

Final Report

Project Title

The Dynamics of Adsorption on Clean and Adsorbate-Modified Transition Metal and Metal Oxide Surfaces

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Abstract

Research directed toward understanding the dynamical factors governing the adsorption of molecules typically involved in heterogeneous catalytic processes has been continued at Harvard. Adsorption is the first step in any catalytic process, and predictions of rates of adsorption are fundamental to calculations of rates of catalytic reactions. Often activation of the bonds within the molecule proceed via a molecular precursor, and the rate of activation is determined by competitive bond activation and desorption of this precursor. Thus predictive capabilities for the adsorption probabilities of hydrocarbons become important for understanding the rates of simple reactions involving alkanes, such as reforming. In this work we have focused on the dynamics of molecular adsorption of low molecular weight alkanes on single crystal surfaces of platinum group metals in order to understand how different physical properties of the metals affect different trapping (adsorption) probabilities of the alkanes. The overall

objective of these studies was to make a quantitative comparison of the molecular probabilities of C₂-C₄ alkanes on different metals in order to assess the effects of the structures of the different alkanes and the intrinsic differences of the metals on the reactivity of the alkanes. This work built on previous studies with platinum and palladium single crystal surfaces for which we were able to apply molecular dynamic simulations to quantitatively predict trapping probabilities of low molecular weight alkanes for palladium directly from measured values of the trapping of ethane (only) on Pt(111). The *trapping* probabilities for the alkanes are higher on Pd(111) due to a larger dissipation of energy to lattice vibrations upon collision, suggesting a general scaling of trapping with the lattice force constant for different metal surfaces, provided the surface structure is not too different. In this grant period we have thus focused on the dynamics of molecular adsorption of low molecular weight alkanes on single crystal surfaces of platinum, palladium, copper, silver and nickel in order to assess this scaling directly. We observe that the trapping of each of the alkanes studied decreases with the lattice stiffness and mass of the metal atom, but not as strongly as predicted by the lattice for constant itself. These observations are in general agreement with the expectations of molecular dynamic simulations, but further theoretical work is needed to understand the trends in detail.

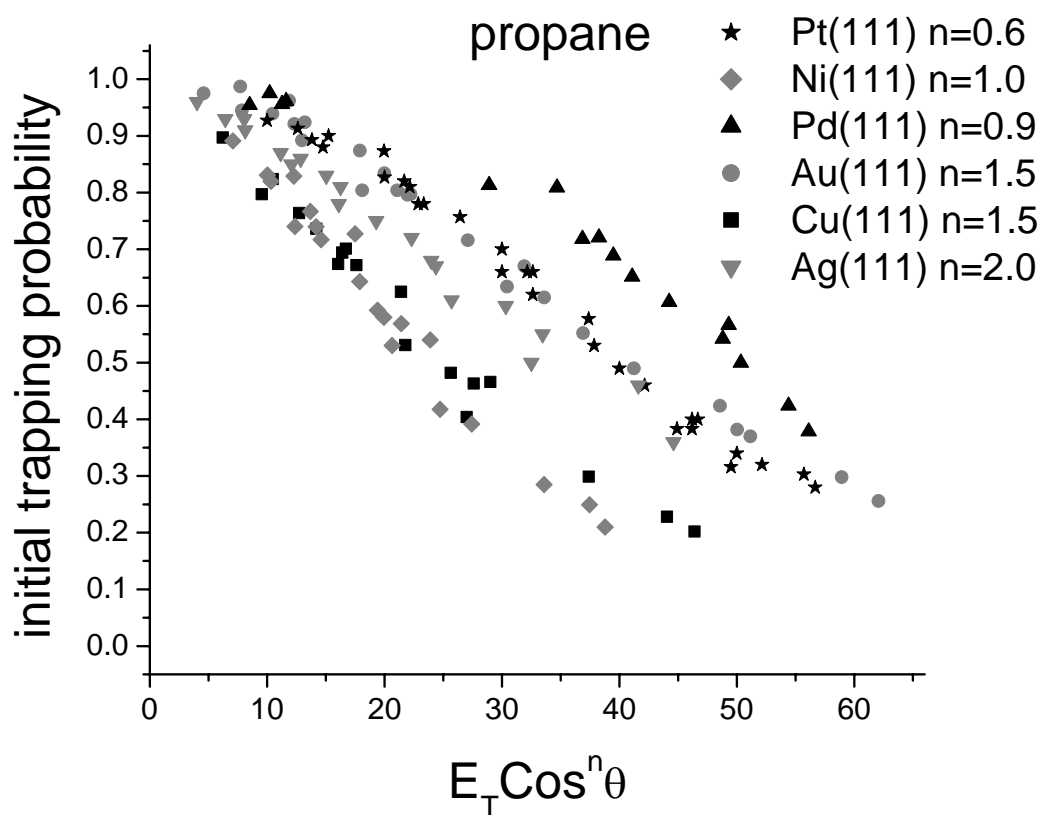
Publications:

1. *The scaling of the trapping probabilities on close-packed surfaces of Pt, Pd, Cu, Ag and Ni*, D. Rampulla and R.J. Madix, in preparation

Report

Over the last few years considerable progress has been made in understanding dissociative adsorption of alkanes on clean metal surfaces. Generally for all but methane, at low incident kinetic energies C-H bond activation proceeds via a molecularly adsorbed precursor, whereas at high kinetic energies direct collisional activation dominates. Collisional activation of methane has been more extensively studied than for higher molecular weight hydrocarbons. At high incident kinetic energies direct collisional activation dominates. In this process bonds within the alkane are broken and reformed with the surface at distances characteristic of bond lengths. At such close distances of approach, energy transfer from the incident molecule to the surface is expected because this distance is substantially closer than the distance of closest approach observed in molecular adsorption, in which substantial energy is dissipated to lattice phonons. We have utilized a combination of molecular beam experiment and molecular dynamics simulations to develop a method for predicting this energy transfer for a variety of metals. We found that, using a Morse potential, the dependence of the trapping probability of ethane on both the incident angle and energy on a single crystal surface of platinum Pt(111) can be quantitatively simulated assuming a united atom description of the molecule. Furthermore, this potential affords an accurate *prediction* of the trapping probabilities of methane, propane, butane and neopentane on platinum surfaces. With this success in mind, we turned to the scaling of trapping probabilities from platinum to other metal surfaces. Since platinum and palladium have similar physical properties,

differing primarily in their atomic mass, we began with Pd(111). We found that the binding energy of the alkanes to Pt(111) and Pd(111) was nearly identical, giving justification to the assumption that the potential parameters found for the alkanes on Pt(111) would be applicable to Pd(111). Indeed, using the same potential parameters derived for Pt(111), we were able to accurately scale these trapping probabilities to the Pd(111) surface. Next we turned our attention to Ni(111). Nickel differs appreciably from platinum and palladium in its physical properties. First, its atomic mass is much less. Second the Ni-Ni force constants are much stronger than either Pt or Pd. The combination of these two differences make the comparison of the trapping probabilities on Ni(111) to those observed on Pt(111) and Pd(111) more difficult. To fit the trapping probabilities of the alkanes on Ni(111) we found that some adjustment of the alkane-Pt potential was necessary. In general, the increased lattice stiffness of the nickel surface leads to a significant reduction in the trapping probabilities of the alkanes on the nickel surface. Thus, trapping is most efficient on Pd(111) and least efficient on Ni(111), with Pt(111) being intermediate in its efficiency.



These trends suggest a relationship between the trapping probability of the alkane and the metal-metal force constant of the surface. The origin of this correlation is that the trapping probability increases with the softness of the metal, as measured by its Debye

temperature, and decreases with the mass of the metal atom. A simple dynamical analysis suggests that the trapping probability might scale inversely with the metal-metal force constant, decreasing with the Debye temperature and with increasing mass of the metal atom. To this end we studied the trapping probabilities of low molecular weight alkanes on Cu(111) and Ag(111) to complement our previous measurements. A summary of these results for propane is shown in figure 1.

Similar results were observed for ethane and butane. E_T is the kinetic energy of the molecule far from the surface and θ is its angle of incidence relative to the surface normal; n is a scaling parameter that best collapses the data for a single surface onto the continuous curve. Clearly the trapping probability is greatest for Pd(111) over the entire range and least for Ni(111). The trapping probability can be grouped generally as follows: Pd(111) > Au(111) \approx Ag(111) \approx Pt(111) > Cu(111) \approx Ni(111).

With the exception of Au(111) the trapping probabilities scale approximately inversely with $M\Theta_D$, where M is the mass of the metal atom and Θ_D is the Debye temperature. We do not currently understand the anomalous behavior of the Au(111) surface. One possible origin is that the Au(111) surface reconstructs to form a structure different from the other metal surfaces. Were this reconstruction to alter the surface Debye temperature of the Au(111) surface significantly (make it stiffer), the results for Au(111) could be rationalized.