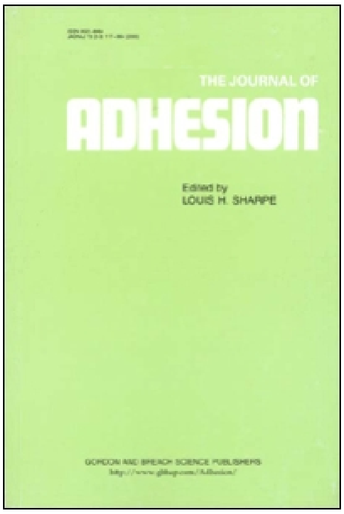

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Influence of the Electronic Structure of the Metal at the Polymer/Metal Interface: A Tentative Interpretation on the Basis of Lewis Acid-Base Reactions

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Influence of the Electronic Structure of the Metal at the Polymer/Metal Interface: A Tentative Interpretation on the Basis of Lewis Acid-Base Reactions*

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In the present paper, we examine the link between theoretical qualitative predictions made on the grounds of the Lewis acid-base concept and the actual interface built between polyamide-6,6 (PA-6,6) and copper, and PA-6,6 and platinum. By using a combination of very-surface-sensitive photoemission spectroscopies and model polymers, it becomes possible to obtain important information about the chemical nature of the polymer/metal interface. Our experiments show a complete dissociative chemisorption of the polymer on Pt, while PA-6,6 retains its chemical integrity on copper.

Keywords: Polymer/metallic surface interaction; regioselectivity; Lewis acid-base interactions; density functional theory (DFT); surface analysis (XPS, UPS)

INTRODUCTION

The thorough characterization of the interfacial region between a metal and an organic polymer has long been a goal in surface science. This stems from the peculiar role played by the metal/polymer interface in

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complex phenomena of technological interest such as adhesion or lubrication [1]. Towards this aim, a need for precise analytical techniques focusing on the interface region and – as far as possible – predictive models has emerged. In this last field, the concept of acids and bases brought about by Lewis at the beginning of the century has been paid some attention [2–5]. This concept states that significant predictive information on the nature of molecular interactions can be gained from the knowledge of isolated systems, and of isolated systems only (*i.e.* prior to their actual interactions). In the field of polymer/metal interactions, this approach is very appealing as it opens the hope towards an *a priori* estimation of the physicochemical behavior of complex polymer/metal assemblies.

In the present paper, we examine the link between theoretical qualitative predictions made on the ground of the Lewis acid-base concept and the actual interface built between polyamide-6,6 (PA-6,6) and copper, and PA-6,6 and platinum. For this purpose, we have designed an integrated installation in which the "reactants" are built, brought into contact and the resulting interface analyzed under ultrahigh vacuum (UHV). Practically, the successive polymer layers are deposited on the metallic substrate by condensation from a melted polymer phase. The resulting samples are characterized using X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS, respectively). This procedure enables a step-by-step following of the growth of the interfacial polymer/metal region. As regards the tentative theoretical modeling of these two metal/polymer interactions, we make use of the fairly recent point of view brought about by the Density Functional Theory (DFT) on the Lewis acid-base concept [6–11]. In short, this model states that: (i) the hardness, η, of the two interacting systems indicates in a relative way the overall predominant nature of the interactions: electrostatic interactions are likely to predominate between "hard" (large η) systems, while charge transfer is the major component between "soft" (low η) systems; (ii) as far as the charge transfer is the major component, the sign of the electron transfer is driven by the difference between the respective chemical potentials, μ, of the two systems: the one of highest μ is the Lewis base (the electron donor), the one with the lowest μ being the Lewis acid (*i.e.* the electron acceptor) [6]; (iii) in the case of an interaction driven by the electronic transfer, the regio-selectivity of the interaction can be determined by the localization of the most intense regions of the Fukui functions $f(r)$ of the two systems [6].

Practically, η, μ and $f(\vec{r})$ for the polymer can be computed from a molecular model. We estimate these quantities on the *N*-methylformamide molecule, which retains the main characteristics of the potentially reactive centers of PA-6,6 *i.e.* the amide group. For the metals, it has been shown that $\mu = -\Phi$, where Φ is the work function of the metal, and $\eta = 1/2\ g(e_F)$ where $g(e_F)$ is the density of occupied states (DOS) at the Fermi level of the metal [7]. As mentioned previously, it is important to recall that the DFT point of view on the Lewis acid-base concept is restricted to the initial steps of the interaction (the so-called non-crossing assumption): the attempt is clearly to "feel" the reaction path as far as possible with the electronic and geometric characteristics of the reactants forced to remain in their unperturbed situation [11]. The purpose of the present work is, thus, to examine whether or not this approach is licit in the instance of PA-6,6/Cu and PA-6,6/Pt interactions.

EXPERIMENTAL

The experiments are carried out in a multitechnique ultrahigh vacuum (UHV) chamber equipped with a sample entry followed by a preparation chamber. This chamber is coupled together with an interaction reactor and an analysis chamber. Figure 1 shows a schematic view of this installation.

PA-6,6 (Aldrich Chemical Co.) dehydrated prior to use (2 hours storage at 100° C under primary vacuum) is introduced in a quartz crucible placed on a heating plate in the interaction reactor. An Alumel-Chromel thermocouple immersed in the melting pot allows a measure of the actual temperature inside the crucible and, thus, the regulation of the melting temperature at ± 2°C using a temperature controller. After outgassing, the polymer is heated to its melting point (280°C) and the metallic substrates are exposed to the chemical vapors during a chosen time. Samples are subsequently transferred *in vacuo* into the attached spectroscopy chamber which is kept at a pressure of 1.33×10^{-8} Pa. A more detailed experimental procedure will be found in a forthcoming paper [12].

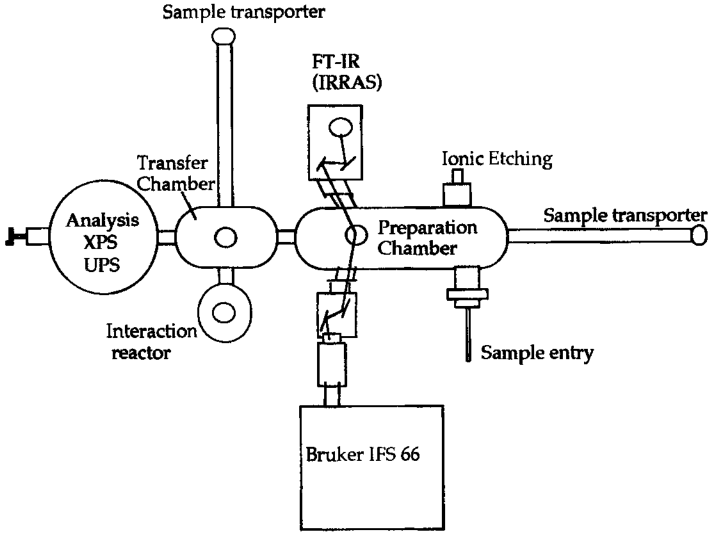

FIGURE 1 Schematic view of the ultrahigh vacuum installation.

The various surfaces and interfaces are characterized by XPS using a Vacuum Generator ESCALAB 210 spectrometer with a monochromatic Al Kα X-ray source (1486.6 eV) radiation. The electronic structures are analyzed by UPS with the He II line (40.8 eV). All spectra of metallic substrates and interfacial samples are referenced to the Fermi level (E_F) of the bare metal surface after ionic etching. Our coatings are thin enough to be charge free.

The metallic substrates are prepared outside the UHV installation. Copper and platinum surfaces are obtained, respectively, by evaporation from a copper (Marz 99.99%)-plated tungsten wire on 2 cm^2 glass plates while platinum substrates are obtained by cathodic pulverisation on 2 cm^2 glass plates. The samples are then directly transferred into the preparation chamber where they are etched (Ar$^+$, 5 keV, 2 minutes). The etching treatment is completed for platinum substrate by heating (230°C) to eliminate carbon contamination. The surfaces are then free of contaminants (in particular free of H_2O, hydrocarbons, fatty acids...). The UPS spectrum of the working copper surface after ionic etching (Fig. 2a) is characterized by a peak centred on 2.5 eV below the Fermi level and a shoulder at 3.34 eV attributed to the degenerated

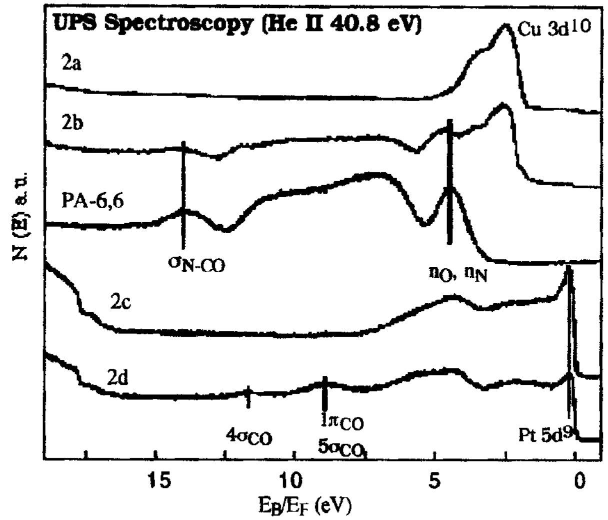

FIGURE 2 UPS spectra (He II, 40.8 eV) of: -a- atomically clean copper substrate after etching (Ar^+, 5KeV, 2 minutes); -b- deposited coating at the interface on copper; -c- atomically clean platinum substrate after etching (Ar^+, 5KeV, 2 minutes) and heating (230°C); -d- deposited coating at the interface on platinum.

$3d^{10}$ levels of the metal. The levels of copper oxide are absent. The spectrum of the working platinum surface after ionic etching and heating corresponds (Fig. 2c) with an atomically clean surface [13] and is characterized by a peak centred on 0.2 eV below the Fermi level and the two shoulders at 2.1 eV and 4.85 eV. The general structure can be attributed to the 5d and 6s levels of the metal [14,15].

EXPERIMENTAL RESULTS

We first examine a whether or not the melting of the polymer induces chemical modifications. No chemical modifications were detected on the IR spectra of the PA-6,6 contained in the crucible and recorded before and after several heating cycles to its melting temperature. The evaporated phase, in the bulk, has a structure equivalent to polyamide [16] and suggests that the polymer does not undergo any degradation after melting. An attribution of the various structures present on the

UPS spectrum (Fig. 3) of the evaporated film was made with the help of *ab-initio* calculations on small model molecules (*N*-methylformamide, *N*-methylacetamide and *N*-methylpropylamide [17]), those molecules being representative of the functional structure (secondary amide) of PA-6,6 molecules. On this spectrum, we shall merely point out the peak emerging at 14.2 eV. This is characteristic of the functional amide group and is attributed to the σ_{N-CO} orbital. Thus, it will be a probe to follow whether or not the amide linkage is affected by the interactions with the substrate.

In order to study the various steps leading to the formation of a polymer film, coatings of different thickness were deposited by varying the time of exposure. At times lower than or equal to 15 s, the films have a thickness smaller than 3 nm (the limit of escape depth for UPS analysis). Under these conditions, we can investigate more precisely the interfacial polymer/metal region. The comparison of the O 1s, N 1s and C 1s core-levels photoelectron spectra of the evaporated coating on copper and platinum at the interface and in the bulk (insert) is shown in Figures 4 and 5. The O 1s interfacial spectrum on copper (Fig. 4a) exhibits a peak at the same binding energy (531.34 eV) as in the bulk and corresponding to the carbonyl oxygen atoms in Pa-6,6 [16]. This result indicates that the carbonyl group does not react with copper atoms. In the N 1s region (Fig. 4b), on the side of the main

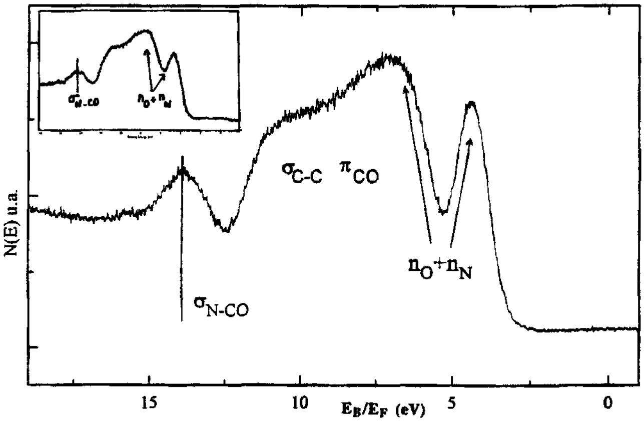

FIGURE 3 UPS spectrum (He II; 40.8 eV) of the bulk of the deposited film (50 nm thick) from the melted polymer on copper substrate. Insert: UPS spectrum of the unevaporated polymer.

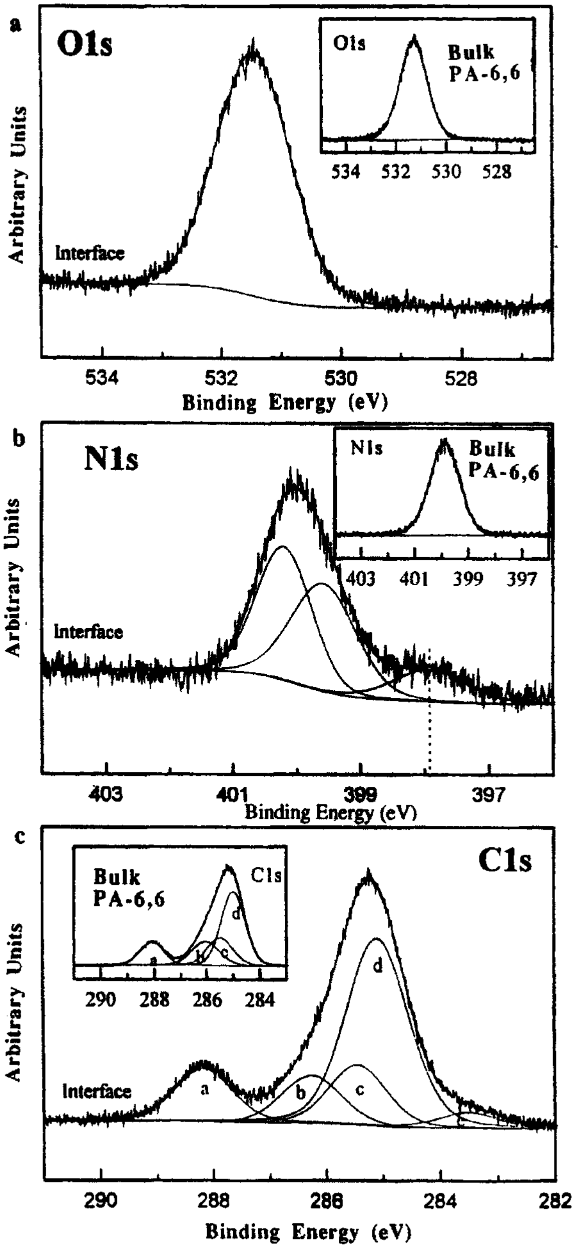

FIGURE 4 XPS spectra (Al Kα 1486.6 eV, monochromatized) of the core levels of the deposited coating at the interface on copper: -a- O 1s photopeak; -b- N 1s photopeak; -c- C 1s photopeak. Insert: core levels of the bulk polymer (50 nm thick).

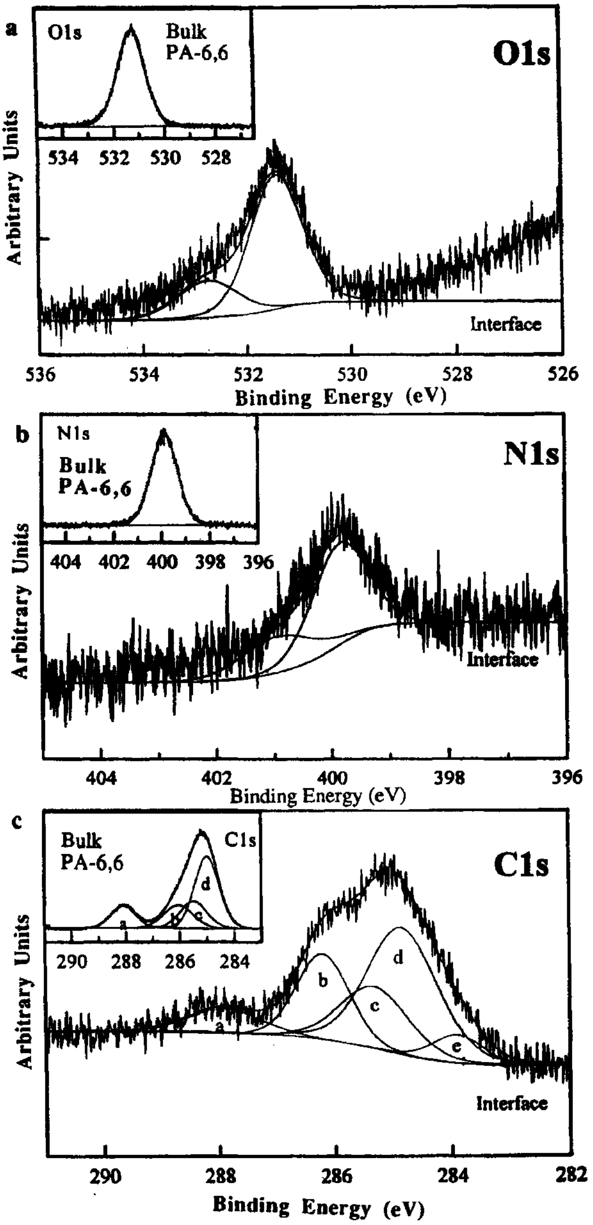

FIGURE 5 XPS spectra (Al Kα 1486.6 eV, monochromatized) of the core levels of the deposited coating at the interface on platinum: -a- O 1s photopeak; -b- N 1s photopeak; -c- C 1s photopeak. Insert: core levels of the bulk polymer (50 nm thick).

peak centered at 399.8 eV, for the polymer/metal interface, new components appear at lower binding energies that we assign to nitrogen atoms in interaction with copper. The deconvoluted C 1s spectrum of the evaporated film shows the same features at the interface as in the bulk but, for the interfacial region (Fig. 4c), we need of an additional peak at lower energy (283.5 eV) to idealize line shapes. This low binding energy contribution can be attributed to an electron-rich carbon resulting from an interaction between the carbon atoms and the copper surface.

The UPS spectra of the coating obtained on copper after 15 s exposure exhibit an electronic structure which can be interpreted as the superposition of the electronic structures of bulk polymer and metal (Fig. 2b). In particular, we see the σ_{N-CO} level at 14.2 eV, which constitutes a probe of the structural integrity of PA-6,6.

The XPS survey recorded on the thinnest coating on Pt indicates that the atomic ratios C:O:N correspond to the stoichiometry 4:1:0.5 and not to the classical 6:1:1 PA-6,6 stiochiometry. In contrast to what we observed on copper for the same experimental conditions, the decomposition of O 1s interfacial spectrum on Pt (Fig. 5a) exhibits two peaks: one at a binding energy of 531.34 eV corresponding to the carbonyl oxygen atoms in PA-6,6 and a second at a higher binding energy (532.76 eV). This one can be related to oxygen atoms from carbonyl moieties adsorbed on a platinum surface [18]. The decomposition of the N 1s spectrum recorded on the interfacial region (Fig. 5b) is fitted correctly with two components: one corresponding to nitrogen atoms of the unperturbed amide function (399.8 eV) and another (400.62 eV) which we attribute to the cleavage of the macromolecules leading to the adsorption of N_xH_y species [19]. This situation differs from what we observe on copper for which the N/Cu interactions lead to a lower binding energy. The C 1s photopeak is very different in the interfacial region (Fig. 5c) compared with the bulk polymer. Firstly, it is necessary to introduce a supplementary component at low binding energy (284.0 eV) to describe the peak fully. This suggests a C-Pt interaction between hydrocarbon moieties and platinum substrate. Secondly, the relative percentages of the different components of the peak are not in the ratio—$\underline{C}H_2/\underline{C}H_2$—CO/$\underline{C}H_2$—NCO/—$\underline{C}$O: 3:1:1:1 anymore as it was in the bulk polymer and on copper but in the ratio 5:2:5:2.5:1. This suggests again the breaking of the amide function of the macromolecule and the preferential adsorption of carbonyl and nitrogen-containing moieties in the very close vicinity of the metallic surface.

The UPS spectrum of the coating obtained on platinum after 15 s exposure and recorded on the side of the sample (Fig. 2d) exhibits an electronic structure quite different from that of bulk PA-6,6. Indeed, we observe the disappearance of the peak at 14.2 eV due to the σ_{N-CO} orbital. Moreover, we distinguish, on the side of the metallic levels, two other structures at 8.95 eV and 11.72 eV which can not be attributed either to the metal or to PA-6,6 levels. On the other hand, those new structures compare favorably with those observed for the adsorption of CO on Pt (111) and correspond to $5\sigma/1\pi$ and 4σ orbitals, respectively [20]. The structure between 4.3 to 6.0 eV reveals, in addition to metallic levels, structures which can be assigned to nitrogen moieties like N_xH_y (n_N: 5.6 eV [19]). It is impossible, however, to identify these exactly. All these observations fully agree with XPS results and suggest that the macromolecule breaks in contact with the platinum substrate and, more specifically, that it is the amide linkage which is broken.

THEORETICAL PROPOSALS VERSUS EXPERIMENTAL RESULTS

Some indications on the first steps of the molecule/metal interactions can be put forth from Lewis acid-base concepts [9,11]: as regards the chemical potentials (μ) of the metallic substrates ($\mu_{Cu} = -4.8$ eV, $\mu_{Pt} = -5.6$ eV) and of the organic phase (μN-methylformamide $= -6.0$ eV), both metals act as Lewis bases towards the organic molecule and copper is more basic than platinum. But, copper bears a filled d-band and has a lower DOS than platinum which has an unfilled d-band. In Lewis acid-base therminology, copper is harder than platinum; this means that its interaction with PA-6,6 is more driven by electrostatic interactions than in the case of platinum, for which the charge transfer component is the dominant term. As far as the overall reactivity can be predicted by such an examination of the first steps of the interaction (the so-called non-crossing assumption) one can predict a plainer chemical modification on platinum than on copper.

Let us now examine the regioselectivity of the interaction. An examination of the Fukui function-as-an-acid of *N*-methylformamide (Fig. 6) [12] indicates that two reactive acidic (in the Lewis sense) sites are present on the secondary amide: the proton of the amide function and the carbonyl carbon (in this order). Thus, the Lewis acid-base interactions are likely to take place between metallic sites/amide protons and/or metallic sites/carbonyl carbon. These interactions constitute the preliminary steps of chemical reactions which can be recognized as a Brønsted proton-exchange reaction (between the amide groups and the metallic surfaces) and a nucleophilic addition (to the carbonyl group), respectively. Thus, the Lewis acid-base approach predicts that the Brønsted acid-base (*i.e.* proton exchange) is the most favorable reaction, and that the nucleophilic addition to the carbonyl groups of PA-6,6 is the other alternative. One can note that this nucleophilic addition involves a significant charge transfer necessary to shift the carbonyl carbon from sp^2 to sp^3, in a way similar to the basic hydrolysis of amides in solution [21].

If we now compare our theoretical predictions with experiment, we see that the Brønsted surface reaction is fairly well compatible with: (i) the gaseous H_2 production observed upon deposition PA-6,6 on copper

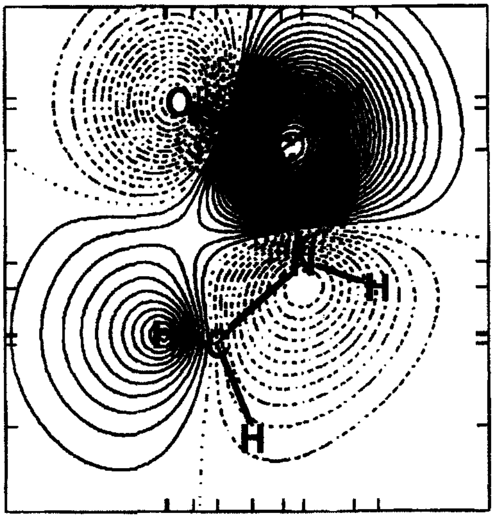

FIGURE 6 Isocontour plots of the Fukui function, as an acid, of *N*-methylformamide [17].

and coming from the protons abstracted from PA-6,6; and (ii) the low-energy N 1s contribution stemming probably from an adsorption of the conjugate Brønsted base (R—N$^-$—(C=O)—R′) on the Cu surface. The chemical integrity of PA-6,6 which is preserved on the Cu surface indicates that the nucleophilic addition does not occur.

As regards platinum the H_2 evolution is harder to trace, as many compounds desorb from the surface upon deposition. However, the result of a final surface covered with CO is consistent with an initial nucleophilic attack of a metallic site to the C=O; this initial reaction leads to transient species which undergo further chemical reactions. One should note that the relative behavior of both metals is consistent with their respective propensity to be involved in large charge transfer, as indicated by their relative hardness. Our experiments tend to confirm this view, showing complete dissociative chemisorption of the polymer on Pt, while PA-6,6 retains its chemical integrity on copper. When the surface reactivity of platinum is neutralized by the adsorption of CO and nitrogen-containing moieties, the polymer grows without degradation. This layer can be considered as a picture, at the molecular scale, of a least cohesive phase at the interface between two materials.

CONCLUSION

The experimental methodology used enables us to detail the evolution of the interfacial chemical structure of PA-6,6 on copper and platinum. It appears that the two ($\mu, f(r)$) parameters we have put forward are relevant to describe and monitor the course and the extent of electronic charge transfer between a metallic surface and an organic molecule. Here, we only compare the reactivity of a given molecule towards two different metallic surfaces. The present work contributes to the illustration of the peculiar role of the DFT chemical potential and Fukui functions in describing surface acid-base reactions. We hope this will contribute to a better understanding of interface reactions.

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