Single-atom catalysts:
a shift in catalysis science due to impact chemical and energy industries

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First clearly identified and termed accordingly by Zhang, Li, Liu and co-workers in 2011, when the team reported that single Pt atoms supported on FeO_x - and not Pt nanoparticles (NPs) - are responsible for the high activity (3 times more active than the NP counterpart) and remarkable stability observed in CO oxidation (1), single-atom catalysis (SAC) is a shift in catalysis science due to shortly impact the chemical and energy industries (2).

Thanks to recent fundamental work of Ananikov and co-workers in Russia (3), we know today that in industrially relevant transition metal catalysis such as in cross-coupling reactions mediated by palladium, mononuclear, cluster and nanoparticle metal species are all involved in catalysis. Commercially available samples of $Pd_2(dba)_3$ contain up to 40% of Pd NPs which, during catalysis, progressively decompose to form Pd complexes and clusters in solution, giving place to a "cocktail" of multiple catalytic species in solution (Figure 1).

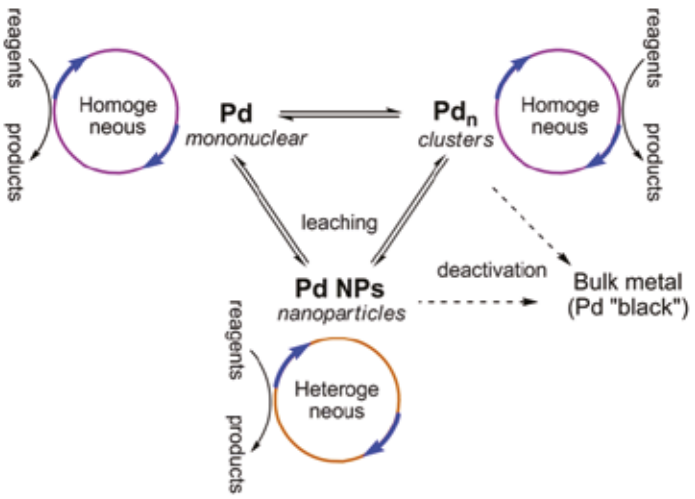

Figure 1. Pd catalysis of cross-coupling reactions using homogeneous Pd complexes involves a cocktail of catalytic species in solution. [Image courtesy of Prof. Valentine P. Ananikov, Russian Academy of the Sciences].

Single-atom catalysis is the ultimate consequence of applying the atom economy approach to heterogeneous catalysis, with full utilization of the available (and costly) metal atoms. A large body of research has been devoted to SAC since the original report. Readers are referred to a recent review article showing its dramatic potential (4). Here, we briefly summarize the two main technical issues remaining prior to widespread uptake of SAC in chemical productions, including hydrogen from water via enhanced electrolysis.

The first is the development of efficient methodologies affording SACs of higher metal load at low cost via repeatable synthetic routes. One could be photodeposition, such as in the case of atomically dispersed Pd_1/TiO_2 with up to 1.5 wt % palladium load, exhibiting >55 higher activity in the hydrogenation of aldehyde at room temperature as well as of C=C bonds, with no no decay in the catalytic activity (9).

Another is the top-down strategy to making single atom catalysts as it happens with the synchronous pyrolysis–deposition route affording Pt atoms on mesoporous metal oxides, starting from a solution containing Pt^{2+}, nitrates and mesoporous template of Pluronic F-127 (10).

The second main issue to be tackled is the stability of single-atom catalysts whose supported atoms, driven by the decrease of metal surface free energy, strongly tend to sinter into aggregated particles with rising temperatures. Again in China, a team led by Li at Tsinghua University has recently discovered that Pd, Pt, Au nanoparticles can actually be transformed to thermally stable single atoms above 900 °C (11).

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SOLAR HYDROGEN FROM ENHANCED WATER ELECTROLYSIS

In the solar economy sun, wind and water will be the main energy sources providing abundant and low cost electricity for all end uses (5), whereas renewable solar hydrogen generated splitting water via electrolysis will emerge as the key clean fuel to power hydrogen fuel cell electric vehicle (FCEVs) (6). In brief, hydrogen refueling stations installed across the world will all make use of water electrolysis to generate and compress on site hydrogen gas at the required 350 or 700 bar at which H_2 is dispensed at hydrogen fuel cell electric cars, buses and (soon) trucks (7).

Today, most water electrolysers use alkaline water electrolysis relying on Ni to mediate both the H_2 evolution reaction at the cathode and O_2 evolution reaction at the anode (nickel-plated mild steel). Advances in the electrocatalytic performance in terms of lower voltage (reduced energy demand), catalyst stability and reduced cost will greatly benefit the uptake of FCEVs.

A joint US-China team of scholars led by Tour discovered as early as of 2015 that single cobalt atoms at the surface of graphene doped with nitrogen efficiently mediate the hydrogen evolution with very low over-potential (30mV) in both basic and acidic conditions (8).

The N-doped graphene molecular sheets supporting the single Co atoms (Figure 2) enable both high electron mobility and stabilize the Co atoms against sintering via strong metal-support interaction. Indeed, the electrocatalyst shows a negligible decrease in activity after 10 hours of accelerated degradation studies in both acid and base conditions.

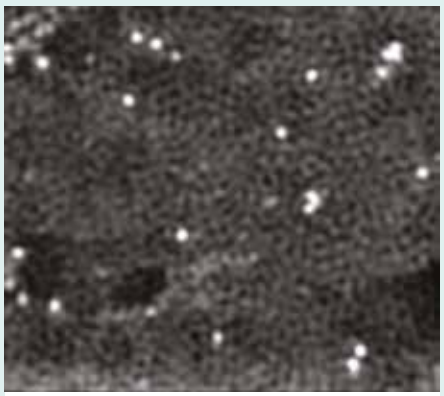

Figure 2. TEM of N-doped graphene functionalized with Co atoms. White spots correspond to Co atoms. [Photo courtesy of Professor James M. Tour, Rice University].

The catalyst synthetic protocol is simple and highly reproducible involving only sonication of graphene oxide (GO) in the presence of $CoCl_2 \cdot 6H_2O$ dissolved in water (weight ratio GO/Co=135:1), followed by freeze-drying to minimize re-stacking of the GO sheets, and calcination under an Ar/NH_3 atmosphere at 750 °C.

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