Nanostructured catalysts prepared

209th ACS National Meeting

ANAHEIM

Ultrafine catalyst particles of transition metals can now be prepared by a new method—sonochemical generation from organometallic precursors.

The sonochemical method facilitates control of particle properties and adjustment of catalytic selectivity for certain reactions, within limits. In addition, some catalysts, such as nanophase metallic carbides, are very difficult to prepare in any other way.

The new sonochemical techniques for catalyst preparation were developed by Kenneth S. Suslick, professor of chemistry at the University of Illinois, Urbana-Champaign. He reported on his research to the Divisions of Petroleum Chemistry and of Fuel Chemistry.

The sonochemical technique involves irradiating a liquid with intense high-frequency sound waves, typically 20 kHz. The waves cause the formation, rapid growth, and implosion of small bubbles in the liquid. Localized temperatures of about 5,000 K and localized pressures of 1,800 atm are typically encountered in such systems. "The energy required for synthesis comes from compressional heating of the gas, and from shock waves generated within the gas bubbles," according to Suslick.

The heating in the bubble is virtually adiabatic (it occurs with very little energy transfer), resulting in the formation of a "hot spot" in the bubble. This permits highly localized high-temperature chemistry within a medium that is at an average low temperature. Because the hot spots are only microns in size, cooling rates in the vicinity of the bubbles exceed 10^{10} K per second.

Suslick notes that several techniques are now being employed to generate nanometer structures. Among them are metal evaporation, reduction of metallic salts, and decomposition of organometallic compounds. However, he says that sonochemical synthesis offers some advantages.

When irradiated with ultrasound, in low-volatility solvents maintained under argon, volatile organometallic precursors yield solids with high surface areas. The solids are agglomerates of nanometer clusters and are very active catalysts for hydrocarbon reforming, carbon monoxide hydrogenation, and other reactions.

Says Suslick, "One of the advantages of sonochemical synthesis is that various forms of nanophase materials can be generated simply by changing the reaction medium." When the precursors are treated in a high-boiling alkane, such as decane or hexadecane, nanostructured powders result. If the same precursors are sonicated in a polymeric ligand, such as polyvinylpyrrolidone, metal colloids result. When the medium includes suspended inorganic oxide supports, such as silica or alumina, nanostructured supported catalysts are obtained.

Recently, molybdenum carbides and tungsten carbides have sparked interest in the catalytic community because of their similarity in catalytic activity to platinum-group metals. The high surface areas needed for catalysts are very difficult to produce in molybdenum and tungsten carbides. The usual procedure is programmed carburization of corresponding nitrides.

However, the carbides can be produced sonochemically by irradiation of the hexacarbonyl in hexadecane at low temperature. The elemental analysis of the resulting carbides confirmed the stoichiometry 2Mo:1C, but some oxygen is also present. Suslick says the formation of Mo_2C results from a disproportionation of carbon monoxide on the active metal surface that forms carbon and carbon dioxide. Electron micrographs of the particles show very porous structures and high-resolution transmission electron microscopy data show that the solids are aggregates of 2-nm particles.

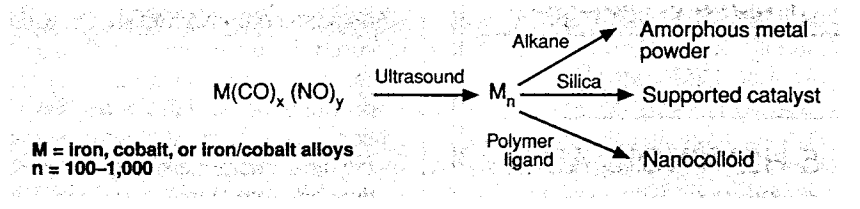
The presence of oxygen in the catalyst particles was cause for concern. Even after heat treatment in helium, about 4% residual oxygen was retained. This presence could have been a potential catalyst poison and was removed by treatment with a 1:1 methane:hydrogen mixture at 300 °C.

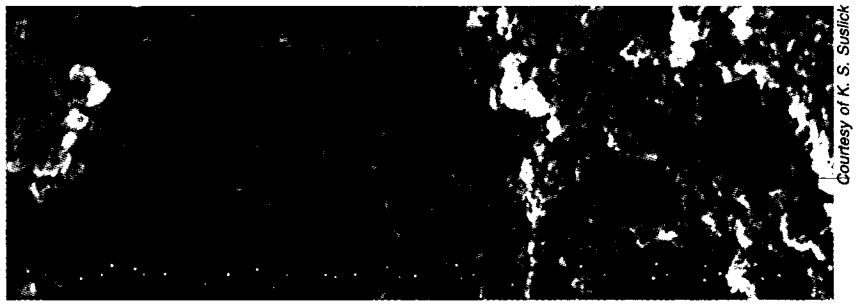
Catalytic activity was tested with the dehydrogenation of cyclohexane to benzene, which was the only product obtained. No hydrogenolysis was detected. One of the interesting properties of the catalysts generated by sonochemistry is that, as formed, they are amorphous. Subsequent heat treatment may induce gradual crystallization.

Iron- and cobalt-based catalysts are traditionally poor dehydrogenation catalysts (although they are very good at cracking cyclohexane to produce methane). But an alloy of iron and cobalt prepared by sonochemistry turns out to be a very good dehydrogenation catalyst. Suslick doesn't know why this is true, but it is a question his group currently is trying to answer.

Joseph Haggin

Ultrasonic synthesis can generate variety of materials





Courtesy of K. S. Suslick

Scanning electron micrograph of amorphous iron generated sonochemically