

A New Route to Intermetallics

Metal silicides and related intermetallic compounds with unusual properties are formed by exposing supported metals to volatile organometallics

A new and general procedure for preparing high surface area, supported alloys and intermetallic compounds has been developed by Lawrence Dubois and Ralph Nuzzo of AT&T Bell Laboratories in Murray Hill, New Jersey. The technique is based on the thermal decomposition of volatile group IIIA and IVA organometallic compounds on the clean surface of supported metals. The technique yields materials with unusual and potentially useful electronic and catalytic properties; it also provides a new way to modify the surface of catalysts in situ. Equally important, a variation of the technique can be used to produce passivating (protective) films on the surface of many metals.

Dubois described the technique at a conference at the University of Delaware's Center for Catalytic Science and Technology.* The first step is the conventional deposition of metal on an alumina or silica support (although the procedure can also be used with bulk metal or thin films). The volatile organometallic is then allowed to contact the surface of the metal at 100° to 300°C; in some cases, this is done in the presence of an excess of hydrogen. The composition of the alloy or intermetallic compound can be varied by changing the time of reaction, concentration of gas, and temperature, or by annealing the product.

In a typical example, silane (SiH_4) might be contacted with a nickel catalyst. The metal itself catalyzes the breakdown of silane. At low temperatures, silyl fragments (SiH_n) can be observed on the surface, but at 300°C the decomposition is complete, and the main product is dinickel silicide (Ni_2Si).

The technique seems to be very general. Among the group IIIA and IVA metals that can be deposited are silicon [as SiH_4 or $(\text{CH}_3)_2\text{SiH}_2$], germanium [as GeH_4 or $(\text{CH}_3)_2\text{GeH}_2$], boron [$\text{BH}_3 \cdot (\text{CH}_3\text{CH}_2)_3\text{N}$], and aluminum [$(\text{CH}_3\text{CH}_2)_3\text{Al}$]. The metals that have been used include iron, cobalt, molybdenum, rhodium, palladium, tungsten, platinum, gold, and silver.

Intermetallic compounds (which differ from alloys in that they have a fixed composition) can, of course, be made by conventional alloying techniques, and some have unusual catalytic properties.

But intermetallic catalysts have previously been prepared by pulverizing bulk material. Such catalysts have surface areas that are at least an order of magnitude lower than those of oxide-supported transition metal catalysts, and they thus have limited commercial utility. Catalysts prepared by the new technique have the desirable high surface areas.

The most thoroughly studied of the intermetallics is nickel disilicide. Dubois and Nuzzo find that the surface of NiSi_2 is characterized by alternating atoms of the two metals, so that there is no direct Ni-Ni or Si-Si bonding. "This type of bonding is very different from that in pure nickel or silicon," says Dubois.

Silanes sharply increase the selectivity of nickel catalysts.

Nickel disilicide has some unusual properties with respect to the binding of small gaseous molecules. Carbon monoxide, for example, binds very strongly to nickel as a molecular species (that is, as intact CO). "In stark contrast," says Dubois, molecular CO interacts only weakly with NiSi_2 and, once bound, dissociates rapidly to atomic carbon and oxygen. This process "is highly uncharacteristic of nickel and other group VIII metal surfaces." This sort of dissociative chemisorption of CO is observed for surfaces of early transition metals, he adds, but those metal surfaces also dissociate molecular hydrogen and nitrogen. NiSi_2 does not bind or dissociate either of those gases, although it does bind atomic hydrogen.

Also unusual is the fact that NiSi_2 disproportionates carbon dioxide to carbon monoxide and atomic oxygen. Many investigators have been searching for a catalytic system that would carry out this reaction; such a catalyst would make it potentially possible to produce hydrocarbons from atmospheric carbon dioxide. The Bell results are a step in this direction. Unfortunately, the reaction is not catalytic; once the surface is saturated, no further dissociation occurs.

With the exception of nickel disilicide's ability to disproportionate carbon

dioxide, these results are very similar to those obtained with heterogeneous catalysts in which there is a strong metal-support interaction (SMSI). SMSI systems are characterized by dramatically altered chemisorption properties and catalytic activity when compared to either a bulk metal or a typical supported catalyst. "In past discussions," says Dubois, "the exact structure of the surfaces in materials displaying SMSI were not known. . . . Our data clearly show that these effects can originate from surface compound formation."

The intermetallic compounds can have some unusual catalytic properties. When cyclohexane is passed over a conventional nickel catalyst on silica at 300°C, for example, about 15 percent is converted to benzene and about 26 percent undergoes hydrogenolysis to a mixture of hydrocarbons, predominantly *n*-hexane; the remaining 59 percent remains unreacted. When the catalyst is first treated with hexamethyldisilane, however, 64 percent of the cyclohexane is converted to benzene and there is no hydrogenolysis. Dubois attributes this change in selectivity to the fact that nickel silicide surfaces do not readily chemisorb hydrogen; hydrogenolysis is therefore inhibited.

A similar increase in selectivity is observed when germanium, boron, or aluminum is added to a nickel catalyst on alumina, but the activity of the catalyst for benzene production is reduced by a factor of between 2 and 10. Some of that activity can be restored, however, by heating the new material at 600°C for an hour. This treatment apparently reorganizes the surface structures to give higher total activity and greater stability with no loss of selectivity.

When both bulk and supported metal silicides are exposed to oxygen, a thin layer of silicon dioxide is formed on the surface and the metal is not oxidized. Similar results can be obtained by exposing metal oxides to silane at elevated temperatures. This layer of silicon dioxide is continuous and tightly bound to the metal and protects the metal from oxidation and other insults. This approach could be useful, Dubois says, for passivating conductors such as gold and copper in electronic devices. Unfortunately, the technique does not work for iron.

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*"New Eyes/New Insights," a daylong symposium, was held on 6 June at the University of Delaware, Newark.