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Deactivation of Pd particles supported on $Nb_2O_5/Cu_3Au(100)$: SFG and TPD studies from UHV to 100 mbar

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Abstract

Structural changes that occur on $Pd–Nb_2O_5/Cu_3Au(100)$ model catalysts upon thermal annealing were followed by sum frequency generation (SFG) and temperature-programmed desorption (TPD) using CO as probe molecule. SFG experiments were performed both under ultrahigh vacuum and mbar pressure. Heating the catalyst to temperatures above 300 K lead to an irreversible 50% decrease in the CO adsorption capacity and modified the remaining adsorption sites. Alterations of the phase between resonant and non-resonant SFG signals upon annealing indicate a change in the electronic structure of the surface, which excludes Pd sintering or migration of Nb_2O_5 over Pd particles to cause the observed effect and rather suggests the formation of "mixed $Pd–NbO_x$" sites. The same changes in surface properties also occur during CO hydrogenation at 1 bar and high temperature, pointing to an involvement of "mixed $Pd–NbO_x$" sites in catalytic reactions.

Keywords: Palladium; Niobium; Clusters; Carbon monoxide; Sum frequency generation; Thermal desorption spectroscopy; Chemisorption; Vibrations of adsorbed molecules

1. Introduction

Niobium-oxide (niobia) containing catalysts are an interesting class of materials and have recently received considerable attention. Niobia itself may be the active phase (unsupported or supported on other oxides), it may serve as support for metal nanoparticles or oxides and may also be used as promoter [1–10]. The most important applications include Fischer–Tropsch synthesis, oxidative dehydrogenation of alkanes, oxidative coupling of methane and others (see below). Studies on high-surface area niobium-oxides inherently carry a high degree of complexity because several stable structures exist (NbO, NbO_2 and Nb_2O_5) and one cannot expect that the resulting surfaces are simple truncations of bulk niobia structures. This is even more so for supported metal oxides, i.e. when two-dimensional thin niobium-oxide layers partly cover a support oxide (e.g. niobia on Al_2O_3, SiO_2, ZrO_2, TiO_2, V_2O_5, etc. [6–8]). Vice versa, Nb_2O_5 was also used as a support for overlayers of vanadium-, chromium-, rhenium-, molybdenum-, and tungsten-oxide [11–16]. These catalysts are active for selective hydrocarbon oxidation, NO_x conversion, alkene isomerization or polymerization, oxidative dehydrogenation, dehydration, partial oxidation of methanol, etc. ([12] and references therein). When Nb_2O_5 was used to support Rh and Ni particles, CO hydrogenation could be carried out with high selectivity to hydrocarbons, while Rh and Ni supported by Al_2O_3, SiO_2 or ZrO_2 yielded more methane [4,8,15–17]. As Nb_2O_5 is a reducible oxide, metal–support interaction (SMSI) was proposed as explanation [15,16]. Co particles on Nb_2O_5 also showed a high selectivity towards long chain hydrocarbons in the Fischer–Tropsch synthesis [11,12,18]. Nb_2O_5 promoted Pd/Al_2O_3, Cr_2O_3, and Mo–V catalysts

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have been successfully tested for the oxidation of volatile organic compounds [19–23].

In order to gain a fundamental understanding of oxide surfaces, well-ordered thin film oxides, grown in ultrahigh vacuum (UHV) under well-controlled conditions, have turned out to be a successful approach ([24–29] and references therein). In contrast to many bulk oxides, thin oxide films exhibit an electric and thermal conductivity that allow the application of electron spectroscopy and temperature-programmed techniques. Furthermore, thin oxide films grown on single crystal substrates are also well-suited for laser spectroscopy [30–36]. Recently, the preparation of well-ordered thin Nb_2O_5 films was reported by Middeke et al. and Starr et al. [37] who have grown a thin niobia film on a $Cu_3Au(1\,0\,0)$ substrate (which was implanted with oxygen) by Nb deposition and subsequent oxidation. The structure of the Nb_2O_5 film was examined by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM), its composition by angular resolved X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). High-resolution electron energy loss spectroscopy (HREELS) and density functional theory (DFT) were applied to confirm the proposed structure. For a complete description we refer to [37], here only a brief summary is given. The Nb_2O_5 oxide film grows two-dimensionally, forming terraces ~100 nm wide, and is ~0.4 nm thick. The film consists of 2/3 ML of a Nb layer above a close packed O layer, on which Nb cations in oxidation state close to 5+ occupy hollow sites and form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. There is another oxygen layer on top of the Nb lattice, leading to a O–Nb–O–Cu_3Au stacking. Due to the square symmetry of the $Cu_3Au(1\,0\,0)$ substrate, there are two domains, rotated by 90°.

In the present study, we have utilized these Nb_2O_5 films to support Pd nanoparticles. In particular, we examine the adsorption of CO by combining temperature-programmed desorption (TPD) and sum frequency generation (SFG), the latter being applied both under UHV and pressures up to 100 mbar. The results on Pd–Nb_2O_5/$Cu_3Au(1\,0\,0)$ model catalysts are compared to previous studies on Pd–Al_2O_3/NiAl(1 1 0) [30,33–36]. In contrast to Pd–Al_2O_3, the Pd–Nb_2O_5 model system undergoes strong structural changes when annealed above 300 K. SFG and TDS indicated changes in the electronic structure of the surface and a strong loss of CO adsorption capacity, pointing to the formation of "mixed Pd–NbO_x" sites. The new surface structure was stable upon repeated annealing and H_2 treatments did not induce further modifications. The Pd–Nb_2O_5 model catalysts were also tested for CO hydrogenation at 1 bar using gas chromatography but no measurable activity was observed.

2. Experimental

The experiments were performed in a UHV system (base pressure $\sim 2 \times 10^{-10}$ mbar) consisting of two sections, (i) a preparation/characterization chamber and (ii) a high-pressure reaction cell [30,34]. The preparation chamber was equipped with an ion sputter gun for surface cleaning, LEED and AES for surface characterization, a quadrupole mass spectrometer (QMS) for TPD measurements, and metal evaporators and a quartz microbalance for deposition of Nb and Pd. The high-pressure cell had CaF_2 windows for SFG measurements and was connected to a gas chromatograph [30].

The $Cu_3Au(1\,0\,0)$ sample crystal was spot-welded by Ta wires to two Mo rods and could be heated resistively to 1300 K and cooled with liquid N_2 to 90 K. Clean $Cu_3Au(1\,0\,0)$ was obtained by cycles of Ar^+ bombardment (1 keV, 5×10^{-6} mbar for 30 min) at 500 K and annealing at 800 K for 5 min. The structure and cleanliness of the surface were examined by LEED and AES. The clean Cu_3Au surface was then sputtered at 300 K with oxygen (1 keV, 7×10^{-7} mbar O_2 for 30 min) followed by annealing at 650 K for 5 min. This treatment implants oxygen into the substrate which seems to prevent Nb/substrate alloying and also creates an oxygen reservoir facilitating the growth of Nb_2O_5 films [37–39].

Nb_2O_5 films of about 0.4 nm thickness were prepared by evaporation of ~1.5–2 Å nominal thickness of (metallic) Nb (from a Nb rod) at 300 K followed by oxidation at 773 K in 1×10^{-6} mbar oxygen for 30 min and annealing at 773 K for 30 min. The well-ordered structure of the Nb_2O_5 film was confirmed by LEED at 90 K, showing a pattern as that reported by Starr et al. [37].

Pd particles were grown on the Nb_2O_5/$Cu_3Au(1\,0\,0)$ substrate at 90 K via Pd deposition (by evaporation of a Pd rod) at a rate of 0.1 nm/min for 6 min, yielding, of course, a nominal Pd thickness of 0.6 nm. According to the analysis of the CO-SFG intensity (see below), the Pd particles were about 3.5 nm in size and exhibited rather rough surfaces. Apparently, the growth (island density) of Pd on Nb_2O_5 and on Al_2O_3 seems roughly comparable, at least at 90 K.

For a full description of SFG theory we refer to [30–36,40,41] and references therein. The SFG signal basically comprises two contributions, a *resonant* part arising from the vibrations of adsorbed molecules, and a *non-resonant background* arising from "off-resonance" SFG signals due to electronic transitions at the interface. As described in detail in [35], the SFG lineshape then depends on the relative magnitudes of both contributions and, in particular, on the *phase* ϕ between them. Since the *phase* ϕ is sensitive to the electronic structure of the substrate, compositional changes at the interface induce changes in ϕ and, consequently, in the SFG lineshape that can be monitored.

SFG vibrational spectroscopy was performed using a Nd:YAG laser (1064 nm, 30 mJ/pulse, 20 ps, 50 Hz) with part of the output converted to 532 nm and 355 nm by a harmonic generator. The 1064 nm and 355 nm beams were mixed in an optical parametric generator/difference frequency generator to produce tunable infrared pulses of about 150 μJ/pulse in the range of 3–6 μm, with resolution of about 5 cm^{-1}. The 532 nm light used for SFG had an energy of about 200 μJ/pulse.