. To date, an increasing number of technical catalysts can be mimicked and various combinations of Pd, Pt, Rh, Ag, Au, bimetallic (Pd/Co, Pd/Ag, Pd/Au), etc nanoparticles supported by Al₂O₃, SiO₂, TiO₂, Fe₃O₄, Nb₂O₅, MgO, etc., have been examined (see e.g. [16,17] and references therein).

* Tel.: +43 1 25077 3813; fax: +43 1 25077 3890.

E-mail address: grupp@imc.tuwien.ac.at.

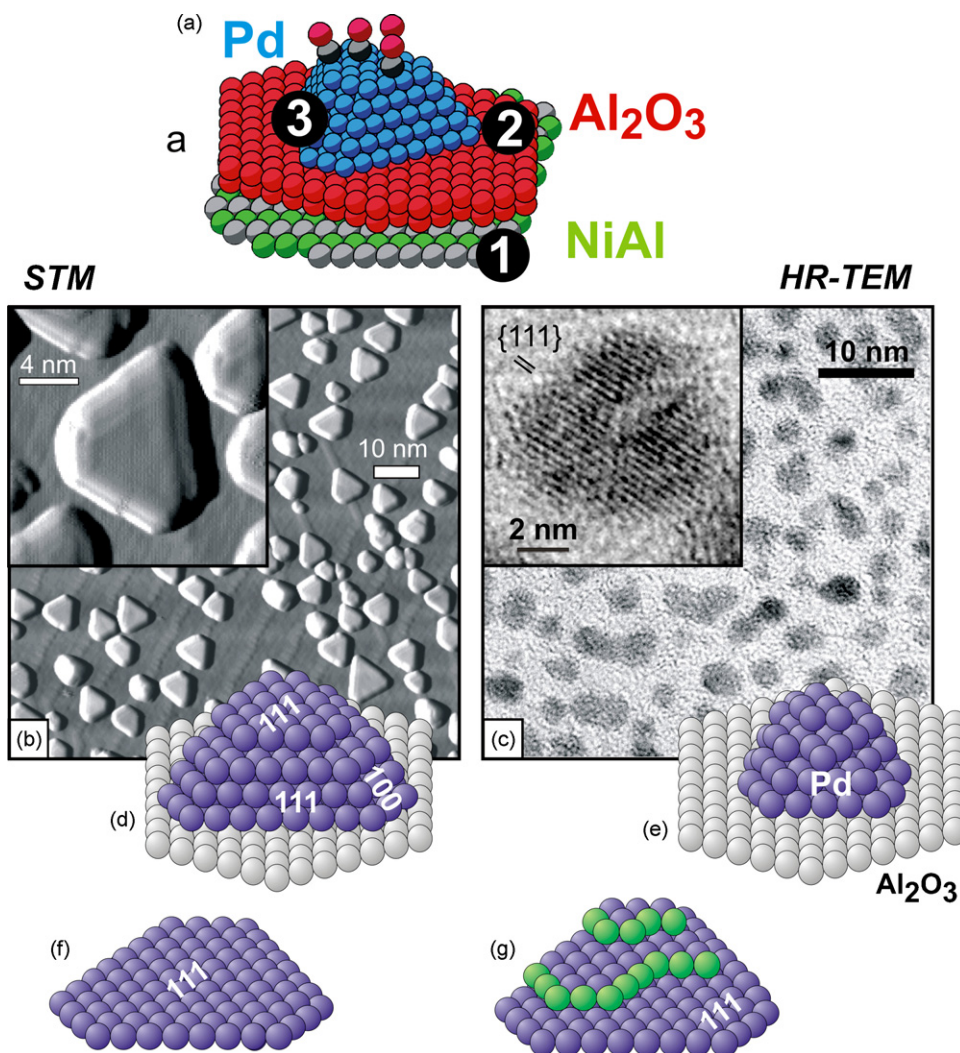


Fig. 1. (a) Graphical illustration of the preparation of Pd nanoparticles supported by $\text{Al}_2\text{O}_3/\text{NiAl}(1\ 1\ 0)$ and of Pd model catalysts with various (surface) morphologies: (b) STM image ($100\ \text{nm} \times 100\ \text{nm}$, adapted from [45,46]) and (c) HRTEM image of Pd nanoparticles, grown at 300 K and 90 K, respectively. The insets show individual particles at higher magnification. Controlling the growth conditions allows preparing Pd particles with different morphology/surface structure, for instance well-faceted truncated cuboctahedra (d) or rougher, defective particles (e). Single crystal surfaces that were used for comparison are also shown: (f) well-ordered Pd(1 1 1) and (g) a “defect-rich” (ion-bombarded) Pd(1 1 1).

Despite the success in the development of model catalyst, studies of their catalytic activity under UHV (e.g. by TPD) are typically very different from the conditions of isothermal, steady state ambient pressure catalytic tests of technical catalysts. Molecular beam studies are probably the best approach to examine reaction kinetics on model catalysts under UHV [18], but due to pressure limitations (operating pressure typically $<10^{-6}$ mbar) the surface coverages may be lower than in the real catalytic process (especially for reactions at elevated temperature), leading to different adsorption site populations. These considerations illustrate the so-called “pressure gap” between surface science and applied catalysis. To circumvent this gap, efforts have been devoted to develop UHV-compatible high-pressure reaction cells and to carry out surface characterization/spectroscopy under non-UHV conditions, i.e. under mbar to atmospheric pressure [17,19–24]. Photon-based methods such as sum frequency generation (SFG) vibrational spectroscopy or polarization-modulation

infrared reflection absorption spectroscopy (PM-IRAS) [17], together with high-pressure X-ray photoelectron spectroscopy (HP-XPS) [25–29] and high-pressure scanning tunneling microscopy (HP-STM) [30–33] are currently among the prime techniques for *in situ* studies of catalytically active surfaces (monitoring “model catalysts at work”).¹ Despite the nanohype one should not forget, however, that studies on single crystals as well as “classical” UHV experiments are still inevitable to interpret and quantify the ambient pressure results.

Combining nanoparticle model catalysts with *in situ* surface spectroscopy at elevated pressure, utilizing suitable UHV systems equipped with high-pressure reaction cells, which are

¹ Here we avoid the term “operando” [34], which refers to simultaneous spectroscopic and kinetic measurements, because “operando” also implies that technically applied reactor types are used (which is not the case for UHV-high pressure cells of model studies).

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