

"The Properties of Supported Metal Catalysts"

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Research Scope and Objectives

The overall scope has been to assemble carefully obtained data on sets of supported metal catalysts and to characterize them physically as well as possible. Catalysts in a given set would differ only in percentage exposed of the metallic component. Catalytic characterization would be accomplished using a number of test reactions via determination of the dependence of activity and selectivity upon supports, percentage exposed, metal particle size, shape, and perfection, and the conditions of preparation and metal reduction. Over the course of the work it has been necessary to add the conditions of pretreatment to this list.

The objective of the work was to produce a cohesive body of information on both catalyst characterization and catalytic activity that would permit unambiguous comparisons of, for example, two (or more) different metals with the same percentage exposed on the same support, the same metal at the same percentage exposed on two (or more) supports, and so on. It was felt that only such systematic research, conducted in the same laboratory using a variety of techniques, could provide a firm basis for the understanding of the nature of structure sensitivity in reactions catalyzed by supported metals.

Description of Research Effort

To date we have prepared graded series of Pt/SiO₂, Pt/Al₂O₃, Pd/SiO₂, Rh/SiO₂ and Co/SiO₂. The first three series have been extensively characterized via hydrogen chemisorption, hydrogen-oxygen titration, X-ray diffraction and EXAFS. Reactions investigated on these catalysts in our laboratory have included the hydrogenolysis of cyclopropane and methylcyclopropane, the hydrogenation of propylene and deuterium exchange with cyclopentane. Other reactions so investigated on the Pt/SiO₂ and Pt/Al₂O₃ have included CO oxidation (Prof. N. W. Cant in Australia), n-hexane reforming (Prof. J. W. Parera in Argentina) and benzene hydrogenation (Profs. J. Barbier and R. Maurel in France).

Our current research is directed toward correspondingly complete characterization, both physical and chemical, of the Rh/SiO₂ and Co/SiO₂ series, and the preparation and characterization of a CoRh/SiO₂ series prepared from heteronuclear carbonyl precursor compounds.

It is felt that there have been several significant contributions of this research over the years. A continuing fruitful effort has been the extensive application Fourier line profile analysis of X-ray data to the characterization of supported metals. Using such methods with conventional diffractometers we have been able to characterize materials such as Pt/SiO₂ and Pd/SiO₂ with percentage exposed as high as 40 (average particle size ca. 2 nm). Use of synchrotron radiation has permitted characterization up to percentage exposed on the order of 80. Reaction experiments, particularly with the hydrogenolysis reactions on supported Pt, have revealed that "structure-sensitivity" is only a relative term. We have demonstrated that it is possible

to change the apparent structure sensitivity of methylcyclopropane hydrogenolysis, for example, at will by altering the conditions of pretreatment in hydrogen. In such cases, the overall correlation in terms of percentage exposed is missing. We incline to the view that the usual model employed for interpretation of structure sensitivity is inadequate, and that the bounding planes of supported metal crystallites are incompletely filled with surface metal atoms (M_s) rather than completely filled. The surface vacancies make adjoining M_s resemble more the M_s at edges rather than M_s in densely packed and incomplete planes. This situation could lead to substantial variation in activity with pretreatment conditions and with the general previous history of the catalyst, as we have observed. The differences in the catalytic behavior of Pt and Pd, even for these simple reactions, is striking and somewhat unexpected. The arbitrary variation of structure sensitivity observed with Pt is suppressed to a large extent with Pd. It has been found that the activity of Pd in hydrogenation and hydrogenolysis reactions is to a significant degree dominated by the formation of β -PdH_{0.7}, which is both structure and temperature sensitive. In-situ X-ray experiments with methylcyclopropane hydrogenolysis demonstrated the existence of multiple steady states of relative hydride-metal compositions, dependent upon the startup conditions of the reaction. Hydride does not form for higher percentage exposed materials (< 30) at temperatures in the range of 273 K, but apparently forms for percentage exposed as high as 80 in the range of 200 K.

Future Research

Since this is the terminal year of this grant, our future research plans are dictated by the necessity to complete the physical and chemical characterization of Rh/SiO₂, Co/SiO₂ and, possibly, CoRh/SiO₂ to the same level of detail as that accomplished for the Pt and Pd series. Related studies are under way in the investigation of the role of halide content on structure sensitivity of hydrogenation, exchange and hydrogenolysis reactions on supported Pt, and in the investigation of the structure sensitive resistance to poisoning of supported Pt and Pd.