Final Report

Project Title

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

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Principal Investigator: Robert J. Madix
Department of Chemical Engineering
381 North-South Mall
Stanford University
Stanford, CA 94305
Email: rjm@chemeng.stanford.edu
Phone: 650-723-2402
FAX: 650-723-9780

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Sponsored Projects Office
Stanford, CA 94306

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Graduate Students: Chai-Ling Kao
Enrique Farfan-Arribas
Ali Alemozafar

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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. Adsorption is the first step in any catalytic process, and predictions of rates of adsorption are fundamental to calculations of rates of catalytic reactions. Dissociative adsorption can occur either directly upon impact with the surface or as the result of the migration of a temporarily trapped species across the surface. Alkane activation exhibits both of these pathways for reaction on metal surfaces. We have focused on the dynamics of dissociative adsorption of low molecular weight alkanes on single crystal surfaces of

platinum group metals. The overall objective of these studies was to make a quantitative comparison of the dissociation probabilities of C_2-C_4 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 reactivity. First, an unusual and somewhat unexpected difference is observed in the reactivity of linear and branched alkanes. Further, the reactivity of each alkane is significantly higher on Pt(111) than on Pd(111). It has also been observed that the *trapping* probabilities for the alkanes are higher on Pd(111) due to a larger dissipation of energy to lattice vibrations upon collision, suggesting that energy dissipation in the reaction coordinate into phonons may be involved in dissociative adsorption. We have thus focused on the dynamics of dissociative adsorption of low molecular weight alkanes on single crystal surfaces of platinum, palladium and nickel in order to assess the role of energy dissipation from the incident molecule and the differences of the reactivity of the different metals. We observe that the reactivity of each of the alkanes studied to date differs by only a small amount. On the contrary, due to the dissipation of incident translational energy to lattice vibrations upon collision, the *trapping* probabilities for the alkanes differ *appreciably* for the three surfaces. There thus appears to be no correlation between the large differences observed in the trapping probabilities and the reactivity of the surfaces for direct collisional activation of the alkanes, suggesting that no significant amount of the incident kinetic energy of the alkane is dissipated from the reaction coordinate into lattice vibrations. Further, the differences in reactivities of different alkanes on these surfaces appears to originate from steric differences in the accessibility of C-H bonds during the collisional encounter with the surface.

Publications:

1. C.L Kao, J.F. Weaver and R.J. Madix, *The Adsorption Dynamics of Small Alkanes on (111) Surfaces of Platinum Group Metals*, Surface Science 557 (2004) 215-230

2. C.L Kao, J.F. Weaver and R.J. Madix, *The Adsorption Dynamics of Small Alkanes on (111) Surfaces of Platinum Group Metals*, Surface Science 557 (2004) 215-230

3. C.L. Kao, A.F. Carlsson and R.J. Madix, *Mass and Lattice Effects in Trapping: Ar, Kr, and Xe on Pt(111), Pd(111) and Ni(111),* Surf. Sci. 565 (2004) 70

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. For these more complex molecules energy can be dissipated from the incident translational energy into other modes of motion, some of

which do not couple into the reaction coordinate, such as lattice vibrations. We have examined this question further.

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.

The degree to which this redirection of energy occurs remains an open question. In an earlier grant period we determined the effects of the molecular mass and structure of C_2 - C_5 alkanes on their probabilities of reaction on Pt(111) and Ir(110). On Ir(110) the precursor mediated process contributes significantly to the reaction over a wide range of energy, and the direct collisional reaction probability is difficult to extract. On Pt(111), however, no precursor-mediated pathway is observed, and the effects of molecular complexity are distinguishable (fig. 1). For ethane, propane, n-butane, and

isobutane the reaction probability scales as $E_t\cos^2\theta_i$.

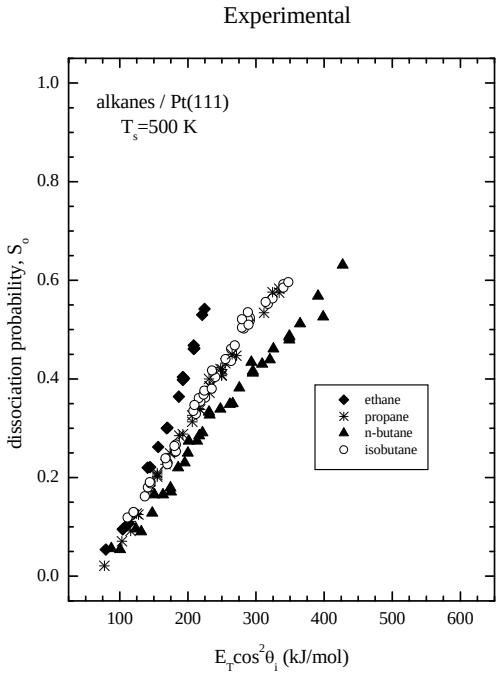

Fig. 1. Dissociative adsorption probabilities for alkanes on Pt(111)

As the molecular weight of the "linear" hydrocarbons is increased, the dissociation probability at a given kinetic energy decreases smoothly. However, the reaction probability for isobutane is greater than for n-butane, and for neopentane (not shown) the reaction probability is even greater, in contrast to what was expected if energy dissipation out of the reaction coordinate due to the excitation of lattice phonons dominates the collisional process prior to C-H bond scission. The trends in reactivity are best explained by differences in the steric factors for primary C-H bond cleavage.

The question remains, however, how reaction probabilities differ on different metal surfaces, how these differences are effected by the differing atomic masses and electronic features of the metals, and whether the effect of steric factors observed on Pt(111) also arise on the other metal surfaces –as they should if they arise from steric factors intrinsic to the molecules. For these reasons we examined the reactions of $C_2 - C_4$ hydrocarbons on Pd(111) and Ni(111) surfaces. These metals have surface structures very similar to Pt(111), and they differ significantly in their dynamical features, such as atomic mass and lattice force constants. Our results for Pd(111) are summarized in figure 2. Significantly, the dissociative reaction probabilities of the alkanes on Pd(111) show the same trend with molecular weight as for Pt(111).

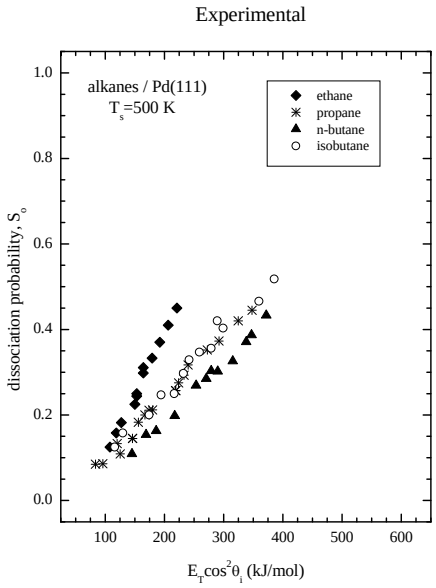

Fig. 2. Dissociative adsorption probabilities for alkanes on Pd(111)

There is a progressive shift of the reaction probabilities of the *linear* alkanes to lower values (at a constant incident normal energy) as the molecular weight increases, but there is a clear increase in the reactivity for *branched* hydrocarbons, relative to the linear hydrocarbon of the same molecular weight – the reactivity of isobutene is greater than that of n-butane. Furthermore, the reaction probabilities on Pd(111) are uniformly less than on Pt(111) (fig. 3). This effect does parallel the behavior observed for the relative values of the trapping probabilities.

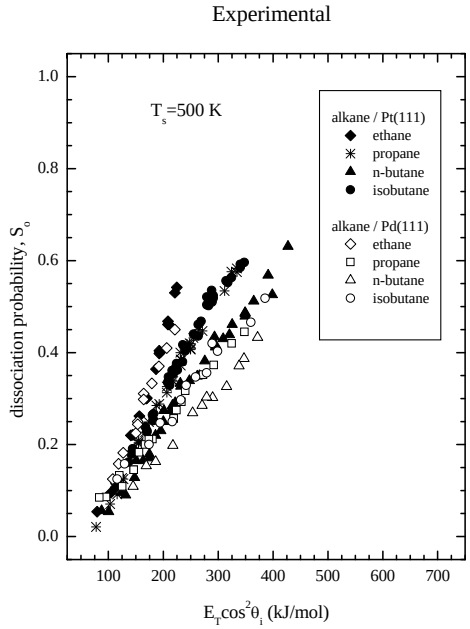

Fig. 3. Comparison of dissociative adsorption probabilities for alkanes on Pt(111) and Pd(111)

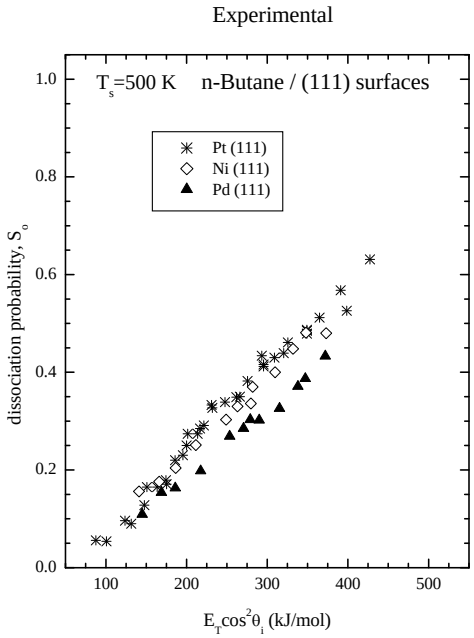

Fig. 4. Comparison of the direct dissociative adsorption probabilities of n-butane on Pt(111), Pd(111) and Ni(111).

However, if there were a significant effect, the reaction probabilities of the alkanes would be lowest on Pd(111) and highest on Ni(111), all else being equal. We have thus measured the energy dependence of direct collisionally activated dissociation of alkanes on both Pd(111) and Ni(111) to determine if the trend in reactivity reflects the substantially different degrees of energy transfer on Pt(111), Pd(111) and Ni(111) surfaces that occurs in molecular adsorption. To date we have completed our studies of reactions of propane and n-butane. We find that the differences in reaction probabilities of these molecules on Pt(111), Pd(111) and Ni(111) are low, suggesting that energy dissipation during the direct collisional activation is not a source of significant difference in the reactivity of the alkanes on these three surfaces.