

Platinum Reactivity Rationalised

Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry

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Now that developments of ab initio calculation methodologies have turned quantum chemistry into a predictive tool for molecular systems involving light elements, a conference was sponsored by NATO and the Société de Chimie Physique in order to review progress on the application of similar methods to transition element systems, including those involving platinum group metals. This book consists of the proceedings of this meeting.

The carbonyl and olefin insertion (β -elimination) reactions in systems relevant to catalytic cycles have been studied by N. Koga and K. Morokuma (Okasaki, Japan). They found that the methyl group migrates in the former reaction and the hydride in the latter. In all these reactions the activation energy and the transition state structure are strongly dependent on the metal as well as on the ligand and other factors. These authors have also studied the oxidative addition/reductive elimination reaction, and claim that with a combination of all these reactions they will soon be able to derive a theoretical model for a complete cycle of homogeneous catalytic reactions, being able to predict how to change activation energies and heats of reaction. They aim to be able to provide a theoretical design mechanism for homogeneous catalysts.

The relevance of applying the principles of co-ordination chemistry to elucidate the detailed surface chemistry on small palladium clusters was described in a paper given by G. Pacchioni and J. Koutecky (Free University of Berlin). The interaction of hydrogen and carbon monoxide with the palladium was investigated, and the spectra predicted using molecular orbital calculations were in excellent agreement with the experimental photoemission spectra obtained for hydrogen and carbon monoxide on palladium.

Molecular orbital calculations have been used by H. Nakatsuji and M. Hada (Kyoto, Japan) to explain the selectivity of small palladium

clusters for the hydrogenation of acetylene impurities in ethylene streams, a reaction used in commercial processing. In this process, the hydrogenation of ethylene does not occur until all the acetylene impurity is converted into ethylene, and hardly any ethane is generated directly from acetylene. These selectivities occur despite the fact that palladium is an even better catalyst for the hydrogenation of pure ethylene. On the basis of the calculations, it is proposed that the explanation lies in the larger heat of adsorption on a palladium surface for acetylene compared with ethylene. Furthermore, acetylene has active π -bonds all around the carbon-carbon axis, whereas ethylene has π -orbitals only in the plane perpendicular to the molecular plane, giving acetylene a bigger potential for bonding to the palladium surface. The ethylene product generated by the hydrogenation of acetylene is coplanar with the active palladium atoms and is repelled from the surface rather than reduced to ethane.

The hydrogenation reaction proceeds in a smooth cycle, involving two steps. The first is the dissociative adsorption of the hydrogen molecule on the palladium surface and the other is the surface reaction between acetylene and hydrogen. Palladium shows catalytic activity in both these steps. Energetically the catalytic role of the palladium is more important in the first, but the second controls selectivity.

Two French theoretical chemists, B. Bigot and C. Minot, described their use of the extended Huckel method to demonstrate the adsorption of hydrogen on small platinum clusters. The energy of first adsorption depends on cluster size, being a maximum at Pt₃/Pt₁.

The conference proceedings show that the application of theoretical approaches is helping to elucidate the mechanism of reactions involving platinum group and other transition metal catalyst systems.

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