SINGLE ATOM CATALYSTS

Separable Suzuki

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There is no shortage of palladium catalysts available to a chemist planning a Suzuki cross-coupling — a number of commercially available complexes are available (with $\text{Pd}(\text{PPh}_3)_4$ being perhaps the best known) and many more tailor-made systems reported in the literature. As with many homogenous systems, however, product isolation and metal contamination can be a concern. And although there are many successful heterogeneous systems, common problems such as metal leaching, aggregation, and deactivation are well-known issues. Now, Javier Pérez-Ramírez and co-workers have attempted to bring together the best of both of these worlds by synthesizing heterogeneous single-atom palladium catalysts.

The palladium was deposited on exfoliated graphitic carbon nitride, and only isolated palladium atoms were observed in the material (Pd-ECN). This was then used for a simple biaryl coupling, with the performance compared to that

of commonly used homogenous systems including $\text{Pd}(\text{PPh}_3)_4$ and Pd(II) complexes. The single atom catalyst showed, as might be expected, a significantly improved stability. However, this was not the only benefit — the performance in terms of rate, conversion, selectivity and purified yield were all higher for the new material.

Further work showed that the rate of biphenyl formation remained constant over at least 13 hours. The best-performing homogenous catalyst ($\text{Pd}(\text{PPh}_3)_4$) completely deactivated over a similar time period, whereas palladium acetate anchored on silica (PdAc-MPES/SiO_2) suffered from very significant metal leaching. Finally, density functional theory and molecular mechanics showed a mechanism not too dissimilar to that observed for molecular catalysts.

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