

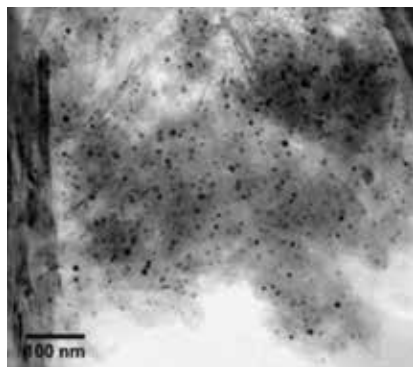


## Recoverable and Cost-Effective Platinum Catalysts for Hydrosilylation Applications

Since the hydrosilylation reaction was first reported in 1947, it has become a key process for the organosilicon industry. Metal-catalyzed hydrosilylation is recognized as one of the most important commercial applications of platinum in homogeneous catalysis.

With an estimated market value of \$18 billion, hydrosilylation products are used in road construction, bridges, pipelines, and other commercial applications, and they are expected to have a major role in emerging applications such as electric vehicles, health, and personal care. However, the organosilicon industry's reliance on depletable platinum-based catalyst systems has necessitated the development of increasingly efficient and cost-effective platinum catalysts. In addition, commercial cost constraints require that catalytic reactions be carried out without solvents and with a high degree of selectivity to lessen the need for additional product purification.

Homogeneous platinum catalysts used in hydrosilylation reactions often



▲ This transmission electron microscope (TEM) image shows platinum graphene nanoplate (Pt-GNP) catalysts. Pt particle size ranges from 4 nm to 8 nm. The high catalytic activity has been attributed to the surface interaction between Pt and graphene that facilitates electron transfer.

account for up to 30% of the final cost of a product (1, 2). However, in most instances, high product viscosity prohibits the recovery of the platinum and the purification of the product. This affects not only the cost of product preparation but also the shelf life of the product itself due to the presence of the catalyst. Thus, the development of a heterogeneous catalyst, which uses a support, would avoid precious metal loss in the product stream through easy separation of the catalyst and product streams in batch and continuous operations, providing a more cost-effective approach that would facilitate platinum recovery while increasing product quality.

The Center for Rational Catalyst Synthesis (CeRCaS) — an Industry-University Cooperative Research Center (IUCRC) funded by the U.S. National Science Foundation (NSF) involving Virginia Commonwealth Univ., the Univ. of South Carolina, the Univ. of California, Davis, and the Univ. of California, Berkeley — has focused on developing and expanding a new method of synthesizing highly active heterogeneous catalysts. One of the methods that CeRCaS employs combines the use of strong electrostatic adsorption techniques with solventless microwave irradiation (SEA-MW) to produce platinum catalysts supported by graphene nanoplates (GNP).

CeRCaS has previously demonstrated that graphene can serve as a semiconductor. The SEA step in the SEA-MW method provides a rational, controllable, and uniform uptake of  $\text{PtCl}_4^{2-}$  metal precursor onto the surface of the GNP support. The sample is then treated with solventless microwave irradiation to facilitate the simul-

taneous reduction of  $\text{PtCl}_4^{2-}$  to form small, well-dispersed Pt nanoparticles and graphene defects or holes that strongly anchor the Pt nanoparticles.

To test the catalyst, CeRCaS's initial evaluations began with the solvent-free hydrosilylation of 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD<sup>3</sup>M) on 1-octene. Under these conditions with low Pt loading (0.00125 mol%), their catalyst was able to produce quantitative conversion to the desired isomer in only 30 min at 40°C and with a catalyst turnover frequency (TOF) of  $4.8 \times 10^6/\text{hr}$ .

CeRCaS found that their catalyst performed with comparative efficiency to the homogeneous industrial benchmark, Karstedt catalyst, which has a TOF of  $5.2 \times 10^6/\text{hr}$ . Furthermore, they found the Pt-GNP catalyst to be effective with a broad range of olefin and siloxane substrates.

Most recently, the CeRCaS collaboration has focused on the attachment of Pt-GNP catalyst to conventional supports such as alumina and silica spheres in order to improve the ease of recovery and facilitate their use in packed bed reactor manufacturing platforms as well as batch reactor systems. They are currently working with manufacturing partners to demonstrate the use of these catalysts on a commercial scale.

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