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Reactivity of 3-hexyne on oxygen modified Ru(001) surfaces: Observation of oxametallacycles by RAIRS

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ABSTRACT

The chemical behaviour of 3-hexyne on oxygen modified Ru(001) surfaces has been analysed under ultrahigh-vacuum, using reflection–absorption infrared spectroscopy (RAIRS). The effects of oxygen coverage, 3-hexyne exposure and adsorption temperature were studied. Two modified Ru(001) surfaces were prepared: Ru(001)-(2 × 2)-O and Ru(001)-(2 × 1)-O that correspond to oxygen coverages (θ_O) of 0.25 and 0.5 ML, respectively. The striking result is the direct bonding to an O atom when the modified surfaces are exposed to a very low dose (0.2 L) of 3-hexyne at low temperature (100 K). For $\theta_O = 0.25$ ML, an unsaturated oxametallacycle [$Ru–O–C(C_2H_5)=C(C_2H_5)–Ru$] is proposed, identified by RAIRS for the first time, through the $\nu C=C$ and νCO modes. Further decomposition at 110 K yields smaller oxygenated intermediates, such as acetyl [μ_3-η^2(C,O)-CH_3CO], co-adsorbed with a small amount of carbon monoxide and non-dissociated species. The temperature at which a fraction of molecules undergoes complete C–C and C–H bond breaking is thus much lower than on clean Ru(001). The ultimate decomposition product observed by RAIRS at 220 K is methylidyne [$\equiv CH$]. Another key observation was that the adsorption temperature is not determinant of the reaction route, contrarily to what occurs on clean Ru(0 0 1): even when 3- hexyne strikes the surface at a rather high temperature (220 K), the multiple bond does not break completely. For $\theta_O = 0.5$ ML, a saturated oxametallacycle [$Ru–O–CH(C_2H_5)–CH(C_2H_5)–Ru$] is also proposed at 100 K, identified by the $\nu_{as}O–C–C$ (at 1043 cm^{-1}) and $\nu_sO–C–C$ (at 897 cm^{-1}) modes, showing that some decomposition with C–H bond breaking occurs. For this oxygen coverage, the reaction temperatures are lower, and the intermediate surface species are less stable.

1. Introduction

The adsorption of organic molecules on metal surfaces has been the focus of an increasing interest, mainly for their potential use in the emerging field of nanotechnology. In particular, the study of the reactivity of unsaturated hydrocarbons on single crystal model systems, performed under idealized conditions, contributes to understand the surface assisted decomposition mechanisms at different temperatures and coverages, which is achieved primarily by the identification of the intermediate species formed and their adsorption geometries [1–3].

Ruthenium, pure and in bimetallic alloys, is a catalyst with remarkable selectivity and characteristic activity [4,5]. The high activity of the Ru(001) surface towards C–H and C–C bond breaking reactions has been evidenced for 1-alkenes, namely in comparison with Pt(111), by lower temperatures of reaction: despite similar decomposition pathways, the same surface species are detected on Pt(111) at temperatures almost 150 K above those observed on Ru(001) [6].

The chemistry of alkynes on clean Ru(001) strongly depends on the chain length and on the position of the triple bond, which plays a determining role in the stability of the surface species and in the decomposition channels. This is particularly important in the case of hexyne isomers, whose decomposition on clean Ru(001) has been recently reviewed [3]. It was proved that 1-hexyne adsorbs at 90 K as a di-σ/π complex, which implies a rehybridisation of the *sp* carbons with bond order reduction [7]. By thermal activation, this complex dehydrogenates (in C1) yielding hexylidyne [$\equiv C(CH_2)_4CH_3$], which further decomposes with formation of surface metallocycles [$\equiv C(CH_2)_4CH_2–$] and [$\equiv C(CH_2)_4C\equiv$]. Eventually (at 300 K), these species undergo complete C–C bond breaking into adsorbed methylidyne [$\equiv CH$]. The hexyne isomers with the triple bond in secondary carbons may follow two decomposition mechanisms: (1) the di-σ/π complex formed at low temperature (~90 K) reacts by breaking the C–C bonds adjacent to the surface anchors; (2) the triple bond breaks completely upon direct adsorption at higher temperature (~220 K), with formation of shorter chain

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alkylidynes. The first mechanism was observed for 2-hexyne, where C1–C2 and C3–C4 bond breaking occurs at 110 K, yielding ethyne di-σ/π complex, methylidyne and propylidyne [$\equiv CCH_2CH_3$] [8]. It was also observed for 3-hexyne, but by annealing to 220 K, ethyne di-σ/π complex and ethylidyne [$\equiv CCH_3$] being formed by C2–C3 and C4–C5 bond breaking [9]. The second proposed decomposition path has been detected for 2-hexyne with formation of ethylidyne and butylidyne [$\equiv CCH_2CH_2CH_3$], and for 3-hexyne with formation of propylidyne that further decomposes into ethylidyne. A schematic representation of the decomposition paths of 3-hexyne on clean Ru(001) is shown in Fig. 1.

The presence of preadsorbed species on transition metal surfaces can inhibit or induce surface reactions, by direct participation in the reaction pathway [10,11], by modification of the surface electronic structure [12], or just by a site blocking effect. An example is the opening of new routes on the surface reactions of C_2H_5 (from C_2H_5I) by potassium adatoms on Rh(111) [13]. Oxygen atoms are known to enhance the chemisorption of short chain alkenes and alkynes, as a consequence of an induced positive charge on the surface that increases the interaction towards the π system [14]. In fact, on Ag(111), the tendency of propene to adsorb as a di-σ (instead of π) complex increases with the surface oxygen load [15]. Chemisorbed oxygen also influences a wide range of reaction mechanisms of hydrocarbons on surfaces, *e.g.*, catalytic oxidation, by involving transient states that provide low energy pathways [16]. So far, the more extensively studied unsaturated hydrocarbon on oxygen modified metal surfaces was ethene [17–20].

On ruthenium single crystals under UHV conditions, oxygen chemisorption leads to a diversity of atomic oxygen ordered structures that eventually lead to the formation of a saturated oxygen monolayer [21–23]. Ru(001) may accommodate large loads of oxygen, even under mild experimental conditions, without decreasing its reactivity [24,25]. In fact, an increase in the reactivity of Ru surfaces was observed when the determining step is the diffusion of adsorbed oxygen atoms, as reported for the oxidation of CO, which follows a Langmuir-Hinshelwood mechanism [26]. Methoxide conversion into formate is also favoured on oxygen modified Ru(001) surfaces with $\theta_O \geqslant 0.5$ ML [27,28]. Other examples include the chemistry of ethyl iodide that, on oxygen-precovered Ru(001), bonds preferentially to Ru sites nearby oxygen adatoms, holding together by Coulomb forces, and being stabilized in new adsorption states [29]. A different reaction channel may also be induced by the presence of oxygen: the C_2H_5 species obtained by dissociation of C_2H_5I yields diethyl ether and, at higher coverage, acetaldehyde, whereas on the clean surface the main decomposition products are $\equiv CCH_3$(adsorbed) and C_2H_6(g) [30].

The amount of oxygen on the surface may be responsible for different chemical behaviours. In fact, ethylene adsorbed on stoichiometric RuO_2(110), formed upon a heavy dosage of the Ru(001) surface with oxygen, presents a reduced reactivity: it desorbs molecularly at 320 K, with a rearrangement from π- to σ-bonded at 260 K [31,32], whereas on the clean surface it reacts at 280 K with formation of ethylidyne [33]. Nevertheless, on the oxygen-rich RuO_2(110) surfaces, ethylene adsorbs molecularly at 85 K and is completely oxidized upon annealing to 500 K, CO_2 being the final product [32]. On the whole, the studies on oxygen modified Ru(001) surfaces may be understood as a bridge to overcome the gap between UHV clean surface conditions and the atmospheric pressure, where the metal surface is oxidized [34].

The purpose of this work is to study the adsorption and thermal decomposition of 3-hexyne on oxygen modified Ru(001) surfaces, based on reflection–absorption infrared spectroscopy (RAIRS), which will lead to a better understanding of the mutual influence of coadsorbates, by comparison with the observations on the clean surface. Two surfaces were prepared: Ru(001)-(2 × 2)-O (for θ_O = 0.25 ML) and Ru(001)-(2 × 1)-O (for θ_O = 0.5 ML), both layers with the oxygen atoms adsorbed on 3-fold hcp sites [22,35–37].

2. Experimental

The experiments were performed in a Kratos Analytical bakeable ultrahigh-vacuum (UHV) chamber (described in detail elsewhere [1]), operating at a base pressure of 10^{-10} Torr, equipped with a low electron energy diffraction (LEED) spectrometer (with a three-grid rear view LEED optics, from SPECS) and with facilities for surface cleaning. The RAIRS data were obtained with a coupled Mattson Research Series 1 FTIR spectrometer, with an external narrow-band MCT detector (4000–800 cm^{-1}), from EG&G Judson. A wire-grid polarizer was placed before the detector window to select exclusively p-polarized light. The spectra were recorded at 4 cm^{-1} resolution, and result from the ratio of 1000 co-added scans to the same number of background scans (for the corresponding oxygen modified surface). All the spectra were obtained keeping the crystal at 90 K, which means that, after thermal activation of the surface layers by annealing to the required temperatures for ∼2 min, the crystal was re-cooled to scan the spectrum. An exception was made for adsorption at 220 K, as the spectra were recorded at this temperature.

The surface was cleaned by several cycles of sputtering (with 2500 eV Ar^+ ions, for 15 min) and annealing to 1200 K (by electron-bombardment heating). The surface cleanliness and smoothness were tested by LEED and by the RAIR spectrum of carbon monoxide adsorbed at 90 K and at saturation coverage [38,39].

The oxygen modified Ru(001) surfaces were prepared by dosing 0.5 and 20 L of O_2 (N48, from Alpha Gaz) at 300 K, followed by annealing to 450 K for 1 min [22]. The LEED images exhibited sharp (2 × 2) patterns, compatible with a long-range ordered atomic oxygen overlayer, that could be either Ru(001)-(2 × 2)-O or Ru(001)-(2 × 1)-O. The effective oxygen coverages were assessed by the RAIR spectra of the probe molecules CO and NO, as in previous works [27,28]. The 0.5 L dose yields a layer with θ_O = 0.25 ML, corresponding to the Ru(001)-(2 × 2)-O structure, whereas 20 L yields θ_O = 0.5 ML, *i.e.*, the Ru(001)-(2 × 1)-O structure.

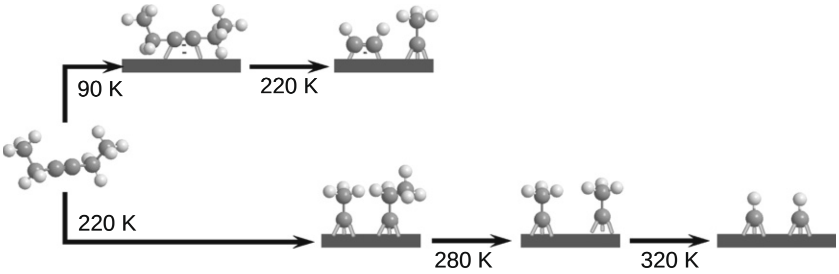

Fig. 1. Decomposition pathways proposed for 3-hexyne on clean Ru(001).