

## Surface Chemistry — Application of Coordination Principles

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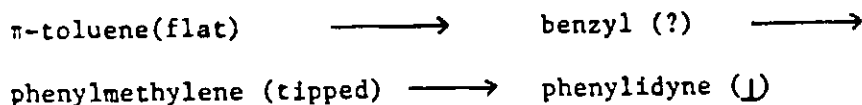
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The objective of this research is to establish the molecular features of the hydrocarbon-metal surface chemistry as a function of surface topography and composition (e.g., carbon, oxygen and sulfur adatom contaminants). Primary focus has been on the factors that sensitively affect carbon-carbon and carbon-hydrogen bond breaking reactions.

The most scientifically significant results from our research to date with nickel and platinum metals is that surface topography is a critical element in C-H bond breaking. By matching hydrocarbons with surface topography, regioselective reactions can be achieved. For example, C-H bond breaking in toluene is fully regioselective on the atomically flat planes of Ni(100) and Ni(111). Using selectively labeled toluene molecules,  $CD_3C_6H_5$  and  $CH_3C_6D_5$ , it was established that all aliphatic C-H bonds are cleaved before any aromatic C-H bonds are broken. The labeling studies and preliminary NEXAFS studies show that toluene binds initially in a plane parallel to the surface plane but then flips up after the first C-H (aliphatic) bond scission. The probable reaction sequence is:



Now we have NEXAFS data that establish a planar configuration for  $\pi$  bound toluene (parallel to surface plane). Also, these studies establish that after scission of aliphatic C-H bonds, the phenyl ring then is normal (or tipped) with respect to the surface plane. Such a configuration disallows aromatic C-H bond scission at moderate conditions.

All the aromatic molecules we have studied with HREELS and NEXAFS data are oriented in a plane parallel to the surface plane. These include benzene, toluene, hexafluorobenzene and benzonitrile on Pt(111). Data for nickel (111) and (100) and for Pd(111) are incomplete but the geometry seems pervasively that parallel to that of the surface plane for the  $\pi$  bound arene.

In contrast to the arenes, pyridine bonds through the nitrogen atom and stands upright on the surface provided the coverage is at least  $\sim 0.05$ . Orientation was established by NEXAFS studies. On Ni(100), equilibrium between molecular pyridine and 2-pyridyl is established at low temperatures as defined through our labeling studies with 2,6- $C_5H_3D_2N$ , 3,5- $C_5H_3D_2N$  and 4- $C_5H_4DN$ :  
$$Ni(100)-NC_5H_5 \rightleftharpoons Ni(100)-\eta^2-NC_5H_4 + Ni(100)-H$$

The major thrust of our program will be studies of heteroaromatic molecules: furan, thiophene and pyrrole using isotopically labeled molecules and HREELS and NEXAFS data to define molecular structure.