

# Metal Nanoparticles for C–H activation

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Contributor: Luigi Vaccaro, Federica Valentini, Oriana Piermatti

The design of highly active metal nanoparticles to be employed as efficient heterogeneous catalysts is a key tool for the construction of complex organic molecules and the minimization of their environmental costs. The formation of novel C–N bonds via C–H activation is an effective atom-economical strategy to access high value materials in pharmaceuticals, polymers, and natural product production.

Keywords: heterogeneous catalysis ; metal nanoparticles ; C–N bond formation ; C–H activation

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## 1. Introduction

Nowadays the development of efficient synthetic strategies to access value-added products in a cost-effective and atom-economical manner is an urgent challenge for modern chemistry. In the context of sustainable chemical production, the use of catalytic methods is therefore of key importance to access reactivity and selectivity that is otherwise inaccessible <sup>[1]</sup> <sup>[2]</sup>.

An effective step-economical catalytic construction of complex organic molecules is based on the use of direct C–H functionalization technologies <sup>[3]</sup><sup>[4]</sup><sup>[5]</sup><sup>[6]</sup>. Avoiding the needs of pre-functionalization substrates, the C–H functionalization methodology offers an effective approach to minimize the waste associated to the preparation of highly reactive building blocks <sup>[3]</sup><sup>[4]</sup><sup>[5]</sup><sup>[6]</sup><sup>[7]</sup><sup>[8]</sup><sup>[9]</sup><sup>[10]</sup><sup>[11]</sup><sup>[12]</sup><sup>[13]</sup><sup>[14]</sup>. The formation of C–metal bonds consecutive to the catalytic C–H bond cleavage increases the reactivity of otherwise inert C–H bonds, steering direct catalytic functionalization <sup>[15]</sup><sup>[16]</sup><sup>[17]</sup>.

In this scenario, several efforts have been dedicated to the development of various transition metal-based catalysts. Although homogeneous metal complexes are highly efficient in C–H activation reactions <sup>[18]</sup><sup>[19]</sup><sup>[20]</sup><sup>[21]</sup><sup>[22]</sup><sup>[23]</sup><sup>[24]</sup><sup>[25]</sup><sup>[26]</sup>, their difficult reusability and the inevitable waste produced from their separation from reaction products constitutes an important limitation for their actual use. To overcome these issues and improve the sustainability of C–H functionalization reactions, the design and use of heterogeneous catalysis is a valid yet challenging option <sup>[27]</sup><sup>[28]</sup><sup>[29]</sup><sup>[30]</sup><sup>[31]</sup><sup>[32]</sup><sup>[33]</sup><sup>[34]</sup><sup>[35]</sup><sup>[36]</sup><sup>[37]</sup><sup>[38]</sup>.

Nanocatalysis have emerged as a well-defined subclass of heterogeneous catalysis that comprehend both colloidal and supported nanoparticles <sup>[39]</sup><sup>[40]</sup><sup>[41]</sup><sup>[42]</sup><sup>[43]</sup>. Tailor-made supports and ligands used for the stabilization of metal nanoparticles (MNPs) play a key role in the design of nanocatalysts, influencing both shape and size. The reduced metal dimension at nanoscale makes MNPs potentially highly effective and desirable catalysts. The peculiar properties of nanometric-sized materials make MNPs interesting for their applications in the development of sustainable protocols for C–H functionalization reactions. In fact, the use of rare precious metals, generally employed in homogeneous catalysis, can be minimized with increased activity at the nanoscale. Indeed, less-reactive non-noble metals also lead to efficient nanocatalytic systems or supports by enhancing their catalytic efficiency. Nanomaterials may also be endowed with specific additional properties that enhance their applicative interest. For example, when MNPs are employed as photocatalysts <sup>[44]</sup><sup>[45]</sup>, light-activation can promote the single electron transfer mechanism (SET), or alternatively, NPs with magnetic properties can be separated from the reaction mixture, simplifying product isolation <sup>[46]</sup><sup>[47]</sup><sup>[48]</sup><sup>[49]</sup><sup>[50]</sup><sup>[51]</sup><sup>[52]</sup><sup>[53]</sup>.

Catalyst design strictly influences the operative mechanism of heterogeneous nanocatalysts, and therefore may affect their recoverability and reusability in addition to the metal contamination in the products <sup>[35]</sup><sup>[36]</sup><sup>[37]</sup><sup>[38]</sup>. Indeed, when MNPs are used in catalysis, the catalytic cycle can take place directly on the nanoparticle surfaces (heterogeneous mechanism) or it can be promoted by some soluble species released in solution (homogeneous mechanism). Generally, in the latter case, effective nanocatalysts are of major interest if the metallic active species returns to the surface at the end of the catalytic cycle, defining a “release and catch” mechanism <sup>[54]</sup><sup>[55]</sup>.

## 2. C–H Amination

Different C–H amination processes have been developed with the use of copper based nanocatalysts, employing as nitrogen sources primary <sup>[56][57]</sup> or secondary <sup>[58][57][59][60]</sup> amines, as well as ammonia <sup>[61]</sup>.

In 2014 Nageswar and coworkers reported the synthesis of 2-substituted benzothiazoles through direct C–H amination catalyzed by magnetic copper ferrite nanoparticles <sup>[59]</sup>. The air-stable CuFe<sub>2</sub>O<sub>4</sub> nanocatalyst can be easily separated from the reaction mixture thanks to its magnetic properties. This feature allowed the authors to efficiently recover and reuse the catalytic system for four consecutive runs without any loss in conversion. Furthermore, XRD, TEM, and SEM analyses confirmed the stability of the copper ferrite nanocatalyst. However, the authors did not envisage any mechanistic proposal regarding the direct C–H amination.

A different protocol for the oxidative amination of benzene to aniline promoted by a Cu(II)-based nanocatalyst in the presence of H<sub>2</sub>O<sub>2</sub> was developed by Bal and coworkers <sup>[61]</sup>. The authors used a bimetallic copper-chromium oxide as a support for Cu(II) NPs (Cu(II)-CuCr<sub>2</sub>O<sub>4</sub>) and tested different reaction conditions to obtain the best selectivity in aniline with the lowest amount of phenol formed as side-product. The catalytic activity remained unchanged for up to five consecutive runs and no metal leaching was detected in solution, suggesting the heterogeneous nature of the catalyst. In addition, the change in conversion during the experiment in the presence of TEMPO as a radical scavenger led the authors to propose a reaction mechanism which involves the formation of NH<sub>2</sub>OH and a subsequent reduction to protonated amino radicals. Different catalytic tests were conducted by varying the ratio between NH<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, proving that the reaction path starts with the C–H bond activation of benzene in presence of H<sub>2</sub>O<sub>2</sub>.

Very recently, the same group employed copper-supported on spherical MnO in the C–H amination of 8-aminoquinoline benzamides <sup>[58]</sup>. In comparison with the results obtained for the amidation reaction, the direct amination proceeds under milder reaction conditions. After 6 h at 100 °C, different products were obtained in excellent yields without the addition of any additives. Only the primary amine and indole were not compatible with the optimized reaction conditions. However, when the reaction was scaled up to gram scale, a comparable yield was recorded in the C–H amination of 8-aminoquinoline benzamides with 4-methylpiperidine. The Cu-MnO was efficiently recycled for five consecutive runs with negligible loss in efficiency associated with the sintering of the impregnated copper.

## 3. C–N Bond Formation in the Synthesis of Heterocycles

Particularly intriguing is the preparation of widely useful heterocycles exploiting direct C–N bond formation. An example is given by the intramolecular oxidative C–H amidation process proposed by Patel and coworkers for the synthesis of 2,3-disubstituted quinazolinones <sup>[62]</sup>. Using CuO nanoparticles, several quinazolinones were obtained from different ortho-halobenzamides and benzylamines in DMF under air *via* an Ullman coupling followed by an oxidative intramolecular C–H amidation. To further confirm the proposed mechanism, the authors performed the reaction under inert atmosphere, obtaining only Ullman's product. The latter was placed under optimized reaction conditions, in the presence of air, affording the desired product and confirming the presence of this intermediate during the reaction. After the recovery and reuse of the CuO nanocatalyst, a slight decrease in catalytic efficiency was observed due to a change in the morphology of the CuO material after the recovery. Indeed, TEM images of the used catalyst showed the presence of particle aggregates formed during the reaction.

In 2014 Ying and coworkers developed eight different palladium NP-based catalysts for the synthesis of carbazoles *via* intramolecular C–H amination <sup>[63]</sup>. The authors investigated the role of the support in Pd stabilization, highlighting the dependence of catalyst reactivity on the interactions between Pd and the support. After testing Ag-Pd/C, Ag@Pd/C, Ag<sub>2</sub>S@Pd/C, Pd/C, Pd/CeO<sub>2</sub>, Pd/TiO<sub>2</sub>, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/SiO<sub>2</sub> in DMSO as a reaction medium, the highest catalytic activity was that of Pd/C. This material was then selected for further optimization. The authors found the use of 4 Å molecular sieves crucial to remove the only byproduct, water, formed during the reaction using O<sub>2</sub> as oxidant. Despite the good tolerability of the Pd/C catalyst for different substrates, during the recycle experiments the conversion dropped by 12% and 50%, respectively for the two subsequent recycles. The drop in catalytic efficiency was explained by TEM analyses that revealed an increase of the particle size distribution from 2–5 nm to 20–30 nm. However, the Pd 3d peaks from XPS analyses before and after the C–H amination process showed no significant modification of the surfaces. By performing a series of hot filtration experiments, with and without oxygen, the authors proposed a homogeneous nature of the catalysis driven by both O<sub>2</sub> and DMSO. Indeed, after the filtration of solid catalyst the reaction proceeded only in presence of oxygen. The role of oxygen reveals to be crucial for the solubilization of Pd(II) active species, probably as Pd-DMSO complexes. The same behavior was also revealed when the CeO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> Pd-supported nanomaterials were employed. The Pd/C, Pd/CeO<sub>2</sub>, and Ag<sub>2</sub>S@Pd/C nanocatalysts presented a higher amount of Pd(II) species than

the other materials. Among these, the inactive Ag<sub>2</sub>S@Pd/C had its Pd(II)-associated peaks shifted to lower values. The authors suggested that the different interactions between Pd(II) and the supports influenced catalytic efficiency, as it is related to the dissolution of palladium in DMSO.

During the same year, Arisawa and coworkers reported the synthesis of *N*-aryl-benzotriazoles via a sequence of 1,7-palladium migration, cyclization, and dealkylation catalyzed by sulfur-modified gold-supported Pd NPs (SAuPd) [64]. The authors focused initially on the choice of the most adequate oxidant to promote the formation of Pd(II) species and found that PhI(OAc)<sub>2</sub> combined with KOAc as a base and DMF as the medium to produce optimal reaction conditions. The protocol is applicable to different substrates; however, recycling or further tests to determine the mechanism and the nature of the catalysis were not reported.

One year later, Kantam and coworkers developed an efficient Pd-based heterogeneous catalyst for the synthesis of *N*-pyridyl indoles [65]. The authors tested different heterogeneous Pd(0) NP-based catalysts and found the role of the nanocrystalline magnesium oxide support beneficial to the reaction using CuCl<sub>2</sub> as oxidant. The developed catalyst (NAP-Mg-Pd(0)) was efficiently recovered and reused for four consecutive runs without loss in efficiency or Pd leaching in solution. Moreover, the comparison of TEM images between the fresh and spent catalysts showed no change in morphology after four cycles. However, further experiments about the reaction mechanism were not reported by the authors.

## 4. Conclusions and Future Outlooks

The direct construction of novel C–N bond is of great interest in different areas leading to an atom-economical strategy to access high-value products. The precious metals, generally used as homogenous catalytic systems, could possibly be replaced with more convenient heterogeneous systems that allow for an easy separation of the catalyst from the reaction mixture, the reuse of the catalytic system and a minimization of product metal contamination.

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