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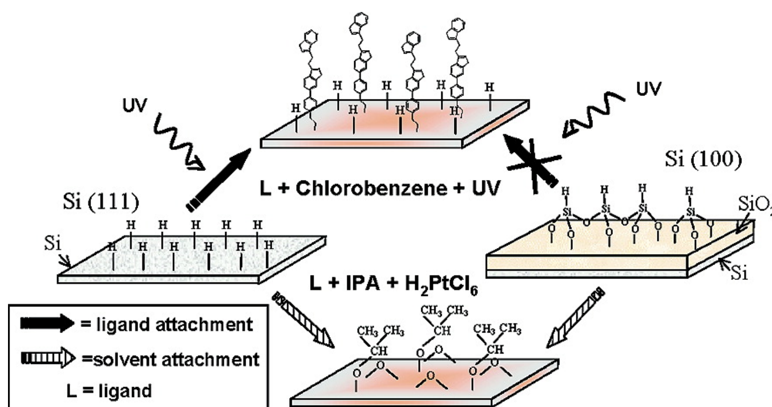

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Controlled Silicon Surface Functionalization by Alkene Hydrosilylation

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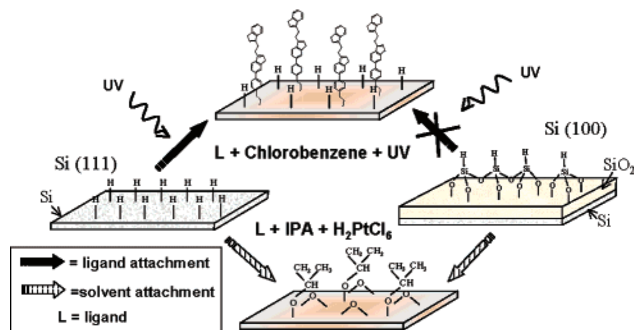
Methods for the controlled organic surface functionalization of inorganic materials are critical for the synthesis of many new classes of hybrid materials. Numerous examples exist in the semiconductor industry and in biomaterials research, where the objective is to combine the mechanical, structural, and electrical properties of the bulk materials with tailored surface characteristics, such as tunable reactivity, biocompatibility, or hydrophobicity. Additionally, there are many emerging applications,[1] such as nanoparticle functionalization and chiral organometallic complexe immobilization, to produce new and efficient catalysts for pharmaceutical syntheses.[2] Methods to immobilize organic ligands based on the reaction of trialkoxysilane with surface silanol groups[3] or the use of Grignard reagents with halogen-terminated surfaces[4,5] have been utilized with mixed success. Such methods generally suffer from problems (e.g., harsh conditions, surface contamination by catalyst), which are difficult to overcome for lack of effective characterization.

Alternatively, surface hydrosilylation of hydrogen-terminated silica (SiO_2) has emerged as a promising new strategy for grafting organic molecules onto inorganic surfaces. However, the process of hydrosilylation is not well understood, partly because of the use of high-surface-area substrate materials, leading to unreliable results and controversy in the field.[6] When a catalyst is used, for example, the Speier catalyst, $H_2[PtCl_6]$, side reactions with the solvent can occur. The catalyst itself may also cause post-contamination of the surface by elemental Pt, which can lead to secondary reactions.[7] The use of ultraviolet (UV) and white light has also been pioneered by Chidsey[8,9] and Buriak[5,10,11] in place of molecular catalysts to induce surface reactions, but UV has not been yet utilized for complex organic ligands. Importantly, the reaction mechanism leading to the attachment of the organic molecules on flat silicon (Si) surfaces with UV light is still unclear.[5]

We present a powerful method, combining the use of *well-defined* surfaces with infrared spectroscopy, to elucidate the mechanisms of surface chemical functionalization, including hydrosilylation reactions. To illustrate the approach, we focus on the complex ligand, 3-[2′-(1*H*-inden-3″-yl)ethyl]-5-(4‴-vinylphenyl)-1*H*-indene ("indene ligand"), a precursor for a metallocene catalyst and an important model compound for surface functionalization.[12] We find that, in contrast to some reports, the Speier catalyst does not always promote the alkene surface hydrosilylation reaction, but fosters instead the reaction of the solvent (e.g., isopropyl alcohol, IPA) with H-terminated silicon surfaces. Importantly, we demonstrate that UV irradiation in chlorobenzene leads to complete immobilization of the indene ligand during surface hydrosilylation reactions on oxide-free surfaces only, thus suggesting electron−hole pair excitons as key to the mechanism of UV-induced surface reaction (Scheme 1).

The key to the present work is the combination of submonolayer sensitivity surface infrared absorption spectroscopy (IRAS) with two types of well-defined, flat hydrogen-terminated Si surfaces:[13]

Scheme 1. Schematic Summary of the Main Mechanisms



(1) *oxide-free*, atomically flat H-terminated Si(111) [H/Si(111)],[14] and (2) *oxidized*, flat silicon surfaces [SiO_2/Si(100)] hydrogenated by reaction with triethoxysilane [H/SiO_2/Si(100)]. The starting surfaces are fully characterized by IRAS, so that a systematic study of all relevant methods can be undertaken, probing each reaction step with IRAS. This is in contrast to the studies cited above, in which the high-surface-area substrates are structurally complex and opaque in the IR spectral region (500−2500 cm^{-1}), most important to unravel chemical mechanisms.

Figure 1 shows that, while the presence of the catalyst H_2PtCl_6 does lead to hydrogen loss on either H/SiO_2/Si(100) (Figure 1a) or H/Si(111) (Figure 1b) surfaces, it promotes the immobilization of the solvent (IPA) instead of the indene ligand! Specifically, any ligand-related modes, such as the indene C−H stretch and bend at ∼3000−3100 and ∼1400−1700 cm^{-1}, are not observed. Instead, there is clear evidence for the formation of Si−O−C modes at 1115 and 1170 cm^{-1} and CH_3 modes in the ∼2900 cm^{-1} region, consistent with alkoxy bonded to the Si surface. Examination of IPA reactivity with H/Si(111) without catalyst (Supporting Information) reveals that alkoxy formation also takes place, although at a lower reaction rate. Figure 1c shows that, when chlorobenzene is used instead of IPA, complete removal of surface hydrogen takes place in the presence of the catalyst, with partial immobilization of the ligand (∼1/4 monolayer, ML). This observation indicates that the catalyst can induce ligand immobilization under conditions when the solvent is stable. However, the surface is also substantially oxidized (broad bands ∼1100 cm^{-1}). Interestingly, Rutherford backscattering measurements of surfaces show that for the case of IPA + catalyst a significant amount of Pt (∼2.5×10^{14} Pt/cm^2) and no measurable Cl are detected, while for chlorobenzene + catalyst, a smaller amount of Pt (∼1×10^{14} Pt/cm^2) remains on the surface together with chlorine (∼2×10^{14} Cl/cm^2). These observations suggest that the catalyst dissociates in the presence of IPA and chlorobenzene, forming $PtCl_2$ in the latter case.

UV irradiation offers a potentially "cleaner" (metal-free) way to foster surface reactions on surfaces. Figure 2b shows that, under UV illumination, ligand immobilization takes place on H/Si(111)

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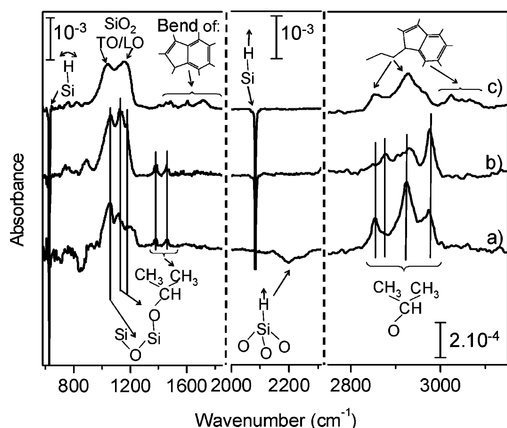

Figure 1. Transmission IR spectra after IPA + H_2PtCl_6 + indene ligand on (a) $H/SiO_2/Si$ and (b) H/Si(111) surfaces, and (c) chlorobenzene + H_2PtCl_6 + indene ligand on H/Si(111). Spectra referenced to H-terminated surfaces prior to treatment.

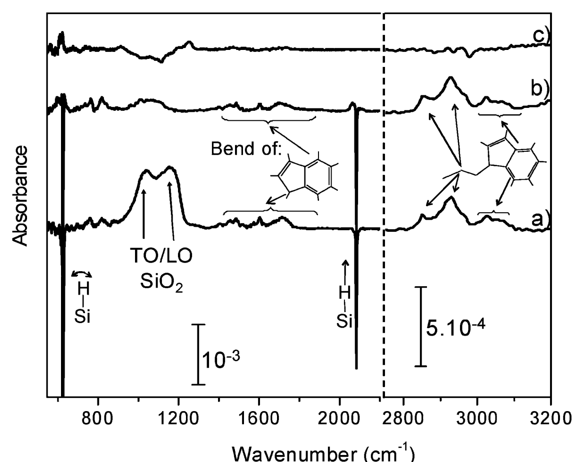

Figure 2. Transmission IR spectra of chlorobenzene and ligand subjected to (a) H_2PtCl_6, (b) UV on H/Si(111), and (c) UV on $H/SiO_2/Si$. Spectra a and b referenced to H/Si(111), and spectrum c to the TES-terminated surface ($H/SiO_2/Si$).

with almost no oxidation (no SiO_2 formation), in contrast to catalyst-induced reactions (Figure 2a). Interestingly, 60% of the surface remains H-terminated, although all possible indene ligands (~30% monolayer) are attached. This indicates that a full coverage of indene ligand cannot react with more than ~30% Si−H ML due to steric interactions among the indene ligand molecules. The absence of oxidation is a direct consequence of substrate Si−H bonds remaining intact between the indene ligand molecules. In fact, this surface is extremely stable, even under harsh SC-1 and SC-2 post-treatments.

Figure 2c shows that, under similar UV treatments of $H/SiO_2/Si(100)$ surfaces, no reaction with the indene ligand occurs! This observation is critical to understand the mechanism of UV-induced dissociation. If UV simply promoted the Si−H photodesorption to form a radical, as proposed earlier,[9] then both H/Si(111) and $H/SiO_2/Si$ surfaces should be functionalized by the ligand. The absence of reaction on the oxidized [$H/SiO_2/Si(100)$] surface indicates that UV radiation excites electron−hole pairs (excitons) in the substrate, which can only diffuse to the surface and promote the ligand reaction for the oxide-free H-terminated surface (i.e., in the absence of an oxide insulating barrier). The exciton mechanism has been previously invoked in the case of Si nanoparticles.[11] For flat silicon surfaces, direct Si−H bond breaking had been suggested instead.[9] The present data do not support a bond breaking mechanism.

In summary, a novel method for probing the mechanism of silica surface functionalization with a wide class of organic molecules (e.g., ligands of chiral catalysts) was presented. This method, using high-sensitivity IR spectroscopy on well-defined surfaces makes it possible to identify unambiguously the reactants and products attached at the surface at *all* stages of the process. Inconsistencies previously observed on high-surface-area materials can thus be precisely addressed. For instance, the knowledge that the H_2PtCl_6 catalyst preferentially induces solvent immobilization in the case of IPA (and other solvents) is essential to optimize ligand immobilization and is directly applicable to high-surface-area materials. Furthermore, the use of model H-terminated silicon surfaces with controllable oxide thickness has provided the strongest confirmation of the role of electron−hole pairs in surface reaction on flat H-terminated Si surfaces, providing quantitative guidelines to optimize ligand attachment on more complex substrates.

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Supporting Information Available: Experimental conditions and infrared data for solvent reactions, UV irradiation time and wavelength dependence on different Si substrates, and stability of the ligand after immobilization. This material is available free of charge via the Internet at http://pubs.acs.org.

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