



Gold-Free Catalysts Promise Efficient Vinyl Acetate Production

Worldwide demand for paints, coatings, and glues makes vinyl acetate (VA) monomer an important chemical with a market value of over \$10 billion per year. The demand for VA is increasing with rising solar energy adoption because VA-based polymers offer a way to encapsulate and protect the solar cells. Given the immense scale of VA manufacturing — about 10 million tons are produced per year — and projected future needs, there is rejuvenated interest in finding more efficient and sustainable VA production processes.

The current industrial process for VA synthesis involves oxidative coupling of gas-phase ethylene and acetic acid molecules on an alkali-promoted palladium-gold (PdAu) bimetallic catalyst supported on silica (SiO_2). The reaction is carried out at 160–180°C and 6–8 atm pressure, in fixed catalyst beds within 1-in. tubes that are several meters long. Feed compositions are typically around 60% ethylene, 15% acetic acid, and 7% O_2 . The reaction can achieve 90% selectivity but at low single-pass ethylene conversions (~7%), which requires separation and large recycle streams of unconverted reactants.

The high cost of Pd (~\$1,000/oz) and Au (~\$2,000/oz) and the leakage of some gold during catalyst production add to the upfront cost of the catalyst. Once the catalyst is in use, metal

leaching usually shortens its lifetime and necessitates catalyst replacement in one to two years, making the heavy use of precious metals unsustainable. Despite years of research, only PdAu alloys have been reported as promising VA synthesis catalysts.

To address the challenges involving the current PdAu catalysts, a team led by Prashant Deshlahra and Charles Sykes of Tufts Univ., funded by the U.S. National Science Foundation (NSF), used a multi-pronged experimental and computational approach that has led to the identification of new VA synthesis catalyst compositions, as well as a potentially broadly applicable method of catalyst preparation.

For example, the team identified copper (Cu), an inexpensive metal (~\$0.30/oz), as an alternative to Au, and their new SiO_2 -supported PdCu catalysts show promising activity and near 100% selectivity for low-oxygen-pressure VA synthesis. Alternatives to Pd were also identified, leading to less-expensive Pd- and Au-free formulations that give rates of more than 30 mole VA/(mole metal-hr) and 90% selectivity, which is similar to the performance of PdAu catalysts tested at identical and industrially relevant feed conditions and conversions. These new catalysts are stable in laboratory tests, which makes them promising drop-in replacements in current processes, and the team is in discussions with potential industrial partners to further assess paths to commercializing new catalyst compositions.

While PdAu catalysts require multistep catalyst preparation, the alloyed PdCu catalysts can be made from a physical mixture of powders with individual supported metals (Pd/ SiO_2 and Cu/ SiO_2) that spontaneously restructures and rapidly

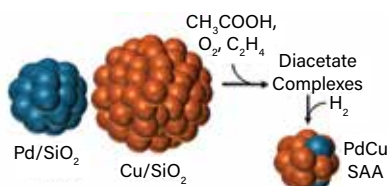
achieves atomic-scale mixing under reaction conditions. Essentially, the gas-phase VA synthesis reactants help synthesize the catalyst itself.

To understand the mechanism of this restructuring, the team used infrared spectroscopic measurements guided by density functional theory; this approach revealed that metal diacetate complexes form under oxidative conditions in the presence of acetic acid. The molecular nature of the diacetate complexes makes them highly mobile and allows rapid mixing. The mixed diacetates, when reduced to metallic form by hydrogen treatment, turn into well-mixed single-atom alloys (SAAs) that are active and selective catalysts. In contrast to typical nanoparticle sintering under reaction conditions, the PdCu SAA nanoparticles were, in fact, smaller than the parent nanoparticles before exposure to reaction conditions. The catalyst restructuring mechanism identified by the team provides an easy method for scalable production of Cu-based VA synthesis catalysts.

Dr. Mikhail Rodkin, an expert in industrial catalysis and a former vice president at BASF, commented, “This work has brought catalysis closer to the goal of ultimate atom efficiency when each valuable atom is an active site. The fact that the catalyst regroups and self-assembles to increase its performance is remarkable. A first-principles approach married to experimentation has produced a valuable catalyst for an important industrial process and is an example of the future of material design.”

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▲ PdCu single-atom alloy (SAA) catalysts spontaneously form when physical mixtures of monometallic nanoparticles are exposed to gas-phase vinyl acetate synthesis conditions.

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