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High-resolution fast X-ray photoelectron spectroscopy study of ethylene interaction with Ir(1 1 1): From chemisorption to dissociation and graphene formation

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ABSTRACT

High-energy resolution fast X-ray photoelectron spectroscopy was used to study the thermal evolution of ethylene on Ir(1 1 1). Temperature programmed photoemission spectra of the C 1*s* and Ir $4f_{7/2}$ core levels were measured in 400 ms/spectrum while ramping the temperature from 170 to 1120 K. The C 1*s* spectra display a large variety of components, assigned to different carbon containing species present on the surface at increasing temperature, namely ethylene, ethylidene, ethylidyne, ethynyl, adsorbed carbon and finally graphene. Components due to the C–H stretch vibration excitation are clearly resolved for C_2H_4, $CHCH_3$ and C_2H_3. The C 1*s* spectra of the last two species display also shifted components that belong to non-equivalent carbon atoms. At temperatures higher than 900 K the narrowing of C 1*s* spectra is caused by graphene formation. Also the Ir $4f_{7/2}$ spectra are strongly affected by the presence of the different species. The clean surface component moves initially towards the bulk peak and shifts back and forth along the series, to recover the binding energy position corresponding to the clean surface when the graphene layer is completely formed. A comparison of ethylene interaction with Ir(1 1 1) and Pt(1 1 1) is presented.

Iridium is a 5d transition metal which exhibits distinctive chemical properties largely employed in several fields, particularly in heterogeneous catalysis. Ir is commonly used to improve the selectivity towards N_2 instead of NO_x production during ammonia oxidation [1]. In addition Ir based catalysts are extensively studied because of their unique catalytic activity for hydrogen production from ammonia and hydrazine [2], free from CO and CO_2, to be used as propellant in satellite propulsion [3]. Moreover, highly dispersed Ir nanoparticles were found to be effective photocatalysts for the production of stoichiometric hydrogen and oxygen by water splitting under visible light irradiation [4].

Because of the high efficiency in C–H bond breaking of small alcohols, such as methanol and ethanol [5], the Ir(1 1 1) surface has recently attracted a lot of attention for the growth of a single graphite layer, named graphene, by hydrocarbon dissociation [6–8]. Whereas the presence of carbon atoms which are not easily hydrogenated, is usually a problem in chemical reactions because it results in surface blockage and catalytic reaction poisoning, the formation of graphene represents a challenge for technological applications in nano-electronics because of the remarkable electronic and transport properties of this two-dimensional carbon system [9]. Because of this, many groups are currently studying different aspects of the graphene on Ir(1 1 1) system, which span from the electronic and structural properties to the understanding of the growth process. A new and atypical growth mechanism was found [10], which involves the creation of dome-shaped carbon nanoislands whose interaction with the Ir substrate takes place only at the cluster edges. It was proposed that this new mechanism of cluster formation, which results in nanosized non-interacting carbon regions, could offer the groundwork for a nanoscale design of graphene-based-systems, in particular for electronic devices making use of quantum dots and nanoribbons [11].

Among hydrocarbons, ethylene is commonly used to produce graphene layers on Ir(1 1 1) with high structural quality. Scanning Tunneling Microscopy (STM) measurements [7,8] have shown that high-temperature ($T > 800$ K) ethylene dissociation results in an incommensurate pattern with a 25.3 Å periodicity and a (9.32×9.32) superstructure, described as a moiré structure. At this temperature the dissociation of C_2H_4 is complete and the interplay between carbon–substrate interaction, surface carbon diffusion

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and graphene–Ir lattice mismatch are the key ingredients for the epitaxial growth. What is still missing in these studies is the understanding of the processes that bring a chemisorbed C_2H_4 molecule to break into C_xH_y fragments first, and in a second moment into C atoms, the building blocks of graphene.

It is important to highlight that already in the '70s Nieuwenhuys et al. [12] reported that heating of the Ir(1 1 1) surface above 1070 K in the presence of hydrocarbons results in the formation of a well-ordered carbonaceous overlayer with (9 × 9) periodicity, whose structure was attributed to "*an hexagonal layer of carbon similar to the structure of the basal plane of graphite deposited on the (1 1 1) Ir surface*". Hydrogen thermal programmed desorption (TPD) spectra indicated that C–H bond breaking take place between 370 and 820 K. Later, Marinova et al. [13,14] using high-resolution electron energy loss spectroscopy (HREELS) reported the formation of ethylidyne (C_2H_3) at 180 K, with the C–C axes parallel to the surface. With increasing the temperature above 300 K these species are converted into a new species with the C–C axis inclined. Complete decomposition of ethylidyne into C_2H species was accomplished by annealing to 500 K, thus suggesting a larger activity of Ir(1 1 1) than Rh(1 1 1), Pd(1 1 1) and Pt(1 1 1) surfaces.

In this work we use the high-energy resolution fast X-ray photoelectron spectroscopy (XPS) technique to shed light into the nature of the different chemical precursor species involved in the formation of graphene on Ir(1 1 1) from ethylene. The changes in the C 1*s* and Ir $4f_{7/2}$ core electron binding energies are used to probe the different chemical species present on the surface as well as the local geometric environment of the substrate atoms. By exploiting the tunability and the high brilliance of the soft X-ray radiation produced at third generation synchrotron light sources, which yields an increase of the photon flux of almost three orders of magnitude with respect to conventional anode-based sources, with much higher energy resolution (<50 meV), it is possible to follow *in situ* and in *real time* the modification of the surface composition during a chemical reaction [15]. The same experimental approach was already successfully employed by Fuhrmann et al. [16] to study the dissociation of ethylene on Pt(1 1 1). Binding energy changes and vibrational signatures of the C 1*s* spectra were used to make the assignment of the different surface species, in particular ethylidyne which forms on Pt(1 1 1) at 290 K and another intermediate species which was tentatively assigned to ethylydene ($CHCH_3$).

The Ir sample, a 6 mm diameter disc oriented along the (1 1 1) direction within 0.1°, was cleaned by repeated cycles of Ar^+ sputtering (T = 300 K, E = 2.5 keV), annealing at 1470 K, oxygen treatments (T = 570–970 K, $p = 1 \times 10^{-7}$ mbar) and a final annealing in H_2 to remove residual oxygen (T = 370–670 K, $p = 1 \times 10^{-7}$ mbar). This procedure yielded a very well ordered and clean surface, as proved by the sharp and low background (1 × 1) low energy electron diffraction (LEED) pattern and by the absence of traces of contaminants in the C 1*s*, S 2*p* and O 1*s* core level regions (detection limit below 0.5% of a monolayer).

The core level photoemission measurements were performed at the SuperESCA beamline of the synchrotron radiation source Elettra in Trieste. C 1*s* and Ir $4f_{7/2}$ core level spectra were acquired at photon energies of 400 and 130 eV, respectively. A Phoibos hemispherical electron energy analyser from SPECS (mean radius of 150 mm) implemented with an home-made delay-line detection system, was used to collect the spectra. The technology of the delay-line detector allows for acquisition times in the ms range when running the analyser in the so-called snap-shot mode, with thousand energy data points per spectrum. The C 1*s* and Ir $4f_{7/2}$ core level spectra of the present work were acquired in 400 ms.

The high sensitivity to the local environment of the narrow C 1*s* and Ir 4*f* core levels, together with the high-energy resolution available (60 and 40 meV for the C 1*s* and Ir 4*f* spectra, respectively), allowed us to perform Temperature Programmed XPS (TP-XPS) experiments [17]. We measured very high quality C 1*s* and Ir $4f_{7/2}$ spectra with unprecedent speed from 180 to 1120 K with a linear ramp of 1.5 K/s. Such a wide temperature range allowed us to follow the dissociation pathways of ethylene till the formation of a well ordered, almost free-standing graphene layer on Ir(1 1 1).

C_2H_4 was dosed onto Ir(1 1 1) kept at 170 K at a background pressure of 1×10^{-7} Torr for 300 s, corresponding to 30 Langmuir (L), to ensure saturation of the surface.

The C 1*s* and Ir 4*f* binding energies are referred to the Fermi level, measured under the same experimental conditions (photon energy, analyser set-up and surface temperature). The photoemission spectra were fitted by convoluting a Doniach–Šunjić (DS) function [18] with a Gaussian to account for the vibrational-unresolved broadening and the instrumental resolution. A linear background was also subtracted. The DS profile contains a Lorentzian distribution arising from the finite core–hole lifetime, and an asymmetry parameter for electron–hole pair excitations at the Fermi level. The C 1*s* lineshape parameters (Lorentzian and Gaussian width and asymmetry) for the different species present on the surface, as well as the distance between the peaks that belong to the same chemical species, were optimised at some selected temperatures and then fixed during the analyses of the TP-XPS data, while the intensities were allowed to vary. It is important to note that the Gaussian width of the individual components can be different not only because of vibrational effects, but also because of inhomogenous broadening. This effect arises from the different local configurations and it is particularly relevant for the atomic carbon species resulting from molecular dissociation at high temperature, as reported in our previous work [10]. The BE positions were also let free, with the constraint explained above.

Fig. 1(a) shows a two-dimensional plot of the time-lapsed C 1*s* spectra acquired while heating the Ir(1 1 1) surface saturated with ethylene at 170 K. The intensity, represented as a density plot by a colour scale, ranges from low (blue) to high (white). The large intensity variations are a clear fingerprint of the presence of distinct features at different BEs.

Fig. 1(b) shows a sequence of C 1*s* spectra at different temperatures, selected from the complete TP-XPS series to figure out the evolution of the surface layer. In the following the fitting procedure as well as the interpretation of the different components are explained in more detail.

The first C 1*s* spectrum of Fig. 1(b) (spectrum (1)) measured at 190 K displays three main components at BE of 282.56, 283.26 and 283.67 eV. While at a first sight only three components are visible, other two extra peaks at 283.06 and 283.83 eV have to be included in the fit in order to achieve a small residual with low modulation. This is confirmed by the fit of the spectrum measured in scanning mode with higher statistics (not shown) just after ethylene adsorption at 170 K before starting the TP-XPS experiment. One has to bear in mind that sharp, well-resolved core level components emerging in the C 1*s* spectra are not necessarily associated with non-equivalent C species, but are expected also because of vibrational excitations of C–H stretching modes in the final state. Hydrocarbons adsorption on transition metal surfaces often results in multi-component C 1*s* spectra related to this effect [16,19–21].

At higher temperature (spectrum (2)) the low BE components (A, shown in black) disappear and only the three higher binding energy peaks (B, shown in grey) are present, shifted by ∼30 meV to higher BE with respect to spectrum (1). The intensity behaviour of the different components as obtained from the analysis clearly indicates that the relative weights of the two peaks in the low BE region and of the three high BE components, are constant such that they behave as a doublet and a triplet, respectively. Let us discuss now what is the meaning of the individual peaks.