476i Silicon Surface Functionalization by Uv-Initiated Alkene Hydrosilylation

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Grafting organic molecules onto inorganic surfaces is one of the most widely used strategies for functionalizing inorganic materials, and the most common approach is based on the reaction of trialkoxysilyl with surface silanol groups. Another common strategy for surface functionalization is the preparation of a chlorinated inorganic surface followed by a reaction with organometallic compounds, mainly Grignard reagents. All these procedures use a simple silanol surface. However, there are considerable disadvantages in using these surfaces for the immobilization of homogeneous catalytic complexes. This has led to the development of a new, alternative catalyst immobilization strategy, i.e., the surface hydrosilylation with commercially available silica particles having a hydrogen-terminated surface, i.e., Si-H.

At this time, there is no detailed understanding of the surface hydrosilylation reaction, and previous investigations have used porous silica particles, which have a rough surface, and limit the analytical characterization of the functionalized silica particles. In addition, inconsistency with the catalyzed surface hydrosilylation reaction remains unexplained.

In our study, a functional H-monolayer on silicon (111) and (100), an atomically flat and well-defined surface, and high-resolution infrared spectroscopy were used to characterize in detail the surface hydrosilylation reaction. The chemical nature of the surfaces before and after chemical functionalization and the surface structures were explicitly defined. This led to the identification of an adverse side reaction between various solvents (such as IPA) and the reactive Si-H surface, which was never reported before and which may explain inconsistencies using this reactions. Using an inert solvent and replacing the Pt-catalyst with UV-initiation significantly improved the applicability of the surface hydrosilylation reaction as a strategy for immobilization of homogeneous catalytic complexes. Detailed results on the surface characterization and on the heterogenization of a homogeneous catalyst are presented. Methods for nano-templating and for creating multi-functional catalytic surfaces are discussed in detail.