Surface Science 623 (2014) 29–40

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Adsorption of CO on bimetallic $Rh_N/Ru(0001)$ layers

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ARTICLE INFO

Article history:
Received 28 August 2013
Accepted 4 January 2014
Available online 14 January 2014

Keywords:
Carbon monoxide
Infrared absorption spectroscopy
Ruthenium
Rhodium
Vibrations of adsorbed molecules
Low energy electron diffraction

ABSTRACT

The adsorption of CO on bimetallic $Rh_N/Ru(0001)$ layers with $N = 0–5$ Rh layers has been investigated using Fourier transform infrared spectroscopy, thermal desorption, and low energy electron diffraction. It is found that the morphology as well as the thickness of these ultra thin Rh films lead to characteristic frequency shifts of the internal CO stretch modes as well as variations of the CO desorption energies. For $N \geq 3$ ML differences with respect to CO adsorption on Rh(111) single crystal substrates are only very minor. Our findings confirm similar observations and conclusions associated with CO on bimetallic $Pt_N/Ru(0001)$ layers. Dependent on the coverage of CO adsorbed on Rh/Ru(0001) monolayer films we identify a series of ordered overlayer structures which have been correlated with characteristic CO vibrational spectra.

1. Introduction

A straightforward approach to tailor catalysts with specific properties in terms of reactivity and selectivity is to deposit thin metal films on a substrate made of another material. Starting with Ru(0001) as a substrate material a number of systems, such as Cu/Ru(0001) [1–3], Pt/Ru(0001) [4–7], Rh/Ru(0001) [8], or Ni/Ru(0001) [9] exhibit pseudomorphic growth for films of monolayer thickness, i.e. the overlayer adopts the lattice constant of the underlying host. The resulting strain [7,10–12] of the deposited film as well as the electronic influence [7,13,14] of the substrate material lead to a substantial change of surface reactivity. For instance, on the well studied $Pt_N/Ru(0001)$ films the sticking probability of O_2 varies substantially with the number N of deposited Pt monolayers (ML) and even vanishes completely for single monolayer films ($N = 1$), even though quite high values are found for pure Pt(111) and Ru(0001) [15]. Similarly, the binding energy of CO on $Pt_N/Ru(0001)$ depends on the Pt film thickness too and is lowest for $N = 1$ [4,7,16].

In this context the present study on the adsorption of CO on $Rh_N/Ru(0001)$ films ranging from the submonolayer regime up to a thickness of 5 ML builds on recent work of ours and others, namely CO on $Pt_N/Ru(0001)$ [4–7]. This comparison in particular comprises the dependence of CO desorption energies, the type of adsorption sites and C–O vibrational frequencies on the Rh film thickness; in this respect we specify to what extent the Rh/Ru interface and strain within the Rh film contribute.

The change in reactivity of bimetallic surfaces with respect to the elemental surfaces has been analyzed by Hammer and Nørskov [10,17–19]. In their *d*-band model the surface modifications are described by the energetic position, ϵ_d, of the metal *d*-band center with respect to the Fermi-Energy, ϵ_F; specifically, the location of ϵ_d is found to correlate with the binding strength between the metal substrate and chemisorbed adsorbates. For the late transition metals lattice expansion (compression) induces a narrowing (broadening) of the *d*-band as well as an up-shift (down-shift) of ϵ_d. The increased (lowered) density of states at ϵ_F then leads to a strengthening (weakening) of the adsorbate–substrate bond.

Rh containing catalysts are particularly interesting for technical applications such as steam reforming for hydrogen production [20], or as catalyst for direct alcohol fuel cells [21,22]. Thus, general knowledge how to influence adsorption/reaction barriers of specific molecules is of great importance to precisely control and adjust catalytic properties of these materials. In this context, CO plays a prominent role as it is a common reaction product within catalytic processes; in the case of low temperature fuel cells it represents an unwanted catalyst poison.

Regarding technical applications our model study may also contribute to the design and understanding of novel catalysts such as e.g. core-shell nano-particles [23]; specifically, grown Rh/Ru(0001) layers would correspond to the (111) facet of a Ru@Rh core-shell nanoparticle.

Unlike the Pt/Ru(0001) system, the literature related to Rh/Ru(0001) is relatively sparse. Regarding the growth of Rh on Ru(0001), He et al. [8] found, using LEED in conjunction with DFT calculations, layer-by-layer growth leading to a pseudomorphic first Rh layer with a lattice mismatch of 0.5%. Yet, they do not provide any information on the evolution

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http://dx.doi.org/10.1016/j.susc.2014.01.002

of the Rh lattice constant for thicker Rh films. We expect, however, that the pseudomorphic structure of Rh_N/Ru(0001) films is retained at least up to the 5th atomic layer, as it is the case for Pt_N/Ru(0001) that exhibits a much larger lattice mismatch of 2.5% [7].

In the past, the adsorption of CO on Ru(0001) has been studied in detail by means of vibrational spectroscopy, thermal desorption and low energy electron diffraction [24–28]. Thereby it was found that CO occupies on-top sites only, independent of surface coverage [24]. At low coverages its internal stretch mode frequency, ν_{C-O}, equals 1988.7 cm^{-1} [24,26]; for $\Theta_{CO} \simeq 0.1$ ML a $\left(\sqrt{3}\times\sqrt{3}\right)R30°-CO$ surface structure starts to develop exhibiting maximum intensity for $\Theta_{CO} \simeq 0.33$ ML which is associated with an IR band at 2030.7 cm^{-1} (at 30 K) and a desorption peak at around 450 K [25,26]. For higher CO exposures incorporation of additional CO in the $\left(\sqrt{3}\times\sqrt{3}\right)$ layer leads to significant repulsive lateral interactions which is associated with a second desorption peak around 390 K. Eventually, saturation is reached at 0.67 ML and a $\left(2\sqrt{3}\times 2\sqrt{3}\right)R30°$ structure is formed [24,27]. In IR spectra the corresponding C–O peak is located at 2060 cm^{-1} [24,28]; a detailed view of the vibrational spectra reveals that the dominant 2060 cm^{-1} band is accompanied by several weaker bands, indicative of on-top bound CO in different local environments (their low intensity is ascribed to intensity borrowing effects [29] rather than an overall low abundance) [28].

Similar to adsorption of CO on Ru(0001), the adsorption of CO on Rh(111) has been studied in detail with a number of surface sensitive methods, including vibrational spectroscopy (HREELS), low energy electron diffraction (LEED), core level photoemission(XPS) and thermal desorption (TDS) [30–33]. With increasing CO coverage several distinct surface structures were observed: $\left(\sqrt{3}\times\sqrt{3}\right)R30°-CO$ (0.33 ML), (4 × 4)-CO (0.5 ML), a so-called split (2 × 2) structure, and (2 × 2)-3CO (0.75 ML) [31]. At low coverages and low temperatures CO starts occupying on-top surface sites with a C–O stretch frequency of about 2015 cm^{-1} [30]. The layers with $\Theta_{CO} = 0.33$ and 0.75 ML are associated with stretching modes of on-top-CO at 2041 and 2070 cm^{-1}, respectively. Starting at 0.5 ML a second C–O stretch mode at 1815 cm^{-1} assigned to 3-fold coordinated CO becomes visible [30]. At saturation coverage ($\Theta_{CO} = 0.75$ ML) its frequency equals 1861 cm^{-1}. In TDS the desorption signal of CO/Rh(111) displays a single peak at around 500 K for coverages up to 0.5 ML. At higher coverages, and along with the growth of the 1861 cm^{-1} peak, a second desorption feature develops at around 400 K. In the range of 0.5–0.75 ML a redistribution of the CO molecules from on-top adsorption sites to 3-fold hollow sites has been identified by Beutler et al. [31,33] with a relative ratio of 1:2 at 0.75 ML. Thus, the (2 × 2) surface unit cell with $\Theta_{CO} = 0.75$ ML contains one on-top and two 3-fold coordinated CO molecules above fcc and hcp sites. This structural arrangement has been confirmed later on using tensor LEED [34], surface X-ray diffraction [35], as well as density functional theory calculations [36–38]. Bridge bonded CO may exist in small quantities at domain boundaries as evidenced by a weak vibrational band at about 1925 cm^{-1} [30,37].

2. Experimental

The experiments were performed in a UHV chamber at a base pressure of $p = 6 \times 10^{-11}$ mbar. The sample is a Ru crystal (5 N purity) with 10 mm in diameter and a thickness of 2 mm, oriented within ±0.1° in the (0001) direction. It can be cooled with liquid He or N_2 and heated up to 1570 K (limited by a type K thermocouple) with linear heating rates of 0.1–10 K/s. The sample was cleaned by Ar^+ sputtering (1.4 keV, 1–1.5 μA) and multiple O_2 dosing cycles combined with flashing the sample up to 1570 K. The Fourier transform infrared spectrometer is a Bruker IFS 66v with evacuable optics ($p < 1$ mbar). Polarized IR radiation is produced by a water cooled blackbody source (Globar) in conjunction with a wire grid polarizer. Within this work a LN_2 cooled MCT (HgCdTe) detector was used, allowing for measurements in the spectral range 750–4000 cm^{-1}. All infrared absorption spectra were taken at a resolution of 2 cm^{-1} with 500–1000 scans coadded at a surface temperature of 85 K (if not specified otherwise). For IRAS measurements the sample was positioned in a dedicated IR-cell, which also contained a titanium sublimation pump. A uniform gas dosage at the IR measurement position is provided by a multi-capillary array (MCA) with individual diameters of ≈10 μm. A liquid N_2 cold trap inserted in the dosing line avoids built-up of metal carbonyl bands at 2075–2090 cm^{-1} at high CO exposures. Our quadrupole mass spectrometer (Balzers QMA 112) is equipped with a Feulner cup [39] (glass enclosure) to preferentially detect signals associated with desorption from the front face of the sample and to enhance the desorption signals.

For Rh deposition an e^--beam evaporator (Rh purity: 4 N) was used. The typical deposition rate was 0.06 ML min^{-1} at a growth temperature (sample) of $T_g = 600$ K. During evaporation the background pressure increases to about 1×10^{10} mbar. The prepared Rh_N/Ru(0001) layers were characterized by monitoring the ν_{C-O} mode of adsorbed CO ($\Theta_{CO} = 0.004$ ML) using IRAS, i.e. analogous to our study of Pt_N/Ru(0001) layers [6,40]. Typical IRAS spectra are depicted in Fig. 1. The top spectrum in panel (A) belongs to CO adsorbed at 85 K on the clean Ru(0001) substrate; the peak at 1988.8 cm^{-1} reproduces the value of the internal C–O stretch on Ru(0001) reported in the literature [24,26]. Spectra (b) and (c) refer to CO on 0.37 ML Rh/Ru(0001) after CO adsorption at 85 K, (b), and after heating to 140 K, (c). Evidently, the two peaks at 1988.8 and 2018.3 cm^{-1} in spectrum (b) can be assigned to Ru-bound CO on clean Ru(0001) areas and to Rh-bound CO on Rh/Ru(0001) terraces, respectively. By heating the sample to $T \geq 120$ K the peak associated with CO on Rh vanishes while the CO/Ru(0001) peak gains intensity (see Fig. 1, panel B), i.e. diffusion of CO from the Rh terraces to the clean Ru(0001) occurs. At 450–500 K the signal of the C–O stretch mode vanishes due to thermal desorption (compare with Fig. 6,). From the relative increase of the integrated intensity of the ν_{C-O} band (CO on Ru(0001) entity) the Rh surface coverage in the submonolayer regime can easily be calculated, allowing a calibration of the deposition flux of our Rh-evaporator. The error of

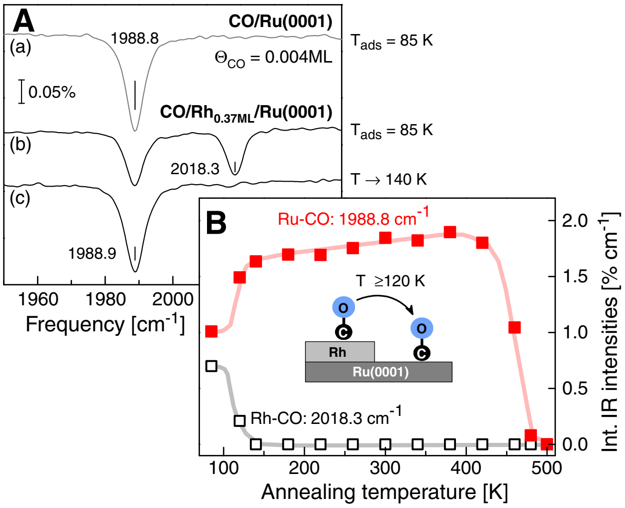

Fig. 1. Sequence of IR-spectra used to derive the amount of deposited Rh. (A): IRAS spectra of 0.004 ML CO ($T_{ads} = 85$ K) on (a) the clean Ru(0001) surface, (b) on $Rh_{0.37\ ML}$/Ru(0001), and (c) after heating the layer in (b) to 140 K (to induce diffusion of Rh-bound CO towards Ru(0001) areas) and recooling to 85 K for data acquisition. The spectra are offset vertically for a better clarity of presentation. (B): Integrated IRAS intensities of the internal C–O stretch bands of Rh-bound (2018.3 cm^{-1}) and Ru-bound (1988.8 cm^{-1}) CO molecules as a function of the annealing temperature (data obtained after recooling to 85 K). At $T > 400$ K thermal desorption of CO sets in. The solid lines are guides to the eye.