

## Surface Science Letters

# A comparative study of the interaction of nickel clusters with buckminsterfullerene, C<sub>60</sub>, and graphite

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Interaction of nickel deposited on multilayer films of C<sub>60</sub> has been investigated in comparison with that on amorphized graphite by employing photoemission spectroscopy. It is shown that unlike with graphite, Ni interacts strongly with C<sub>60</sub> causing large changes in C(1s) and C(2p) binding energies. The increase in the Ni(2p) binding energy at small Ni coverages is also far greater on C<sub>60</sub> than on graphite.

## 1. Introduction

Buckminsterfullerene, C<sub>60</sub>, owing its stability to the geodesic properties inherent in a truncated icosahedral hollow cage [1,2], provides an interesting substrate for the study of the interaction of transition metals such as Ni. Because of the unusual  $\pi$ -states and the large electron affinity of C<sub>60</sub> [3], we would expect it to interact with transition metals deposited on it. It is indeed known that the surface of C<sub>60</sub>, unlike that of graphite, gets readily oxygenated on exposure to oxygen [4]. Similarly, nitrogen adsorbs strongly on the surface of C<sub>60</sub> while there is no interaction with graphite [5]. We therefore considered it necessary to carry out a comparative study of the interaction of Ni with the surfaces of C<sub>60</sub> and amorphized graphite. For this purpose, we have examined the changes brought about in the core-level spectra and the valence bands on depositing Ni on these two substrates at different coverages. The study has indeed revealed that Ni interacts strongly with C<sub>60</sub> but not with graphite, an observation of possible relevance to heterogeneous catalysis.

## 2. Experimental

Buckminsterfullerene, C<sub>60</sub>, was prepared by contact-arc vapourization [6] using a locally fabricated generator [7] followed by purification by column chromatography [2,8]. The product was characterized by mass spectroscopy, <sup>13</sup>C NMR spectroscopy and UV-visible spectroscopy [2,7]. A solution of C<sub>60</sub> in *n*-hexane was allowed to evaporate on a gold foil giving a multilayer film of C<sub>60</sub>. An amorphized carbon surface was prepared by annealing polycrystalline graphite at 600 K, followed by sputtering with 6 kV Ar ions.

Electron spectroscopic measurements were carried out with a VG-ESCA 3 Mk II spectrometer fitted in a sample preparation chamber at a base pressure  $\sim 4 \times 10^{-10}$  Torr. AlK $\alpha$  (1486.6 eV) and He II (40.8 eV) radiations were employed for the XPS and UPS measurements respectively. Different coverages of nickel were deposited in situ at room temperature under UHV conditions in the preparation chamber of the spectrometer by resistive evaporation of high purity (99.9%) Ni metal wound on a tungsten filament which was thoroughly degassed. Core level C(1s) and Ni(2p) spectra were recorded for the different Ni coverages along with the He II va-

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lence band. The coverages of the Ni were quantified by means of the intensity of the Ni(2p<sub>3/2</sub>) feature,  $I_{Ni}$ , relative to that of the C(1s) signal of the support,  $I_C$ . The  $I_{Ni}/I_C$  ratios so obtained provide a measure of the amount of Ni deposited or the Ni cluster size. The surface coverage at the lowest  $I_{Ni}/I_C$  ( $\sim 0.1$ ) employed by us was  $5 \times 10^{13}$  atoms cm<sup>-2</sup> as estimated by the method of Carley and Roberts [9]; this corresponds roughly to 80 Ni atoms per cluster.

### 3. Results and discussion

We first examined the variation in the Ni(2p<sub>3/2</sub>) binding energy relative to bulk Ni (852.9 eV) with the Ni coverage in order to characterize the nature of the metal clusters deposited on the substrates. In fig. 1 we show plots of  $\Delta E$  Ni(2p<sub>3/2</sub>) against  $I_{Ni}/I_C$  on both C<sub>60</sub> and amorphized graphite substitutes. The  $\Delta E$  (2p<sub>3/2</sub>) increases with the decrease in  $I_{Ni}/I_C$  on the graphite surface; at the smallest coverage studied by us, the shift is around  $\sim 0.7$  eV. The increase in the 2p binding energy relative to the bulk accompanying

the decrease in the coverage or the cluster size, signifies the occurrence of a metal to non-metal transition. That is, at small Ni coverages, the deposited clusters are on average, non-metallic. The increase in the Ni(2p) binding energy with decrease in Ni coverage arises because the core-hole created in the photoemission process is more poorly screened in the small clusters compared to the bulk metal causing a reduction in the relaxation energy. What is noteworthy is that the increase in the Ni(2p) binding energy is significantly larger on the C<sub>60</sub> support than on graphite for an equivalent Ni coverage. Thus, at the smallest coverage,  $\Delta E$  Ni(2p<sub>3/2</sub>) is  $\sim 1.0$  eV on C<sub>60</sub>. This implies that the core-hole is more weakly screened on the C<sub>60</sub> substrate and is consistent with the fact that C<sub>60</sub> is less conducting than graphite.

When Ni is deposited on the amorphized graphite substrate no change occurs in the C(1s) binding energy of graphite at all coverages. However, when Ni is deposited on the C<sub>60</sub> support, we observe a progressive decrease in the C(1s) binding energy with increasing Ni coverage, showing a maximum shift of  $\sim 0.4$  eV at large Ni coverages (fig. 2). This observation suggests that as Ni is deposited on the C<sub>60</sub> film, the carbon

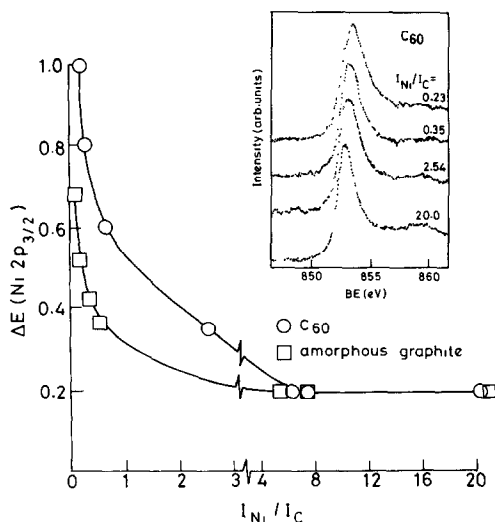


Fig. 1. Variation of the Ni(2p<sub>3/2</sub>) binding energy (relative to the bulk Ni value) with the Ni coverage ( $I_{Ni}/I_C$ ) on C<sub>60</sub> and amorphized graphite substrates. Each experimental point represents an independent measurement on a freshly deposited cluster. Inset shows Ni(2p<sub>3/2</sub>) spectra on C<sub>60</sub>.

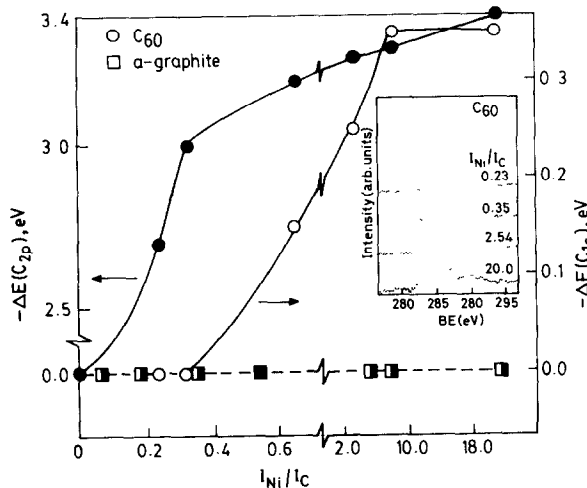


Fig. 2. Variation of the C(1s) and C(2p) binding energies of C<sub>60</sub> with Ni coverage ( $I_{Ni}/I_C$ ) relative to those of the clean substrate. Note that the C(1s) and C(2p) binding energies do not change with Ni coverage in the case of the graphite substrate. Inset shows C(1s) spectra of C<sub>60</sub> at different Ni coverages.

atoms acquire a slight negative charge. The C(1s) binding energy at high Ni coverages (284.5 eV) is slightly higher than that of carbidic carbon (284.2 eV).

In fig. 3, we show the evolution of the Ni(3d) band in the valence region with the increase in the coverage of Ni on an amorphized graphite substrate. The broad feature due to C(2p) is centered around 9.5 eV relative to  $E_F$ . The Ni(3d) band shifts to lower energies with increase in Ni coverage, but no additional features develop in the C(2p) region due to interaction of the graphite surface with Ni. However, when Ni is deposited on the C<sub>60</sub> film, we observe a feature derived from C(2p) at a lower binding energy (fig. 4). The position of this feature progressively shifts to lower binding energy with the increase in Ni coverage. We suggest that this new C(2p) feature arises from the interaction of Ni atoms with C<sub>60</sub>. In the case of the C<sub>60</sub> substrate also, the Ni(3d) band shifts to higher binding energies with decrease in Ni coverage. In the inset of fig. 4 we

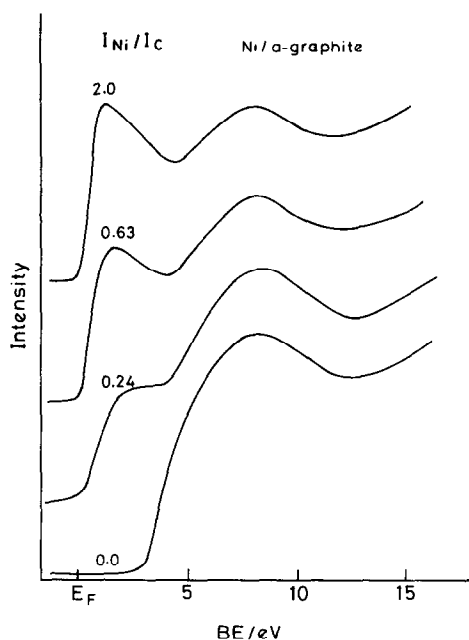


Fig. 3. He II valence band spectra of Ni clusters deposited on amorphized graphite at different coverages. All spectra are normalized to equal height at the top of C(2p) band of the blank graphite substrate.

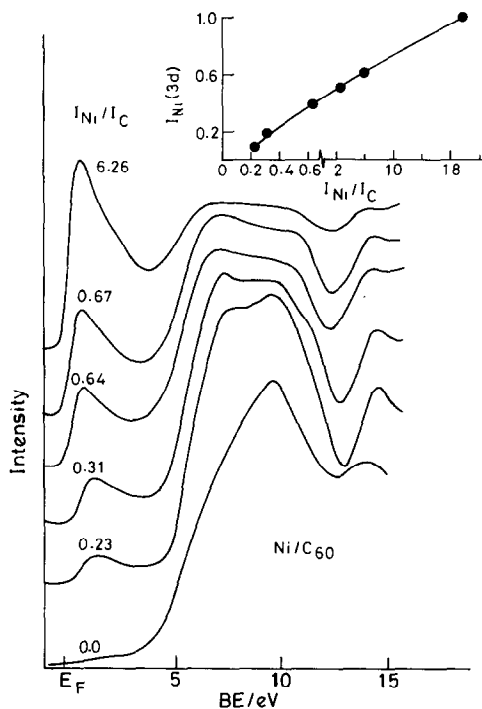


Fig. 4. He II valence band spectra of Ni clusters deposited on a multilayer C<sub>60</sub> film. Note that the new C(2p) feature moving towards lower binding energy with increase in Ni coverage. Inset shows the variation of the intensity of the Ni(3d) band with  $I_{Ni}/I_C$ .

show the variation of the Ni(3d) band intensity with Ni coverage; we see that the intensity approaches zero at the smallest coverage showing the cluster size to be very small.

In fig. 2 we have plotted the shift in the binding energy of the new C(2p) feature (relative to the binding energy of 9.5 eV of pure C<sub>60</sub>) against the Ni coverage. We notice that it shifts by  $\sim 3.4$  eV at large coverages. The progressive decrease in the binding energies of the C(1s) and the C(2p) levels on the C<sub>60</sub> surface with the increase in  $I_{Ni}/I_C$  as well as the higher Ni(2p<sub>3/2</sub>) binding energies on C<sub>60</sub> imply that at low coverages, the Ni atom forms a "complex" with the  $\pi$ -system of C<sub>60</sub>. With increase in Ni coverage, more  $\pi$ -bonds of C<sub>60</sub> interact with the metal atoms giving rise to the observed shifts in binding energies. These results suggest a likely role for C<sub>60</sub> in heterogeneous catalysis.

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