135f Kinetics and Mechanism for Alkyl Monolayer Growth on Hydrogenated Si Surfaces

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We have recently found that self-assembled monolayers of decane can be grown on hydrogenated silicon surfaces with gaseous 1-decene at millibar pressures and moderate surface temperature, and have characterized the growth kinetics experimentally using in situ total reflection Fourier transform infrared spectroscopy. The growth kinetics have been proposed to follow a chain mechanism in which an alkene molecule adsorbs onto a dangling bond site and then reacts with a neighboring hydrogen atom to produce an adsorbed alkyl group and regenerate a surface dangling bond. For our experimental conditions, the measured kinetics are well described by the chain mechanism, but only under the limiting condition that alkene desorption is much faster than both adsorption and hydrogenation. In this talk, we focus on density functional theory (DFT) calculations that corroborate the proposed chain mechanism and provide estimates of the elementary rate coefficients that govern the surface reaction kinetics. The computed rate coefficients support the assumption of fast alkene desorption for the growth pressures and temperatures that were investigated experimentally, and are in good agreement with the measured values. From these computations, we estimate that a hydrogenated silicon surface with about 0.1% dangling bond sites would be needed to initiate SAM growth at the rates observed.