

A photoelectron spectroscopic study of the interaction of oxygen, nitrogen and transition metals with C₆₀ films

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Evidence is presented for the strong interaction of oxygen and nitrogen with solid films of buckminsterfullerene based on core-level spectroscopic studies. Cr, Ni and Cu deposited on C₆₀ films interact strongly giving rise to large changes in the C(1s) and C(2p) binding energies as well as the (2p) binding energies of the transition metals.

The chemistry of buckminsterfullerene, C₆₀, has attracted world-wide attention in the last few months. C₆₀ exhibits many novel properties. It undergoes facile one-electron reduction to give various anionic species^{1,2} and produce singlet oxygen with high quantum yields³. It is reported that C₆₀ gets oxidised by solid O₂ on exposure to low or high energy photons⁴. Interaction of C₆₀ with N₂ has not been studied hitherto although one would expect interesting adsorbed species to be formed on the surface, considering that strongly bound molecular species with a bond order between 1 and 2 have been found on a carbided Ni surface^{5,6}. We have studied the interaction of N₂ with multilayer C₆₀ films by employing X-ray photoelectron spectroscopy. For the purpose of comparison, we have examined the interaction of O₂ with C₆₀ films. We have also investigated the interaction of chromium, nickel and copper clusters deposited on C₆₀ films, since we felt that transition metal atoms may bind strongly by the π system of C₆₀. We have employed core-level spectra of the transition metal and C₆₀ as well as the valence bands to examine the C₆₀-transition metal interaction.

Materials and Methods

C₆₀, prepared by the contact-arc vapourization of graphite in a He atmosphere by employing a locally fabricated generator⁷, was purified by chromatography⁸ and the identity ascertained by mass spectrometry, UV-visible spectroscopy and ¹³C NMR spectroscopy. Layers of C₆₀ were deposited on a polycrystalline Au foil. Photoelectron spectra were recorded with a VG ESCA 3 MkII spectrometer fitted with a sample preparation

chamber, by employing Al K α (1486.6 eV) or HeII (40.8 eV) radiation under an operating vacuum of $\sim 4 \times 10^{-10}$ torr. The C(1s), O(1s) and N(1s) binding energies were referenced with respect to the Au(4f) binding energy (84.0 eV). The C₆₀ films were exposed to N₂ and O₂ under different conditions in the sample preparation chamber. Different coverages of Ni, Cr or Cu were deposited on the C₆₀ film by resistive evaporation of the metal, the quantity deposited being determined by the I_M/I_C intensity ratio (of the transition metal 2p_{3/2} and C 1s levels). For the purpose of comparison we have examined all these systems by employing amorphized graphite substrate.

Results and Discussion

Nitrogen

In Fig. 1 we show the N(1s) spectrum of N₂ adsorbed on a multilayer film of C₆₀ at 80K. We observe a single sharp feature around 400.6 eV, unlike N₂ adsorbed on most transition metal surfaces (in the γ -state⁶) wherein two relatively broad features around 401 eV and 405 eV are generally found due to the screened and the unscreened final states respectively⁶. A single N(1s) feature in the 399-400 eV range is found on transition metal surfaces when N₂ is strongly chemisorbed in the α -state⁶ with a N-N bond order between 1 and 2. We believe that the N(1s) peak around 400.6 eV found at 80K on the C₆₀ films is due to a strongly chemisorbed molecular species, I, the sharpness of the feature being suggestive of the presence of a well-defined single species (Note that graphite does not interact with N₂ at 80K or 300K). The absence of a feature due to the unscreened state also suggests that the N₂ species

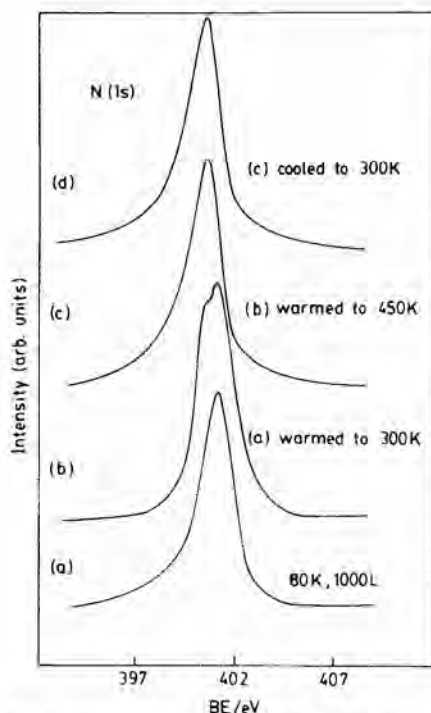


Fig. 1—N(1s) spectra of N₂ adsorbed on C₆₀.

does not desorb even at 300K, unlike the weakly chemisorbed γ -species on transition metal surfaces which desorbs well below 300K. The N(1s) spectrum at 300K (Fig. 1) also shows the emergence of a new sharp feature at a lower binding energy (400.2 eV). This would represent another chemisorbed state, II, of N₂ on C₆₀. On warming at 450K, we only see the 400.2 eV feature indicating that species I completely transforms to II. We consider the occurrence of such chemisorbed states of N₂ on C₆₀ to be most interesting. It is possible that the structure of this species is one where a weakened N-N bond (1.3-1.4 Å long) is lying side-on on a C-C bond of C₆₀. We have not found any evidence for the formation of dissociated nitrogen species on C₆₀ up to 450K.

Oxygen

Unlike in the case of N₂, C₆₀ films exposed to oxygen or air (without any special irradiation) show evidence for reactive interaction with a O(1s) feature around 532.5 eV at 300K (Fig. 2) due to oxygenated C₆₀, probably involving an epoxide-like linkage as in graphitic oxide, rather than a carbonyl function. Accordingly, the 532.5 eV feature remains on the surface even at 450K. Graphite itself does not interact with oxygen at 300K; oxidation of graphite occurs only on interaction with atomic oxygen or oxygen plasma⁹. It is likely that the oxidation of C₆₀ probably occurs

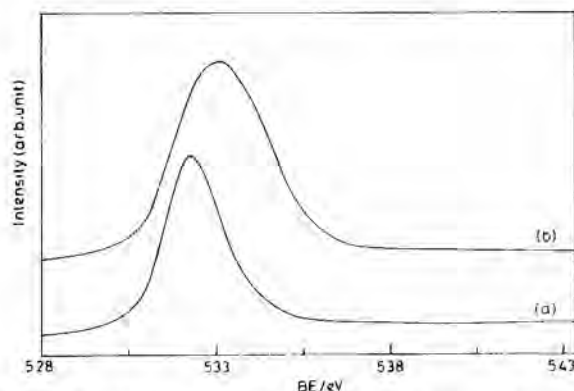


Fig. 2—O(1s) spectrum of O₂ adsorbed on C₆₀: (a) C₆₀ film exposed to oxygen at 300K; (b) O₂ adsorbed at 80K in (a) showing physisorbed species; on warming to 300K spectrum (a) is found again.

through the O₂⁻ species¹⁰ (O 1s, 534.2 eV) initially formed on the surface on adsorption of O₂ at low temperatures; the O₂ species disappears below 200K from the surfaces of clean as well as oxygenated C₆₀.

Nickel

As mentioned earlier, the coverages of the Ni were quantified by means of the intensity of the Ni(2p_{3/2}) 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 size¹¹. The surface coverage at the lowest I_{Ni}/I_C (~ 0.1) employed by us was 5 × 10¹³ atoms cm⁻² as estimated by the method of Carley and Roberts¹²; this corresponds roughly to 80 Ni atoms per cluster.

We first examined the variation in the Ni (2p_{3/2}) 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. 3 we show plots of ΔE Ni (2p_{3/2}) against I_{Ni}/I_C on both C₆₀ and amorphized graphite substrates. The ΔE (2p_{3/2}) increases with the decrease in I_{Ni}/I_C on the graphite surface; at the smallest coverage studied by us, the shift is around ~ 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

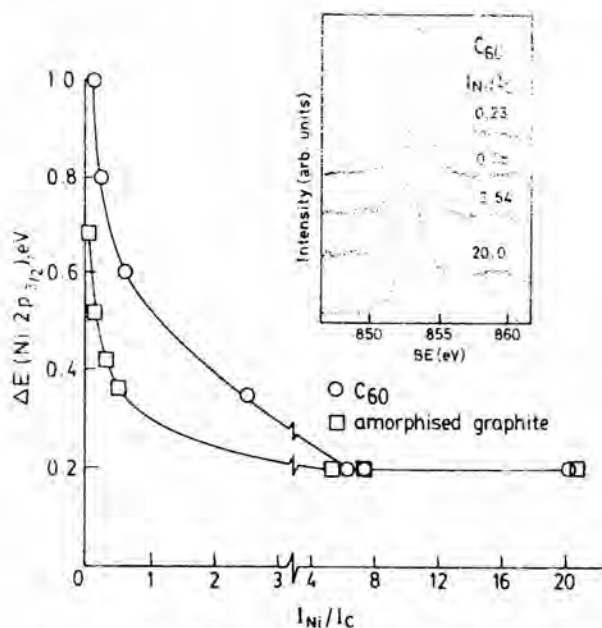


Fig. 3—Variation of the Ni($2p_{3/2}$) binding energy (relative to the bulk Ni value) with the Ni coverage (I_{Ni}/I_C) on C_{60} and amorphized graphite substrates. Each experimental point represents an independent measurement on a freshly deposited cluster. Inset shows Ni($2p_{3/2}$) spectra on C_{60}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

the Ni($2p$) binding energy is significantly larger on the C_{60} support than on graphite for an equivalent Ni coverage¹³. Thus, at the smallest coverage, ΔE Ni ($2p_{3/2}$) is ~ 1.0 eV on C_{60} . This implies that the core-hole is more weakly screened on the C_{60} substrate and is consistent with the fact that C_{60} 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_{60} support, we observe a progressive decrease in the C(1s) binding energy (relative to the value of 284.9 eV of C_{60}) with increasing Ni coverage, showing a maximum shift of ~ 0.4 eV at large Ni coverages (Fig. 4). This observation suggests that as Ni is deposited on the C_{60} film, the carbon atoms acquire a slight negative charge¹³. The C(1s) binding energy at large Ni coverages (284.5 eV) is slightly higher than that of carbidic carbon (284.2 eV).

In Fig. 5, 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. This new C($2p$) feature is considered the C($2p$) region due to interaction of the graphite surface with Ni. However, when Ni is deposited

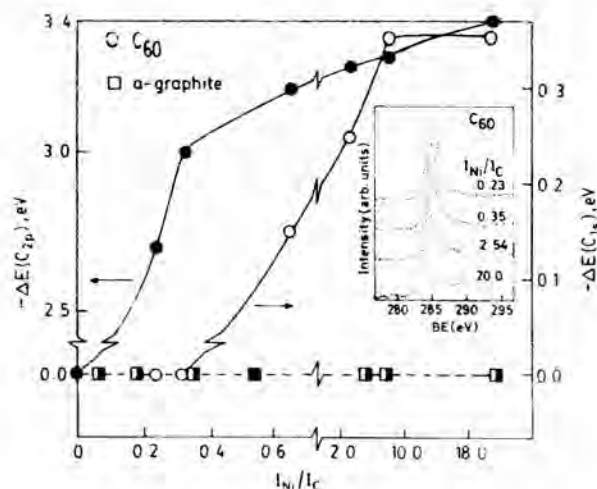


Fig. 4—Variation of the C(1s) and C(2p) binding energies of C_{60} with Ni coverage (I_{Ni}/I_C) relative to those of the clean substrate. Note that the C(1s) and C(2p) binding energies do not change with Ni coverage in the case of the graphite substrate. Inset shows C(1s) spectra of C_{60} at different Ni coverages.

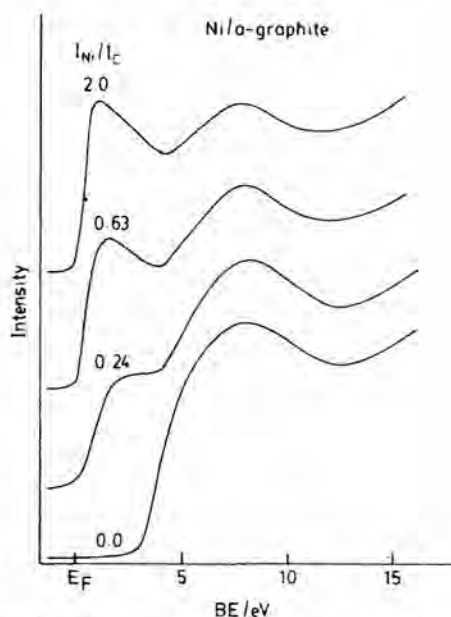


Fig. 5—HeII valence band spectra of Ni clusters deposited on amorphized graphite at different coverages. All spectra are normalized to equal height at the top of C($2p$) band of the blank graphite substrate.

on the C_{60} film, we observe a feature derived from C($2p$) at a lower binding energy (Fig. 6). The position of this feature progressively shifts to lower binding energy with the increase in Ni coverage. This new C($2p$) feature is considered to result from the interaction of Ni atoms with

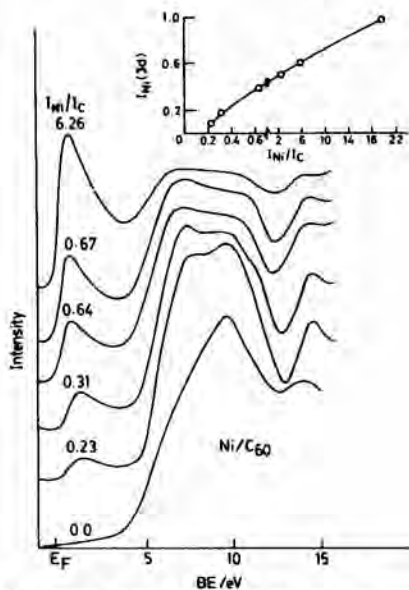


Fig. 6—HeII valence band spectra of Ni clusters deposited on a multilayer C₆₀ film. Note the new C(2*p*) feature moving towards lower binding energy with increase in Ni coverage. Inset shows the variation of the intensity of the Ni(3*d*) band with I_{Ni}/I_C .

C₆₀¹³. In the case of the C₆₀ substrate also, the Ni(3*d*) band shifts to higher binding energies with decrease in Ni coverage. In the inset of Fig. 6 we show the variation of the Ni(3*d*) 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. 4 we have plotted the shift in the binding energy of the new C(2*p*) feature (relative to the binding energy of 9.5 eV of pure C₆₀) against the Ni coverage. We notice that it shifts by ~ 3.4 eV at large coverages. The progressive decrease in the binding energies of the C(1*s*) and the C(2*p*) levels in the C₆₀ surface with the increase in I_{Ni}/I_C as well as the higher Ni (2*p*_{3/2}) binding energies on C₆₀ imply that at low coverages, the Ni atom forms a "complex" with π -system of C₆₀. With increase in Ni coverage, more π -bonds of C₆₀ interact with the metal atoms giving rise to the observed shifts in binding energies.

Chromium and copper

In Fig. 7 we show the variation of the shift in the Cr(2*p*_{3/2}) binding energy, ΔE , relative to the bulk metal (574.3 eV) with Cr coverage on both C₆₀ and amorphized graphite substrates. The shift increases with decrease in coverage or cluster size. Furthermore, the shift is much larger on C₆₀ than on amorphized graphite for any given coverage. The maximum ΔE found for the smallest coverage studied by us is around 1.2 eV. This

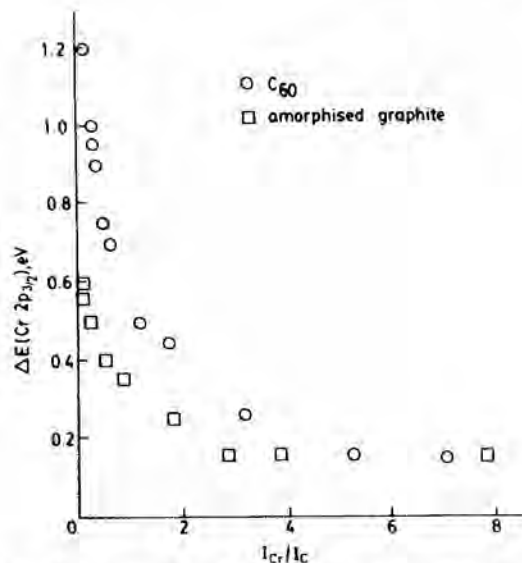


Fig. 7—Variation of the Cr(2*p*_{3/2}) binding energy (relative to bulk Cr) with Cr coverage I_{Cr}/I_C on C₆₀ and amorphized graphite substrates.

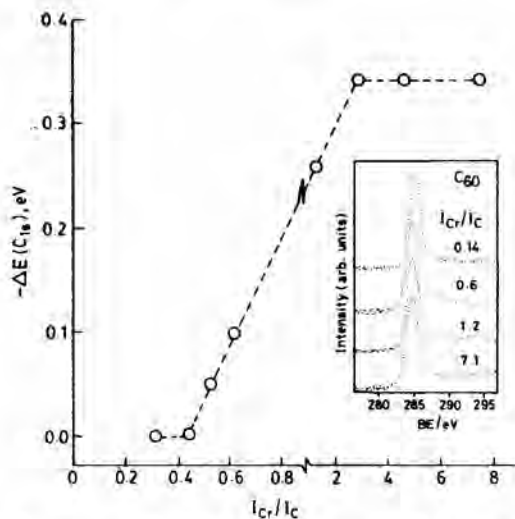


Fig. 8—Variation of C(1*s*) binding energy of C₆₀ with Cr coverage (I_{Cr}/I_C) relative to the clean substrate. In the inset we show C(1*s*) spectra.

shift is larger than that found with Ni (Fig. 3). The C(1*s*) binding energy of C₆₀ also shifts progressively to lower binding energies with increasing Cr coverage showing a maximum shift of ~ 0.35 eV for large Cr coverage (Fig. 8). In the inset of the Fig. 8, we have shown the C(1*s*) spectra of C₆₀ for different coverages of Cr. It appears that the interaction of Cr with C₆₀ is similar to that of Ni, involving strong metal-carbon bonding.

We have also studied the interaction of C₆₀ films with Cu at different coverages. Here again

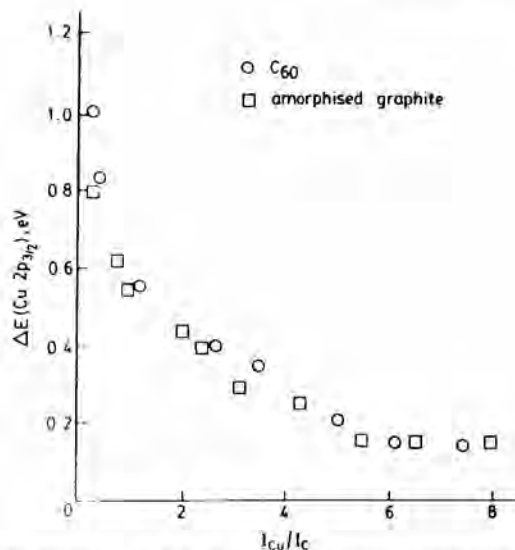


Fig. 9—Variation of Cu($2p_{3/2}$) binding energy (relative to bulk Cu) with Cu coverage (I_{Cu}/I_C) on C_{60} and amorphized graphite substrates.

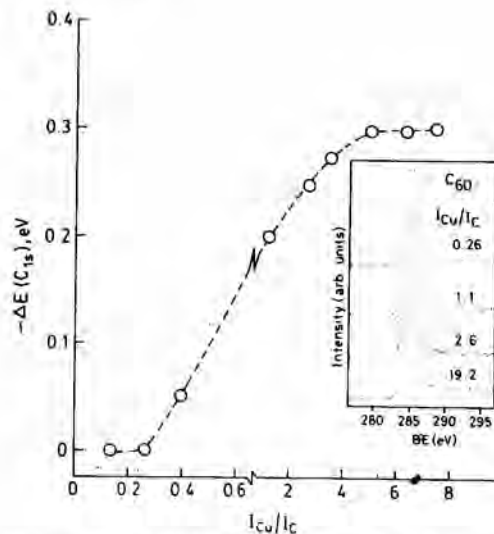


Fig. 10—Variation of C($1s$) binding energy of C_{60} with Cu coverage (I_{Cu}/I_C). In the inset we show C($1s$) spectra.

we find large shifts in the Cu($2p_{3/2}$) binding energies relative to the bulk metal (933.1 eV) with the decrease in Cu coverage. In Fig. 9, we show the shifts of $2p_{3/2}$ binding energy for various coverage of Cu deposited on C_{60} as well as amorphized graphite supports. In the case of Cu, unlike with Ni and Cr, we see little difference with the two supports. The C($1s$) binding energy of the C_{60} however decreases by ~ 0.3 eV for the highest Cu deposition (Fig. 10) suggesting strong interaction between Cu clusters and C_{60} . The present study on the interaction of Ni, Cr and Cu clusters with C_{60} shows the interaction to be uniformly strong and suggests that C_{60} may have a role in heterogeneous catalysis¹³.

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