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Structure and Bonding between an Aryl Group and Metal Surfaces

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Merging different branches of chemistry into a new avenue of research always generates great enthusiasm and interest among chemists. Using aryldiazonium salts to graft single or multiple layers of aryl groups onto carbon, semiconductor, and metal surfaces exemplifies this idea. In this case, the well-established organic chemistry of diazonium ions was applied to an electrode, and the resulting surface chemistry generated an exciting new area of exploration.[1] Recent work by Tour and co-workers[2] forwent the electrochemical cell and employed spontaneous grafting, which advanced this field to a new level. Potential applications of these methods range from functionalization of carbon nanotubes[3] and porous carbon[4] to molecular electronics[5] and metal protection.[6]

Metals that were aryl-grafted by diazonium salts so far include Fe, Co, Ni, Pd, Pt, Zn, Cu, and Au.[1,2] This list is expected to grow quickly in the next few years. A covalent bond between an aryl group and a nonmetal surface, such as glassy carbon or silicon, can be easily visualized, but the nature of the bond on a metal surface is subject to current debate. The polycrystalline nature of the metal samples examined by grafting has made definitive evidence difficult to obtain. On the other hand, surface scientists have prepared C_6H_5 (the simplest aryl group) on single-crystal surfaces by heat-, photo-, or electro-induced dissociation of adsorbed benzene or halobenzene molecules and examined them under ultrahigh vacuum (UHV) conditions with a variety of techniques. However, the majority of the work has been limited to the surfaces of Cu, Ag, and Au,[7] and the nature of the C_6H_5−metal bond is still controversial from those UHV experiments. Therefore, there is a fundamental lack of understanding of the bonding of aryl groups to metal surfaces.

It is our goal here to explore the structure and bonding of aryl groups on metal surfaces and bridge UHV and grafting research by broadening the scope of metals examined but still using well-defined surfaces. By using first principles density functional theory (DFT) simulations,[8] which to the best of our knowledge has not been attempted for aryl−surface systems, we can examine metals across the periodic table and gain insight into the aryl−metal bonding stability. We selected four metals (Fe, Pd, Cu, and Au) from the experimental list and added one "unexperimented" early transition metal (Ti) for our theoretical examination. We studied their closest-packed surfaces. For comparison, we also examined the hydrogen-passivated Si(111) surface, as was also done in the experiments.

We started with 10−15 initial configurations of the phenyl group (C_6H_5) on the high-symmetry sites of the surfaces and optimized their structures. We found that both an upright (perpendicular) configuration and a stable tilted or flat-lying (parallel) configuration exist for the phenyl group on each of the metal surfaces examined. The most stable structures for the two orientations are shown in Figures 1 and 2, and the energetics are displayed in Table 1. The adsorption energies shown clearly indicate that the interaction is chemical in nature, that is, it is chemisorption. The bond strength at the C_6H_5/Si(111) interface is well within the territory of covalent bonds. For the metals, the binding strength with C_6H_5 decreases from Ti to Cu with the increasing number of d-electrons. This trend usually correlates with the center of the d-band.[9] In other words, the metal d-band shifts further below the Fermi level with the increasing number of d-electrons, effectively decreasing the bonding between surfaces and adsorbates. This trend is true for both orientations. Here we can think of the upright fashion as a tendency to a favor carbon−metal (C−M) σ-bond, while the tilted or flat-lying fashion to favor a C−M π-bond. The relative energetics indicates that Fe demarcates the transition metals with respect to binding with C_6H_5; that is, the metals to the left of Fe on the periodic table favor a C−M π-bond, and the metals to the right of Fe favor a C−M σ-bond. This trend agrees well with the fact that experimentally realized metals by diazonium grafting fall to the right of Fe because C−M σ-bonds facilitate the perpendicular growth of aryl layers.

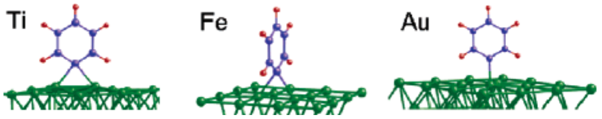

Figure 1. Optimized structures of phenyl groups on metal surfaces for the upright configuration. Carbon atoms in blue, H in red, and metal atoms in green (only the top layer is shown). Same color scheme is used in all subsequent figures.

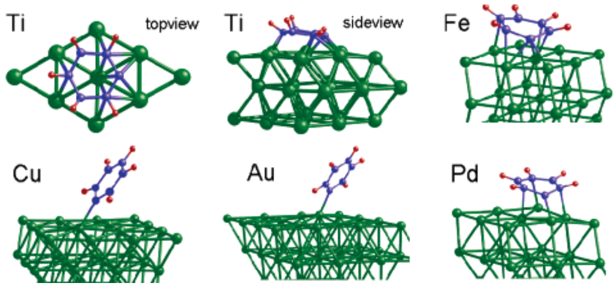

Figure 2. Optimized structures of phenyl groups on metal surfaces for the tilt or flat-lying configurations.

Table 1. Energetics of C_6H_5 on Solid Surfaces[a]

		upright		tilted or flat-lying	
surface	lattice type	E_{ad}[b]	site	E_{ad}	θ (°)[c]
Ti(0001)	hcp	64.7	bridge	106.7	72
Fe(110)	bcc	41.0	bridge	41.4	69
Cu(111)	fcc	27.9	bridge	24.4	40
Au(111)	fcc	24.0	atop	17.6	38
Pd(111)	fcc	37.3	atop	25.9	72
Si(111):H[d]	diamond	70.0	atop		

[a] C_6H_5 coverage is at 0.111 molecules per surface atom for all surfaces here. [b] $E_{ad} = E(\text{surface}) + E(C_6H_5) - E(C_6H_5/\text{surface})$, kcal/mol. [c] Angle between the C_6H_5 molecular plane (determined by the carbon atom without a hydrogen and the other two carbon atoms at its meta-positions) with respect to the surface normal. [d] Hydrogenated Si(111) surface.

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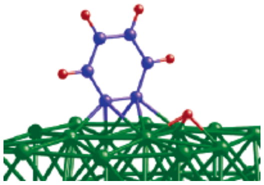

Figure 3. C_6H_5 underwent β-dehydrogenation on Ti(0001).

In the flat-lying fashion, C_6H_5 is strongly adsorbed on Ti(0001) and structurally distorted with elongated C−C bonds (one C−C bond increased as much as 0.1 Å). Three H atoms are significantly moved off the phenyl molecular plane, indicating that the carbon atoms on the phenyl ring are converted to sp^3 hybridization. The carbon without a hydrogen atom is found to have a formal charge of −1.20 e, while the remaining five carbon atoms have a charge of −0.4 to −0.70 e, supporting the idea of sp^3 rehybridization. Moreover, we found that some initial guesses for C_6H_5 on Ti(0001) led to β-dehydrogenation of C_6H_5, resulting in C_6H_4 and H on the surface (Figure 3). Dissociation did not happen on any other metal surfaces investigated here. Both the strong C−M π-bond and the dissociation of C_6H_5 on Ti(0001) apparently result from the strong affinity of Ti for C. It is well-known that early transition metals can form very stable carbides. Therefore, we expect that the behavior of grafting aryl layers on early transition metals will be very different from other transition metals. Our work invites experiments with these metals.

We found that C_6H_5 equally prefers the flat-lying fashion as much as the upright one on Fe(110). In the upright configuration, C_6H_5 is bonded to two neighboring Fe atoms at a bridge site, instead of being atop one Fe atom. The tilted configuration of C_6H_5 on Cu(111) is predicted to be almost as stable as the upright one. The predicted tilt angle (40°) agrees reasonably well with experiment (47 ± 5°).[7g] Kinetic analysis of C_6H_5 desorption to form biphenyl yielded a barrier of 23 kcal/mol on Cu(111) and 26.6 kcal/mol on Ag(111).[7e] These energies are in line with the chemisorption energies calculated here for the Cu group metals. Against the previous assumption of the formation of a phenyl anion on Cu(111),[7c] we found that the phenyl carbon has a formal charge of only −0.25 e. It is a little surprising that a stable flat-lying structure of C_6H_5 also exists on Pd(111). We will clarify this point in a future paper by comparing with Ni and Pt.

Because grafting aryl groups using diazonium chemistry has been employed mainly by solution and electrochemical methods, traditional UHV surface science techniques have yet to be used extensively to investigate aryl−metal surface systems prepared by grafting. Nevertheless, X-ray photoelectron spectroscopy studies were carried out to study aryl groups on iron and other surfaces,[1h,2,10] and we expect other techniques, such as high-resolution electron energy loss spectroscopy, will provide more direct evidence of surface bonding for aryl-grafted metal surfaces.

In conclusion, using first principles DFT-GGA methods, we have clearly shown that the bond between C_6H_5 and metal surfaces is chemical in nature. We have profiled a trend across the periodic table for transition metals, which shows decreasing phenyl−metal bond strength from left to right. It is found that early transition metals favor the flat-lying configuration, while late transition metals prefer the upright fashion. It is also found that the phenyl group can undergo β-dehydrogenation on early transition-metal surfaces. Because of the versatile organic chemistry of the aryl group, modifying solid surfaces with diazonium grafting holds great promises for various applications. We hope that our work catalyzes further theoretical and experimental research in this exciting new area.

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Supporting Information Available: Coordinates for all the stable structures of C_6H_5 on surfaces and dissociated C_6H_5 on Ti(0001) (PDF). This materials is available free of charge via the Internet at http://pubs.acs.org.

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(8) We used the Vienna Ab Initio Simulation Package (VASP)[11] to perform DFT calculations with planewave bases and periodic boundary conditions and within the generalized gradient approximation (GGA) for electron exchange and correlation. Projector-augmented wave (PAW) method was used within the frozen core approximation to describe the electron−core interaction.[12] We used the PBE functional[13a] for all geometry optimizations and report the RPBE energetics for those PBE-optimized structures here because RPBE−GGA appears to give a better description of atomization energies of molecules and adsorption energetics.[13b] DFT−PBE optimized lattice parameters were used for Ti (hcp, a = 2.923 Å, c = 4.627 Å), Fe (bcc, a = 2.834 Å), Cu (fcc, a = 3.632 Å), Pd (fcc, a = 3.955 Å), Au (fcc, a = 4.170 Å), and Si (diamond, a = 5.468 Å). The surfaces were modeled with four or five layers of atoms together with a 17 Å thick vacuum layer. The top two substrate layers were allowed to relax with the adsorbed phenyl layer. The force tolerance was set at 0.025 eV/Å. A converged 450 eV kinetic energy cutoff was used. A 4 × 4 × 1 Monkhorst−Pack k-mesh was employed to sample the Brillouin zone of the (3 × 3) lateral cell of all surfaces. Spin-polarized calculations were performed for iron surfaces. Formal charge on atoms were determined according to Bader's atom-in-molecule method, as implemented by Henkelman et al.[14]

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