

## Recent Developments in Organoplatinum Chemistry

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Literature Seminar

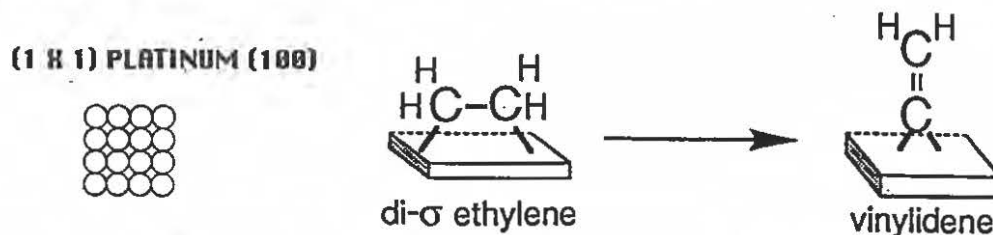
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Surface-adsorbate interactions are central to heterogeneous catalytic processes and better understanding of these interactions will lead to more efficient utilization and more effective design of catalytic processes [1]. In the past, surface science has relied heavily upon inorganic chemistry for interpretation of experimental data [2]. As surface science has evolved, so too has the need for useful inorganic molecular models, and these needs may be best met through an understanding of the current developments in surface science. Platinum, more than any other single metal, has played a significant role in heterogeneous catalysis and surface studies, and thus provides examples of many of these developments. Therefore, recent developments in surface organoplatinum chemistry hold particular relevance for inorganic chemists.

The surface of a metal can affect an adsorbate in many ways (e.g., bond scission, bond formation, bond localization, isomerization) and frequently the predominance of one event over another is site dependent. Somorjai's study of n-hexane over five different platinum faces showed marked structure dependencies for aromatization, which took place at a greater rate over Pt(111) faces, and internal C - C bond scission, whose rate was enhanced on the Pt(100) surface. This work demonstrates the importance of a hexagonal arrangement of surface atoms for optimal catalytic activity toward the production of aromatics [3].

The localization of benzene double bonds on Pt(111) was investigated by Van Hove and Somorjai using LEED techniques. In this pioneering work, it was postulated that benzene adopts  $C_{2v}$  symmetry and becomes buckled when adsorbed to the Pt(111) surface [4].

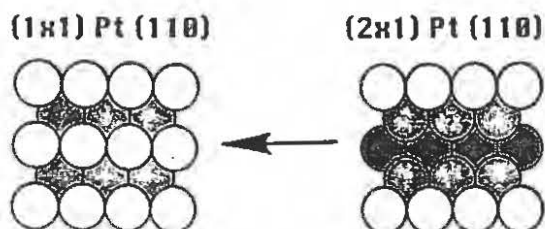
The study of ethylene bonding modes on various metal surfaces is not a new area of investigation [5], yet after nearly thirty years of experiment, questions remain, and site and temperature dependencies of these modes are areas of active inquiry. TPD and EELS comparisons of ethylene bonded to the (5 x 20) and (1 x 1) reconstructed faces of Pt(100) show a preference for ethynylidyne formation on the hexagonal sites of the (5 x 20) surface and vinylidene formation on the (1 x 1) surface [6]. On both surfaces a di-sigma ethylene configuration is favored at low temperatures [7]. The behavior of ethylene on the (5 x 20)Pt(100) surface was, as expected, very similar to the bonding of ethylene on Pt(111) due to the presence on both surfaces of hexagonal arrangements of atoms. However, the square arrangement of atoms on the (1 x 1)Pt(100) face exhibits very different behavior, with ethylene forming vinylidene and quad-acetylene intermediates [8].



An adsorbate can, and often does, have profound effects on the surface arrangement of atoms [9]. The surface is dynamic and often reconstructs simply because it is no longer in a bulk environment in order to minimize the surface free-energy. This is a well known phenomenon and has been so for many years. The predominant reconstruction type is that which produces a closer packed hexagonal surface atom arrangement from Pt(100) and Pt(110) faces [10]. Recently, work by Zehner and Gibbs has shown that even clean Pt(111) faces recon-

struct at temperatures which are 65% of the bulk melting temperature [11]. Such studies underscore the dynamic and fluid nature of a surface.

Adsorbates can remove the reconstruction of a clean metal surface, or alternatively can induce such a reconstruction. Ferrer and Bonzel developed a method to produce an unreconstructed Pt(110) surface in an effort to make such a surface accessible for study [12]. The procedure is an adgas-induced removal of the (2 x 1) reconstruction that is the predominant species on most Pt(110) surfaces. Schwartz and Schmidt followed the (1 x 1) to "hex" phase transition induced by the reaction of carbon monoxide and nitrogen monoxide on Pt(100) surfaces [13]. They found that surface structure had a significant effect on reaction rate and that the rate of dinitrogen production oscillated with a frequency that was dependent on the rate of surface reconstruction.



In similar work, Ertl et al. investigated the kinetic oscillations and faceting associated with the catalytic oxidation of carbon monoxide on a Pt(110) surface [14]. Their work revealed a repeating cycle of adgas induced reconstruction followed by a thermal reordering process.

For many heterogeneous catalytic processes there is more than one adsorbate species present on the surface, so adsorbate-adsorbate interactions cannot be ignored. One of the simplest effects of a coadsorbate is site-blocking. It may also be one of the most informative for inorganic chemists interested in synthesis of model compounds for surface reactions. The study of bismuth coadsorbed with ethylene on Pt(111) yielded information about the size of the surface site needed for ethylene adsorption (4 atoms) and the size needed for the decomposition of ethylene (5-6 atoms) [15]. It seems that this information would be helpful to those who design metal cluster compounds.

Adsorbates may also induce ordering of coadsorbate molecules as is the case of carbon monoxide coadsorbed with benzene. Somorjai's work used LEED analysis to determine that CO induces ordering of benzene and lowering of its symmetry to  $C_{2v}$ . However, it appears that the ring remains planar [16].

Perhaps the most dramatic effect of coadsorbates is that seen with alkali coadsorbates. Recent work has suggested that Cs atoms coadsorbed on Pt(111) surfaces induce a dipole moment in cyclic hydrocarbons sufficient to reverse the metal-hydrocarbon dipole [17].

## References

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