

Adsorption Energies of Molecules and Molecular Fragments on Pt(111)

We also plan to measure the heats of adsorption of various species on Pt(111). We will study species of interest in catalysis, whose adsorption energies cannot be measured by TPD (i.e., those with high dissociation probabilities). The adsorption reactions to be studied include:

- (1) $c\text{-C}_5\text{H}_{8,g} \rightarrow \text{di-}\sigma\text{-}c\text{-C}_5\text{H}_{8,a}$, at 100-180K;
- (2) $c\text{-C}_6\text{H}_{10,g} \rightarrow \text{di-}\sigma\text{-}c\text{-C}_6\text{H}_{10,a}$, at 100-180K;
- (3) $c\text{-C}_6\text{H}_{10,g} \rightarrow \pi\text{-allyl } c\text{-C}_6\text{H}_9,a + \text{H}_a$, at 240-260K;
- (4) $c\text{-C}_6\text{H}_{10,g} \rightarrow \text{benzene}_a + 4\text{H}_a$, at 310K, low coverage;
- (5) $\text{benzene}_g \rightarrow \text{benzene}_a$, at 100-300K;
- (6) $2\text{H}_2\text{O}_g + \text{O}_a \rightarrow 2\text{OH}_a + \text{H}_2\text{O}_a$, at 170K; and,
- (7) $2\text{CH}_3\text{OH}_g + \text{O}_a \rightarrow 2\text{CH}_3\text{O}_a + \text{H}_2\text{O}_a$, at 170K.

Here the subscript "a" refers to gas and "g" is adsorbed phase. The temperature following the reaction is that temperature range where this reaction is known to occur with nearly unit sticking probability on Pt(111) at low coverages [16-22] [23-25]. While David King's group has performed beautiful, pioneering adsorption calorimetry on Pt(111) [26], his capabilities on Pt(111) crystals are limited to room temperature measurements and high vapor pressure gases. (He has made cryogenic measurements on Ni(100) [3], but Ni can be annealed at lower temperature than Pt(111). Annealing Pt would destroy the pyroelectric detector in King's approach.) Thus, these proposed experiments can not be performed by King's group.

In the first two reactions, two C-Pt σ bonds replace the C-C double bond, so these energetics should directly reveal the strength of C-Pt σ bonds. The change in this adsorption energy between ethylene (measured already by King's group [26], and the larger molecules should reveal if the other parts of these larger molecules interact with the surface.

Since the heat of hydrogen adsorption is fairly well known on Pt(111) from TPD [27, 28], reactions (3-4) should reveal the heats of formation of π -allyl $c\text{-C}_6\text{H}_9,a$ and adsorbed benzene. The later value can be checked more directly through the energy of reaction (5), which should tell us also if our heat of adsorption of hydrogen used in analyzing reactions (3) and (4) was correct. The bonding strengths of aromatic rings to Pt(111) should be revealed by the heat of reaction (5).

Reactions (6) and (7) should reveal the heats of formation of CH_3O_a and OH_a , since the heats of adsorption of oxygen and water are already fairly well estimated from TPD data [29, 30]. These values will in turn tell us the strength of Pt-O sigma bonds. It should be noted that the heat of formation of OH_a has been indirectly estimated from kinetic data [31].

These energies can be used to make predictions about the kinetics of various catalytically interesting elementary steps. For example, the difference in energies for reactions (2) and (3) should give us the energy of the reaction: $c\text{-C}_6\text{H}_{10,a} \rightarrow \pi\text{-allyl } c\text{-C}_6\text{H}_9,a + \text{H}_a$. This is a rapid dehydrogenation reaction whose kinetics we have measured [19]. Its activation energy is about 14 kcal/mol [19]. The reverse process is much slower, and difficult to measure. Its activation energy, however, should just be 14 kcal/mol minus this reaction energy. Since the heat of adsorption of cyclohexane is known [32], these energetics should also show us relative energetic stabilities of many of the key adsorbed intermediates in the catalytic dehydrogenation of cyclohexane to benzene.

To perform these experiments, we will be adding a molecular beam to one of our calorimeters (see below), so that we can extend our adsorption energy measurements to

molecules and not just metal atom beams. The molecular beam to be added has been designed to operate with low vapor pressure molecules, such as those above. The only other single crystal adsorption calorimeter in the world with a molecular beam is in David King's group at Cambridge in England, and it only handles high vapor pressure gases. Thus, we will be adding a new dimension to the world's capability in adsorption calorimetry.

REFERENCES:

3. Dixon-Warren, S.J., *et al.*, *Pyroelectric Single Crystal Adsorption Microcalorimetry at Low Temperatures: Oxygen on Ni(100)*. Surf. Sci., 1994. **307-309**: p. 16-22.
16. Jiang, L.Q. and B.E. Koel, *Hydrocarbon Trapping and Condensation on Pt(111)*. J. Phys. Chem. Lett., 1992. **96**: p. 8694.
17. Campbell, C.T., *et al.*, *Probing Ensemble Effects in Surface Reactions: I. Site-Size Requirements for the Dehydrogenation of Cyclic Hydrocarbons on Pt(111) Revealed by Bismuth Site Blocking*. J. Phys. Chem., 1989. **93**: p. 806-814.
18. Campbell, J.M., S.G. Seimanides, and C.T. Campbell, *Probing Ensemble Effects in Surface Reactions: II. Benzene Adsorption on Clean and Bismuth-Covered Pt(111)*. J. Phys. Chem., 1989. **93**: p. 815-826.
19. Henn, F.C., *et al.*, *The Decomposition of Cyclohexene on Pt(111): A BPTDS and HREELS Study*. J. Phys. Chem., 1992. **96**: p. 5965-5974.
20. Henn, F.C., P.J. Dalton, and C.T. Campbell, *Probing Ensemble Effects in Surface Reactions: IV. Cyclopentene Adsorption on Clean and Bismuth-Covered Pt(111)*. J. Phys. Chem., 1989. **93**: p. 836-846.
21. Berlowitz, P., *et al.*, *Temperature-Programmed Desorption Study of Ethylene on a Clean, a H-Covered, and an O-Covered Pt(111) Surface*. Langmuir, 1985. **1**: p. 206.
22. Windham, R.G., M.E. Bartram, and B.E. Koel, *Coadsorption of Ethylene and Potassium on Pt(111). I. Formation of a π -Bonded State of Ethylene*. J. Phys. Chem., 1988. **92**: p. 2862.
23. Creighton, J.R. and J.M. White, *The Decomposition of H₂O on Oxygen-Covered Pt(111): Thermal and Vibrational Excitation Effects*. Surf. Sci., 1984. **136**: p. 449.
24. Mitchell, G.E. and J.M. White, *Identification of the Intermediate in the Water Formation Reaction on Pt(111)*. Chem. Phys. Lett., 1987. **135**: p. 84.
25. Sexton, B.A., *Methanol Decomposition on Platinum (111)*. Surf. Sci., 1981. **102**: p. 271.
26. Brown, W.A., R. Kose, and D.A. King, *Femtomole Adsorption Calorimetry on Single-Crystal Surfaces*. Chem. Rev., 1998. **98**: p. 797-831.
27. Norton, P.R., J.A. Davies, and T.E. Jackman, *Absolute Coverage and Isosteric Heat of Adsorption of Deuterium on Pt(111) Studied by Nuclear Microanalysis*. Surf. Sci., 1982. **121**: p. 103.
28. Poelsma, B., G. Mechttersheimer, and G. Comsa, Surf. Sci., 1981. **111**: p. 519.
29. Campbell, C.T., *et al.*, *A Molecular Beam Study of the Interactions of O₂ with a Pt(111) Surface*. Surf. Sci., 1981. **107**: p. 220-236.
30. Gland, J.L., G.B. Fisher, and E.B. Kollin, J. Catal., 1982. **77**: p. 263.
31. Anton, A.B. and D.C. Cadogan, *The Mechanism and Kinetics of Water Formation on Pt(111)*. Surf. Sci. Lett., 1990. **239**: p. L548.
32. Rodriguez, J.A. and C.T. Campbell, *Probing Ensemble Effects in Surface Reactions: III. Cyclohexane Adsorption on Clean and Bismuth-Covered Pt(111)*. J. Phys. Chem., 1989. **93**: p. 826-835.