

# **Design of High-Performance Alloy catalysts: Enhancing Activity and Switching Selectivity by the Incorporation of Palladium into Gold Nanoparticles**

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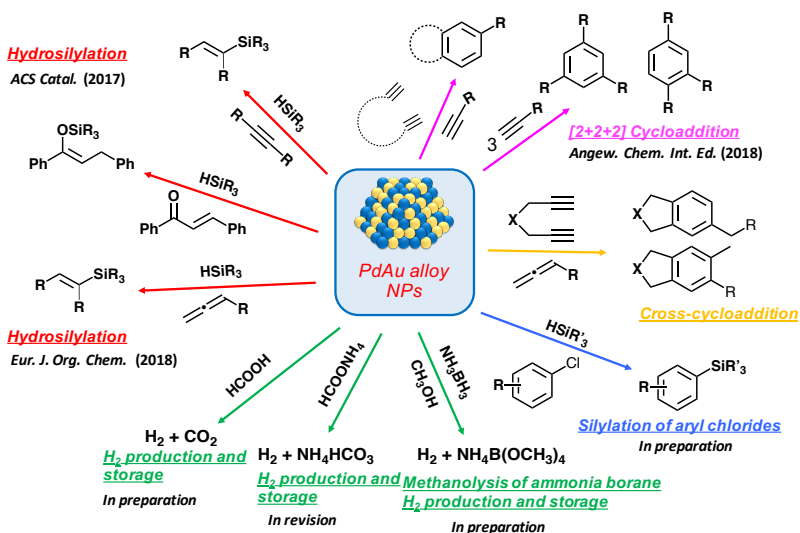
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The development of a novel catalytic system that can operate under mild conditions would be very important with regard to both synthetic and green chemistry. In this respect, the use of supported metal nanoparticles (NPs) as a heterogeneous catalyst is intriguing due to their high stability and high reusability, and the ease with which the catalysts can be separated from the products. On the other hand, considerable attention has recently been focused on the catalysis of alloy NPs in the field of synthetic chemistry. Alloy NPs, which are composed of two or more kinds of metals, may exhibit unique catalytic functions due to their completely different electronic states and structural conformations compared to the original monometallic NPs. Accordingly, we have rationally designed environmentally-benign supported alloy catalysts.

We recently reported that supported PdAu alloy catalyst functioned as an efficient catalyst for the hydrosilylation of  $\alpha,\beta$ -unsaturated ketones and alkynes under mild reaction conditions, whereas monometallic Pd and Au NP catalysts were totally ineffective<sup>1</sup>. Supported PdAu alloy catalysts also efficiently catalyzed the hydrosilylation of allenes to form alkenylsilanes<sup>2</sup>. Stratakis reported that the reaction at 65 °C with Au/TiO<sub>2</sub> catalyst proceeded smoothly to give the corresponding terminal alkenylsilane as a main product with high selectivity, but only a trace amount of products was obtained by the reaction with Au/TiO<sub>2</sub> catalyst at room temperature<sup>3</sup>. On the other hand, supported PdAu alloy catalyst showed high activity even under ambient conditions. Interestingly, the incorporation of Pd atoms into Au NPs drastically changed the regiochemistry of the products, and the main product in the reaction with PdAu alloy catalysts turned out to be the internal alkenylsilane. These results clearly indicated that the incorporation of Pd atoms into Au NPs not only remarkably enhanced the catalytic activity but also drastically changed the product selectivity. In addition to hydrosilylations, versatile and practical [2+2+2] cycloadditions of substituted alkynes were achieved with the use of supported Pd–Au alloy catalysts<sup>4</sup>.

We have developed supported PdAu alloy catalysts for a highly efficient and reversible hydrogen storage-release process based on the reversible reactions involving ammonium formate and bicarbonate. Supported PdAu alloy catalysts showed a higher activity than supported Pd catalyst in bicarbonate hydrogenation to storage hydrogen storage and formate dehydrogenation to produce hydrogen under ambient conditions even without additives such as base<sup>5</sup>.

In this lecture, based on detailed characterization and kinetic analysis, the relationship between the catalytic performance of supported PdAu alloy catalysts (Scheme 1) and the structure and electronic states of PdAu alloy NPs is discussed.



Scheme 1. Catalysis by supported PdAu alloy catalyst.

## References

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