MASTER

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SUPPORTED CATALYSTS: SYNTHESIS AND CHARACTERIZATION

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The usual procedure for making metal supported catalysts is to impregnate porous solids with metal salt solutions and then to subject the dried product to thermal treatment. The particle size is varied by sintering while alloy preparation is based on simultaneous or successive impregnation of different salt solutions. These procedures are for the most part empirical and their physics and chemistry difficult to unravel.

The research scope of the project is the synthesis of both metal and support in aqueous solution as monodisperse colloidal and sub-colloidal particles, adsorption of the metal particles on the supports and isolation of the supported catalyst by centrifugation, drying, and thermal treatment. At each stage of the synthesis the preparations are characterized by a broad spectrum of physical and chemical techniques. Ultra-high resolution electron microscopy permits studying the process to its ultimate level--the visualization of atoms and their clusters.

The objective of the project was to make, by a reproducible and well-defined method, monodisperse metal catalysts of varying particle size and definite alloy composition for use in various processes for preparing useful fuels. These preparations should use the minimum amount of precious metals for maximum catalytic effect and at the same time minimize catalyst inactivation.

The basic scientific question is the determination of the effect of size and alloy composition on the catalytic activity for different reactions.

Extensive researches in the Princeton laboratories during the last three decades have established the principles governing the synthesis in aqueous solution of colloidal metals (1), their alloys (2), alumina(3), silica (4), and (in part) zeolite supports (5). Each stage of the process could be characterized by a variety of classical and recently developed techniques. The incisive tool in this characterization is the electron microscope, the latest versions being capable of visualizing individual atoms and clusters. The program established the basic steps in the synthesis: nucleation, growth and coagulation. By proper choice of experimental conditions, these steps could be isolated, studied and controlled.

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The nucleation process is one of polymerization-condensation of the starting inorganic monomer. Silicic acid or hydrated aluminum ions polymerize individually to form long polymeric chains. These, in the case of alumina, can be made to form fibers and plates. In the case of silica they can be made to form soft gels, hard gels or hard monodisperse spheres of controlled size. In the case of metal systems the metal ion and the organic reducing agent form co-polymers which, on reaching a certain size, undergo internal redox reaction to produce the colloidal metal. Using different metal ions, colloidal alloys can be formed. These polymers have been isolated in the case of gold and now are being studied for platinum, palladium and their alloys. Their formation was investigated by the STEM electron microscope at Brookhaven, (courtesy of Dr. J. Wall), where atoms and clusters of atoms can be resolved (6).

The growth step is carried out by inoculating a solution containing a potential reducing agent (such as gold chloride or palladium chloride and hydroxyl amine) with nuclei of either platinum, gold, or palladium. In this way by control of the proportion of the nuclei to the ion, the gold and palladium can be grown to the desired size and gold layered on platinum or palladium. Platinum can be grown on platinum by inoculating a hydrogen-platinum chloride system with platinum nuclei. The law of growth was determined.

The stability (7) of these colloidal sols is controlled by the electric charge on the particles which counteracts the effect of van der Waals' attraction. The charge is determined by adsorbed ions and can be controlled both in magnitude and in sign. The ionic atmosphere around each particle is controlled by the ionic strength of the solution. This has permitted us to verify the Smoluchovski formula for kinetics of cluster formation and the Verwey Overbeek relation for colloid stability. It has further permitted us to determine experimentally the Hammacker constant. Control of the charge on both metal particle and support permits localization of particles on the support.

The characterization of the materials so prepared can be made both in solution and in the solid phase. The techniques employed are optical absorption, light-scattering, viscosity, ultra-centrifugation, conventional electron microscopy (20 Å resolution), ultra-high resolution electron microscopy permitting visualization of individual atoms and atomic lattices in individual particles (6), laser Raman spectroscopy (8), electron spin resonance (9) and carbon-13 NMR (10) of adsorbed molecules. In solution, hydrogen peroxide decomposition kinetics was studied and the number of active centers determined by progressive poisoning using mercuric chloride (11). The turn-over number was compared with that of catalase. In the gas phase hydrogenation of olefins was investigated. The number of active centers was determined by a progressive

poisoning technique developed in our laboratories (12). This number was compared to the number of centers that chemisorb oxygen, carbon monoxide and hydrogen. Furthermore, this number was found to be the same as the number of surface atoms. The nature of the olefin was varied: ethylene, propylene, cyclohexene, butene and benzene. A variety of poisons was examined. Hydrogen-deuterium reaction was also investigated. This work was carried out for platinum and palladium particles of varying size and platinum-gold, platinum-palladium alloys (13). The turn-over number was found to be independent of particle size down to 20 Å but varying with alloy composition.

Absorption of hydrogen atoms (14) from the gas phase by calcium fluoride was established and the location of the hydrogen atoms in the lattice determined by electron spin resonance. The behavior of hydrogen atoms in silica support and platinum-on-silica was also studied. Electric fields in zeolite supports were determined by electron spin resonance studies of the rare earth ions in these materials.

Patent implications are being pursued.

Work was also carried on synthesis of colloidal particles for cancer therapy. A method was found for solubilizing insoluble platinum II compounds.

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