



HAL
open science

Earth-Abundant d-Block Metal Nanocatalysis for Coupling Reactions in Polyols

Marc Camats, Daniel Pla, Montserrat Gomez

► **To cite this version:**

Marc Camats, Daniel Pla, Montserrat Gomez. Earth-Abundant d-Block Metal Nanocatalysis for Coupling Reactions in Polyols. Recent advances in nanoparticle catalysis, 2020. hal-03011363

HAL Id: hal-03011363

<https://hal.science/hal-03011363>

Submitted on 18 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chapter 8

Earth-Abundant D-Block Metal Nanocatalysis for Coupling Reactions in Polyols



Marc Camats, Daniel Pla, and Montserrat Gómez

Abstract Green Chemistry concepts have directed chemists to conceive and develop sustainable procedures, from the starting materials choice through reaction and analysis conditions, including suitable engineering aspects, to the impact of products, comprising recycling, and waste management. Industrial processes in Fine and Pharmaceutical Chemistry sector have high E factors compared to oil and bulk chemicals industry. Thus, the development of catalytic methods leading to high added value products is crucial, as well as waste minimization through selective transformations. Catalysts from 3d metals, compared to “heavy” metals, are greener, although a combination of different approaches is needed for efficient and viable processes. In contrast to 4d and 5d metals, catalysis with earth-abundant metals is less developed, even less concerning nanocatalysts. Metal nanoparticles, due to their unique electronic and structural properties, induce original reactivities allowing a plethora of transformations. Besides, solvents, present in most steps, represent a major economic and environmental concern. In addition, they can have a dramatic influence on the stabilization of MNP and hence, a huge impact on catalytic activity and recycling. This chapter gives a perspective on 3d metal-based nanocatalysts in polyols applied in couplings, reactions present in many methodologies to produce fine chemicals in a sustainable fashion.

AQ1

Keywords 3d metals · Metal nanoparticles · Catalysis · Couplings · Polyols

Dedicated to Prof. Guillermo Muller for his thorough contributions in Organometallic Chemistry and Homogeneous Catalysis.

M. Camats · D. Pla · M. Gómez (✉)
Laboratoire Hétérochimie Fondamentale et Appliquée (UMR 5069), Université de Toulouse,
CNRS, 118 Route de Narbonne, 31062 Toulouse Cedex 9, France
e-mail: gomez@chimie.ups-tlse.fr

D. Pla
e-mail: pla@lhfa.fr

© Springer Nature Switzerland AG 2020
P. W. N. M. van Leeuwen and C. Claver (eds.), *Recent Advances in Nanoparticle Catalysis*,
Molecular Catalysis 1, https://doi.org/10.1007/978-3-030-45823-2_8

1

8.1 Introduction

AQ2

In the 1990s, a ground-breaking movement concerning the Earth preservation for future generations has appeared. In Chemistry, these actions led to the Green Chemistry concept (“Green Chemistry” by Paul et al. [57], Warner et al. [128] articulated through the 12 Green Chemistry Principles [6]; shortly after, the Sandestin declaration established the bases of the Green Engineering Principles [8]. Without any doubt, catalysis is one of the most important pillars of Green approaches [7]. Analyzing the evolution of metal-based catalysis, involving homogeneous and heterogeneous systems, it is evident to conclude that definitely the twentieth century has been the century of “heavy” metal-based catalysts, *i.e.*, catalytic processes concerning 4d and 5d metals (such as Mo, Ru, Rh, Ir, Pd, Pt, Au ...), as internationally acknowledged by the Nobel Prizes in 2005 (Y. Chauvin, R. H. Grubbs and R. R. Schrock) and 2010 (R. F. Heck, E.-i. Negishi and A. Suzuki) for the development of metathesis processes (mainly Mo- and Ru-based catalysts) and Pd-catalyzed couplings in organic synthesis, respectively (www.nobelprize.org/prizes/chemistry/2005/summary; www.nobelprize.org/prizes/chemistry/2010/summary). Nevertheless, nature has exploited earth abundant 3d metals (Fe, Ni, Cu, Zn ...), leading to metalloenzymes which exhibit a prominent specificity [15]. In coherence to a sustainable development, researches on the design of manufactured catalysts with first-row transition metals have exponentially grown since the 2000s (see the contributions collected in the special issue “First row metals and catalysis” of Chemical Reviews, 2019) [2, 4, 46, 48, 64, 78, 100, 123, 129] (Fig. 8.1).

On the other hand, solvents represent one of the major concerns for chemical transformations (employed in synthesis, extractions, purifications, analyses...), in particular volatile organic compounds which are generally toxic showing different levels of harmfulness and danger, submitted to severe regulations. Alternative solvents (water, ionic liquids and deep eutectic solvents, alcohols, supercritical fluids,

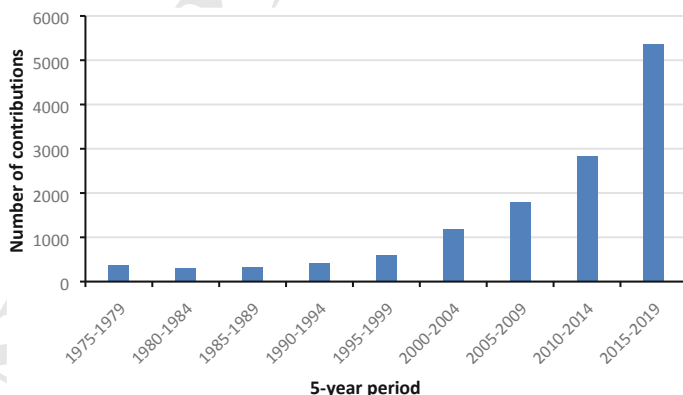


Fig. 8.1 Published contributions per 5-year period for first-row transition metals used in catalysis (data collected from SciFinder Database since 1975 up to July 2019)

renewable solvents, combination of different solvents...) and solvent-free chemistry are useful and efficient approaches for many applications, needing investment and effort to adapt the current processes to the new reaction conditions [68]. In the frame of this chapter, we are interested in polyols, largely used in the industrial sector (highlighting the production of polymers such as polyurethanes, polyvinyl alcohol ...), because they present lower environmental impact than low-weight and volatile organic compounds, and they are particularly attractive for the synthesis and stabilization of nano-sized metal clusters.

Focusing on this type of nanomaterials, well-defined metal-based nanoparticles (objects showing dimensions in the range 1–100 nm) have known a huge expansion since the 1980s due to their distinctive properties, both physical and chemical, in comparison to molecular and bulk materials. Actually, this is a consequence of their electronic and structural features, making possible a vast number of applications [110, 121, 133], in particular in catalysis [1, 54, 88, 110, 111]. Even though metal nanoparticles (MNPs) have been largely applied in classical heterogeneous catalysis, with crucial participation in industrial processes mainly those related to oil area [136], nanocatalysis, which concerns MNPs dispersed in a solvent have been only developed since the end of the last century. This exponential growth has benefited of the recent advances in characterization techniques (including operando approaches) which has permitted the design of catalysts at nanometric scale by means of controlling morphology and surface state of nanoobjects [5, 9, 62, 89]. Noticeably, reproducible synthetic methodologies are crucial for their further applications [106, 122]. The chemical strategies (commonly named bottom-up syntheses) often include solvents, from conventional organic compounds to alternative ones (showing a lower environmental impact), such as water [20, 109], ionic liquids [104], scCO_2 , [30, 99, 134], polyols [22, 38, 41]. It is important to mention that solvents may be involved in different aspects, for example, as reducing agents, stabilizers, or medium for trapping nanocatalysts preserving their morphology during the catalytic transformation and thus facilitating their recycling. This is the case when polyols are present. In 1989, the polyol methodology was for the first time reported by Fiévet and coworkers where metal salts were reduced in ethylene glycol, obtaining well-defined MNPs [42, 43]. In this method, the polyol acts as solvent, reducing agent, and stabilizer when higher polyols are involved (e.g., polyphenols or polysaccharides), which prevents the agglomeration of MNPs in solution [34, 41].

These privileged physicochemical properties favor the preparation of tailor-made first-row transition metal nanocatalysts and derived nanocomposites in a controlled manner. Rational catalyst design is essential for the preparation of well-defined clusters and nanoparticles with optimal properties in terms of redox control, cooperative effects, and increased surface areas, all of them are key factors for catalysis. Beyond the dual catalytic behavior related to both surface and reservoir of molecular species, nanocatalysis brings novel reaction manifolds due to the unique structural properties of MNPs, particularly their differential electronic structure as compared to bulk metals (e.g., facilitating single electron transfer processes via the Fermi level for electrons [40]).

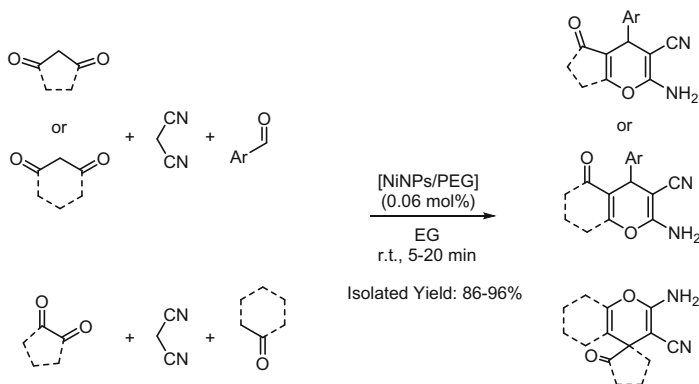
91 In the present contribution, we focus on the recent advances in 3d metal nanocat-
92 alysts (for a recent review, see: [127]), involving polyols acting as stabilizer and/or
93 reaction medium for coupling reactions, Carbon–Carbon and Carbon–Heteroatom
94 bond formation processes, including multicomponent syntheses.

95 8.2 Carbon–Carbon Bond Formation

96 C–C cross-coupling reactions have been largely dominated by palladium-based cat-
97 alyzed processes due to their efficiency and versatility. In particular, the ability of
98 this metal to stabilize different kinds of species (complexes, nanoparticles, extended
99 surfaces) and its relatively high robustness under many different reaction conditions
100 has permitted the elucidation of the corresponding mechanisms [17, 119, 124]. From
101 a sustainable chemistry point of view, the use of first-row transition metals is obvi-
102 ously preferred and a huge research has been developed in the last years (for instance,
103 see the contributions published in the Accounts of Chemical Research special issue
104 “Earth Abundant Metals in Homogeneous Catalysis,” [26]).

105 8.2.1 Lewis Acid-Catalyzed Coupling Reactions

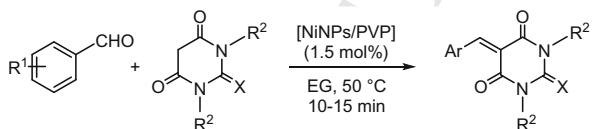
106 Heterocyclic motifs are present in a large variety of naturally occurring products
107 along with industrial compounds [35, 58, 65, 101]. Multicomponent reactions rep-
108 resent an environmentally friendly approach to prepare polyfunctional compounds,
109 in particular heterocycle derivatives, via one-pot processes involving three or more
110 reactants, with high atom economy and easy implementation [18, 130, 138]. These
111 transformations are often promoted by Lewis acids, which favor the kinetics direct-
112 ing the reaction pathway and in consequence improving the selectivity [49]. In this
113 frame, Khurana and coworkers reported nickel nanoparticles (NiNPs) stabilized by
114 polyethylene glycol (PEG-4000) and prepared by polyol-based methodology using
115 ethylene glycol in the presence of NaBH₄, which was applied in the synthesis of
116 spiropyrans [72], interesting materials particularly due to their unique molecular
117 switch triggering structural isomerization under the effect of different external stimuli
118 (light, mechanical stress, temperature...) [74, 82, 131]. They were synthesized by a
119 multicomponent reaction, constituted of a tandem Knoevenagel-cyclo-condensation
120 involving ninhydrin (or related cyclic dicarbonyl compounds), malonitrile, and dime-
121 done (or related 1,3-dicarbonyl derivatives) (Scheme 8.1). The role of the nanocat-
122 alyst (mean size: ca. 7 nm determined by TEM) was evidenced by different control
123 tests; in the absence of nickel, the reaction was much slower (some hours vs. some
124 minutes) and the use of Ni powder (particle size <150 μm) led to moderate yields
125 after 8 h of reaction. Ethylene glycol was a convenient solvent permitting a straight-
126 forward biphasic extraction of products by a biphasic system (using ethyl acetate
127 as immiscible soluble with ethylene glycol), preserving the catalyst dispersed in the



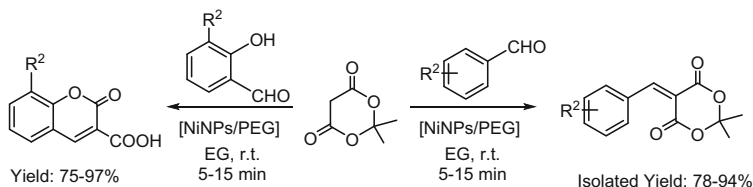
Scheme 8.1 Synthesis of spiroyrans by a multicomponent reaction catalyzed by NiNPs and stabilized by PEG in ethylene glycol [72]

128 diol. NiNPs were efficiently reused up to 3 times. Authors postulated that nickel
129 activates carbonyl and nitrile groups.

130 The same authors previously reported Knoevenagel condensations of barbituric
131 or Meldrum acid and aromatic aldehydes in EG, catalyzed by NiNPs and stabilized
132 by PVP (polyvinylpyrrolidone) [70] and PEG [71], respectively (Scheme 8.2).



X = O, S
 R₁ = H, F, Cl, Br, CH=CH, CH₃, OH...
 R₂ = H, CH₃, Ph
 (R₁ in different positions; also
 polysubstituted aromatic groups)

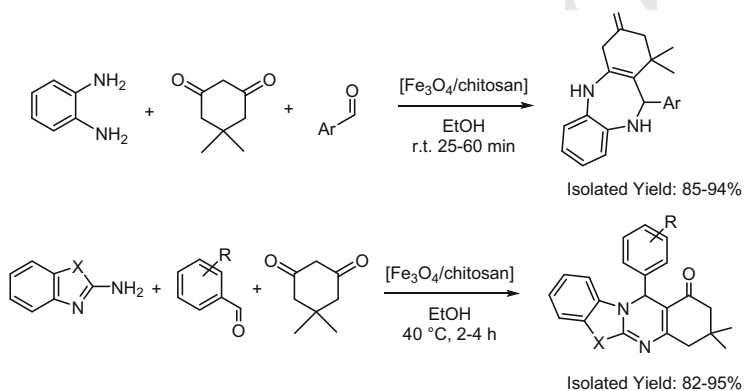


R¹ = H, Cl, CH=CH, CH₃, OCH₃, OH...
 R² = H, CH₃, Ph
 (R¹ and R² in different positions; also
 polysubstituted aromatic groups)

Scheme 8.2 NiNPs stabilized by polymers catalyzed Knoevenagel condensations in ethylene glycol [70, 71]

133 Maleki and coworkers synthesized Fe_3O_4 nanoparticles stabilized by the biopolymer
 134 chitosan coming from chitin (polymer of *N*-acetylglucosamine) to be applied in
 135 three-component reactions yielding benzodiazepines [85] and benzimidazoloquinazolinones
 136 [83] (Scheme 8.3), which present biological and pharmacological activities
 137 [24, 56]. For both types of reactions, the catalyst was recycled up to four times pre-
 138 serving its catalytic performance, being ethanol the most appropriate solvent for these
 139 catalytic reactions. Authors proposed a similar pathway for both transformations.

140 In Fig. 8.2, the postulated mechanism for the synthesis of benzimidazo[2,3-
 141 *b*]quinazolinones is illustrated. The reaction most likely starts by a Knoevenagel



Scheme 8.3 Three-component reactions catalyzed by Fe_3O_4 nanoparticles stabilized by chitosan [83, 85]

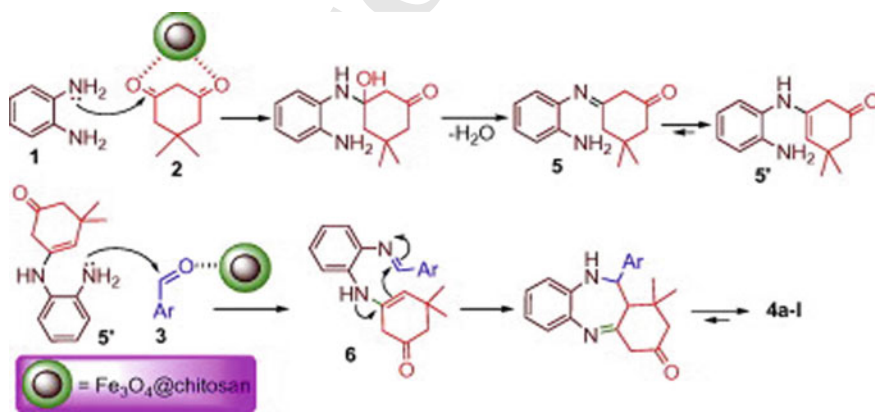


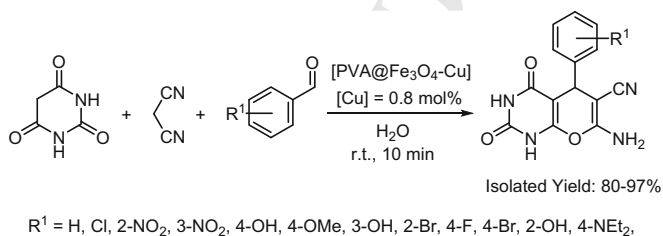
Fig. 8.2 Proposed mechanism for Fe-based catalyzed synthesis of benzimidazo[2,3-*b*]quinazolinones. Reprinted from [83] with permission from Elsevier 2015, license no. 4639401066332

142 condensation between the aromatic aldehyde and dimedone; the resulting α,β -
 143 unsaturated ketone reacts with the 2-aminobenzimidazole or its corresponding thio-
 144 derivative via a Michael addition, giving an acyclic compound which undergoes a fur-
 145 ther intramolecular cyclization. Similar catalysts were also applied for the synthesis
 146 of 2-amino-4H-chromenes [107] and highly substituted pyridines [84].

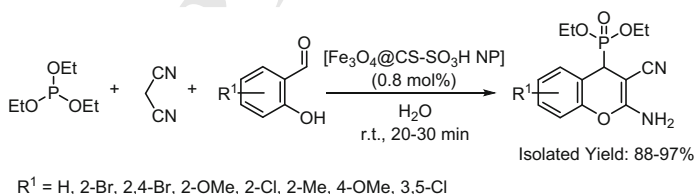
147 Although the Lewis acid properties of Fe_3O_4 have proven to be useful for the
 148 synthesis of heterocycles, these properties seem to be enhanced in the presence of
 149 Cu(II) (Scheme 8.4) [86]. This catalytic system was reused 6 times with slight yield
 150 loss (first run: 98%; sixth run: 91%).

151 An interesting variant of this reactivity was reported by Kassanee, showing that
 152 chromenylphosphonates could also be prepared in a similar manner in water with
 153 high yields and short reaction times (20–30 min), using functionalized magnetite
 154 with modified sulfo-chitosan (Scheme 8.5) [92].

155 Authors propose a mechanism catalyzed by hydrogen–heteroatom (nitrogen or
 156 oxygen) interactions, where water is not an innocent solvent (Fig. 8.3). Simi-
 157 lar behavior has been observed with magnetite functionalized with sulfo-PEG,
 158 $\text{Fe}_3\text{O}_4@ \text{PEG-SO}_3\text{H}$ [87].



Scheme 8.4 Synthesis of pyrano[2,3-d]pyrimidines catalyzed by Fe_3O_4 modified with polyvinyl alcohol (PVA) and doped with Cu(II) salts [86]



Scheme 8.5 Synthesis of 2-amino-4H-chromen-4-ylphosphonates catalyzed by $\text{Fe}_3\text{O}_4@ \text{CS-SO}_3\text{H}$ nanoparticles [92]

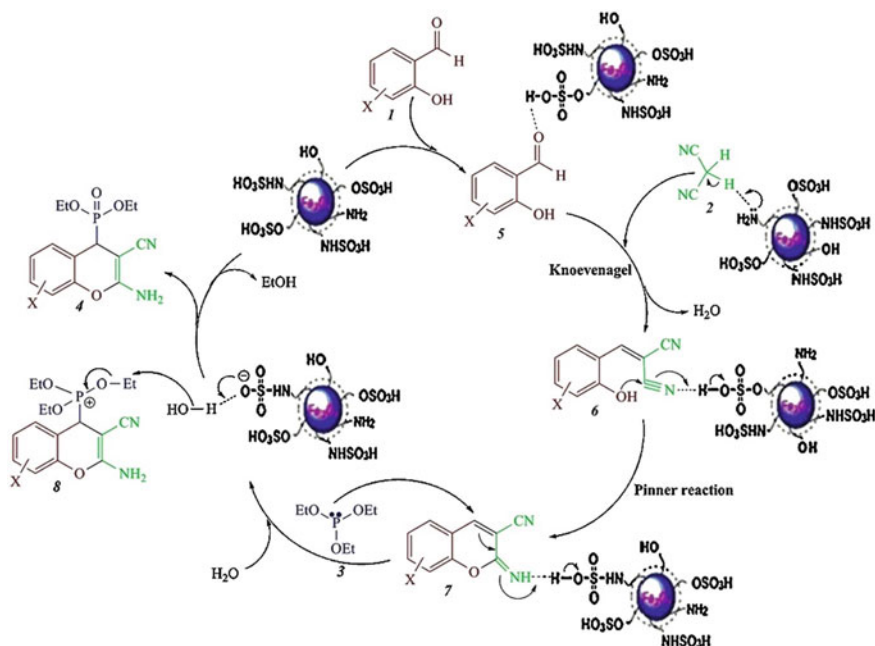


Fig. 8.3 Plausible mechanism for the synthesis of 2-amino-4H-chromen-4-ylphosphonates catalyzed by functionalized magnetite, $\text{Fe}_3\text{O}_4@\text{CS-SO}_3\text{H}$ nanoparticles. Reprinted from [92], Copyright 2013, with permission from Elsevier, license no. 4640241387630

8.2.2 Cross-Coupling Reactions

159

160 The upbringing of d-block transition metals in catalyzed cross-coupling reactions
 161 is gaining ground against palladium thanks to their larger abundance than noble
 162 metals. The Sonogashira–Hagihara cross-coupling reaction enables the formation
 163 of a C–C bond between an sp^2 -carbon halide (aryl or vinyl) and a terminal alkyne
 164 [116]. This transformation was initially described with a Pd(0) catalyst and a Cu(I)
 165 co-catalyst, but Cu alone [75, 79, 120] or other transition metals have been reported
 166 as efficient catalysts for this transformation (Ni [14, 102, 103], Fe [66], Co [115]),
 167 fueling the important role of abundant metals in C–C bond forming reactions. Gaining
 168 a better understanding on the physicochemical processes leading to the formation
 169 of MNPs is key for the design of nanocatalysts with defined morphology [50, 96],
 170 notably when catalyst heterogenization with solid supports such as zeolites, titania,
 171 montmorillonite and carbonaceous materials is required. Robustness and catalytic
 172 activity of tailor-made nanostructured catalysts outperform in many cases classical
 173 ones [90].

174 **C(sp)-C(sp²) Sonogashira cross-coupling** Since synthesis of copper(I) acetylide,
 175 the first organometallic copper complex described in 1859 [19], the reactivity of
 176 copper toward the activation of terminal alkyne groups has yielded a number of

177 interesting transformations for the synthesis of propargylic compounds [33]. The
178 search of catalytic versions is key for exploiting the privileged reactivity of this
179 metal from the point of view of sustainability [36]. Recent reports on the singular
180 π -activation of alkynes leveraged by zero-valent CuNPs reveal the importance of
181 this coordination in catalysis [31, 96].

182 In this context, the cross-coupling of terminal alkynes and acyl chlorides has been
183 reported by Bhosale et al. using a Cu/Cu₂O catalyst prepared from Cu(OAc)₂ in one-
184 step under microwave irradiation (3 min, 600 W) in 1,3-propanediol. The as-prepared
185 catalytic material exhibited an irregular morphology that combines tubular domains
186 and spherical particles ranging from 70 to 110 nm in size (Fig. 8.4) of a mixture of
187 Cu(0) and Cu₂O as confirmed by high-resolution XPS analysis [16].

188 Taking into account the paramount importance that metal traces might have in
189 catalysis, it is crucial to determine their contribution and potential cooperative effects.
190 Firouzabadi et al. described the use of spherical paramagnetic Fe₃O₄ NPs (<30 nm
191 in diameter) in ethylene glycol under ligand-free conditions for the Sonogashira–
192 Hagihara reaction for the synthesis of (hetero)aryl alkynes from terminal alkynes and
193 haloarenes (e.g., heteroaryl bromides, aryl iodides, Scheme 8.6) [44, 45]. In order
194 to ascertain the role of Fe₃O₄ NPs as catalyst, the authors determined the traces of
195 Pd, Ni, Cu, and Co present both in the reagents and solvent. Thus, the contamination
196 concerning the above-mentioned metals was found to be 130 ppb Pd, 45 ppb Ni,
197 24 ppb Cu, and 21 ppb Co for K₂CO₃; as well as 20 ppb Pd, 33 ppb Cu, 27 ppb Ni,

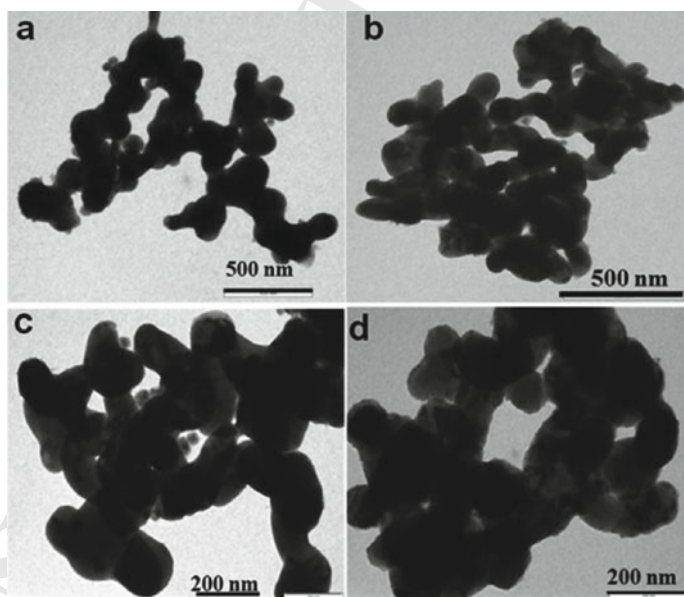
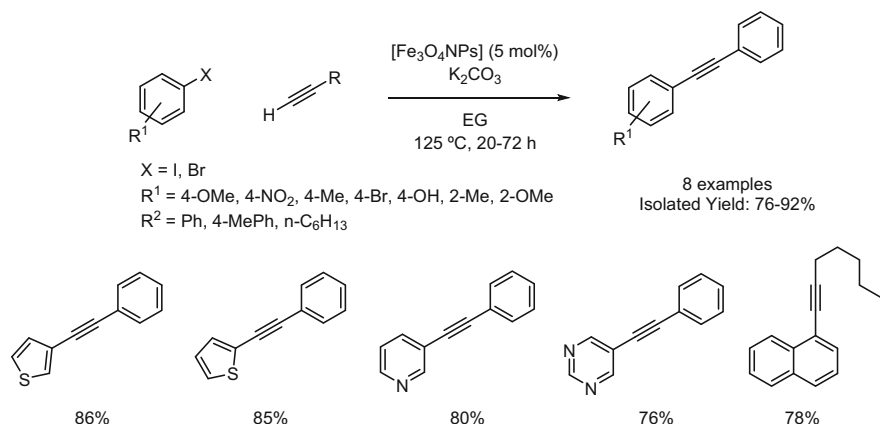


Fig. 8.4 TEM micrographs of Cu/Cu₂O NPs. Reproduced with permission from Royal Society of Chemistry 2014, license no. 4639380035278



Scheme 8.6 Fe_3O_4 NPs catalyzed Sonogashira-Hagihara coupling reaction in EG [44]

198 and 24 ppb Co for ethylene glycol by ICP analyses. As catalyst controls, different
 199 metal salts [e.g., $\text{Pd}(\text{OAc})_2$, CuCl , NiCl_2 , CoCl_2] at concentrations ranging from 200
 200 to 1500 ppb were tested, but the catalytic activity of Fe_3O_4 NPs at 5 mol% loadings
 201 proved to be superior [44]. The magnetic properties of Fe_3O_4 NPs allowed an easy
 202 catalyst recycling with only an overall 2% yield decrease after five consecutive runs.

203 An example of bimetallic nanocatalyst for Sonogashira cross-coupling reaction
 204 featuring PdCo NPs supported on graphene has been described by Dabiri et al. [29].
 205 The synthesis of this nanocomposite was carried out following the polyol method-
 206 ology. In particular, the co-reduction of PdCl_2 and CoCl_2 was performed in ethy-
 207 lene glycol, which acted as reducing and stabilizing agent for the immobilization
 208 of NPs on the 3D graphene support (Fig. 8.5). XPS analysis of the as-prepared
 209 nanocomposite revealed the presence of zero-valent Pd and Co (binding energies at
 210 335.67 and 341.49 eV corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$; as well as 781.53
 211 and 798.16 eV corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$), which match the literature
 212 values for PdCo alloys. Higher oxidation states, namely Pd(II), Co(II), and Co(III)
 213 were also detected, the latter arising from an oxidation on the NPs surface [29]. The
 214 prepared PdCo nanocomposite exhibited high catalytic activity for Sonogashira and
 215 Suzuki cross-coupling reactions of aryl halides with terminal alkynes and boronic
 216 acids, respectively, in water. Moreover, the catalyst was recycled up to seven times
 217 without loss in catalytic activity.

218 Aluminosilicate-based materials such as montmorillonite are largely used as cata-
 219 lyst supports. Liu et al. have recently described the co-immobilization of Cu and Pd on
 220 a montmorillonite-chitosan matrix. According to the authors, the resulting bimetallic
 221 CuPd nanocomposite features Pd coexisting in both Pd(0) and Pd(II) valence states,
 222 as well as Cu mainly in its Cu(II) as determined by XPS. However, the presence of
 223 Cu(0) and Cu(I) cannot be excluded relying solely on this technique. The as-prepared

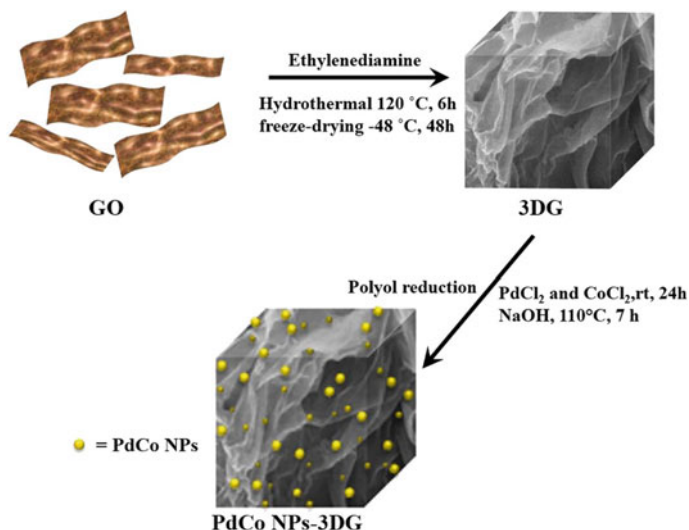


Fig. 8.5 Synthesis of PdCo NPs supported on graphene. Reproduced with permission from Ref. [29]. Copyright 2016 Wiley, license no. 4639270206261

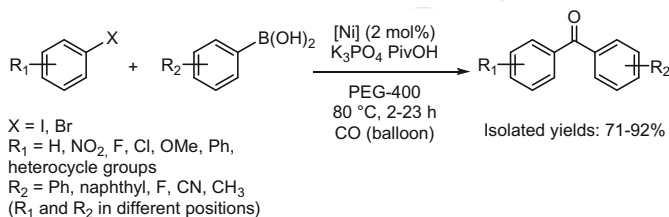
nanocomposite containing spherical PdNPs below 3 nm in diameter catalyzed Sonogashira couplings of haloarenes and alkynes in 1,2-dimethoxyethane/H₂O, although Cu leaching resulted in an activity decrease upon recycling [80].

Alternatively, the stabilization of Pd at higher oxidation states could be achieved via the formation of stable Pd-*N*-heterocyclic carbene complexes. Yavuz et al. have recently reported Sonogashira cross-coupling reaction catalyzed by in situ generated Pd-1*H*-benzo[*d*]imidazolium complexes [from Pd(OAc)₂ and Cs₂CO₃], and CuNPs in PEG300 [132]. However, authors did not characterize the catalyst employed.

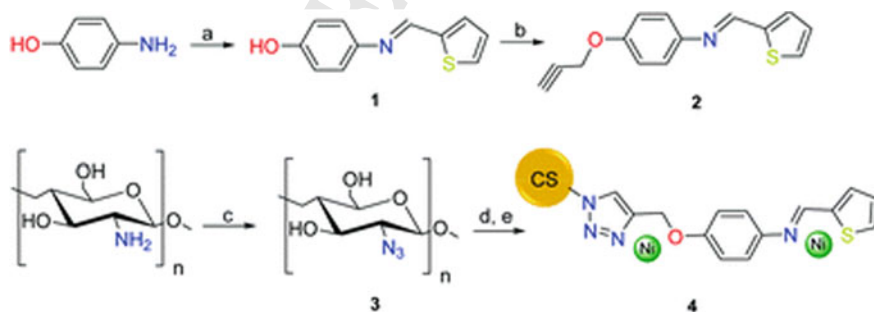
Suzuki–Miyaura-type cross-coupling During the last years, the controlled synthesis of NiNPs has drawn attention to several research groups, the main challenge being the exclusive preparation of zero-valent nickel nanomaterials due to the facile oxidation of Ni(0) species. Consequently, the lack of control of nickel oxidation in preformed nanoparticles is a persistent issue, as shown by several authors. Among them, one finds Tilley and coworkers in the synthesis of nickel nanocubes from Ni(acac)₂ under H₂ [77]; Hyeon's group in the preparation of NiNPs under thermal decomposition [98]; and Zarbin and coworkers in the synthesis of NiNPs following the polyol approach [97]. Chaudret and coworkers published an efficient method for the synthesis of nickel(0) nanorods, from [Ni(COD)₂] under hydrogen atmosphere [27]. More recently, zero-valent NiNPs were successfully prepared in neat glycerol, without exhibiting any oxide shell on their surface thanks to the low solubility of molecular oxygen in glycerol; these nanocatalysts were, in particular, highly efficient for the semi-hydrogenation of alkynes [105]. However, Ni-based nanoparticles have been scarcely applied in C–C cross-coupling reactions. Their efficiency is particularly remarkable when they are formed in situ, as proven by Lipshutz and coworkers using

248 NiNPs generated in water in the presence of appropriate surfactants (acting as stabilizers) and the Grignard reagent MeMgBr to activate the pre-catalyst ($[\text{NiCl}_2\text{L}_n]$,
 249 where L is a (di)phosphine and $n = 1$ or 2), which were successfully applied in
 250 Suzuki–Miyaura couplings [61]. Simultaneously, Han and coworkers reported Ni-
 251 catalyzed carbonylative Suzuki-based reactions in PEG (Scheme 8.7) [135], process
 252 leading to biaryl ketones, motif present in different types of compounds (drugs,
 253 photosensitizers ...). They compared the reactivity between preformed and in situ
 254 generated NiNPs, evidencing that those formed in situ were more active, probably
 255 because the latter are smaller, showing less aggregation than the preformed ones.
 256 Authors carried out control tests (with Hg and CS_2) in order to prove the nature of
 257 the catalytically active species (in the presence of both additives, the reaction did not
 258 work), concluding that the activity observed agrees with a surface-like reactivity.
 259

260 Preformed NiNPs stabilized by triazole-modified chitosan were active nanocatalysts for Suzuki–Miyaura reactions between aryl halides and phenyl boronic acid
 261 derivatives (Scheme 8.8) [59].
 262

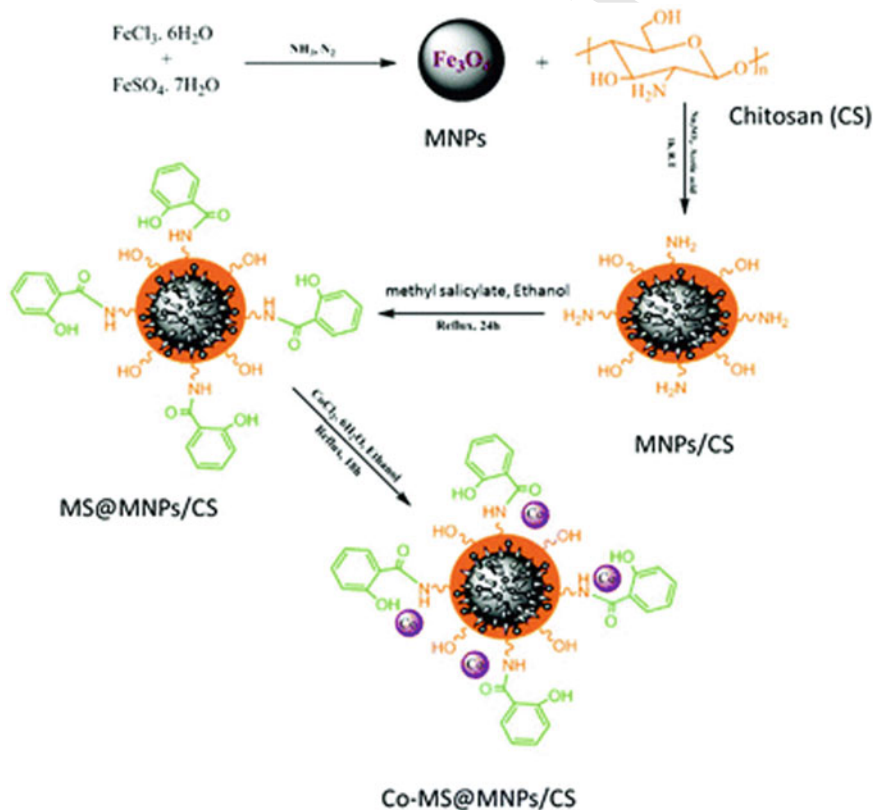


Scheme 8.7 In situ generated NiNPs in PEG-400 applied in carbonylative Suzuki coupling reactions [135]



Scheme 8.8 Synthetic path for the synthesis of NiNPs stabilized by modified chitosan: **a** thiophene-2-carbaldehyde, MeOH, reflux, 3 h; **b** propargyl bromide, K_2CO_3 , acetone, 50 °C, 24 h; **c** triflyl azide, aqueous $\text{HCl} \cdot \text{NaHCO}_3$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, MeOH, r.t., 5 d; **d** 2, CuI, DMF/THF (1 : 1), r.t., 72 h; **e** $\text{NiCl}_2/\text{EtOH}$ solution, 12 h, r.t., then hydrazine hydrate, r.t., 2 h. New journal of chemistry by Center national de la recherche scientifique (France); Royal Society of Chemistry (Great Britain) Reproduced with permission of ROYAL SOCIETY OF CHEMISTRY in the format Book via Copyright Clearance Center, license no. 4639350882762 [59]

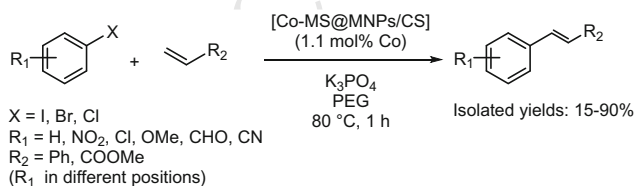
263 **Heck–Mizoroki-type cross-coupling** Since the pioneering and independent works
 264 from Gilman and Lichtenwalter [55], and Kharasch [69] in the 1930s and 1940s,
 265 concerning the homocoupling reaction of Grignard reagents promoted by cobalt(II)
 266 salts, scarce works were carried out up to the 1990s [21] and references therein.
 267 Cobalt complexes have proven their efficiency for the formation of $C(sp^2)–C(sp^2)$
 268 bonds; particularly, Co-based catalysts are interesting for cross-couplings where
 269 alkyl halides are involved, because β -hydrogen elimination of alkyl intermediates is
 270 not favored in contrast to the analogous Pd and Ni organometallic species. In the
 271 frame of the present contribution, Co(II) anchored to chitosan-functionalized Fe_3O_4
 272 NPs has found applications in Heck- and Sonogashira-type couplings [60]. Fe_3O_4
 273 NPs containing chitosan were modified by reaction with methyl salicylate to give
 274 amide-phenol groups at their surface, which coordinate $CoCl_2$ (Scheme 8.9).



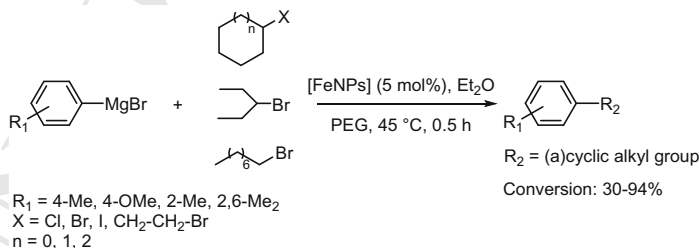
Scheme 8.9 Preparation of co-based nanocatalyst immobilized on Fe_3O_4 nanoparticles modified by chitosan. Green Chemistry by Royal Society of Chemistry (Great Britain) Reproduced with permission of ROYAL SOCIETY OF CHEMISTRY in the format Book via Copyright Clearance Center, license no. 4639360400827 [60]

This represents an example of molecular-like catalytic reactivity using functionalized nanoparticles as support. For the Heck-type reaction, the catalyst was efficient for the coupling of aryl halides (chloro, bromo, iodo) with styrene or methyl acrylate using PEG as solvent (Scheme 8.10). In contrast to the non-functionalized Fe₃O₄ NPs, the functionalized ones were more active and could be recycled up to five times preserving their efficiency, without metal leaching. The Sonogashira-type coupling between aryl halides (bromo, iodo) and phenylacetylene derivatives gave moderate yields under harsher conditions than those used for the Heck couplings.

Kumada-type cross-coupling Kumada–Tamao–Corriu reaction, coupling between a Grignard reagent and an organic halide, was initially reported using Ni-based catalysts [28, 118]; other efficient systems such as those based on palladium and iron, have proven their efficacy, the main part of them involving molecular catalysts, but more recently copper, nickel, and palladium nanoparticles have been used as well ([63, 91] and references therein). Iron, representing the second more abundant metal in the Earth's crust, has found interesting applications in C–C couplings [3, 12, 95]. The main part of reported works assumes the contribution of molecular intermediate species in the catalytic transformation, but also nanoparticles have been identified for low oxidation states (zero-valent FeNPs should be more stable under catalytic conditions than organometallic Fe(0) complexes) and it has been postulated that they act as a reservoir of molecular species exhibiting higher oxidation state [10]. Bedford and coworkers studied the reaction of alkyl halides with aryl Grignard compounds catalyzed by in situ generated FeNPs from FeCl₃ in the presence of PEG-14000 (Scheme 8.11 and Fig. 8.6) [11]. Authors proved that the Grignard reagent acted as



Scheme 8.10 Heck–Mizoroki-type couplings catalyzed by Co(II) supported on functionalized Fe₃O₄ nanoparticles (see Scheme 8.9) [60]



Scheme 8.11 C(sp²)-C(sp³) cross-coupling catalyzed by FeNPs stabilized by PEG [11]

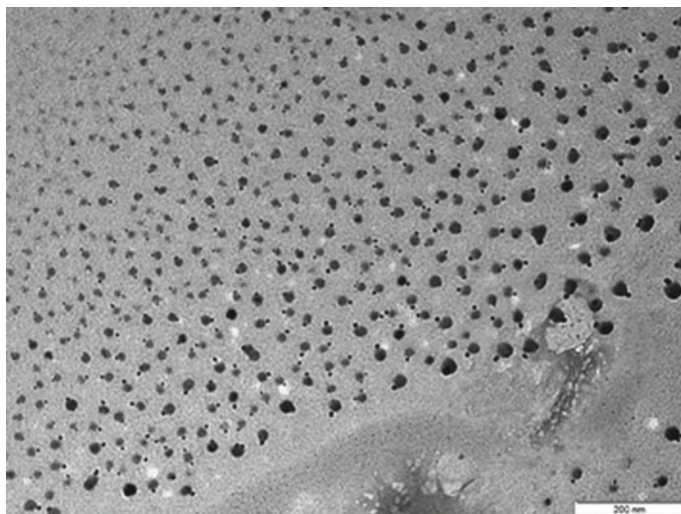


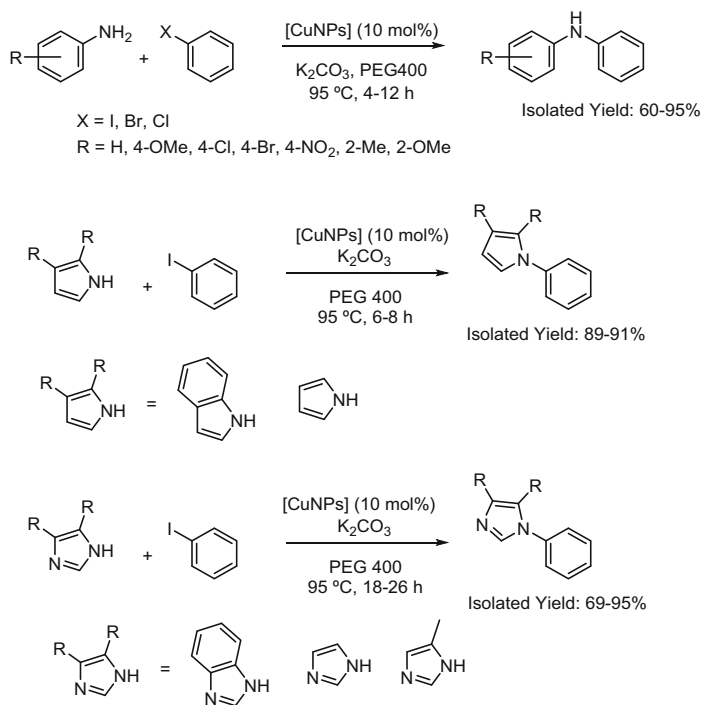
Fig. 8.6 TEM image corresponding to FeNPs generated in situ from FeCl_3 in the presence of 1,6-bis(diphenylphosphino)hexane with $4\text{-MeC}_6\text{H}_4\text{MgBr}$. Reproduced with permission of ROYAL SOCIETY OF CHEMISTRY in the format Book via Copyright Clearance Center, license no. 4640081165587 [11]

298 reducing agent. Preformed FeNPs/PEG (diameter in the range 7–13 nm, determined
299 by TEM) afforded the same reactivity as those formed in situ.

300 8.3 Carbon–Heteroatom Bond Formation

301 The activation of C–halogen bonds has been overwhelmingly used in the function-
302 alization of arenes. Since the discovery of Ullmann’s coupling in 1901, copper has
303 been one of the most used earth-abundant metals in both C–C and C–heteroatom
304 couplings (original paper of Ullmann: [125]; recent reviews: [13, 94, 108]). How-
305 ever, many applications of this reactivity are especially limited due to the use of
306 hazardous solvents such as DMF and DMSO. A lot of interest has been put into
307 transforming this reactivity into greener approaches. In this context, considerable
308 efforts have been recently developed in nanocatalytic systems capable of working
309 in friendly environmental conditions [67, 127], polyols being alternative solvents of
310 interest [39].

311 This strategy has been successfully applied in a wide range of C–N couplings using
312 many different nitrogen-based reagents. Kidwai and coworkers applied preformed
313 unsupported CuNPs in the *N*-arylation of aryl halides with anilines using PEG400
314 as solvent (Scheme 8.12) [73]. A large scope of aniline derivatives and also NH
315 heterocycles was carried out.



Scheme 8.12 CuNPs catalyzed C–N cross-couplings of anilines and NH heterocycles with aryl halides in PEG400 [73]

316 Graphene oxide functionalized with carboxamide groups (f-GO) was an efficient
 317 support to coordinate Cu(II) salts and further reducing them to give CuNPs immobi-
 318 lized on the solid. This CuNPs on f-GO were then treated with Fe₃O₄ nanoparticles
 319 leading to a magnetic catalytic material, which enhanced the catalyst recyclability
 320 (Fig. 8.7) [112].

321 The as-prepared heterogenized nanocatalyst was applied to Ullmann-type cou-
 322 pling for the synthesis of *N*-aryl amines using a deep eutectic solvent (choline chlo-
 323 ride:glycerol = 1:2) (Scheme 8.13). Authors compared the efficiency of this catalytic
 324 system with other CuNPs, both supported and unsupported, concluding that their
 325 catalyst led to higher yields under smoother conditions. However, the recycling was
 326 moderate (up to 3 times without loss of activity).

327 The work of our group on the preparation of small CuNPs ($d_{\text{mean}} = 1.7\text{--}2.4\text{ nm}$)
 328 in glycerol from the reduction of Cu(II) and Cu(I) precursors with PVP as stabilizer
 329 and under low pressure of H₂ (3 bar) avoided the formation of oxidized by-products
 330 coming from the solvent (Fig. 8.8). This approach represents the first report toward
 331 the synthesis of well-defined and stable CuNPs by a bottom-up strategy thanks to
 332 the low solubility of O₂ in this medium, circumventing the formation of oxide shells
 333 [31].

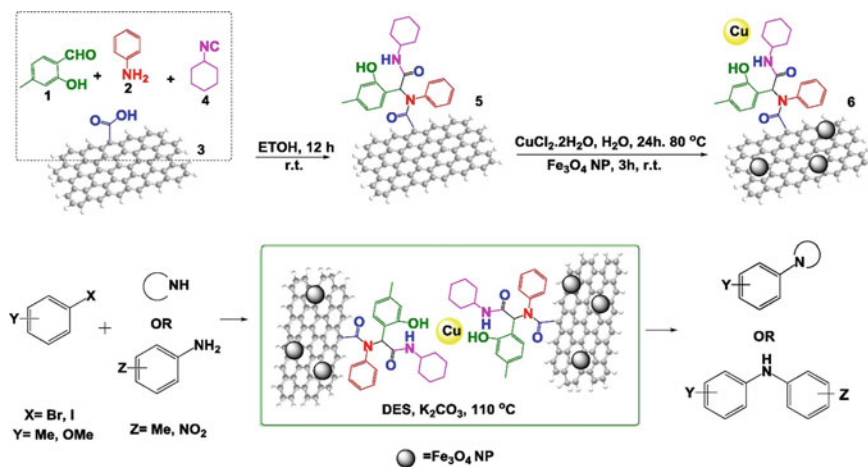
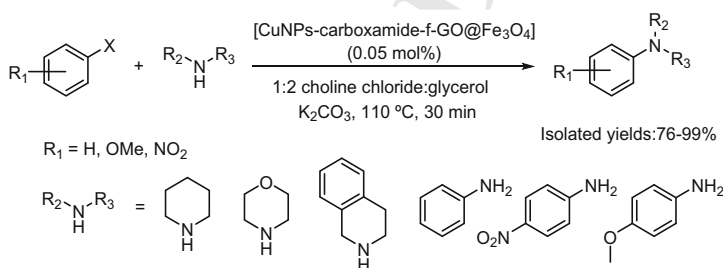


Fig. 8.7 Illustration of the synthesis of CuNPs immobilized on f-GO containing Fe₃O₄ NPs (top) with the application in C–N bond formation processes (bottom). Reprinted from [112], Copyright 2018, with permission from Elsevier, license no. 4640121432056



Scheme 8.13 CuNPs immobilized on a magnetic-modified graphene oxide (see Fig. 8.7) catalyzed C–N couplings of secondary amines and anilines [112]

334 **CuA** nanoparticles were successfully applied in C–N couplings and in the synthesis of propargyl amines through different strategies, such as cross-dehydrogenative
335 couplings and multicomponent reactions, both A³ (aldehyde–alkyne–amine) and
336 KA² (ketone–alkyne–amine) (Scheme 8.14). Authors carried out spectroscopic
337 monitoring (UV-vis and FTIR analyses) concluding that the C–N coupling follows a
338 surface reactivity, without formation of Cu(I) molecular species, like phenylethynylcopper(I),
339 which would be poisoned by the presence of amines.
340

341 The selection of alternative aldehydes bearing heteroatoms in position 2 of the ring
342 (e.g., 2-aminobenzaldehyde, 2-hydroxybenzaldehyde and 2-pyridinecarbaldehyde)
343 provided a direct entry to the synthesis of heterocycles, namely indolizines, benzo-
344 furans and quinolines via a **CuA**-catalyzed A³-cycloisomerization tandem processes
345 (Scheme 8.15).

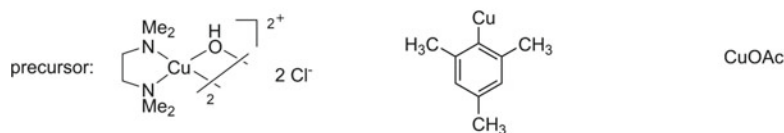
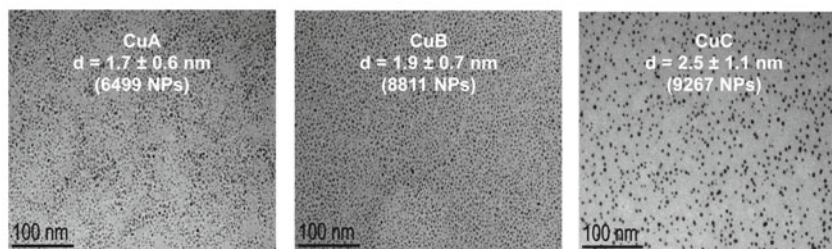
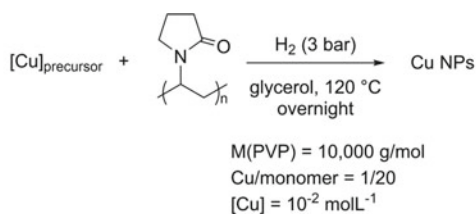


Fig. 8.8 Synthesis of CuNPs in glycerol from different copper precursors stabilized by the polymer PVP (top) and the corresponding TEM images of the different nanoparticles (bottom). Adapted with permission from [31], Copyright 2017 Wiley, license no. 4640130742799

346 Moreover, Shah et al. have recently reported the A^3 -coupling reaction for the
 347 synthesis of propargylamines and pyrrolo[1,2-*a*]quinolines using a heterogenized
 348 Cu catalyst (CuNPs@ZnO–polythiophene) at low catalyst loadings (Scheme 8.16).
 349 Notably, the cyclization only takes place in an intramolecular fashion and no Cu
 350 leaching was detected in the EG reaction medium after catalyst filtration (ICP
 351 analyses).

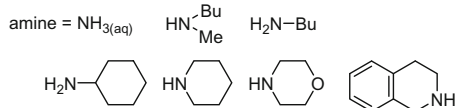
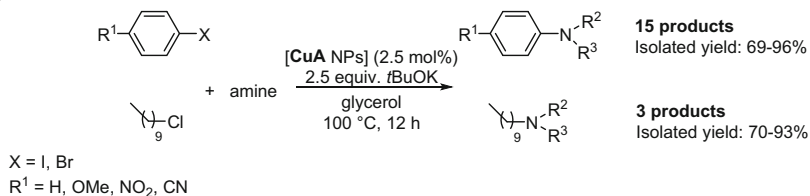
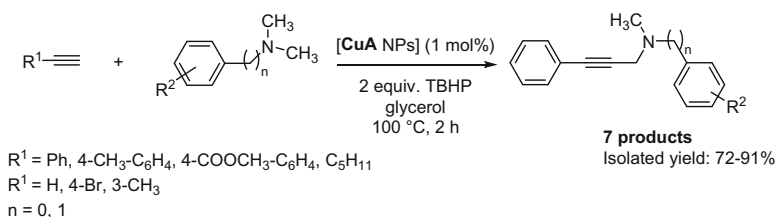
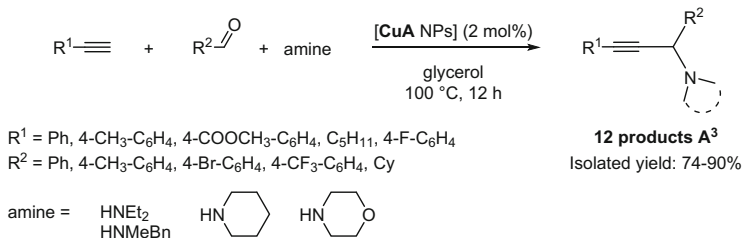
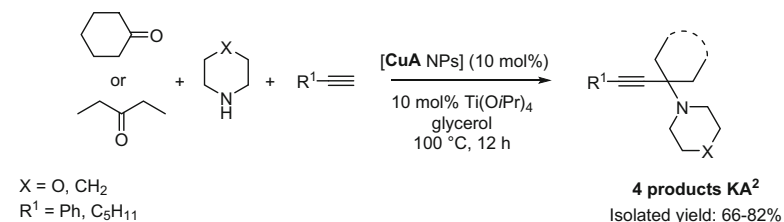
352 Preformed Cu_2O nanoparticles (mean diameter: ca. 5 nm, Fig. 8.9) were applied
 353 in the coupling between iodoaryl derivatives and different nitrogen-based reagents,
 354 such as aryl and alkyl amines, but also aqueous ammonia, in glycerol [23]. This
 355 nanocatalyst was also efficient for the synthesis of thioethers through C–S couplings.

356 This nanocatalyst has also been applied for the activation of terminal alkyne groups
 357 toward azide–alkyne cycloaddition reaction (CuAAC) in glycerol (Scheme 8.17)
 358 [23].

359 Furthermore, Sharghi and Aberi reported the application of Cu_2O NPs in the
 360 synthesis of indazole derivatives through a three-component strategy in PEG300
 361 (Scheme 8.18) [114].

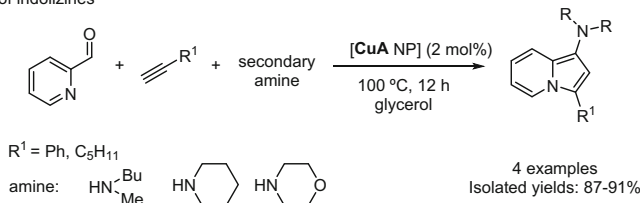
362 Cu-based catalysts in polyol medium have also found interesting applications in
 363 C–S bond formation processes, as proved by our group using Cu_2O nanoparticles
 364 [23]. Primo, García, and coworkers reported the synthesis of Cu-based nanoparticles
 365 stabilized by chitosan, mainly constituted of Cu(0) but surrounded by a thin layer

a) Synthesis of amines and anilines

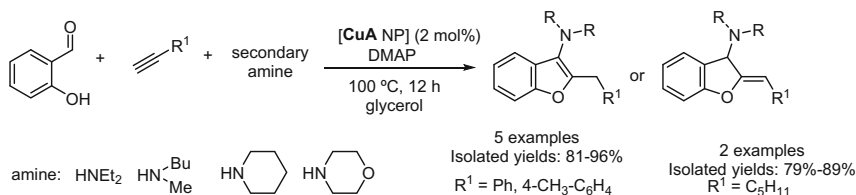
b) Cross-dehydrogenative coupling catalyzed by **CuA** NPs in glycerolc) A³ coupling catalyzed by **CuA** NPs in glycerold) **CuA**-catalyzed KA² multicomponent processes

Scheme 8.14 CuA NPs catalyzed C–N couplings and multicomponent reactions [31]

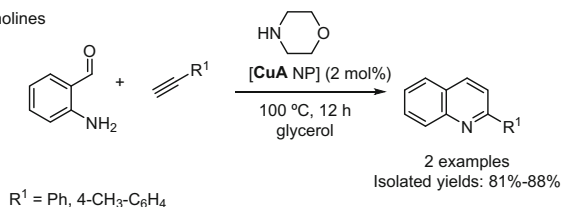
a) Synthesis of indolizines



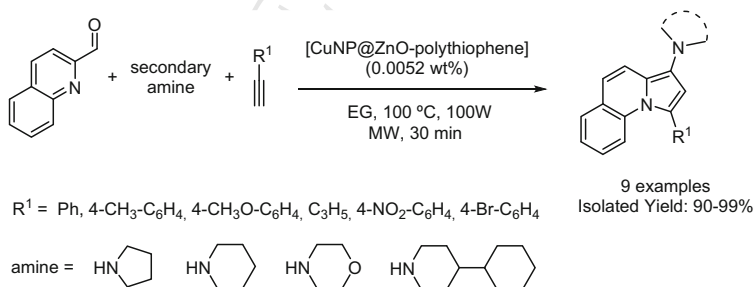
b) Synthesis of benzofurans



c) Synthesis of quinolines



Scheme 8.15 Synthesis of indolizines, benzofurans, and quinolines catalyzed by CuA NPs in glycerol [31]



Scheme 8.16 CuNPs@ZnO-polythiophene catalyzed synthesis of pyrrolo[1,2-a]quinolines in EG under microwave irradiation [113]

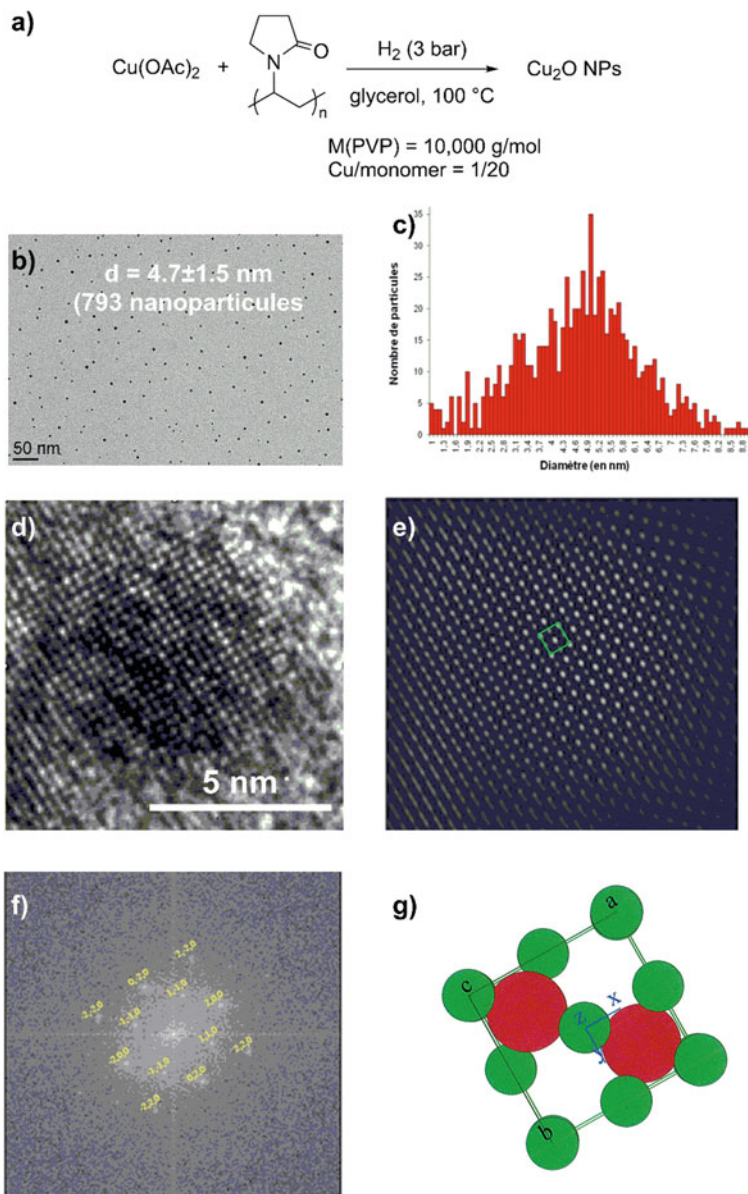
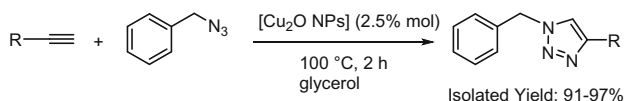
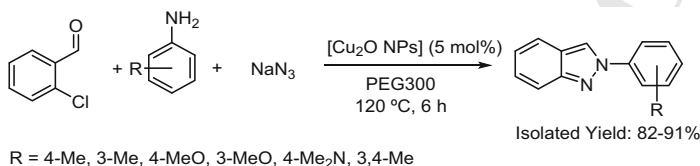


Fig. 8.9 Synthesis of Cu_2O NPs in glycerol and characterization after isolation at solid state and re-dispersion in glycerol. **a** Synthesis scheme; **b** TEM micrograph in glycerol; **c** size distribution histogram; **d** HR-TEM micrograph of one single particle of Cu_2O ; **e** electronic diffraction spots by fast Fourier transform of a single particle; **f** filtered image showing the zone axis $[0\ 0\ 1]$; **g** cartoon of Cu_2O cubic structure. Adapted with permission from [23], Copyright 2014 Wiley, license no. 4640200545968



R = Ph, Cy, n-Bu, t-Bu, (CH₂)₃-CH₂-OH, CH₂CH₂-OH, (CH₃)₂C-OH, (CH₂)₅-CH₂OH, CH₂-NMe₂,

Scheme 8.17 Cu₂O NPs catalyzed azide-alkyne cycloaddition in glycerol [23]



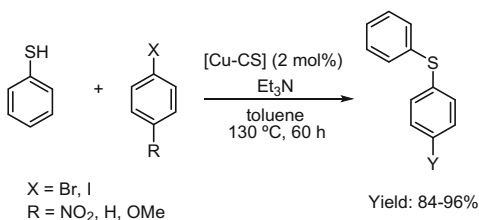
R = 4-Me, 3-Me, 4-MeO, 3-MeO, 4-Me₂N, 3,4-Me

Scheme 8.18 Cu₂O nanoparticles catalyzed the synthesis of 2H-indazoles [114]

of copper oxides as proven by XPS [47]. This nanocatalyst was applied in the C–S coupling of aryl halides and thiophenol, being more active for iodo than bromo and chloro arenes, for the latter ones they were only active for aryl halides containing electron withdrawing substituents (Scheme 8.19). Authors observed that halide anions released to the medium during the catalytic reaction can act as poison for CuNPs, in addition to promoting metal leaching.

Generally speaking, C–O couplings are more challenging reactions mainly due to the limited functional compatibilities and the need of activated substrates [76, 117]. Besides, the use of polyol medium adds another difficulty because the solvent can compete with the substrate. In this frame, Biegi and Ghiasbeigi have recently reported the synthesis and full characterization of functionalized magnetite with isonicotinic acid with the aim of coordinating Cu(I) precursors (Fig. 8.10) [51]. The resulting catalytic material was efficiently applied to the synthesis of phenol and aniline derivatives (TOF up to 4494 h⁻¹), using a mixture of PEG and water as solvent (PEG:H₂O = 2:1) (Scheme 8.20). The catalytic phase was recycled up to 5 times with slight loss of yield, although the 30% copper loss reported by the authors after the fourth run was substantial (Cu content of catalyst before use: 57,037.8 ppm; after 4th run: 40,297.3 ppm).

Scheme 8.19 CuNPs stabilized by chitosan applied in C–S couplings [47]



X = Br, I
R = NO₂, H, OMe

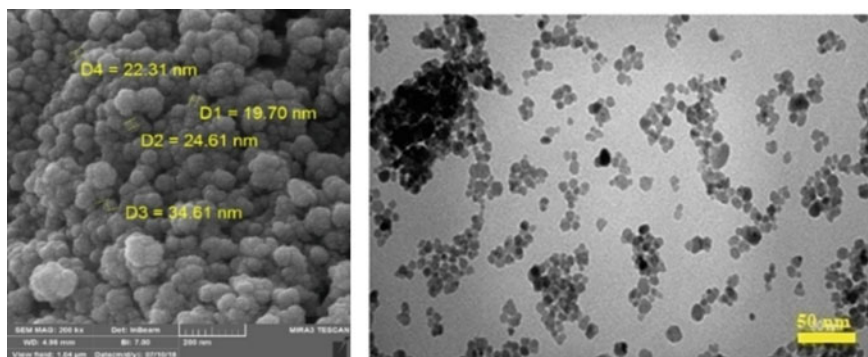
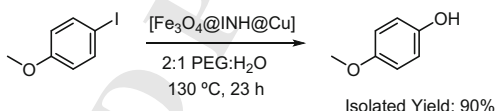


Fig. 8.10 SEM (left) and TEM (right) images of Cu(I) grafted to Fe₃O₄ modified by isonicotinic groups. Reprinted with permission from [51], Copyright 2019 Wiley, license no. 4640160235060

Scheme 8.20 Synthesis of phenols catalyzed by Cu-based catalyst supported on modified Fe₃O₄ [51]



8.4 Conclusions and Outlook

This chapter describes the use of nanocatalysts from Earth-abundant metals in polyol media applied in C–C and C–heteroatom coupling reactions. Despite the interesting reports mentioned in this contribution, nanocatalysis based on d-block transition metals in polyols is still in its infancy. This is an exponentially growing research field that exploits the non-innocent physicochemical properties of polyols as reducing, stabilizing, and dispersing agents in the quest for tailor-made nanocatalysts and nanocomposites with enhanced properties as compared to classical ones. In the framework of the development of greener and more sustainable processes, Cu, Ni, Co, and Fe nanocatalysts in polyol media represent key alternatives to overcome the dependence on the scarcity of noble metals in use currently for both academic and industrial purposes.

The Lewis acidity properties of 3d-transition metals confer them suitable properties as (co)catalysts to effect new transformations by means of (i) Lewis acid base-adduct formation, thereby accelerating slow elementary steps, (ii) pK_a of the reaction modulation (e.g., release of a Brønsted acid, proton transfer processes), or (iii) activating the catalyst precursors or off-cycle catalyst species by tuning its coordination sphere by anion abstraction. This chapter describes the reports on Ni, Cu, and Fe Lewis acid mediated transformations in polyol medium, but contributions from other abundant metals will surely appear in the literature in the years to come.

On the other hand, the abundance and redox properties of 3d-metal-oxide-based materials confer them large applicability as supports for catalysts. In particular, the

406 magnetic properties of Fe_2O_3 and Fe_3O_4 as supports enable the recovery of the pre-
407 pared composite materials. For instance, the use of such supports for the preparation
408 of heterogenized Pd catalysts for C–C cross-coupling reactions and hydrogenations
409 in polyol medium has been widely reported (for selected articles, see: [37, 52, 53,
410 81, 126, 137]). Other supports based on 3d-transition metals such as TiO_2 [93], CuO
411 [25], and ZnO [113] have also been used for the same purpose. This heterogenization
412 strategy efficiently enables the recoverability of the catalytic materials by magnetic
413 separation, and also in some cases, the enhancement of TON is observed due to the
414 synergy between catalyst and support. Furthermore, polymetallic systems merit fur-
415 ther studies to exploit the cooperative effects between active metal centers in polyol
416 medium [32]. The intrinsic properties of polyols in terms of favoring 3D organization
417 via supramolecular interactions, their suitable oxidation potentials for the reduction
418 of transition metal salts and organometallic complexes, as well as their dispersing
419 abilities via solvation interactions, which often trigger an activity increase, confer
420 them unique properties in nanocatalysis.

421 From a structural point of view, 3d -metals based-species present several oxidation
422 states, often leading to paramagnetic intermediates of challenging elucidation. Given
423 the specificity developed by nature in biocatalyzed transformations involving 3d-
424 transition metals and the demonstrated efficiency of nanocatalysts discussed herein
425 (e.g., Cu NPs for Sonogashira and C–heteroatom couplings, Ni NPs for Suzuki, Co
426 NPs for Heck–Mizoroki, Fe NPs for Kumada-like couplings ...), the fundamental and
427 applied research in this field foresees new reactivities and deep mechanistic insights
428 taking advantage of the cutting-edge in operando techniques available nowadays.

429 References

- 430 1. Adil SF, Assal ME, Khan M, Al-Warthan A, Siddiqui MRH, Liz-Marzán LM (2015) Bio-
431 genic synthesis of metallic nanoparticles and prospects toward green chemistry. *Dalton Trans*
432 44(21):9709–9717. <https://doi.org/10.1039/C4DT03222E>
- 433 2. Ai W, Zhong R, Liu X, Liu Q (2019) Hydride Transfer reactions catalyzed by cobalt complexes.
434 *Chem Rev* 119(4):2876–2953. <https://doi.org/10.1021/acs.chemrev.8b00404>
- 435 3. Alice W, Axel Jacobi von W (2013) Iron(0) nanoparticle catalysts in organic synthesis. *Curr*
436 *Org Chem* 17(4):326–335. <https://doi.org/10.2174/1385272811317040003>
- 437 4. Alig L, Fritz M, Schneider S (2019) First-row transition metal (de)hydrogenation catalysis
438 based on functional pincer ligands. *Chem Rev* 119(4):2681–2751. [https://doi.org/10.1021/](https://doi.org/10.1021/acs.chemrev.8b00555)
439 [acs.chemrev.8b00555](https://doi.org/10.1021/acs.chemrev.8b00555)
- 440 5. An K, Alayoglu S, Ewers T, Somorjai GA (2012) Colloid chemistry of nanocatalysts: a
441 molecular view. *J Colloid Interface Sci* 373(1):1–13
- 442 6. Anastas P, Eghbali N (2010) Green chemistry: principles and practice. *Chem Soc Rev*
443 39(1):301–312. <https://doi.org/10.1039/B918763B>
- 444 7. Anastas PT, Kirchhoff MM, Williamson TC (2001) Catalysis as a foundational pillar of green
445 chemistry. *Appl Catal A* 221(1):3–13. [https://doi.org/10.1016/S0926-860X\(01\)00793-1](https://doi.org/10.1016/S0926-860X(01)00793-1)
- 446 8. Anastas PT, Zimmerman JB (2003) Peer reviewed: design through the 12 principles of green
447 engineering. *Environ Sci Technol* 37(5):94A–101A. <https://doi.org/10.1021/es032373g>
- 448 9. Astruc D (2008) Nanoparticles and catalysis. Wiley

- 449 10. Bedford RB (2015) How low does iron go? Chasing the active species in Fe-catalyzed cross-
450 coupling reactions. *Acc Chem Res* 48(5):1485–1493. [https://doi.org/10.1021/acs.accounts.](https://doi.org/10.1021/acs.accounts.5b00042)
451 [5b00042](https://doi.org/10.1021/acs.accounts.5b00042)
- 452 11. Bedford RB, Betham M, Bruce DW, Davis SA, Frost RM, Hird M (2006) Iron nanoparticles
453 in the coupling of alkyl halides with aryl Grignard reagents. *Chem Commun* 13:1398–1400.
454 <https://doi.org/10.1039/b601014h>
- 455 12. Bedford RB, Brenner PB (2015) The development of iron catalysts for cross-coupling
456 reactions. In: Bauer E (ed) *Iron catalysis II*. Springer International Publishing, Cham, pp
457 19–46
- 458 13. Beletskaya IP, Cheprakov AV (2004) Copper in cross-coupling reactions: the post-Ullmann
459 chemistry. *Coord Chem Rev* 248(21):2337–2364. <https://doi.org/10.1016/j.ccr.2004.09.014>
- 460 14. Beletskaya IP, Latyshev GV, Tsvetkov AV, Lukashev NV (2003) The nickel-catalyzed
461 Sonogashira-Hagihara reaction. *Tetrahedron Lett* 44(27):5011–5013. [https://doi.org/10.1016/](https://doi.org/10.1016/S0040-4039(03)01174-2)
462 [S0040-4039\(03\)01174-2](https://doi.org/10.1016/S0040-4039(03)01174-2)
- 463 15. Beller M (2019) Introduction: first row metals and catalysis. *Chem Rev* 119(4):2089. [https://](https://doi.org/10.1021/acs.chemrev.9b00076)
464 doi.org/10.1021/acs.chemrev.9b00076
- 465 16. Bhosale MA, Sasaki T, Bhanage BM (2014) A facile and rapid route for the synthesis of
466 Cu/Cu₂O nanoparticles and their application in the Sonogashira coupling reaction of acyl
467 chlorides with terminal alkynes. *Catal Sci Technol* 4(12):4274–4280. [https://doi.org/10.1039/](https://doi.org/10.1039/C4CY00868E)
468 [C4CY00868E](https://doi.org/10.1039/C4CY00868E)
- 469 17. Biffis A, Centomo P, Del Zotto A, Zecca M (2018) Pd metal catalysts for cross-couplings and
470 related reactions in the 21st century: a critical review. *Chem Rev* 118(4):2249–2295. [https://](https://doi.org/10.1021/acs.chemrev.7b00443)
471 doi.org/10.1021/acs.chemrev.7b00443
- 472 18. Biggs-Houck JE, Younai A, Shaw JT (2010) Recent advances in multicomponent reactions for
473 diversity-oriented synthesis. *Curr Opin Chem Biol* 14(3):371–382. [https://doi.org/10.1016/j.](https://doi.org/10.1016/j.cbpa.2010.03.003)
474 [cbpa.2010.03.003](https://doi.org/10.1016/j.cbpa.2010.03.003)
- 475 19. Boettger R (1859) Ueber die Einwirkung des Leuchtgases auf verschiedene Salzsolutio-
476 nen, insbesondere auf eine ammoniakalische Kupferchlorürlösung. *Justus Liebigs Ann Chem*
477 109(3):351–362. <https://doi.org/10.1002/jlac.18591090318>
- 478 20. Bulut S, Fei Z, Siankevich S, Zhang J, Yan N, Dyson PJ (2015) Aqueous-phase hydrogenation
479 of alkenes and arenes: the growing role of nanoscale catalysts. *Catal Today* 247:96–103.
480 <https://doi.org/10.1016/j.cattod.2014.09.002>
- 481 21. Cahiez G, Moyeux A (2010) Cobalt-catalyzed cross-coupling reactions. *Chem Rev*
482 110(3):1435–1462. <https://doi.org/10.1021/cr9000786>
- 483 22. Chahdoura F, Favier I, Gómez M (2014) Glycerol as suitable solvent for the synthesis of
484 metallic species and catalysis. *Chem Eur J* 20(35):10884–10893. [https://doi.org/10.1002/](https://doi.org/10.1002/chem.201403534)
485 [chem.201403534](https://doi.org/10.1002/chem.201403534)
- 486 23. Chahdoura F, Pradel C, Gómez M (2014) Copper(I) oxide nanoparticles in glycerol: a conven-
487 ient catalyst for cross-coupling and azide-alkyne cycloaddition processes. *ChemCatChem*
488 6(10):2929–2936. <https://doi.org/10.1002/cctc.201402214>
- 489 24. Chakraborty S, Shah NH, Fishbein JC, Hosmane RS (2011) A novel transition state analog
490 inhibitor of guanase based on azepinomycin ring structure: synthesis and biochemical assess-
491 ment of enzyme inhibition. *Bioorg Med Chem Lett* 21(2):756–759. [https://doi.org/10.1016/](https://doi.org/10.1016/j.bmcl.2010.11.109)
492 [j.bmcl.2010.11.109](https://doi.org/10.1016/j.bmcl.2010.11.109)
- 493 25. Chattopadhyay K, Dey R, Ranu BC (2009) Shape-dependent catalytic activity of copper
494 oxide-supported Pd(0) nanoparticles for Suzuki and cyanation reactions. *Tetrahedron Lett*
495 50(26):3164–3167. <https://doi.org/10.1016/j.tetlet.2009.01.027>
- 496 26. Chirik P, Morris R (2015) Getting down to earth: the renaissance of catalysis with abundant
497 metals. *Acc Chem Res* 48(9):2495. <https://doi.org/10.1021/acs.accounts.5b00385>
- 498 27. Cordente N, Respaud M, Senocq F, Casanove M-J, Amiens C, Chaudret B (2001) Synthesis
499 and magnetic properties of nickel nanorods. *Nano Lett* 1(10):565–568. [https://doi.org/10.](https://doi.org/10.1021/nl10100522)
500 [1021/nl10100522](https://doi.org/10.1021/nl10100522)
- 501 28. Corriu RJP, Masse JP (1972) Activation of Grignard reagents by transition-metal complexes.
502 A new and simple synthesis of trans-stilbenes and polyphenyls. *J Chem Soc Chem Commun*
503 3:144a. <https://doi.org/10.1039/C3972000144A>

- 504 29. Dabiri M, Vajargahy MP (2017) PdCo bimetallic nanoparticles supported on three-
505 dimensional graphene as a highly active catalyst for sonogashira cross-coupling reaction.
506 Appl Organomet Chem 31(4):e3594. <https://doi.org/10.1002/aoc.3594>
- 507 30. Dahl JA, Maddux BLS, Hutchison JE (2007) Toward greener nanosynthesis. Chem Rev
508 107(6):2228–2269. <https://doi.org/10.1021/cr050943k>
- 509 31. Dang-Bao T, Pradel C, Favier I, Gómez M (2017) Making copper(0) nanoparticles in glycerol:
510 a straightforward synthesis for a multipurpose catalyst. Adv Synth Catal 359(16):2832–2846.
511 <https://doi.org/10.1002/adsc.201700535>
- 512 32. Dang-Bao T, Pradel C, Favier I, Gómez M (2019) Bimetallic nanocatalysts in glycerol for
513 applications in controlled synthesis. a structure–reactivity relationship study. ACS Appl. Nano
514 Mater 2(2):1033–1044. <https://doi.org/10.1021/acsanm.8b02316>
- 515 33. Díez-González S (2016) Chapter three—copper(I)–acetylides: access, structure, and relevance
516 in catalysis. In: Pérez PJ (ed) Advances in *organometallic chemistry*, vol 66. Academic Press,
517 pp 93–141
- 518 34. Dong H, Chen YC, Feldmann C (2015) Polyol synthesis of nanoparticles: status and options
519 regarding metals, oxides, chalcogenides, and non-metal elements. Green Chem 17(8):4107–
520 4132. <https://doi.org/10.1039/C5GC00943J>
- 521 35. Eicher T, Hauptmann S, Speicher A (2013) The chemistry of heterocycles: structures,
522 reactions, synthesis, and applications. Wiley
- 523 36. Evano G, Blanchard N, Toumi M (2008) Copper-mediated coupling reactions and their appli-
524 cations in natural products and designed biomolecules synthesis. Chem Rev 108(8):3054–
525 3131. <https://doi.org/10.1021/cr8002505>
- 526 37. Fakhri A, Naghipour A (2018) Organometallic polymer-functionalized Fe₃O₄ nanoparticles
527 as a highly efficient and eco-friendly nanocatalyst for C–C bond formation. Trans Met Chem
528 43(5):463–472. <https://doi.org/10.1007/s11243-018-0233-5>
- 529 38. Favier I, Pla D, Gómez M (2018) Metal-based nanoparticles dispersed in glycerol: an efficient
530 approach for catalysis. Catal Today 310:98–106. <https://doi.org/10.1016/j.cattod.2017.06.026>
- 531 39. Favier I, Pla D, Gómez M (2019) Palladium nanoparticles in polyols: synthesis, catalytic
532 couplings and hydrogenations. Chem Rev. <https://doi.org/10.1021/acs.chemrev.9b00204>
- 533 40. Favier I, Toro M-L, Lecante P, Pla D, Gómez M (2018) Palladium-mediated radical homo-
534 coupling reactions: a surface catalytic insight. Catal Sci Technol 8(18):4766–4773. <https://doi.org/10.1039/C8CY00901E>
- 535 41. Fiévet F, Ammar-Merah S, Brayner R, Chau F, Giraud M, Mammeri F, Viau G (2018)
536 The polyol process: a unique method for easy access to metal nanoparticles with tailored
537 sizes, shapes and compositions. Chem Soc Rev 47(14):5187–5233. [https://doi.org/10.1039/](https://doi.org/10.1039/C7CS00777A)
538 [C7CS00777A](https://doi.org/10.1039/C7CS00777A)
- 539 42. Fievet F, Lagier JP, Blin B, Beaudoin B, Figlarz M (1989) Homogeneous and heterogeneous
540 nucleations in the polyol process for the preparation of micron and submicron size metal
541 particles. Solid State Ion 32–33:198–205. [https://doi.org/10.1016/0167-2738\(89\)90222-1](https://doi.org/10.1016/0167-2738(89)90222-1)
- 542 43. Fievet F, Lagier JP, Figlarz M (2013) Preparing monodisperse metal powders in micrometer
543 and submicrometer sizes by the polyol process. MRS Bull 14(12):29–34. [https://doi.org/10.](https://doi.org/10.1557/S0883769400060930)
544 [1557/S0883769400060930](https://doi.org/10.1557/S0883769400060930)
- 545 44. Firouzabadi H, Iranpoor N, Gholinejad M, Hoseini J (2011) Magnetite (Fe₃O₄) nanoparticles-
546 catalyzed sonogashira-hagihara reactions in ethylene glycol under ligand-free conditions. Adv
547 Synth Catal 353(1):125–132. <https://doi.org/10.1002/adsc.201000390>
- 548 45. Firouzabadi H, Iranpoor N, Gholinejad M, Hoseini J (2011b) Magnetite (Fe₃O₄)
549 nanoparticles-catalyzed Sonogashira-Hagihara reactions in ethylene glycol under ligand-free
550 conditions. [Erratum to document cited in CA154:310261]. Adv Synth Catal 353(7):1027.
551 <https://doi.org/10.1002/adsc.201190017>
- 552 46. Formenti D, Ferretti F, Scharnagl FK, Beller M (2019) Reduction of nitro compounds
553 using 3d-non-noble metal catalysts. Chem Rev 119(4):2611–2680. [https://doi.org/10.1021/](https://doi.org/10.1021/acs.chemrev.8b00547)
554 [acs.chemrev.8b00547](https://doi.org/10.1021/acs.chemrev.8b00547)
- 555 47. Frindy S, El Kadib A, Lahcini M, Primo A, Garcia H (2015) Copper nanoparticles stabilized in
556 a porous chitosan aerogel as a heterogeneous catalyst for C–S cross-coupling. ChemCatChem
557 7(20):3307–3315. <https://doi.org/10.1002/cctc.201500565>

- 559 48. Gandeepan P, Müller T, Zell D, Cera G, Warratz S, Ackermann L (2019) 3d transition metals for
560 C-H activation. *Chem Rev* 119(4):2192–2452. <https://doi.org/10.1021/acs.chemrev.8b00507>
- 561 49. Ganem B (2009) Strategies for innovation in multicomponent reaction design. *Acc Chem Res*
562 42(3):463–472. <https://doi.org/10.1021/ar800214s>
- 563 50. Gawande MB, Goswami A, Felpin F-X, Asefa T, Huang X, Silva R, Varma RS (2016) Cu and
564 Cu-based nanoparticles: synthesis and applications in catalysis. *Chem Rev* 116(6):3722–3811.
565 <https://doi.org/10.1021/acs.chemrev.5b00482>
- 566 51. Ghiasbeigi E, Soleiman-Beigi M (2019) Copper immobilized on isonicotinic acid hydrazide
567 functionalized nano-magnetite as a novel recyclable catalyst for direct synthesis of phenols
568 and anilines. *Chem Select* 4(12):3611–3619. <https://doi.org/10.1002/slct.201803770>
- 569 52. Gholinejad M, Zareh F, Najera C (2018) Nitro group reduction and Suzuki reaction catalysed
570 by palladium supported on magnetic nanoparticles modified with carbon quantum dots gener-
571 ated from glycerol and urea. *Appl Organomet Chem* 32(1):e3984. <https://doi.org/10.1002/aoc.3984>
- 572 53. Ghorbani-Choghamarani A, Tahmasbi B, Moradi P (2016) Palladium-S-propyl-2-
573 aminobenzothioate immobilized on Fe₃O₄ magnetic nanoparticles as catalyst for Suzuki
574 and Heck reactions in water or poly(ethylene glycol). *Appl Organomet Chem* 30(6):422–430.
575 <https://doi.org/10.1002/aoc.3449>
- 576 54. Ghosh Chaudhuri R, Paria S (2012) Core/shell nanoparticles: classes, properties, synthesis
577 mechanisms, characterization, and applications. *Chem Rev* 112(4):2373–2433. <https://doi.org/10.1021/cr100449n>
- 578 55. Gilman H, Lichtenwalter M (1939) Relative reactivities of organometallic compounds. XXV.
579 Coupling reaction with halides of group VIII metals. *J Am Chem Soc* 61(4):957–959. <https://doi.org/10.1021/ja01873a056>
- 580 56. Grasso S, Micale N, Monforte A-M, Monforte P, Polimeni S, Zappalà M (2000) Synthesis
581 and in vitro antitumour activity evaluation of 1-aryl-1*H*,3*H*-thiazolo[4,3-*b*]quinazolines. *Eur*
582 *J Med Chem* 35(12):1115–1119. [https://doi.org/10.1016/S0223-5234\(00\)01195-8](https://doi.org/10.1016/S0223-5234(00)01195-8)
- 583 57. Anastas PT, Warner JC (2000) Green chemistry. *Org Process Res Dev* 4(5):437–438. <https://doi.org/10.1021/op000054t>
- 584 58. Haji M (2016) Multicomponent reactions: a simple and efficient route to heterocyclic
585 phosphonates. *Beilstein J Org Chem* 12:1269–1301. <https://doi.org/10.3762/bjoc.12.121>
- 586 59. Hajipour AR, Abolfathi P (2017) Novel triazole-modified chitosan@nickel nanoparticles:
587 efficient and recoverable catalysts for Suzuki reaction. *New J Chem* 41(6):2386–2391. <https://doi.org/10.1039/C6NJ03789E>
- 588 60. Hajipour AR, Rezaei F, Khorsandi Z (2017) Pd/Cu-free Heck and Sonogashira cross-coupling
589 reaction by Co nanoparticles immobilized on magnetic chitosan as reusable catalyst. *Green*
590 *Chem* 19(5):1353–1361. <https://doi.org/10.1039/C6GC03377F>
- 591 61. Handa S, Slack ED, Lipshutz BH (2015) Nanonickel-catalyzed Suzuki–Miyaura cross-
592 couplings in water. *Angew Chem Int* 54(41):11994–11998. <https://doi.org/10.1002/anie.201505136>
- 593 62. Heiz U, Landman U (2007) *Nanocatalysis*. Springer, Berlin
- 594 63. Heravi MM, Zadsirjan V, Hajiabbasi P, Hamidi H (2019) Advances in Kumada–Tamao–Corriu
595 cross-coupling reaction: an update. *Monatsh Chem* 150(4):535–591. <https://doi.org/10.1007/s00706-019-2364-6>
- 596 64. Irrgang T, Kempe R (2019) 3d-metal catalyzed N- and C-alkylation reactions via borrowing
597 hydrogen or hydrogen autotransfer. *Chem Rev* 119(4):2524–2549. <https://doi.org/10.1021/acs.chemrev.8b00306>
- 598 65. Joule JA, Mills K (2010) *Heterocyclic chemistry*. Wiley
- 599 66. Kataria M, Pramanik S, Kaur N, Kumar M, Bhalla V (2016) Ferromagnetic α -Fe₂O₃ NPs: a
600 potential catalyst in Sonogashira–Hagihara cross coupling and hetero-Diels–Alder reactions.
601 *Green Chem* 18(6):1495–1505. <https://doi.org/10.1039/C5GC02337H>
- 602 67. Kaushik M, Moores A (2017) New trends in sustainable nanocatalysis: emerging use of earth
603 abundant metals. *Curr Opin Green Sustain Chem* 7:39–45. <https://doi.org/10.1016/j.cogsc.2017.07.002>
- 604
605
606
607
608
609
610
611
612

- 613 68. Kerton F, Marriott R (2013) Alternative solvents for green chemistry. *Roy Soc Chem* 2
- 614 69. Kharasch MS, Fields EK (1941) Factors determining the course and mechanisms of grignard
- 615 reactions. IV. The effect of metallic halides on the reaction of aryl grignard reagents and
- 616 organic halides 1. *J Am Chem Soc* 63(9):2316–2320. <https://doi.org/10.1021/ja01854a006>
- 617 70. Khurana JM, Vij K (2010) Nickel nanoparticles catalyzed Knoevenagel condensation of aro-
- 618 matic aldehydes with barbituric acids and 2-thiobarbituric acids. *Catal Lett* 138(1):104–110.
- 619 <https://doi.org/10.1007/s10562-010-0376-2>
- 620 71. Khurana JM, Vij K (2011) Nickel nanoparticles catalyzed chemoselective Knoevenagel con-
- 621 densation of Meldrum's acid and tandem enol lactonizations via cascade cyclization sequence.
- 622 *Tetrahedron Lett* 52(28):3666–3669. <https://doi.org/10.1016/j.tetlet.2011.05.032>
- 623 72. Khurana JM, Yadav S (2012) Highly monodispersed PEG-stabilized Ni nanoparticles:
- 624 proficient catalyst for the synthesis of biologically important spiroopyrans. *Aust J Chem*
- 625 65(3):314–319. <https://doi.org/10.1071/CH11444>
- 626 73. Kidwai M, Mishra NK, Bhardwaj S, Jahan A, Kumar A, Mozumdar S (2010) Cu nanoparti-
- 627 cles in PEG: a new recyclable catalytic system for N-arylation of amines with aryl halides.
- 628 *ChemCatChem* 2(10):1312–1317. <https://doi.org/10.1002/cctc.201000062>
- 629 74. Klajn R (2014) Spiropyran-based dynamic materials. *Chem Soc Rev* 43(1):148–184. <https://doi.org/10.1039/C3CS60181A>
- 630 75. Kotovshchikov YN, Latyshev GV, Lukashev NV, Beletskaya IP (2015) Alkynylation of
- 631 steroids via Pd-free Sonogashira coupling. *Org Biomol Chem* 13(19):5542–5555. <https://doi.org/10.1039/C5OB00559K>
- 632 76. Kunz K, Scholz U, Ganzer D (2003) Renaissance of Ullmann and Goldberg reactions—
- 633 progress in copper catalyzed C-N-C-O- and C-S-coupling. *Synlett* 2003(15):2428–2439.
- 634 <https://doi.org/10.1055/s-2003-42473>
- 635 77. LaGrow AP, Ingham B, Cheong S, Williams GVM, Dotzler C, Toney MF, Tilley RD (2012)
- 636 Synthesis, alignment, and magnetic properties of monodisperse nickel nanocubes. *J Am Chem*
- 637 *Soc* 134(2):855–858. <https://doi.org/10.1021/ja210209r>
- 638 78. Langeslay RR, Kaphan DM, Marshall CL, Stair PC, Sattelberger AP, Delferro M (2019)
- 639 Catalytic applications of vanadium: a mechanistic perspective. *Chem Rev* 119(4):2128–2191.
- 640 <https://doi.org/10.1021/acs.chemrev.8b00245>
- 641 79. Liori AA, Stamatopoulos IK, Papastavrou AT, Pinaka A, Vougioukalakis GC (2018) A sus-
- 642 tainable, user-friendly protocol for the Pd-free sonogashira coupling reaction. *Eur J Org Chem*
- 643 2018(44):6134–6139. <https://doi.org/10.1002/ejoc.201800827>
- 644 80. Liu Q, Xu M, Zhao J, Yang Z, Qi C, Zeng M, Wang B (2018) Microstructure and catalytic
- 645 performances of chitosan intercalated montmorillonite supported palladium (0) and copper
- 646 (II) catalysts for Sonogashira reactions. *Int J Biol Macromol* 113:1308–1315. <https://doi.org/10.1016/j.ijbiomac.2018.03.066>
- 647 81. Liu X, Zhao X, Lu M (2015) A highly water-dispersible and magnetically separable palladium
- 648 catalyst based on functionalized poly(ethylene glycol)-supported iminophosphine for Suzuki-
- 649 Miyaura coupling in water. *Appl Organomet Chem* 29(6):419–424. <https://doi.org/10.1002/aoc.3308>
- 650 82. Lukyanov BS, Lukyanova MB (2005) Spiropyran: synthesis, properties, and applica-
- 651 tion (review). *Chem Heterocycl Compd* 41(3):281–311. [https://doi.org/10.1007/s10593-005-](https://doi.org/10.1007/s10593-005-0148-x)
- 652 [0148-x](https://doi.org/10.1007/s10593-005-0148-x)
- 653 83. Maleki A, Aghaei M, Ghamari N (2015) Synthesis of benzimidazolo[2,3-b]quinazolinone
- 654 derivatives via a one-pot multicomponent reaction promoted by a chitosan-based composite
- 655 magnetic nanocatalyst. *Chem Lett* 44(3):259–261. <https://doi.org/10.1246/cl.141074>
- 656 84. Maleki A, Jafari AA, Yousefi S, Eskandarpour V (2015) An efficient protocol for the one-pot
- 657 multicomponent synthesis of polysubstituted pyridines by using a biopolymer-based magnetic
- 658 nanocomposite. *C R Chim* 18(12):1307–1312. <https://doi.org/10.1016/j.crci.2015.09.002>
- 659 85. Maleki A, Kamalzare M (2014) An efficient synthesis of benzodiazepine derivatives via a one-
- 660 pot, three-component reaction accelerated by a chitosan-supported superparamagnetic iron
- 661 oxide nanocomposite. *Tetrahedron Lett* 55(50):6931–6934. [https://doi.org/10.1016/j.tetlet.](https://doi.org/10.1016/j.tetlet.2014.10.120)
- 662 [2014.10.120](https://doi.org/10.1016/j.tetlet.2014.10.120)

- 667 86. Maleki A, Niksefat M, Rahimi J, Taheri-Ledari R (2019) Multicomponent synthesis
668 of pyrano[2,3-d]pyrimidine derivatives via a direct one-pot strategy executed by novel
669 designed cooperated Fe₃O₄@polyvinyl alcohol magnetic nanoparticles. *Mater Today Chem*
670 13:110–120. <https://doi.org/10.1016/j.mtchem.2019.05.001>
- 671 87. Maleki A, Zand P, Mohseni Z, Firouzi-Haji R (2018) Green composite nanostructure
672 (Fe₃O₄@PEG-SO₃H): Preparation, characterization and catalytic performance in the efficient
673 synthesis of β-amino carbonyl compounds at room temperature. *Nano-Struct Nano-Objects*
674 16:31–37. <https://doi.org/10.1016/j.nanoso.2018.03.012>
- 675 88. Martínez-Prieto LM, Chaudret B (2018) Organometallic ruthenium nanoparticles: synthesis,
676 surface chemistry, and insights into ligand coordination. *Acc Chem Res* 51(2):376–384.
677 <https://doi.org/10.1021/acs.accounts.7b00378>
- 678 89. *Metal Nanoclusters in Catalysis and Materials Science: The Issue of Size Control* (2011).
679 Elsevier Science, Amsterdam
- 680 90. Mitrofanov AY, Murashkina AV, Martín-García I, Alonso F, Beletskaya IP (2017) Formation
681 of C–C, C–S and C–N bonds catalysed by supported copper nanoparticles. *Catal Sci Technol*
682 7(19):4401–4412. <https://doi.org/10.1039/C7CY01343D>
- 683 91. Moglie Y, Mascaró E, Nador F, Vitale C, Radivoy G (2008) Nanosized iron- or copper-
684 catalyzed homocoupling of aryl, heteroaryl, benzyl, and alkenyl grignard reagents. *Synth*
685 *Commun* 38(22):3861–3874. <https://doi.org/10.1080/00397910802238726>
- 686 92. Mohammadi R, Kassaee MZ (2013) Sulfochitosan encapsulated nano-Fe₃O₄ as an effi-
687 cient and reusable magnetic catalyst for green synthesis of 2-amino-4H-chromen-4-yl
688 phosphonates. *J Mol Catal A: Chem* 380:152–158. <https://doi.org/10.1016/j.molcata.2013.09.027>
- 690 93. Mondal P, Bhanja P, Khatun R, Bhaumik A, Das D, Manirul Islam S (2017) Palladium nanopar-
691 ticles embedded on mesoporous TiO₂ material (Pd@MTiO₂) as an efficient heterogeneous
692 catalyst for Suzuki–Coupling reactions in water medium. *J Colloid Interface Sci* 508:378–386.
693 <https://doi.org/10.1016/j.jcis.2017.08.046>
- 694 94. Mondal S (2016) Recent advancement of Ullmann-type coupling reactions in the formation
695 of C–C bond. *ChemTexts* 2(4):17. <https://doi.org/10.1007/s40828-016-0036-2>
- 696 95. Nakamura E, Hatakeyama T, Ito S, Ishizuka K, Ilies L, Nakamura M (2013) Iron-catalyzed
697 cross-coupling reactions. *Org React* 1–210
- 698 96. Nasrollahzadeh M, Sajjadi M, Ghorbannezhad F, Sajadi SM (2018) A review on recent
699 advances in the application of nanocatalysts in A³ coupling reactions. *Chem Rec* 18(10):1409–
700 1473. <https://doi.org/10.1002/tcr.201700100>
- 701 97. Neiva EGC, Bergamini MF, Oliveira MM, Marcolino LH, Zarbin AJG (2014) PVP-capped
702 nickel nanoparticles: synthesis, characterization and utilization as a glycerol electrosensor.
703 *Sens Actuator B Chem* 196:574–581. <https://doi.org/10.1016/j.snb.2014.02.041>
- 704 98. Park J, Kang E, Son SU, Park HM, Lee MK, Kim J, Hyeon T (2005) Monodisperse nanopar-
705 ticles of Ni and NiO: synthesis, characterization, self-assembled superlattices, and catalytic
706 applications in the Suzuki coupling reaction. *Adv Mater* 17(4):429–434. <https://doi.org/10.1002/adma.200400611>
- 707 99. Patete JM, Peng X, Koenigsmann C, Xu Y, Karn B, Wong SS (2011) Viable methodologies
708 for the synthesis of high-quality nanostructures. *Green Chem* 13(3):482–519. <https://doi.org/10.1039/C0GC00516A>
- 710 100. Peng J-B, Wu F-P, Wu X-F (2019) First-row transition-metal-catalyzed carbonylative trans-
711 formations of carbon electrophiles. *Chem Rev* 119(4):2090–2127. [https://doi.org/10.1021/](https://doi.org/10.1021/acs.chemrev.8b00068)
712 [acs.chemrev.8b00068](https://doi.org/10.1021/acs.chemrev.8b00068)
- 713 101. Pozharskii AF, Soldatenkov AT, Katritzky AR (2011) Heterocycles in industry and technology.
714 In: Pozharskii AF, Soldatenkov AT, Katritzky AR (eds) *Heterocycles in life and society*, pp
715 209–246
- 716 102. Prabhu RN, Lakshmi Praba J (2017) A nickel(II) thiosemicarbazonato complex: synthesis,
717 structure, electrochemistry, and application in catalytic coupling of terminal alkynes with
718 arylboronic acids. *Transit Metal Chem* 42(7):579–585. [https://doi.org/10.1007/s11243-017-](https://doi.org/10.1007/s11243-017-0162-8)
719 [0162-8](https://doi.org/10.1007/s11243-017-0162-8)
- 720

- 721 103. Prabhu RN, Ramesh R (2016) Square-planar Ni(II) thiosemicarbazonato complex as an easily
722 accessible and convenient catalyst for Sonogashira cross-coupling reaction. *Tetrahedron Lett*
723 57(44):4893–4897. <https://doi.org/10.1016/j.tetlet.2016.09.049>
- 724 104. Pechtl MHG (2017) *Nanocatalysis in ionic liquids*. Wiley-VCH, Weinheim
- 725 105. Reina A, Favier I, Pradel C, Gómez M (2018) Stable Zero-Valent nickel nanoparti-
726 cles in glycerol: synthesis and applications in selective hydrogenations. *Adv Synth Catal*
727 360(18):3544–3552. <https://doi.org/10.1002/adsc.201800786>
- 728 106. Roucoux A, Schulz J, Patin H (2002) Reduced transition metal colloids: a novel family of
729 reusable catalysts? *Chem Rev* 102(10):3757–3778. <https://doi.org/10.1021/cr010350j>
- 730 107. Safari J, Javadian L (2015) Ultrasound assisted green synthesis of 2-amino-4H-chromene
731 derivatives catalyzed by Fe₃O₄-functionalized nanoparticles with chitosan as a novel
732 and reusable magnetic catalyst. *Ultrason Sonochem* 22:341–348. [https://doi.org/10.1016/j.](https://doi.org/10.1016/j.ultsonch.2014.02.002)
733 [ultsonch.2014.02.002](https://doi.org/10.1016/j.ultsonch.2014.02.002)
- 734 108. Sambiagio C, Marsden SP, Blacker AJ, McGowan PC (2014) Copper catalysed Ullmann type
735 chemistry: from mechanistic aspects to modern development. *Chem Soc Rev* 43(10):3525–
736 3550. <https://doi.org/10.1039/C3CS60289C>
- 737 109. San K, Shon Y-S (2018) Synthesis of Alkanethiolate-capped Metal nanoparticles using alkyl
738 thiosulfate ligand precursors: a method to generate promising reagents for selective catalysis.
739 *Nanomaterials* 8(5):346. <https://doi.org/10.3390/nano8050346>
- 740 110. Schmid G (2011) *Nanoparticles: from theory to application*. Wiley
- 741 111. Serp, P., Philippot, K., Somorjai, G. A., & Chaudret, B. (2012). *Nanomaterials in Catalysis*:
742 Wiley
- 743 112. Shaabani A, Afshari R (2018) Magnetic Ugi-functionalized graphene oxide complexed with
744 copper nanoparticles: Efficient catalyst toward Ullman coupling reaction in deep eutectic
745 solvents. *J Colloid Interface Sci* 510:384–394. <https://doi.org/10.1016/j.jcis.2017.09.089>
- 746 113. Shah AP, Sharma AS, Jain S, Shimpi NG (2018) Microwave assisted one pot three component
747 synthesis of propargylamines, tetra substituted propargylamines and pyrrolo[1,2-a]quinolines
748 using CuNPs@ZnO-PTH as a heterogeneous catalyst. *New J Chem* 42(11):8724–8737. [https://](https://doi.org/10.1039/C8NJ00410B)
749 doi.org/10.1039/C8NJ00410B
- 750 114. Sharghi H, Aberi M (2014) Ligand-free copper(I) oxide nanoparticle catalyzed three-
751 component synthesis of 2H-indazole derivatives from 2-halobenzaldehydes, amines and
752 sodium azide in polyethylene glycol as a green solvent. *Synlett* 25(8):1111–1115. [https://](https://doi.org/10.1055/s-0033-1340979)
753 doi.org/10.1055/s-0033-1340979
- 754 115. Song J-Y, Zhou X, Song H, Liu Y, Zhao H-Y, Sun Z-Z, Chu W-Y (2018) Visible-light-assisted
755 cobalt-2-(hydroxyimino)-1-phenylpropan-1-one complex catalyzed Pd/Cu-free Sonogashira-
756 Hagihara cross-coupling reaction. *ChemCatChem* 10(4):758–762. [https://doi.org/10.1002/](https://doi.org/10.1002/cctc.201701253)
757 [cctc.201701253](https://doi.org/10.1002/cctc.201701253)
- 758 116. Sonogashira K (2002) Development of Pd–Cu catalyzed cross-coupling of terminal acetylenes
759 with sp²-carbon halides. *J Organomet Chem* 653(1):46–49. [https://doi.org/10.1016/S0022-](https://doi.org/10.1016/S0022-328X(02)01158-0)
760 [328X\(02\)01158-0](https://doi.org/10.1016/S0022-328X(02)01158-0)
- 761 117. Swamy KCK, Kumar NNB, Balaraman E, Kumar KVPP (2009) Mitsunobu and related
762 reactions: advances and applications. *Chem Rev* 109(6):2551–2651. [https://doi.org/10.1021/](https://doi.org/10.1021/cr800278z)
763 [cr800278z](https://doi.org/10.1021/cr800278z)
- 764 118. Tamao K, Sumitani K, Kumada M (1972) Selective carbon-carbon bond formation by cross-
765 coupling of Grignard reagents with organic halides. Catalysis by nickel-phosphine complexes.
766 *J Am Chem Soc* 94(12):4374–4376. <https://doi.org/10.1021/ja00767a075>
- 767 119. Thomas AA, Denmark SE (2016) Pre-transmetalation intermediates in the Suzuki-Miyaura
768 reaction revealed: the missing link. *Science* 352(6283):329–332. [https://doi.org/10.1126/](https://doi.org/10.1126/science.aad6981)
769 [science.aad6981](https://doi.org/10.1126/science.aad6981)
- 770 120. Thomas AM, Sujatha A, Anilkumar G (2014) Recent advances and perspectives in copper-
771 catalyzed Sonogashira coupling reactions. *RSC Adv* 4(42):21688–21698. [https://doi.org/10.](https://doi.org/10.1039/C4RA02529F)
772 [1039/C4RA02529F](https://doi.org/10.1039/C4RA02529F)
- 773 121. Thota S, Crans DC, Mei W, Wu Q (2018) Applications of metal nanoparticles in
774 medicine/metal nanoparticles as anticancer agents. In: *Metal nanoparticles*. Wiley-VCH
775 Verlag GmbH & Co. KGaA, pp 169–190

- 776 122. Torimoto T, Kameyana T, Kuwabata S (2017) Top-down synthesis methods for nanoscale
777 catalysts. In: Prechtl MHG (ed) Nanocatalysis in ionic liquids. Wiley-VCH, Weinheim, pp
778 171–205
- 779 123. Trammell R, Rajabimoghadam K, Garcia-Bosch I (2019) Copper-promoted functionalization
780 of organic molecules: from biologically relevant Cu/O₂ model systems to organometallic
781 transformations. *Chem Rev* 119(4):2954–3031. <https://doi.org/10.1021/acs.chemrev.8b00368>
- 782 124. Tsuji J (2004) Palladium reagents and catalysts: new perspectives for the 21st century. Wiley,
783 West Sussex
- 784 125. Ullmann F, Bielecki J (1901) Ueber synthesen in der biphenylreihe. *Ber Dtsch Chem Ges*
785 34(2):2174–2185. <https://doi.org/10.1002/cber.190103402141>
- 786 126. Veisi H, Najafi S, Hemmati S (2018) Pd(II)/Pd(0) anchored to magnetic nanoparticles (Fe₃O₄)
787 modified with biguanidine-chitosan polymer as a novel nanocatalyst for Suzuki-Miyaura
788 coupling reactions. *Int J Biol Macromol* 113:186–194. <https://doi.org/10.1016/j.ijbiomac.2018.02.120>
- 789 127. Wang D, Astruc D (2017) The recent development of efficient Earth-abundant transition-metal
790 nanocatalysts. *Chem Soc Rev* 46(3):816–854. <https://doi.org/10.1039/C6CS00629A>
- 791 128. Warner JC, Cannon AS, Dye KM (2004) Green chemistry. *Environ Impact Assess Rev*
792 24(7):775–799. <https://doi.org/10.1016/j.eiar.2004.06.006>
- 793 129. Wei D, Darcel C (2019) Iron catalysis in reduction and hydrometalation reactions. *Chem Rev*
794 119(4):2550–2610. <https://doi.org/10.1021/acs.chemrev.8b00372>
- 795 130. Wender PA (2014) Toward the ideal synthesis and molecular function through synthesis-
796 informed design. *Nat Prod Rep* 31(4):433–440. <https://doi.org/10.1039/C4NP00013G>
- 797 131. Xia H, Xie K, Zou G (2017) Advances in spiroopyrans/spirooxazines and applications based
798 on fluorescence resonance energy transfer (FRET) with fluorescent materials. *Molecules*
799 22(12):2236
- 800 132. Yavuz K, Kuecukbay H (2018) Efficient and green catalytic system incorporating new
801 benzimidazolium salts for the Sonogashira cross-coupling reaction. *Appl Organomet Chem*
802 32(1):n/a. <https://doi.org/10.1002/aoc.3897>
- 803 133. Yonezawa T (2018) Application 78—preparation of metal nanoparticles and their application
804 for materials. In: Naito M, Yokoyama T, Hosokawa K, Nogi K (eds) Nanoparticle technology
805 handbook, 3rd edn. Elsevier, pp 829–837
- 806 134. Zhang Y, Erkey C (2006) Preparation of supported metallic nanoparticles using supercritical
807 fluids: a review. *J Supercrit Fluids* 38(2):252–267. <https://doi.org/10.1016/j.supflu.2006.03.021>
- 808 135. Zhong Y, Gong X, Zhu X, Ni Z, Wang H, Fu J, Han W (2014) In situ generated nickel
809 nanoparticle-catalyzed carbonylative Suzuki reactions of aryl iodides with arylboronic acids
810 at ambient CO pressure in poly(ethylene glycol). *RSC Adv* 4(108):63216–63220. <https://doi.org/10.1039/C4RA10739J>
- 811 136. Zhou B, Hermans S, Somorjai GA (2004) Nanotechnology in catalysis. Kluwer/Plenum, New
812 York
- 813 137. Zhou L, Gao C, Xu W (2010) Robust Fe₃O₄/SiO₂-Pt/Au/Pd magnetic nanocatalysts with mul-
814 tifunctional hyperbranched polyglycerol amplifiers. *Langmuir* 26(13):11217–11225. <https://doi.org/10.1021/la100556p>
- 815 138. Zhu J, Bienaymé H (2006) Multicomponent reactions. Wiley