Boundary Layer Dynamics in Mixed Hydrocarbon Thin Films on Metal Surfaces

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Obtaining an improved understanding of such diverse phenomena as adhesion,[1] lubrication,[2,3] surface and interface induced organizations of molecular assemblies,[4,5] and heterogeneous catalysis[6] depends crucially on developing a clearer picture of the underlying dynamical properties of adsorbate-modified interfaces. Hydrocarbon assemblies on Pt(111) serve as an extremely useful model for examining the nature of transport dynamics exhibited in thin organic films. Ease of variation of the components in these bilayer assemblies provides a controlled investigation of the effects of chain length, shape, and isotopic labeling.

N-alkanes are known to organize readily on Pt(111) at low temperatures and produce a well-defined model organic film. The structural scheme shown in Figure 1 illustrates a model of this structure for a monolayer of n-octane, as a representative example, which is consistent with all the data presently available (primarily from RAIRS and LEED).[7,8,9]
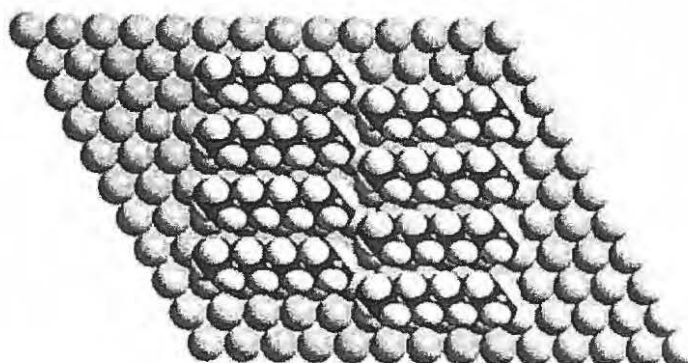

Figure 1.

The dynamic processes occurring in hydrocarbon assemblies can be evidenced and quantified using spectroscopic methods.[10] Reflection absorption infrared (RAIR) spectroscopy is sensitive not only to the identity of the adsorbates but also the orientation of the molecules, due to the selection rule imposed by the metal surface. An ordered array of hydrocarbons such as that described above would give a RAIR spectrum which differs significantly from that observed for an isotropic arrangement of the chains. Further, the direct C-H···metal contacts induce significant perturbations of the vibrational frequencies relative to those of an unbound molecule, allowing the determination of the location of the species. To distinguish molecules initially present at the surface from those initially in the second layer, isotopic labeling of the hydrocarbons was utilized.

Figure 2 shows representative RAIR difference spectra for an assembly of n-octane on Pt(111) pre-covered with n-octane(d_{18}). As can be seen by the pattern of features in the spectra, the initially surface bound n-octane(d_{18}) (2100 – 2300 cm^{-1}) is displaced from the surface by n-octane. The changes in the stretching modes in the C-H region (2800 – 3000 cm^{-1}) indicate the presence of n-octane at the platinum surface.

This dynamic process was investigated for systems with varying chain lengths and shape asymmetries. Regardless of the initial deposition order, the longer or linear hydrocarbon chain (in the systems with shape asymmetry involving linear and cyclic alkanes) was retained at the surface. This demonstrates the low temperature mobility of the molecules within this ordered assembly.[11]
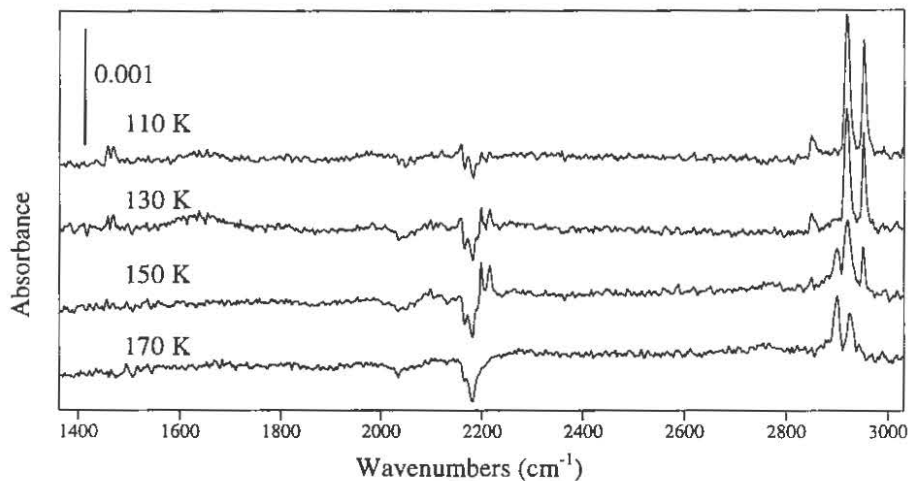

Figure 2.

Temperature programmed desorption (TPD) experiments provide quantitation of the dynamic processes occurring in alkane assemblies. TPD spectra for desorption of n-octane(d_{18}) species from a system of cyclooctane on n-octane(d_{18}) is shown in Figure 3. The low temperature feature corresponds to desorption of non-surface contacting n-octane(d_{18}), where the higher temperature feature corresponds to desorption of surface bound n-octane(d_{18}). The increase in the size of the low temperature feature indicates that a small fraction of n-octane(d_{18}) is displaced from the surface by cyclooctane.
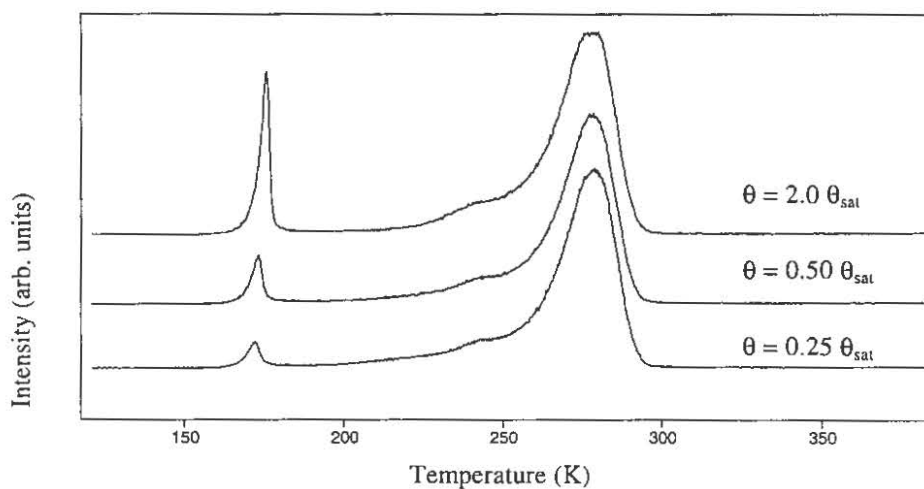

Figure 3.

The characteristics of the alkane molecular assemblies deduced from spectroscopic investigations, which include a large molecular mobility and attractive lateral interactions, become important when considering the desorption of these adsorbates from the Pt(111) surface. A simple first order desorption model does not account for these contributions to the desorption process.[12] Using a first order desorption rate to predict the desorption activation energies for the series of n-alkanes, hexane through decane, results in an unreasonable scaling of segmental surface interaction energies. Based on this model, the activation energy per carbon unit decreases rapidly with increasing chain length. This decrease in energy implies that the surface interaction energy for each methylene is less than the methylene segmental desorption activation energy for non-surface contacting species (the latter have a lower binding energy).[13] This simplistic desorption model is best applies to simple systems without strong coverage dependence of either the activation energy or the pre-exponential factor,[14,15] lateral interactions,[16] desorption precursor states[17] and other complex desorption processes.[18] From investigations of the dynamics in alkane assemblies, it is clear that these properties are significant in this desorption process.

The simplest desorption process incorporating both the facile diffusion of alkanes on the Pt(111) surface and attractive lateral interactions is a desorption process dominated by molecules at domain perimeters Although overly simplistic, the resulting half order desorption rate predicts the appropriate surface segmental interaction energies for n-alkane desorption from Pt(111), and suggests that even small deviations from the ideal adsorbates assumed by the first order desorption model can lead to inaccurate predictions of desorption energetics.

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