

## Review Article

# Recent Developments in Nanostructured Palladium and Other Metal Catalysts for Organic Transformation

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Nanocatalysis is an emerging field of research and is applicable to nearly all kinds of catalytic organic conversions. Nanotechnology is playing an important role in both industrial applications and academic research. The catalytic activities become pronounced as the size of the catalyst reduces and the surface area-to-volume ratio increases which ultimately enhance the activity and selectivity of nanocatalysts. Similarly, the morphology of the particles also has a great impact on the activity and selectivity of nanocatalysts. Moreover, the electronic properties and geometric structure of nanocatalysts can be affected by polar and nonpolar solvents. Various forms of nanocatalysts have been reported including supported nanocatalysts, Schiff-based nanocatalysts, graphene-based nanocatalysts, thin-film nanocatalysts, mixed metal oxide nanocatalysts, magnetic nanocatalysts, and core-shell nanocatalysts. Among a variety of different rare earth and transition metals, palladium-based nanocatalysts have been extensively studied both in academia and in the industry because of their applications such as in carbon-carbon cross-coupling reactions, carbon-carbon homocoupling reactions, carbon-heteroatom cross-coupling reactions, and C-H activation, hydrogenation, esterification, oxidation, and reduction. The current review highlights the recent developments in the synthesis of palladium and some other metal nanocatalysts and their potential applications in various organic reactions.

## 1. Introduction

After realizing the unique morphological, structural, and optoelectrical characteristics of nanomaterials, their wide range of applications has been explored in various fields [1]. These include environmental, energy harnessing, biomedical sector, and catalysis [2–7]. The chemical process that involves the use of nanomaterials as a catalyst can be termed as nanocatalysis, while the nanomaterial can be termed as nanocatalyst. Based on their morphologies, nanocatalysts can be classified into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures [8]. The control dimensions of these materials induced specific physicochemical characteristics, which make them special for the catalysis industry [9]. More recently, researchers show significant inclination to use nanocatalysts in advance heterogeneous and homoge-

nous catalysis applications [10]. A number of reviews in the area gave an insightful view into the prospects of nanostructured catalysis [11–14]. The catalyst system composed of nanoparticles/nanocomposites showed greater catalytic activity and selectivity because of its morphology and nano-dimensional characteristics. Though many materials have been utilized as nanocatalysts in industries, transition metal NPs have received significant attention due to their unique physicochemical characteristics, abundant availability, and more importantly, consumer-friendly costs. It is well established that the size, morphology, and solvents play a key role in the catalytic activity, selectivity, and stability of the nanocatalysts [15].

The present review is an attempt to realize the current development and prospects in nanostructured catalysts, especially for organic synthesis. The beginning portion of the review is dedicated to the effect of various factors on the

overall performance of nanocatalysts. This is followed by a critical overview of organic transformations, with a few case studies on Pd, Pt, Fe, Cu, Ag, Au, and Zn NPs, as well as other examples. In the later part of the review, some insights are provided through the Conclusion along with a few future recommendations about the future potential of nanostructured catalysts.

## 2. Factors Affecting the Performance of Nanocatalysts

There are several factors that affect the performance of nanocatalysts. However, this section will mainly focus on three important factors which include particle size, particle shape, and solvent.

**2.1. Particle Size Effect of Nanocatalysts.** Over the past few years, significant research has been conducted to identify the effect of nanoparticle size on catalytic performance for various chemical transformations [16]. As the particle size decreases, their surface area-to-volume ratio is enhanced, allowing more atoms on the surface to take part in the reaction [17]. As a result, improved catalyst activity and selectivity can be achieved. The particle size is very important for the development of highly active and selective catalysts as well as for the reduction of catalyst loading. Yoo et al. found better electrocatalytic and electronic properties by decreasing the size of Pt/TiO<sub>2</sub> nanocatalysts [18]. Bond and Thompson discovered that the catalytic activity of gold nanoparticles depends on their size, support system, and synthesis methods [19]. The gold catalyst is composed of very small-sized particles (<5 nm) and is supported by TiO<sub>2</sub>. Before such discovery, gold was assumed to be the least catalytically active metal. Li et al. synthesized palladium nanoparticle-graphene hybrids and investigated the catalytic activities of such Pd-graphene hybrids in Suzuki reaction under aerobic and aqueous conditions [20]. It was observed that a palladium-graphene hybrid with a 4 nm particle size of palladium gave a 100% yield along with 95.5% selectivity. However, a palladium-graphene hybrid with a 15 nm particle size of palladium gave a 93.7 yield along with 95.2% selectivity.

**2.2. Particle Shape Effect of Nanocatalysts.** The shaped-controlled synthesis of catalytic materials is widely regarded to control some important physicochemical properties of nanocatalysts [21]. Many reports are available in the literature in this regard. For instance, hemispherical gold nanoparticles gave better results as compared to spherical-shaped gold nanoparticles for the oxidation of carbon monoxide (CO) even at low temperature [22]. In 2005, Henry reported a brief review with practical examples regarding the effect of nanoparticle shape on their properties in numerous developing technologies [23]. Narayanan and El-Sayed synthesized tetrahedral- and cubic-shaped platinum nanoparticles and studied the relationship of shape reactivity [24]. Shape control is significantly reported for photocatalytic applications in the literature. Khan and Qurashi synthesized highly controlled platelet-shaped copper vanadate nanocatalysts for PEC water splitting and compared the results

with NPs of conventional shape. It was determined that the shape-controlled copper vanadate enhanced the light trapping properties of the catalyst and hence enhanced the photoelectrochemical performance of the catalyst [25].

Similarly, shape-controlled NPs are also found useful in organic conversion to some extent. As reported by Luo et al., shape-controlled synthesis of Rh-based nanocrystals and supported Rh-based nanocatalysts was found efficient in heterogeneous conversions such as in methane conversion and olefin hydroformylation [26].

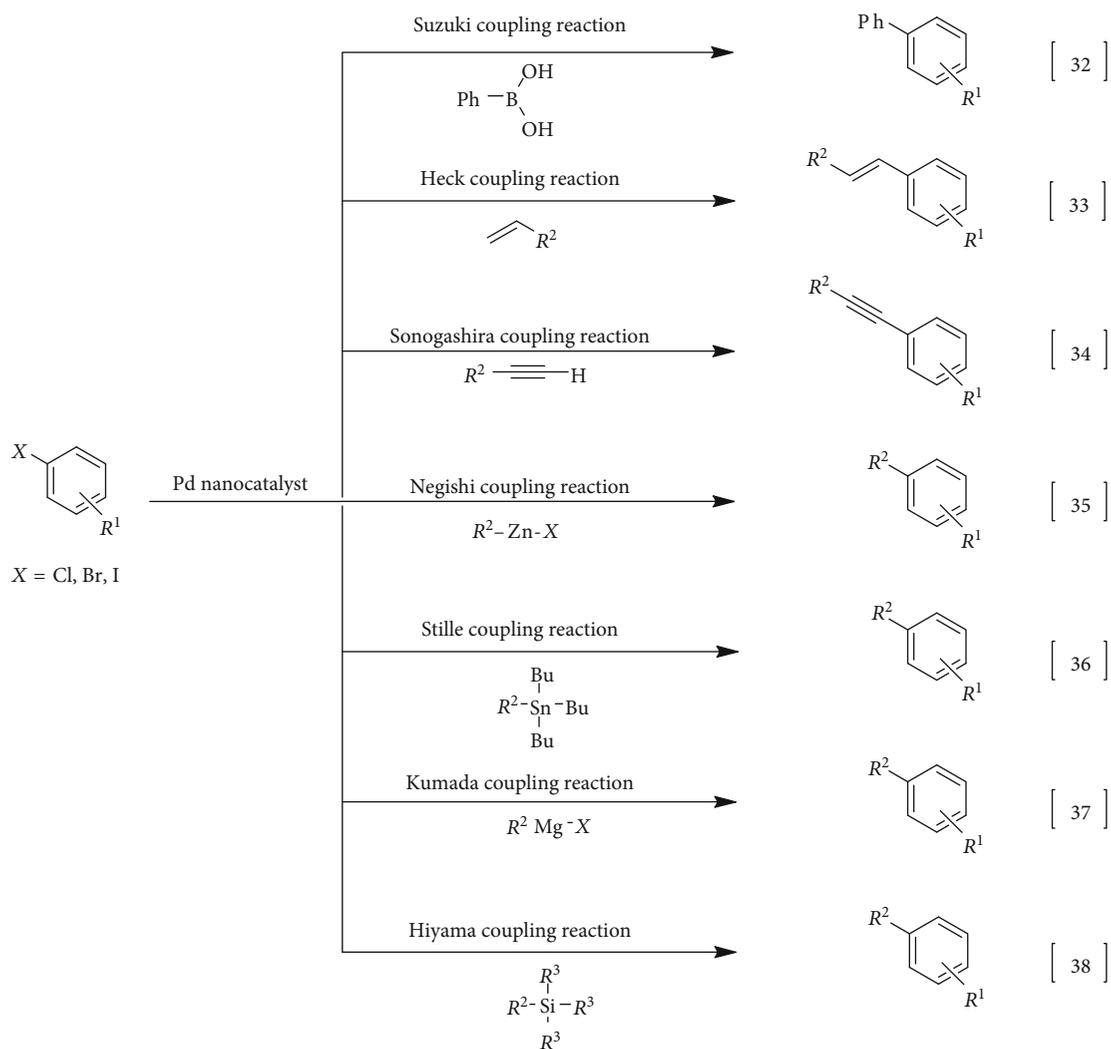
**2.3. Solvent Effect on Nanocatalysts.** A solvent has a significant impact on the reaction pathway, reaction energy, and activation energy. The geometric structure and the electronic properties of nanoparticles can be influenced by the interaction of a solvent and metal atoms. Dufour et al. reported the effects of solvents on the electronic and structural properties of small gold clusters [27]. Li and Liu demonstrated the geometrical, electronic, and photocatalytic properties of titania anatase nanoparticles in aqueous media [28]. A comprehensive study of the effects of polar and nonpolar solvents on electronic and geometrical properties of nanocatalysts was conducted by Hou et al., and it was noted that a polar solvent has a great impact on the properties of nanocatalysts. It was observed that the ionization potential decreased by increasing the polarity of the solvent. Therefore, it was easier for neutral species to donate an electron in the solvent. Moreover, the electron-donating ability of a neutral species is considerably increased in a polar solvent as compared to that in a nonpolar solvent [29]. Recently, Chowdhury et al. synthesized palladium nanoparticles in an aqueous dimethyl formamide (DMF) solvent with a changing composition of DMF. Different shapes and geometries of palladium nanoparticles, such as hexagonal, cuboidal, and triangular plates, were obtained by varying the composition of DMF. It was emphasized that the various geometries of palladium nanoparticles are due to the blocking and interaction of DMF to some planes of nanoparticles leading to different geometries [30].

## 3. Major Nanocatalysts for Organic Synthesis

A huge number of metals have been investigated for organic transformations, and these metals showed better results in the formation of pharmaceuticals, fine chemicals, and new materials [31]. Among the varieties of different rare earth and transition metals, palladium is one of the most widely used transition metal for carbon-carbon coupling reactions, and palladium-based nanocatalysts have been extensively studied both in academia and in industry because of their applications such as in sensors, fuel cell catalysts, hydrogen storage, dechlorination, and organic transformations. Therefore, we mainly focused on the current development of palladium-based nanocatalysts for cross-coupling reactions. However, some other metals which have been successfully applied in this field have also been highlighted.

### 3.1. Palladium-Based Nanocatalyst

**3.1.1. Palladium-Based Nanocatalysts for Carbon-Carbon Cross-Coupling Reactions.** Palladium-assisted nanocatalysts



SCHEME 1: Palladium-based nanocatalysts for carbon-carbon cross-coupling reactions.

for carbon-carbon bond formation including Suzuki [32], Heck [33], Sonogashira [34], Negishi [35], Stille [36], Kumada [37], and Hiyama [38] cross-coupling reactions (Scheme 1) have made a huge impact on organic reactions because of mild reaction conditions and tolerance to various functional groups [39]. Such kinds of reactions showed extensive applications in the formation of pharmaceuticals, agrochemicals, and other important industrial products [40].

Among the various carbon-carbon coupling reactions, Suzuki, Heck, and Sonogashira reactions are the most important reactions and play a central role in the formation of natural products, pharmaceutical, and agrochemicals [41]. Table 1 lists the various metal nanoparticles for catalyzing Suzuki, Heck, and Sonogashira cross-coupling reactions.

<sup>a</sup>Isolated yield. <sup>b</sup>GC yield. <sup>c</sup>Yield after work-up.

Within the framework of carbon-carbon cross-coupling reactions, the Suzuki reaction is the most extensively used reaction and it has been the benchmark for identifying the catalytic activity of newly prepared metal nanoparticles. In 2008, Kim et al. synthesized bimetallic nanoparticles (Pd-Ag, Pd-Ni, and Pd-Cu) on carbon support through the  $\gamma$ -irradiation technique for Suzuki and Heck cross-coupling

reactions [52]. The catalytic efficiency of these supported bimetallic nanoparticles in Suzuki reaction were in the order of Pd-Cu/C > Pd/C > Pd-Ag/C > Pd-Ni/C based on the reaction yield 97.5% > 96.7% > 92.3% > 38.5%, respectively.

The various metal nanocatalysts used in the Suzuki reaction are listed in Table 2.

<sup>a</sup>Isolated yield. <sup>b</sup>GC yield.

**3.1.2. Mechanism of Cross-Coupling Reactions.** The reactants meet on a palladium atom and become so close together that reaction takes place. The major role of palladium and the other metals is to enable and encourage two coupling partners to undergo a chemical reaction. In 1972, Kumada et al. suggested that the catalytic cycle of a cross-coupling reaction occurs in three steps including oxidative addition, transmetalation, and reductive elimination (Scheme 2) [67].

The reaction mechanism usually begins with the zero-valent palladium (Pd<sup>0</sup>) which undergoes oxidative addition (step 1) by reacting with an organic electrophile to form a Pd (II) species [68]. Usually, step 1 is the rate-determining step in this three-step catalytic cycle. Subsequently, transmetalation (step 2) occurs in the presence of a base for the

TABLE 1: Palladium-based nanocatalysts for carbon-carbon coupling reactions.

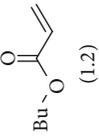
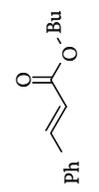
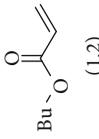
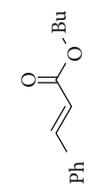
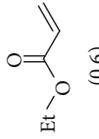
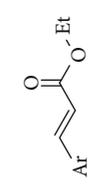
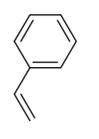
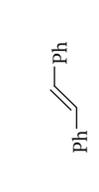
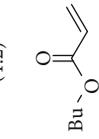
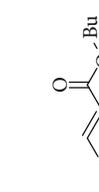
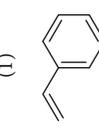
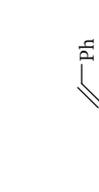
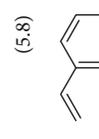
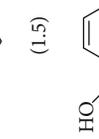
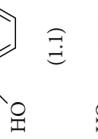
Catalyst (amount)	Substrate (1 mmol)	Substrate (2 mmol)	Coupling product	Base	Solvent	T (°C)	Time (h)	Reaction name	Yield (%)	Ref.
Pd-SMU-MNPs (8 mg)	PhI (1)	 (1.2)		K <sub>2</sub> CO <sub>3</sub>	DMF	120	1.5	Heck	95 <sup>a</sup>	[42]
Fe <sub>3</sub> O <sub>4</sub> @CS-Schiff-based Pd catalyst (10 mg)	PhI (1)	 (1.2)		Et <sub>3</sub> N	DMF	120	0.3	Heck	98 <sup>a</sup>	[43]
Stabilized Pd-NPs (1 mol%)	ArI (0.5)	 (0.6)		CsCO <sub>3</sub>	DMF	110	2	Heck	95 <sup>a</sup>	[41]
Pd/NH <sub>2</sub> -SiO <sub>2</sub> (0.05 mol%)	PhI (1)	 (1.2)		K <sub>2</sub> CO <sub>3</sub>	DMF	110-120	2	Heck	95 <sup>a</sup>	[44]
Pd-PVP-Fe (0.004 g)	PhBr (1)	 (1)		K <sub>2</sub> CO <sub>3</sub>	DMF	RT	0.5	Heck	91 <sup>a</sup>	[33]
OXDH-Pd-NPs (0.0091 mmol)	ArI (6.3)	 (5.8)		Na <sub>2</sub> CO <sub>3</sub>	NMP:H <sub>2</sub> O (1:1)	80	0.5	Heck	97 <sup>a</sup>	[45]
Au/Pd-NPs (0.3 mol%)	PhI (1)	 (1.5)		K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	80	8	Heck	89 <sup>c</sup>	[46]
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /isoniazide/Pd (10 mg)	PhI (1)	 (1.1)		K <sub>2</sub> CO <sub>3</sub>	EtOH:H <sub>2</sub> O (1:1)	25	0.5	Suzuki	96 <sup>a</sup>	[47]
Pd-NP-HNG (0.025 mol%)	PhI (1)	 (1.3)		K <sub>2</sub> CO <sub>3</sub>	EtOH:H <sub>2</sub> O (1:1)	60	2.5	Suzuki	98 <sup>a</sup>	[48]

TABLE I: Continued.

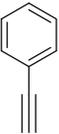
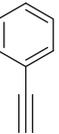
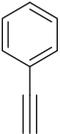
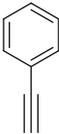
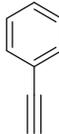
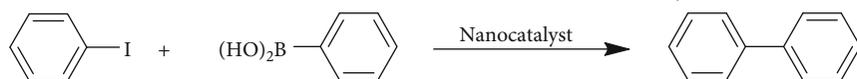
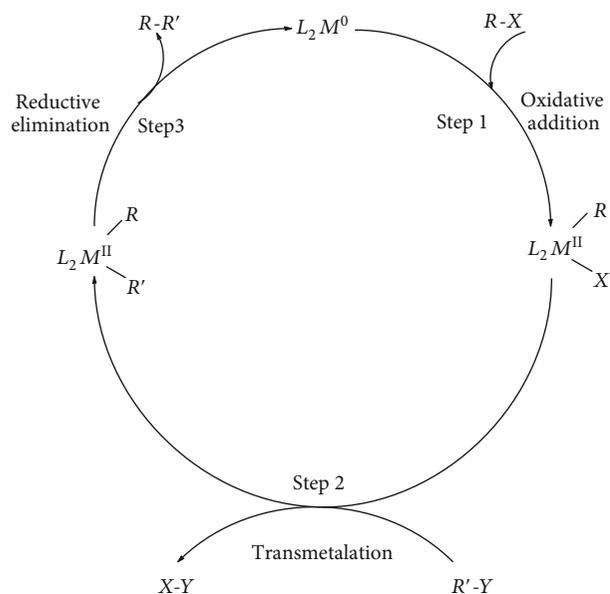
Catalyst (amount)	Substrate (1 mmol)	Substrate (2 mmol)	Coupling product	Base	Solvent	T (°C)	Time (h)	Reaction name	Yield (%)	Ref.
PdCo ANP-PPI-g-graphene (0.004 g)	PhI (1)	 (1)	 Ph	K <sub>2</sub> CO <sub>3</sub>	None	25	1	Sonogashira	99 <sup>b</sup>	[49]
Pd tripods (2 mol%)	PhI (0.49)	 (0.74)	 Ph	KOH	H <sub>2</sub> O	100	6	Sonogashira	93 <sup>a</sup>	[50]
Pd@MWCNTs (1 mmol%)	PhI (1)	 (1.2)	 Ph	K <sub>2</sub> CO <sub>3</sub>	MeOH : H <sub>2</sub> O (3 : 1)	Reflux	2.5	Sonogashira	71 <sup>a</sup>	[51]
Pd/NH <sub>2</sub> -SiO <sub>2</sub> (0.05 mol%)	PhI (1)	 (1.5)	 Ph	K <sub>2</sub> CO <sub>3</sub>	EG	120	2	Sonogashira	98 <sup>a</sup>	[44]
Stabilized Pd-NPs (1 mol%)	PhI (0.5)	 (0.6)	 Ph	Cs <sub>2</sub> CO <sub>3</sub>	MeOH	90	22	Sonogashira	91 <sup>a</sup>	[41]

TABLE 2: Suzuki reaction with various metal nanocatalysts



Nanocatalyst (amount)	PhI	PhB(OH) <sub>2</sub>	Base	Solvent	T (°C)	Time (h)	Yield (%)	Ref.
Pd-SMU-MNPs (6 mg)	1	1	K <sub>2</sub> CO <sub>3</sub>	PEG	50	0.5	97 <sup>a</sup>	[42]
Cu-C (0.1 mol%)	1	1.2	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	50	3	96 <sup>a</sup>	[53]
Fe <sub>3</sub> O <sub>4</sub> NPs/IL/Pd(0) (0.2 mol%)	1	1.1	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O/EtOH (1 : 1)	RT	0.25	96 <sup>a</sup>	[54]
Au-graphene (1 mol%)	1	1.2	NaOH	H <sub>2</sub> O	100	4	85 <sup>b</sup>	[55]
Pd/TiO <sub>2</sub> (0.7 mol%)	1	1.1	Na <sub>2</sub> CO <sub>3</sub>	NMP : H <sub>2</sub> O (2.5 : 1)	120	4	97 <sup>a</sup>	[56]
Ru/Al <sub>2</sub> O <sub>3</sub> (5 mol%)	1	1.5	NaOH	DME/H <sub>2</sub> O (1 : 1)	60	1	96 <sup>a</sup>	[57]
Pd@MWCNTs (1 mmol%)	1	1.2	K <sub>2</sub> CO <sub>3</sub>	MeOH : H <sub>2</sub> O (3 : 1)	Reflux	2.5	84 <sup>b</sup>	[51]
PVP-stabilized Pd-NPs (0.07 mol%)	0.5	0.75	K <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> O : EtOH (3 : 1)	90	24	97 <sup>b</sup>	[58]
Pd/NH <sub>2</sub> -SiO <sub>2</sub> (0.05 mol%)	1	1.2	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O (2 mL)	60-70	1	96 <sup>a</sup>	[44]
Fe <sub>3</sub> O <sub>4</sub> @CS-Schiff-based Pd catalyst (10 mg)	1	1.2	K <sub>2</sub> CO <sub>3</sub>	PEG	80	0.17	98 <sup>a</sup>	[43]
Pd-Ni@Fe <sub>3</sub> O <sub>4</sub> (0.0026 mol% of Pd and 0.001 mol% of Ni)	0.5	0.75	K <sub>2</sub> CO <sub>3</sub>	EtOH	80	0.25	94 <sup>a</sup>	[59]
Pd/r-GO NP thin film	1	1.2	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	80	0.25	>99 <sup>a</sup>	[60]
LDH-DS-Pd(0) (0.5 mol%)	1	1.2	K <sub>2</sub> CO <sub>3</sub>	DMF/H <sub>2</sub> O 6 mL (5 : 1, v/v)	80	5	93 <sup>a</sup>	[61]
Pd@MTiO <sub>2</sub> (0.03 g)	1	1.2	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	70	3	99 <sup>b</sup>	[62]
Carbon nanocomposite Pd catalyst (1 mol%)	0.5	0.6	K <sub>2</sub> CO <sub>3</sub>	DMF/H <sub>2</sub> O (2 : 1)	100	1.5	97 <sup>b</sup>	[63]
Core-shell-like Ni-Pd/CB catalyst (5.5 mg, 0.1 mol% Pd)	2.5	2.75	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (1 : 1)	30	0.5	90 <sup>a</sup>	[64]
Au-G nanocomposite (0.05 g)	1	1.5	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	RT	4	99 <sup>b</sup>	[65]
Sr/Alg/CMC/GO/Au (0.005 mol%)	2	2.4	NaOH	H <sub>2</sub> O	80	4	98 <sup>a</sup>	[66]
OXDH-Pd-NPs (0.0091 mmol)	5.41	4.92	Na <sub>2</sub> CO <sub>3</sub>	1,4 Dioxane/water (1 : 1)	80	1	98 <sup>a</sup>	[45]
Stabilized Pd-NPs (1 mol%)	0.5	0.75	KF	DMF : H <sub>2</sub> O (1 : 1)	RT	24	93 <sup>a</sup>	[41]



SCHEME 2: The proposed mechanism of cross-coupling reactions.

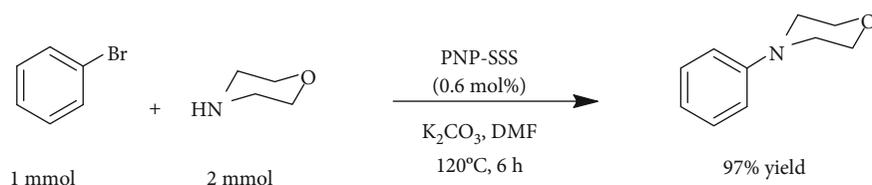
transfer of  $R'$  towards a less electropositive metal. In this step, both coupling partners join the same metal center while removing the functional groups. At the end (step 3), reductive elimination occurs which leads to the formation of a

new carbon-carbon bond as well as the regeneration of a zero-valent palladium species which is ready for another cycle. An unsaturated organic species was found to undergo a faster coupling reaction by following the order vinyl > phenyl > phenyl > alkynyl > alkyl > alkyl.

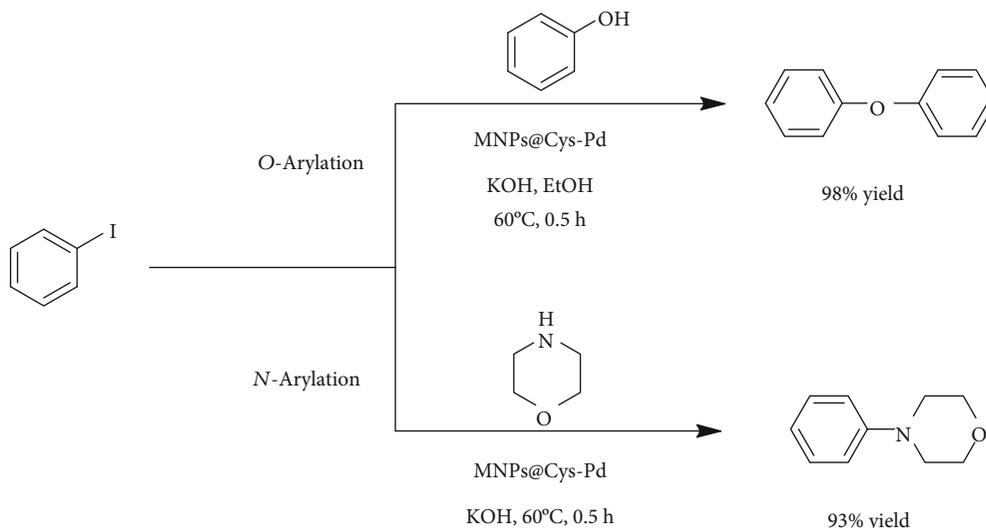
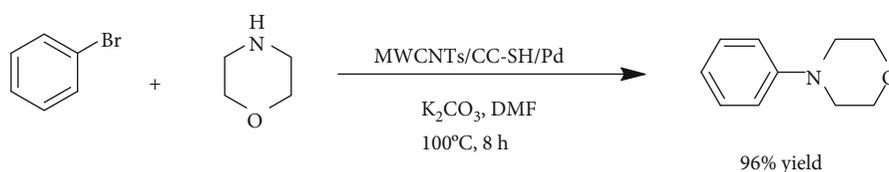
**3.1.3. Palladium-Based Nanocatalysts for Carbon-Heteroatom Cross-Coupling Reactions.** Palladium nanocatalysts have been successfully applied in carbon-heteroatom cross-coupling reactions such as in Buchwald-Hartwig amination. Recently, Panahi et al. reported an immobilized palladium nanocatalyst on a silica-starch substrate (PNP-SSS) as an effective catalyst for carbon-nitrogen cross-coupling reactions through Buchwald-Hartwig amination with excellent catalytic activity and reusability [69] (Scheme 3).

Most recently, Hajipour et al. studied the efficiency of a palladium nanocatalyst supported on cysteine-functionalized magnetic nanoparticles for *N*- and *O*-arylation reactions in environmentally friendly conditions [70]. The authors claimed that the synthesized palladium catalyst system exhibited excellent recyclability with no substantial deactivation even after ten cycles (Scheme 4).

Similarly, Veisi et al. also reported a carbon-heteroatom cross-coupling reaction using a palladium nanocatalyst immobilized on carbon nanotubes and observed no change in catalytic activity for up to six cycles (Scheme 5) [71].



SCHEME 3: Buchwald-Hartwig amination using PNP-SSS [69].

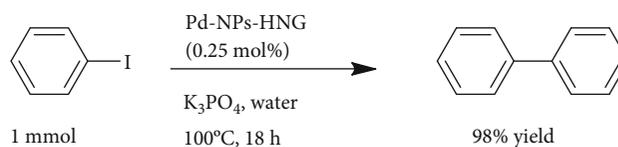
SCHEME 4: *N*- and *O*-arylation using a cysteine-supported palladium nanocatalyst.

SCHEME 5: C-N cross-coupling reaction using a palladium nanocatalyst immobilized on carbon nanotubes.

**3.1.4. Palladium-Based Nanocatalysts for Carbon-Carbon Homocoupling Reactions.** The biaryl formation is a very important reaction in the field of catalysis, total synthesis, fine chemicals, and supramolecular chemistry [72]. The bond between two aryl groups is often available in natural products, dyes, medicine, and agrochemicals. The copper-catalyzed homocoupling reaction is a well-known method for the construction of biaryls, but it requires harsh reaction conditions. Movahed et al. reported palladium nanoparticles on nitrogen-doped graphene (Pd-NP-HNG) for an Ullmann-type homocoupling reaction in water (Scheme 6) [48].

Recently, Rafiee et al. reported the synthesis of a palladium nanocatalyst immobilized on a magnetic few-layer graphene support which they applied on cross- and homocoupling reactions [73]. The catalyst system was found to be active up to six runs with no loss of its catalytic activity (Scheme 7).

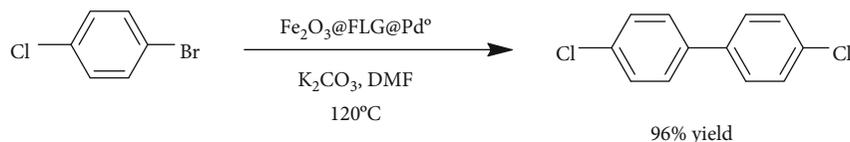
Liu et al. prepared a series of polyaniline-supported palladium nanocatalysts for the Ullmann homocoupling reaction of aryl iodides to form biaryls. It was observed that the cata-



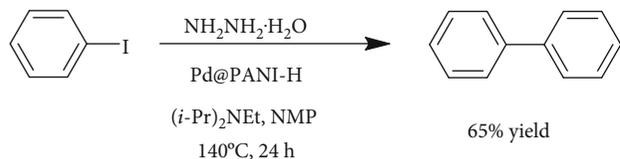
SCHEME 6: Ullmann homocoupling reaction using Pd-NP-HNG nanocatalysts [48].

lyst activity can be tuned by introducing electron-donating groups (Scheme 8) [74].

**3.1.5. Palladium-Based Nanocatalyst for Hydrogenation Reactions.** A palladium catalyst has faster hydrogenation and dehydrogenation processes and are also used in petroleum cracking. A variety of hydrogenation reactions are conducted by palladium nanocatalysts. A palladium nanocatalyst has the capability to combine with a wide range of ligands for highly selective organic reactions. Research is more focused on supported palladium nanoparticles due to their excellent



SCHEME 7: Homocoupling reaction of 4-chloro-1-bromo benzene using a  $\text{Fe}_2\text{O}_3\text{@FLG@Pd}^0$  catalyst.



SCHEME 8: Ullmann homocoupling reaction using a  $\text{Pd@PANI-H}$  catalyst.

efficiencies and faster rate of reaction. Chang et al. reported on palladium nanoparticles entrapped in aluminum oxyhydroxide for the hydrogenation of nitroaromatics and solid alkenes (Scheme 9) [75].

The same catalyst ( $\text{Pd}/\text{AlO}(\text{OH})$ ) was also used by Fry and O'Connor with different concentrations for the hydrogenation of unsaturated esters [76]. The palladium nanoparticles entrapped in aluminum oxyhydroxide were found to be selective without reducing other functionalities in the molecule.

**3.1.6. Palladium-Based Nanocatalysts for the Dichromate Reduction Reaction.** In 2013, Tu et al. synthesized polyvinylpyrrolidone-stabilized palladium nanoparticles (PVP-Pd) through a chemical reduction protocol for Pd-catalyzed dichromate reduction [77]. Chromium exists in two oxidation states which are (Cr-VI) and (Cr-III) (Scheme 10). Among these two oxidation states, hexavalent chromium (Cr-VI) is a highly toxic and carcinogenic species. However, trivalent chromium (Cr-III) is comparatively non-toxic and even small quantities of (Cr-III) are required by the human body as an essential nutrient. Many reports appeared in the literature on the reduction of (Cr-VI) by using iron nanoparticles, aluminum oxide, titanium oxide, mixed transition metal nanoparticles, palladium nanoparticles, etc. [78]. Yang et al. demonstrated the application of tobacco mosaic virus-templated palladium nanoparticles for the reduction of (Cr-VI) and claimed that such a nanocatalyst system can be applied in different kinds of catalytic reactions [79].

**3.1.7. Supported Palladium Nanoparticles.** Palladium nanoparticles can lose their catalytic activity due to aggregation or precipitation. Therefore, stabilizers such as ligands, polymers, or surfactants are useful to control agglomeration and precipitation [80]. A variety of palladium nanoparticles that have appeared in the literature have described the advantages of supported systems such as carbon nanotubes [81], colloidal support [82], silica [83], metal nanoparticle support [84], polymers [85], carbon [86], and graphene [87]. Palladium nanoparticles supported onto different materials increase the surface-to-volume ratio of the composite and improve the catalytic activity and selectivity of the heteroge-

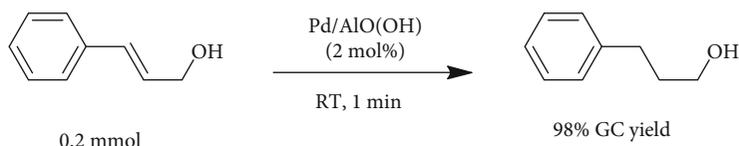
neous catalyst. Palladium nanoparticles either in colloidal form or deposited form have been successfully applied as a catalyst for different kinds of reactions. Liew et al. reported a new catalyst system of palladium nanoparticles (XL-HGPd) (Scheme 11) with the help of a cross-linking method [88]. Such a catalyst system was easy to recover and showed excellent recyclability with continuously high catalytic activities.

Liu et al. prepared palladium nanoparticles (1–5 nm) with the help of a helical backbone containing poly(*N,N*-dialkylcarbodiimide) (PDHC-Pd) as a polymeric gel for stabilizing a palladium nanocatalyst. Such a composite material was found to be very active for the Suzuki reaction under regular heating or microwave irradiation (Scheme 12) [89].

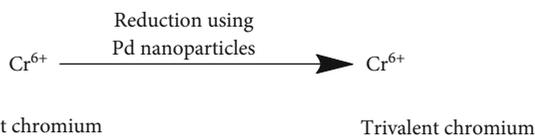
The catalyst was recycled for the second, third, fourth, and fifth time and reaction yields were 93%, 95%, 92%, and 90%, respectively. Palladium nanocatalysts with carbon nanomaterial support have been successfully applied for glucose oxidation reaction [90]. Glucose is considered as an emerging energy source for fuel cell technology improvement in order to fulfill the green energy requirement.

**3.2. Platinum-Based Nanocatalysts.** Platinum catalysts have been extensively used in pharmaceutical, chemical, electronic, petrochemical, and fuel cell applications [91]. Such catalysts have shown excellent catalytic and electrical activities as well as corrosion-resistant properties. Platinum-based catalysts have been successfully applied in sensors [92], fuel cells [93], methanol oxidation [94], and petroleum industries [95]. Platinum-based nanomaterials have shown remarkable properties because of their stability in different conditions. Just like other metal nanocatalysts, the activities of platinum-based nanocatalysts also depend on the size and shape of the catalyst. Several methods are available in the literature for the synthesis of platinum nanoparticles such as physical methods [96], solvothermal [97] and hydrothermal [98] approaches, sol-gel [99], and an electrodeposition [100] process. The morphology and properties of a platinum-based nanomaterial such as optical, magnetic, and catalytic properties can be tailored by changing the starting material and reaction parameters [101]. Narayanan and El-Sayed reported the Suzuki reaction between iodobenzene and phenylboronic acid to catalyze using platinum nanocatalysts (Scheme 13) [102].

**3.3. Iron-Based Nanocatalysts.** Iron, as a backbone of infrastructure, received great interest because of excellent magnetic and catalytic properties [103]. Due to their magnetic property, iron-based nanocatalysts can be easily separated by an external magnet after the completion of a reaction [104]. Iron oxide nanoparticles with various structures and morphologies have been widely used for drug delivery



SCHEME 9: Hydrogenation reaction in the presence of (Pd/AIO(OH)) nanocatalysts [75].



SCHEME 10: Reduction of hexavalent chromium (Cr-VI) to trivalent chromium (Cr-III).

[105], biosensor [106], medical [107], and water treatment [108] applications, as well as other applications. Iron oxide nanoparticles have multiple advantages because of their low price and inherent biocompatibility. The synthetic scheme of iron nanoparticles plays a key role in terms of morphologies and chemical and physical properties [109]. Within the framework of different nanoparticles, ferromagnetic iron and cobalt nanoparticles and their oxides and alloys were found to be the most favorable probes for different applications [110].

2,4-Dichlorophenol is a toxic material and is present in both wastewater and soil. Li et al. successfully degraded 2,4-dichlorophenol by either Fenton oxidation or reductive dechlorination with the help of various iron-based nanoparticles [111]. In 2005, Park et al. reported a new synthetic way for the synthesis of monodisperse nanoparticles of iron oxide with a size of 6-13 nm [112]. The synthesis of 6-13 nm particle size was accomplished by the additional growth of the monodisperse nanoparticles of iron oxide. There are several methods available in the literature for the synthesis of iron nanoparticles; however, iron pentacarbonyl decomposition is the most widely used method because of ease of handling and because it only has carbon monoxide as a byproduct. Some other methods are also available in the literature such as the reduction of organic or inorganic salts [113], mechanical methods, and decomposition of other unstable iron compounds [114]. Jagadeesh et al. describe the synthesis of iron oxide-based nanocatalysts for the hydrogenation of nitroarenes to anilines with excellent activity and selectivity (Scheme 14) [115].

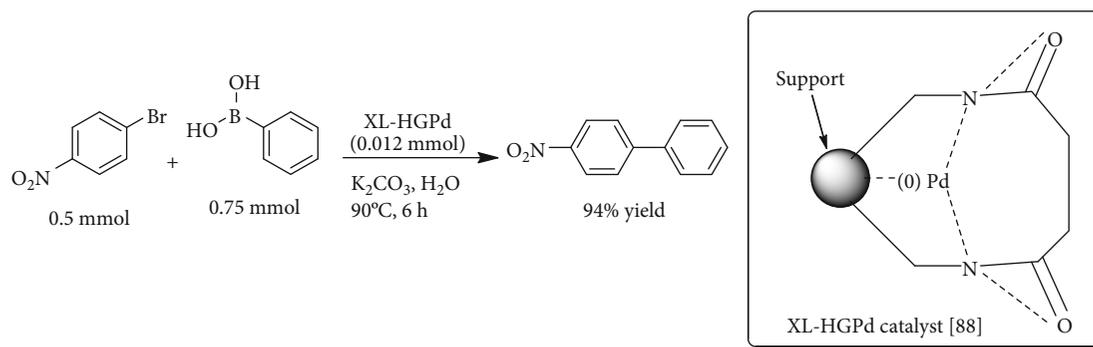
**3.4. Copper-Based Nanocatalysts.** Copper-based nanocatalysts have received considerable attention because of their high activity and low reaction temperature [116]. The activity of the Cu-based nanocatalyst can be influenced by synthetic protocol, composition, temperature, pressure, concentration, and reactor type [117]. Various methods are available in the literature to synthesize Cu-based nanocatalysts such as hydrothermal [118], coprecipitation [119], homogenous precipitation [120], and impregnation [121]. Recently Lamei et al. reported a green nontoxic catalyst material to comprise nanowires and nanoparticles embedded in a carbonaceous

matrix [53]. Such a Cu-based ligand-free nanocatalyst system was applied to the Suzuki coupling reaction with excellent activity and no significant loss of activity observed even after four cycles (Scheme 15).

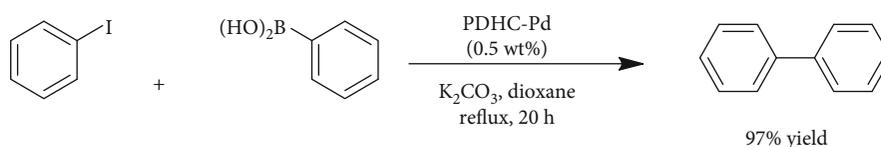
**3.5. Gold-Based Nanocatalysts.** Since the pioneering studies of Haruta et al. [122], gold nanocatalysts have become widely used nanoparticles for oxidation [123], reduction [124], hydrogenation [125], homocoupling [126], degradation of organic pollutants [127], and electrochemical sensor applications [128]. In order to expose more atoms on the surface, gold nanoparticles are usually dispersed on a suitable support such as activated carbon [129], starch [130], silica [131], metal oxide [132], and resin [133]. Gold along with magnetic nanoparticles such as catalytic support has gained much attention due to its superparamagnetic properties and environmentally friendly nature. The gold-magnetic nanocatalyst (Au-Fe<sub>3</sub>O<sub>4</sub>) has shown excellent catalytic activity in various organic reactions such as oxidation of CO [134] and reduction of H<sub>2</sub>O<sub>2</sub> [135]. Lin and Doong synthesized Au-Fe<sub>3</sub>O<sub>4</sub> nanocatalysts through iron-oleate decomposition in the presence of Au seeds. The catalyst system was successfully applied in the reduction of nitrophenol with excellent activity and selectivity (Scheme 16) [136].

**3.6. Silver-Based Nanocatalysts.** Silver nanoparticles have been successfully applied in optics, medicine, catalysis, and sensors [137]. Silver-based nanocatalysts are continuously being developed due to their strong absorption in the region of visible light which is easily detectable through a UV-visible spectrophotometer. In terms of organic reactions, silver nanocatalysts are used in reduction reactions [138], alkylation [139], degradation [140], reduction [141], and synthesis of fine chemicals [142]. Recently, Mandi et al. reported the synthesis of supported silver nanocatalysts via acrylic acid polymerization and subsequent immobilization with silver nanoparticles to form nanocomposite Ag-MCP-1. The nanocomposite material was used in a reductive coupling reaction of nitrobenzene with alcohols in the presence of a hydrogen source such as glycerol (Scheme 17) [143].

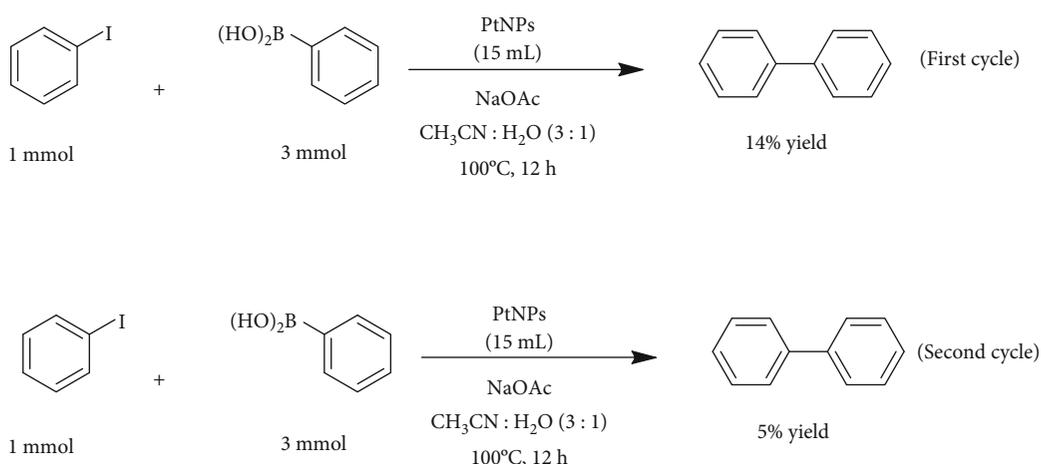
Apart from colloidal Ag nanoparticles, 1D and 2D structures of Ag and their composites have also shown huge prospects in catalytic conversion. Ag nanowires and copper oxide-embedded Ag nanowires showed excellent and rapid catalytic activity [144]. The activity and selectivity of such composites were reported to be ecofriendly and distinguished. However, Ag nanowires possessed 40% conversion efficiency along with 95% selectivity, and copper oxide-embedded Ag nanowires showed much higher activity and stability compared to individual metal oxides or metal nanowires [145]. Such demonstration paves way for further



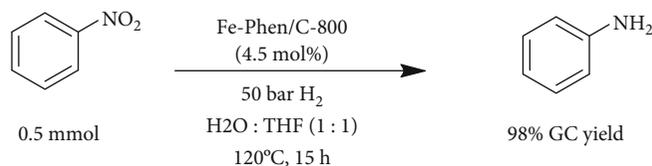
SCHEME 11: Suzuki reaction catalyzed by an XL-HGPd nanocatalyst [88].



SCHEME 12: Suzuki reaction in the presence of PDHC-Pd nanocatalysts [89].



SCHEME 13: Suzuki reaction between iodobenzene and phenylboronic acid catalyzed using platinum nanocatalysts [102].

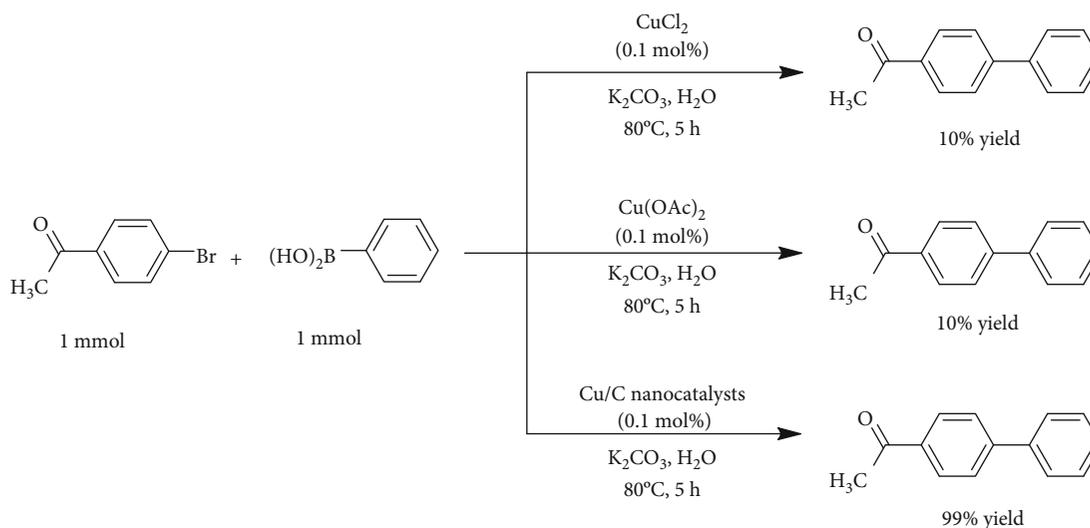


SCHEME 14: Hydrogenation of nitrobenzene to aniline using iron nanocatalysts [115].

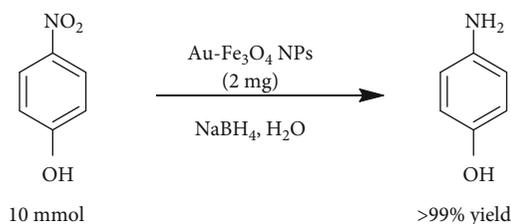
efficient designs and innovative applications of metal oxide-embedded 1D and 2D materials as new nanocatalysts for organic conversion.

**3.7. Zinc-Based Nanocatalysts.** The nanocomposite system containing zinc oxide mixed with other metal oxides has

been a material of choice due to several applications such as the production of biodiesel [146], CO<sub>2</sub> conversion [147], aldehyde oxidation [148], hydrogen production [118], transesterification [149], wastewater treatment [150], azo dye decoloration [151], and chemoselective acetylation [152]. The activity and selectivity of the zinc oxide-based



SCHEME 15: Suzuki coupling reaction using different copper catalysts [53].

SCHEME 16: Reduction of nitrophenol using gold-magnetic nanocatalysts (Au-Fe<sub>3</sub>O<sub>4</sub>) [136].

nanocatalysts rely on size and morphology of the synthesized material. Different methods are available in the literature to describe the synthetic procedures for controlling the size and morphology of the zinc oxide nanocatalysts such as coprecipitation [119], microwave assisted [153], combustion [154], ion exchange, and vapor phase transport [155]. In 2015, Saikia et al. reported the synthesis of zinc oxide nanocatalysts through the leaf extract of *Carica papaya* and its application in the synthesis of oxime derivatives [156]. The reaction was run without a solvent under microwave irradiation to form an oxime with an excellent yield and with a recycle capability up to 5th run (Scheme 18).

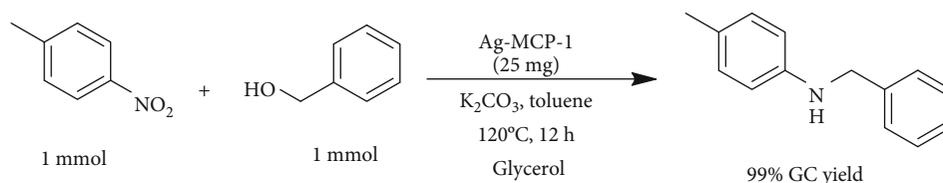
#### 4. Future Prospects and Challenges

Carbon-carbon cross-coupling protocols such as Suzuki, Heck, and Sonogashira reactions are industrially important reactions, and a review of the literature reveals that these reactions are catalyzed by precious metals including palladium or gold nanoparticles. Therefore, it is highly anticipated that the focus of research will be on the development of either metal-free or nonnoble metal nanocatalysts with high activity and selectivity for carbon-carbon cross-coupling reactions. Nanocatalysts are known to have high activity and selectivity, but they suffer from instability and reusability issues. One way to achieve high stability and reusability is for the nanocatalyst to have a strong interaction with the support system

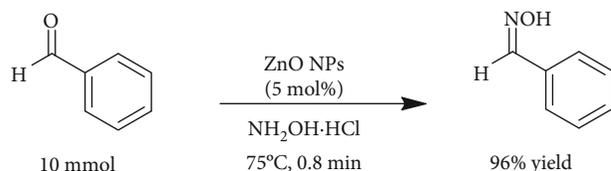
which can prevent an aggregation problem. To achieve this, the support system should have chelating properties to bind the nanoparticles more strongly. Severe conditions such as high-temperature reactions can cause the leaching of metal in the nanocatalysts. Initially, it was thought that the leaching process mainly occurs with nanocatalysts containing the palladium metal. However, in recent times, a number of reports appeared in the literature describing the leaching of other noble metals in nanocatalysts. Therefore, the development of new nanocatalysts that can bear harsh conditions is highly desirable. As depicted earlier, the shape and size of the nanocatalyst have a great impact on their catalytic properties and stabilities. Hence, new methods with a well-controlled size and shape of the nanocatalysts need to be developed. The multistep synthesis using a costly starting material and low yield hinders their commercial applications. Such synthetic protocols need to be replaced with a facile route, a green process, and large-scale production with high quality.

#### 5. Conclusion

In this review, we highlighted the recent progress on the design and development of nanocatalysts and discussed their catalytic application in important organic reactions. The synthetic procedure of nanocatalysts contains various metals such as Pd, Pt, Fe, Cu, Au, Ag, and Zn and have been reviewed along with their important applications. Among the various metals, the palladium-based nanocatalysts are the most widely investigated material for coupling reactions. Palladium nanocatalysts either with a suitable support or as mixed metal oxides are known to increase the surface-to-volume ratio of the composite and improve the catalytic activity and selectivity of the heterogeneous catalyst. The industrially important organic reactions such as carbon-carbon bond coupling reactions, carbon-heteroatom bond coupling reactions, carbon-carbon homocoupling reactions, hydrogenation, reduction, and oxime formation reactions have been reviewed. Similarly, the Suzuki reaction has been a benchmark to explore the catalytic activities of newly



SCHEME 17: Reductive amination reaction between 4-methylnitrobenzene and benzyl alcohol using a Ag-MCP-1 nanocatalyst [143].



SCHEME 18: Conversion of aldehyde/ketone into oximes using zinc oxide nanocatalysts [156].

synthesized palladium-based nanocatalysts. The future prospects that need to be addressed, on the basis of literature review, have also been highlighted at the end. Consequently, this review article may help on the design and development of new nanocomposite catalysts containing a well-defined shape and size with high activity, selectivity, stability, and reusability. This literature search will also help to identify the best support system for high-performance supported nanocatalysts. Due to the ease of synthesis, high activity, and selectivity, more nanocatalyst systems will be developed in the near future for organic conversion.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

## Acknowledgments

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## References

- [1] L. A. Kolahalam, I. K. Viswanath, B. S. Diwakar, B. Govindh, V. Reddy, and Y. L. Murthy, "Review on nanomaterials: synthesis and applications," *Materials Today: Proceedings*, 2019.
- [2] B. R. Cuenya and F. Behafarid, "Nanocatalysis: size- and shape-dependent chemisorption and catalytic reactivity," *Surface Science Reports*, vol. 70, no. 2, pp. 135–187, 2015.
- [3] M. S. Kamal, A. A. Adewunmi, A. S. Sultan, M. F. Al-Hamad, and U. Mehmood, "Recent advances in nanoparticles enhanced oil recovery: rheology, interfacial tension, oil recovery, and wettability alteration," *Journal of Nanomaterials*, vol. 2017, Article ID 2473175, 15 pages, 2017.
- [4] L. Li, H. Yang, D. Zhou, and Y. Zhou, "Progress in application of CNTs in lithium-ion batteries," *Journal of Nanomaterials*, vol. 2014, Article ID 187891, 8 pages, 2014.
- [5] R. Liu, Q. Zhao, Y. Li, G. Zhang, F. Zhang, and X. Fan, "Graphene supported Pt/Ni nanoparticles as magnetically separable nanocatalysts," *Journal of Nanomaterials*, vol. 2013, Article ID 602602, 7 pages, 2013.
- [6] Y. Xu, Y. Liang, L. Jiang, H. Wu, H. Zhao, and D. Xue, "Preparation and magnetic properties of ZnFe<sub>2</sub>O<sub>4</sub> nanotubes," *Journal of Nanomaterials*, vol. 2011, Article ID 525967, 5 pages, 2011.
- [7] L. Song, Y. Han, F. Guo et al., "Mesoporous nickel-based zeolite capsule complex with Fe<sub>3</sub>O<sub>4</sub> as electrode for advanced supercapacitor," *Journal of Nanomaterials*, vol. 2018, Article ID 9813203, 13 pages, 2018.
- [8] V. V. Pokropivny and V. V. Skorokhod, "New dimensionality classifications of nanostructures," *Physica E: Low-dimensional Systems and Nanostructures*, vol. 40, no. 7, pp. 2521–2525, 2008.
- [9] E. González, J. E. Villegas, D. Jaque, E. Navarro, and J. L. Vicent, "Fabrication of 2D, 1D and 0D ordered metallic nanostructures," *Vacuum*, vol. 67, no. 3, pp. 693–698, 2002.
- [10] D. Astruc, F. Lu, and J. R. Aranzas, "Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis," *Angewandte Chemie International Edition*, vol. 44, no. 48, pp. 7852–7872, 2005.
- [11] A. Makawana, C. B. Sangani, Y.-F. Yao, Y.-T. Duan, P.-C. Lv, and H.-L. Zhu, "Recent developments of metal and metal oxide nanocatalysts in organic synthesis," *Mini Reviews in Medicinal Chemistry*, vol. 16, no. 16, pp. 1303–1320, 2016.
- [12] J. Choi and G. C. Fu, "Transition metal-catalyzed alkyl-alkyl bond formation: another dimension in cross-coupling chemistry," *Science*, vol. 356, no. 6334, article eaaf7230, 2017.
- [13] N. V. Tzouras, I. K. Stamatopoulos, A. T. Papastavrou, A. A. Liori, and G. C. Vougioukalakis, "Sustainable metal catalysis in CH activation," *Coordination Chemistry Reviews*, vol. 343, pp. 25–138, 2017.
- [14] M. M. Lorion, K. Maindan, A. R. Kapdi, and L. Ackermann, "Heteromultimetallic catalysis for sustainable organic syntheses," *Chemical Society Reviews*, vol. 46, no. 23, pp. 7399–7420, 2017.
- [15] N. Sharma, H. Ojha, A. Bharadwaj, D. P. Pathak, and R. K. Sharma, "Preparation and catalytic applications of nanomaterials: a review," *RSC Advances*, vol. 5, no. 66, pp. 53381–53403, 2015.
- [16] T. P. N. Tran, A. Thakur, D. X. Trinh, A. T. N. Dao, and T. Taniike, "Design of Pd@graphene oxide framework nanocatalyst with improved activity and recyclability in Suzuki-Miyaura cross-coupling reaction," *Applied Catalysis A: General*, vol. 549, pp. 60–67, 2017.

- [17] Y.-Y. Yu, Q.-W. Cheng, C. Sha, Y.-X. Chen, S. Naraginti, and Y.-C. Yong, "Size-controlled biosynthesis of FeS nanoparticles for efficient removal of aqueous Cr(VI)," *Chemical Engineering Journal*, vol. 379, article 122404, 2019.
- [18] S. J. Yoo, T.-Y. Jeon, K.-S. Lee, K.-W. Park, and Y.-E. Sung, "Effects of particle size on surface electronic and electrocatalytic properties of Pt/TiO<sub>2</sub> nanocatalysts," *Chemical Communications*, vol. 46, no. 5, pp. 794–796, 2010.
- [19] G. C. Bond and D. T. Thompson, "Catalysis by gold," *Catalysis Reviews*, vol. 41, no. 3-4, pp. 319–388, 1999.
- [20] Y. Li, X. Fan, J. Qi et al., "Palladium nanoparticle-graphene hybrids as active catalysts for the Suzuki reaction," *Nano Research*, vol. 3, no. 6, pp. 429–437, 2010.
- [21] E. Dube and T. Nyokong, "Effect of gold nanoparticle shape on the photophysicochemical properties of sulphur containing metallophthalocyanines," *Journal of Molecular Structure*, vol. 1181, pp. 312–320, 2019.
- [22] M. Haruta, "Nanoparticulate gold catalysts for low-temperature CO oxidation," *ChemInform*, vol. 35, no. 48, 2004.
- [23] C. R. Henry, "Morphology of supported nanoparticles," *Progress in Surface Science*, vol. 80, no. 3, pp. 92–116, 2005.
- [24] R. Narayanan and M. A. El-Sayed, "Effect of nanocatalysis in colloidal solution on the tetrahedral and cubic nanoparticle shape: electron-transfer reaction catalyzed by platinum nanoparticles," *The Journal of Physical Chemistry B*, vol. 108, no. 18, pp. 5726–5733, 2004.
- [25] I. Khan and A. Qurashi, "Shape controlled synthesis of copper vanadate platelet nanostructures, their optical band edges, and solar-driven water splitting properties," *Scientific Reports*, vol. 7, no. 1, article 14370, 2017.
- [26] L. Luo, H. Li, Y. Peng, and C. Feng, "Recent advances in Rh-based nanocatalysts for heterogeneous reactions," *ChemNanoMat*, vol. 4, 2018.
- [27] F. Dufour, B. Fresch, O. Durupthy, C. Chaneac, and F. Remacle, "Ligand and solvation effects on the structural and electronic properties of small gold clusters," *The Journal of Physical Chemistry C*, vol. 118, no. 8, pp. 4362–4376, 2014.
- [28] Y.-F. Li and Z.-P. Liu, "Particle size, shape and activity for photocatalysis on titania anatase nanoparticles in aqueous surroundings," *Journal of the American Chemical Society*, vol. 133, no. 39, pp. 15743–15752, 2011.
- [29] M. Hou, Q. Mei, and B. Han, "Solvent effects on geometrical structures and electronic properties of metal Au, Ag, and Cu nanoparticles of different sizes," *Journal of Colloid and Interface Science*, vol. 449, pp. 488–493, 2015.
- [30] S. R. Chowdhury, P. S. Roy, and S. K. Bhattacharya, "Room temperature synthesis of polyvinyl alcohol stabilized palladium nanoparticles: solvent effect on shape and electrocatalytic activity," *Nano-Structures & Nano-Objects*, vol. 14, pp. 11–18, 2018.
- [31] Y. Zhu and N. S. Hosmane, "Nanocatalysis: recent advances and applications in boron chemistry," *Coordination Chemistry Reviews*, vol. 293–294, pp. 357–367, 2015.
- [32] A. Y. Khormi, T. A. Farghaly, and M. R. Shaaban, "Pyrimidyl formamidine palladium(II) complex as a nanocatalyst for aqueous Suzuki-Miyaura coupling," *Heliyon*, vol. 5, no. 3, article e01367, 2019.
- [33] E. Rafiee, M. Joshaghani, and P. G.-S. Abadi, "Effect of a weak magnetic field on the Mizoroki-Heck coupling reaction in the presence of wicker-like palladium-poly(N-vinylpyrrolidone)-iron nanocatalyst," *Journal of Magnetism and Magnetic Materials*, vol. 408, pp. 107–115, 2016.
- [34] S. Rohani, G. M. Ziarani, A. Ziarati, and A. Badii, "Designer 3D CoAl-layered double hydroxide@N, S doped graphene hollow architecture decorated with Pd nanoparticles for Sonogashira couplings," *Applied Surface Science*, vol. 496, article 143599, 2019.
- [35] A. Balanta, C. Godard, and C. Claver, "Pd nanoparticles for C-C coupling reactions," *Chemical Society Reviews*, vol. 40, no. 10, pp. 4973–4985, 2011.
- [36] T. Tamoradi, A. Ghorbani-Choghamarani, and M. Ghadermazi, "Synthesis of a new Pd(0)-complex supported on magnetic nanoparticles and study of its catalytic activity for Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives," *Polyhedron*, vol. 145, pp. 120–130, 2018.
- [37] D. Astruc, "Palladium nanoparticles as efficient green homogeneous and heterogeneous carbon-carbon coupling precatalysts: a unifying view," *Inorganic Chemistry*, vol. 46, no. 6, pp. 1884–1894, 2007.
- [38] A. R. Hajipour and P. Abolfathi, "Nickel embedded on triazole-modified magnetic nanoparticles: a novel and sustainable heterogeneous catalyst for Hiyama reaction in fluoride-free condition," *Catalysis Communications*, vol. 103, pp. 92–95, 2018.
- [39] A. Trzeciak and A. Augustyniak, "The role of palladium nanoparticles in catalytic C-C cross-coupling reactions," *Coordination Chemistry Reviews*, vol. 384, pp. 1–20, 2019.
- [40] M. J. Mphahlele and M. M. Maluleka, "Advances in metal-catalyzed cross-coupling reactions of halogenated quinazolines and their quinazoline derivatives," *Molecules*, vol. 19, no. 11, pp. 17435–17463, 2014.
- [41] D. Ganapathy and G. Sekar, "Palladium nanoparticles stabilized by metal-carbon covalent bond: an efficient and reusable nanocatalyst in cross-coupling reactions," *Catalysis Communications*, vol. 39, pp. 50–54, 2013.
- [42] A. Ghorbani-Choghamarani, B. Tahmasbi, N. Noori, and S. Faryadi, "Pd-S-methylisothiourea supported on magnetic nanoparticles as an efficient and reusable nanocatalyst for Heck and Suzuki reactions," *Comptes Rendus Chimie*, vol. 20, no. 2, pp. 132–139, 2017.
- [43] A. Naghipour and A. Fakhri, "Heterogeneous Fe<sub>3</sub>O<sub>4</sub>@chitosan-Schiff base Pd nanocatalyst: fabrication, characterization and application as highly efficient and magnetically-recoverable catalyst for Suzuki-Miyaura and Heck-Mizoroki C-C coupling reactions," *Catalysis Communications*, vol. 73, pp. 39–45, 2016.
- [44] P. Veerakumar, M. Velayudham, K.-L. Lu, and S. Rajagopal, "Silica-supported PEI capped nanopalladium as potential catalyst in Suzuki, Heck and Sonogashira coupling reactions," *Applied Catalysis A: General*, vol. 455, pp. 247–260, 2013.
- [45] M. Panchal, A. Kongor, V. Mehta, M. Vora, K. Bhatt, and V. Jain, "Heck-type olefination and Suzuki coupling reactions using highly efficient oxalix[4]arene wrapped nanopalladium catalyst," *Journal of Saudi Chemical Society*, vol. 22, no. 5, pp. 558–568, 2017.
- [46] M. Nasrollahzadeh and A. Banaei, "Hybrid Au/Pd nanoparticles as reusable catalysts for Heck coupling reactions in water under aerobic conditions," *Tetrahedron Letters*, vol. 56, no. 3, pp. 500–503, 2015.

- [47] F. Heidari, M. Hekmati, and H. Veisi, "Magnetically separable and recyclable  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{isoniazide}/\text{Pd}$  nanocatalyst for highly efficient synthesis of biaryls by Suzuki coupling reactions," *Journal of Colloid and Interface Science*, vol. 501, pp. 175–184, 2017.
- [48] S. K. Movahed, M. Dabiri, and A. Bazgir, "Palladium nanoparticle decorated high nitrogen-doped graphene with high catalytic activity for Suzuki-Miyaura and Ullmann-type coupling reactions in aqueous media," *Applied Catalysis A: General*, vol. 488, Supplement C, pp. 265–274, 2014.
- [49] A. Shaabani and M. Mahyari, "PdCo bimetallic nanoparticles supported on PPI-grafted graphene as an efficient catalyst for Sonogashira reactions," *Journal of Materials Chemistry A*, vol. 1, no. 32, pp. 9303–9311, 2013.
- [50] Y.-T. Chu, K. Chanda, P.-H. Lin, and M. H. Huang, "Aqueous phase synthesis of palladium tripod nanostructures for Sonogashira coupling reactions," *Langmuir*, vol. 28, no. 30, pp. 11258–11264, 2012.
- [51] M. Radtke, S. Stumpf, B. Schröter, S. Höppener, U. S. Schubert, and A. Ignaszak, "Electrodeposited palladium on MWCNTs as "semi-soluble heterogeneous" catalyst for cross-coupling reactions," *Tetrahedron Letters*, vol. 56, no. 27, pp. 4084–4087, 2015.
- [52] S.-J. Kim, S.-D. Oh, S. Lee, and S.-H. Choi, "Radiolytic synthesis of Pd-M (M = Ag, Ni, and Cu)/C catalyst and their use in Suzuki-type and Heck-type reaction," *Journal of Industrial and Engineering Chemistry*, vol. 14, no. 4, pp. 449–456, 2008.
- [53] K. Lamei, H. Eshghi, M. Bakavoli, S. A. Rounaghi, and E. Esmaeili, "Carbon coated copper nanostructures as a green and ligand free nanocatalyst for Suzuki cross-coupling reaction," *Catalysis Communications*, vol. 92, pp. 40–45, 2017.
- [54] H. Veisi and A. Kakanejadifard, "Immobilization of palladium nanoparticles on ionic liquid-triethylammonium chloride functionalized magnetic nanoparticles: as a magnetically separable, stable and recyclable catalyst for Suzuki-Miyaura cross-coupling reactions," *Tetrahedron Letters*, vol. 58, no. 45, pp. 4269–4276, 2017.
- [55] Y. Li, X. Fan, J. Qi et al., "Gold nanoparticles-graphene hybrids as active catalysts for Suzuki reaction," *Materials Research Bulletin*, vol. 45, no. 10, pp. 1413–1418, 2010.
- [56] M. Nasrollahzadeh and S. M. Sajadi, "Green synthesis, characterization and catalytic activity of the Pd/TiO<sub>2</sub> nanoparticles for the ligand-free Suzuki-Miyaura coupling reaction," *Journal of Colloid and Interface Science*, vol. 465, pp. 121–127, 2016.
- [57] Y. Na, S. Park, S. B. Han, H. Han, S. Ko, and S. Chang, "Ruthenium-catalyzed Heck-type olefination and Suzuki coupling reactions: studies on the nature of catalytic species," *Journal of the American Chemical Society*, vol. 126, no. 1, pp. 250–258, 2004.
- [58] P. M. Uberman, L. A. Pérez, G. I. Lacconi, and S. E. Martín, "PVP-stabilized palladium nanoparticles electrochemically obtained as effective catalysts in aqueous medium Suzuki-Miyaura reaction," *Journal of Molecular Catalysis A: Chemical*, vol. 363, pp. 245–253, 2012.
- [59] N. Ghanbari, S. J. Hoseini, and M. Bahrami, "Ultrasonic assisted synthesis of palladium-nickel/iron oxide core-shell nanoalloys as effective catalyst for Suzuki-Miyaura and p-nitrophenol reduction reactions," *Ultrasonics Sonochemistry*, vol. 39, pp. 467–477, 2017.
- [60] S. J. Hoseini, M. Dehghani, and H. Nasrabadi, "Thin film formation of Pd/reduced-graphene oxide and Pd nanoparticles at oil-water interface, suitable as effective catalyst for Suzuki-Miyaura reaction in water," *Catalysis Science & Technology*, vol. 4, no. 4, pp. 1078–1083, 2014.
- [61] L. Shiyong, Q. Zhou, Z. Jin, H. Jiang, and X. Jiang, "Dodecyl-sulfate anion embedded layered double hydroxide supported nanopalladium catalyst for the Suzuki reaction," *Chinese Journal of Catalysis*, vol. 31, no. 5, pp. 557–561, 2010.
- [62] P. Mondal, P. Bhanja, R. Khatun, A. Bhaumik, D. Das, and S. M. Islam, "Palladium nanoparticles embedded on mesoporous TiO<sub>2</sub> material (Pd@MTiO<sub>2</sub>) as an efficient heterogeneous catalyst for Suzuki-coupling reactions in water medium," *Journal of Colloid and Interface Science*, vol. 508, pp. 378–386, 2017.
- [63] M. Shokouhimehr, T. Kim, S. W. Jun et al., "Magnetically separable carbon nanocomposite catalysts for efficient nitroarene reduction and Suzuki reactions," *Applied Catalysis A: General*, vol. 476, pp. 133–139, 2014.
- [64] J. Xia, Y. Fu, G. He, X. Sun, and X. Wang, "Core-shell-like Ni-Pd nanoparticles supported on carbon black as a magnetically separable catalyst for green Suzuki-Miyaura coupling reactions," *Applied Catalysis B: Environmental*, vol. 200, pp. 39–46, 2017.
- [65] P. Mondal, N. Salam, A. Mondal, K. Ghosh, K. Tuhina, and S. M. Islam, "A highly active recyclable gold-graphene nanocomposite material for oxidative esterification and Suzuki cross-coupling reactions in green pathway," *Journal of Colloid and Interface Science*, vol. 459, pp. 97–106, 2015.
- [66] M. Thomas, M. U. D. Sheikh, D. Ahirwar, M. Bano, and F. Khan, "Gold nanoparticle and graphene oxide incorporated strontium crosslinked alginate/carboxymethyl cellulose composites for o-nitroaniline reduction and Suzuki-Miyaura cross-coupling reactions," *Journal of Colloid and Interface Science*, vol. 505, pp. 115–129, 2017.
- [67] Y. Kiso, K. Yamamoto, K. Tamao, and M. Kumada, "Asymmetric homogeneous hydrosilylation with chiral phosphine-palladium complexes," *Journal of the American Chemical Society*, vol. 94, no. 12, pp. 4373–4374, 1972.
- [68] J. K. Stille and K. S. Y. Lau, "Mechanisms of oxidative addition of organic halides to group 8 transition-metal complexes," *Accounts of Chemical Research*, vol. 10, no. 12, pp. 434–442, 1977.
- [69] F. Panahi, F. Daneshgar, F. Haghghi, and A. Khalafi-Nezhad, "Immobilized Pd nanoparticles on silica-starch substrate (PNP-SSS): efficient heterogeneous catalyst in Buchwald-Hartwig C-N cross coupling reaction," *Journal of Organometallic Chemistry*, vol. 851, pp. 210–217, 2017.
- [70] A. R. Hajipour, Z. Khorsandi, and S. F. M. Metkazini, "Palladium nanoparticles supported on cysteine-functionalized MNPs as robust recyclable catalysts for fast O- and N-arylation reactions in green media," *Journal of Organometallic Chemistry*, vol. 899, article 120793, 2019.
- [71] H. Veisi, P. Safarimehr, and S. Hemmati, "Buchwald-Hartwig C-N cross coupling reactions catalyzed by palladium nanoparticles immobilized on thio modified-multi walled carbon nanotubes as heterogeneous and recyclable nanocatalyst," *Materials Science and Engineering: C*, vol. 96, pp. 310–318, 2019.
- [72] S. Santra, P. Ranjan, S. K. Mandal, and P. K. Ghorai, "Living nanocatalyst for effective synthesis of symmetrical biaryls," *Inorganica Chimica Acta*, vol. 372, no. 1, pp. 47–52, 2011.

- [73] F. Rafiee, P. Khavari, Z. Payami, and N. Ansari, "Palladium nanoparticles immobilized on the magnetic few layer graphene support as a highly efficient catalyst for ligand free Suzuki cross coupling and homo coupling reactions," *Journal of Organometallic Chemistry*, vol. 883, pp. 78–85, 2019.
- [74] Y. Liu, D. Tang, K. Cao, L. Yu, J. Han, and Q. Xu, "Probing the support effect at the molecular level in the polyaniline-supported palladium nanoparticle-catalyzed Ullmann reaction of aryl iodides," *Journal of Catalysis*, vol. 360, pp. 250–260, 2018.
- [75] F. Chang, H. Kim, B. Lee, S. Park, and J. Park, "Highly efficient solvent-free catalytic hydrogenation of solid alkenes and nitro-aromatics using Pd nanoparticles entrapped in aluminum oxy-hydroxide," *Tetrahedron Letters*, vol. 51, no. 32, pp. 4250–4252, 2010.
- [76] D. Fry and K. O'Connor, "The solvent-less hydrogenation of unsaturated esters using 0.5% Pd/Al (O) OH as a catalyst," *The Chemical Educator*, vol. 18, pp. 144–146, 2013.
- [77] W. Tu, K. Li, X. Shu, and W. W. Yu, "Reduction of hexavalent chromium with colloidal and supported palladium nanocatalysts," *Journal of Nanoparticle Research*, vol. 15, no. 4, pp. 1–9, 2013.
- [78] C. Yang, J. H. Meldon, B. Lee, and H. Yi, "Investigation on the catalytic reduction kinetics of hexavalent chromium by viral-templated palladium nanocatalysts," *Catalysis Today*, vol. 233, pp. 108–116, 2014.
- [79] C. Yang, A. K. Manocchi, B. Lee, and H. Yi, "Viral templated palladium nanocatalysts for dichromate reduction," *Applied Catalysis B: Environmental*, vol. 93, no. 3, pp. 282–291, 2010.
- [80] S. Karaboga and S. Özkar, "Nanoalumina supported palladium(0) nanoparticle catalyst for releasing H<sub>2</sub> from dimethylamine borane," *Applied Surface Science*, vol. 487, pp. 433–441, 2019.
- [81] J. V. Rojas and C. H. Castano, "Production of palladium nanoparticles supported on multiwalled carbon nanotubes by gamma irradiation," *Radiation Physics and Chemistry*, vol. 81, no. 1, pp. 16–21, 2012.
- [82] I. Miguel-García, Á. Berenguer-Murcia, T. García, and D. Cazorla-Amorós, "Effect of the aging time of PVP coated palladium nanoparticles colloidal suspensions on their catalytic activity in the preferential oxidation of CO," *Catalysis Today*, vol. 187, no. 1, pp. 2–9, 2012.
- [83] X. Le, Z. Dong, X. Li, W. Zhang, M. Le, and J. Ma, "Fibrous nano-silica supported palladium nanoparticles: an efficient catalyst for the reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol under mild conditions," *Catalysis Communications*, vol. 59, pp. 21–25, 2015.
- [84] M. Gholinejad and A. Aminianfar, "Palladium nanoparticles supported on magnetic copper ferrite nanoparticles: the synergistic effect of palladium and copper for cyanation of aryl halides with K<sub>4</sub>[Fe(CN)<sub>6</sub>]," *Journal of Molecular Catalysis A: Chemical*, vol. 397, pp. 106–113, 2015.
- [85] M. M. Dell'Anna, V. F. Capodiferro, M. Mali et al., "Highly selective hydrogenation of quinolines promoted by recyclable polymer supported palladium nanoparticles under mild conditions in aqueous medium," *Applied Catalysis A: General*, vol. 481, no. 0, pp. 89–95, 2014.
- [86] C. Shang, W. Hong, J. Wang, and E. Wang, "Carbon supported trimetallic nickel-palladium-gold hollow nanoparticles with superior catalytic activity for methanol electrooxidation," *Journal of Power Sources*, vol. 285, pp. 12–15, 2015.
- [87] M. Gómez-Martínez, E. Buxaderas, I. M. Pastor, and D. A. Alonso, "Palladium nanoparticles supported on graphene and reduced graphene oxide as efficient recyclable catalyst for the Suzuki-Miyaura reaction of potassium aryltrifluoroborates," *Journal of Molecular Catalysis A: Chemical*, vol. 404–405, pp. 1–7, 2015.
- [88] K. H. Liew, W. Z. Samad, N. Nordin et al., "Preparation and characterization of HypoGel-supported Pd nanocatalysts for Suzuki reaction under mild conditions," *Chinese Journal of Catalysis*, vol. 36, no. 5, pp. 771–777, 2015.
- [89] Y. Liu, C. Khemtong, and J. Hu, "Synthesis and catalytic activity of a poly(*N,N*-dialkylcarbodiimide)/palladium nanoparticle composite: a case in the Suzuki coupling reaction using microwave and conventional heating," *Chemical Communications*, no. 4, pp. 398–399, 2004.
- [90] C.-C. Chen, C.-L. Lin, and L.-C. Chen, "Functionalized carbon nanomaterial supported palladium nano-catalysts for electrocatalytic glucose oxidation reaction," *Electrochimica Acta*, vol. 152, pp. 408–416, 2015.
- [91] R. Serra-Maia, S. Chastka, M. Bellier, T. Douglas, J. D. Rimstidt, and F. M. Michel, "Effect of particle size on catalytic decomposition of hydrogen peroxide by platinum nanocatalysts," *Journal of Catalysis*, vol. 373, pp. 58–66, 2019.
- [92] W. Liu, K. Hiekel, R. Hübner, H. Sun, A. Ferancova, and M. Sillanpää, "Pt and Au bimetallic and monometallic nanostructured amperometric sensors for direct detection of hydrogen peroxide: influences of bimetallic effect and silica support," *Sensors and Actuators B: Chemical*, vol. 255, pp. 1325–1334, 2017.
- [93] J. Lin, V. Kamavaram, and A. Kannan, "Synthesis and characterization of carbon nanotubes supported platinum nanocatalyst for proton exchange membrane fuel cells," *Journal of Power Sources*, vol. 195, no. 2, pp. 466–470, 2010.
- [94] C. Berghian-Grosan, T. Radu, A. R. Biris et al., "Platinum nanoparticles coated by graphene layers: a low-metal loading catalyst for methanol oxidation in alkaline media," *Journal of Energy Chemistry*, vol. 40, pp. 81–88, 2020.
- [95] H. Gobara, R. S. Mohamed, F. H. Khalil, M. S. El-Shall, and S. A. Hassan, "Various characteristics of Ni and Pt-Al<sub>2</sub>O<sub>3</sub> nanocatalysts prepared by microwave method to be applied in some petrochemical processes," *Egyptian Journal of Petroleum*, vol. 23, no. 1, pp. 105–118, 2014.
- [96] E. Gharibshahi, E. Saion, A. Ashraf, and L. Gharibshahi, "Size-controlled and optical properties of platinum nanoparticles by gamma radiolytic synthesis," *Applied Radiation and Isotopes*, vol. 130, pp. 211–217, 2017.
- [97] J. Lai, W. Niu, R. Luque, and G. Xu, "Solvothermal synthesis of metal nanocrystals and their applications," *Nano Today*, vol. 10, no. 2, pp. 240–267, 2015.
- [98] Y. Yang, L.-M. Luo, J.-J. Du et al., "Facile one-pot hydrothermal synthesis and electrochemical properties of carbon nanospheres supported Pt nanocatalysts," *International Journal of Hydrogen Energy*, vol. 41, no. 28, pp. 12062–12068, 2016.
- [99] A. Chen and P. Holt-Hindle, "Platinum-based nanostructured materials: synthesis, properties, and applications," *Chemical Reviews*, vol. 110, no. 6, pp. 3767–3804, 2010.
- [100] F. Ye, W. Hu, T. Zhang, J. Yang, and Y. Ding, "Enhanced electrocatalytic activity of Pt-nanostructures prepared by electrodeposition using poly(vinyl pyrrolidone) as a shape-control agent," *Electrochimica Acta*, vol. 83, pp. 383–386, 2012.

- [101] K. A. Manbeck, N. E. Musselwhite, L. M. Carl et al., "Factors affecting activity and selectivity during cyclohexanone hydrogenation with colloidal platinum nanocatalysts," *Applied Catalysis A: General*, vol. 384, no. 1-2, pp. 58–64, 2010.
- [102] R. Narayanan and M. A. El-Sayed, "Effect of colloidal nanocatalysis on the metallic nanoparticle shape: the Suzuki reaction," *Langmuir*, vol. 21, no. 5, pp. 2027–2033, 2005.
- [103] C. Dai, C. Wang, R. Hu et al., "Photonic/magnetic hyperthermia-synergistic nanocatalytic cancer therapy enabled by zero-valence iron nanocatalysts," *Biomaterials*, vol. 219, article 119374, 2019.
- [104] A. R. Hajipour and P. Abolfathi, "Nickel embedded on triazole-modified magnetic nanoparticles: a novel and sustainable heterogeneous catalyst for Hiyama reaction in fluoride-free condition," *Catalysis Communications*, vol. 103, pp. 92–95, 2017.
- [105] M. Hałupka-Bryl, M. Bednarowicz, B. Dobosz et al., "Doxorubicin loaded PEG-b-poly(4-vinylbenzylphosphonate) coated magnetic iron oxide nanoparticles for targeted drug delivery," *Journal of Magnetism and Magnetic Materials*, vol. 384, pp. 320–327, 2015.
- [106] L. Li, C. Zeng, L. Ai, and J. Jiang, "Synthesis of reduced graphene oxide-iron nanoparticles with superior enzyme-mimetic activity for biosensing application," *Journal of Alloys and Compounds*, vol. 639, pp. 470–477, 2015.
- [107] H. J. Kim, S.-M. Lee, K.-H. Park, C. H. Mun, Y.-B. Park, and K.-H. Yoo, "Drug-loaded gold/iron/gold plasmonic nanoparticles for magnetic targeted chemo-photothermal treatment of rheumatoid arthritis," *Biomaterials*, vol. 61, pp. 95–102, 2015.
- [108] D.-W. Cho, H. Song, F. W. Schwartz, B. Kim, and B.-H. Jeon, "The role of magnetite nanoparticles in the reduction of nitrate in groundwater by zero-valent iron," *Chemosphere*, vol. 125, pp. 41–49, 2015.
- [109] A. Saritha, B. Raju, D. N. Rao, A. Roychowdhury, D. Das, and K. A. Hussain, "Facile green synthesis of iron oxide nanoparticles via solid-state thermolysis of a chiral, 3D anhydrous potassium tris(oxalato)ferrate(III) precursor," *Advanced Powder Technology*, vol. 26, no. 2, pp. 349–354, 2015.
- [110] J. Castelló, M. Gallardo, M. A. Busquets, and J. Estelrich, "Chitosan (or alginate)-coated iron oxide nanoparticles: a comparative study," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 468, pp. 151–158, 2015.
- [111] R. Li, Y. Gao, X. Jin, Z. Chen, M. Megharaj, and R. Naidu, "Fenton-like oxidation of 2,4-DCP in aqueous solution using iron-based nanoparticles as the heterogeneous catalyst," *Journal of Colloid and Interface Science*, vol. 438, pp. 87–93, 2015.
- [112] J. Park, E. Lee, N.-M. Hwang et al., "One-nanometer-scale size-controlled synthesis of monodisperse magnetic iron oxide nanoparticles," *Angewandte Chemie*, vol. 117, no. 19, pp. 2932–2937, 2005.
- [113] L. C. Varanda, M. Jafelicci, P. Tartaj et al., "Structural and magnetic transformation of monodispersed iron oxide particles in a reducing atmosphere," *Journal of Applied Physics*, vol. 92, no. 4, pp. 2079–2085, 2002.
- [114] F. Dumestre, B. Chaudret, C. Amiens, P. Renaud, and P. Fejes, "Superlattices of iron nanocubes synthesized from  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ ," *Science*, vol. 303, no. 5659, pp. 821–823, 2004.
- [115] R. V. Jagadeesh, T. Stemmler, A.-E. Surkus, H. Junge, K. Junge, and M. Beller, "Hydrogenation using iron oxide-based nanocatalysts for the synthesis of amines," *Nature Protocols*, vol. 10, no. 4, pp. 548–557, 2015.
- [116] J. Wu, G. Gao, Y. Li, P. Sun, J. Wang, and F. Li, "Highly chemoselective hydrogenation of lactone to diol over efficient copper-based bifunctional nanocatalysts," *Applied Catalysis B: Environmental*, vol. 245, pp. 251–261, 2019.
- [117] H. Ajamein, M. Haghghi, R. Shokrani, and M. Abdollahifar, "On the solution combustion synthesis of copper based nanocatalysts for steam methanol reforming: effect of precursor, ultrasound irradiation and urea/nitrate ratio," *Journal of Molecular Catalysis A: Chemical*, vol. 421, pp. 222–234, 2016.
- [118] S. B. Bagherzadeh and M. Haghghi, "Plasma-enhanced comparative hydrothermal and coprecipitation preparation of  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  nanocatalyst used in hydrogen production via methanol steam reforming," *Energy Conversion and Management*, vol. 142, pp. 452–465, 2017.
- [119] S. Allahyari, M. Haghghi, A. Ebadi, and S. Hosseinzadeh, "Ultrasound assisted co-precipitation of nanostructured  $\text{CuO}-\text{ZnO}-\text{Al}_2\text{O}_3$  over HZSM-5: effect of precursor and irradiation power on nanocatalyst properties and catalytic performance for direct syngas to DME," *Ultrasonics Sonochemistry*, vol. 21, no. 2, pp. 663–673, 2014.
- [120] J. Baneshi, M. Haghghi, N. Jodeiri, M. Abdollahifar, and H. Ajamein, "Homogeneous precipitation synthesis of  $\text{CuO}-\text{ZrO}_2-\text{CeO}_2-\text{Al}_2\text{O}_3$  nanocatalyst used in hydrogen production via methanol steam reforming for fuel cell applications," *Energy Conversion and Management*, vol. 87, pp. 928–937, 2014.
- [121] S. Danwittayakul and J. Dutta, "Two step copper impregnated zinc oxide microball synthesis for the reduction of activation energy of methanol steam reformation," *Chemical Engineering Journal*, vol. 223, pp. 304–308, 2013.
- [122] M. Haruta, N. Yamada, T. Kobayashi, and S. Iijima, "Gold catalysts prepared by coprecipitation for low-temperature oxidation of hydrogen and of carbon monoxide," *Journal of Catalysis*, vol. 115, no. 2, pp. 301–309, 1989.
- [123] J. Papavasiliou, "Interaction of atomically dispersed gold with hydrothermally prepared copper-cerium oxide for preferential CO oxidation reaction," *Catalysis Today*, 2019.
- [124] L. Qin, G. Zeng, C. Lai et al., "Synthetic strategies and application of gold-based nanocatalysts for nitroaromatics reduction," *Science of the Total Environment*, vol. 652, pp. 93–116, 2018.
- [125] X. Sun, F. Li, J. Shi et al., "Gold nanoparticles supported on  $\text{MgO}_x-\text{Al}_2\text{O}_3$  composite oxide: an efficient catalyst for selective hydrogenation of acetylene," *Applied Surface Science*, vol. 487, pp. 625–633, 2019.
- [126] A. Monopoli, A. Afzal, C. di Franco et al., "Design of novel indium oxide supported gold nanocatalysts and their application in homocoupling of arylboronic acids," *Journal of Molecular Catalysis A: Chemical*, vol. 386, pp. 101–107, 2014.
- [127] H. S. Devi, N. R. Singh, H. P. Singh, and T. D. Singh, "Facile synthesis of biogenic gold nanocatalyst for efficient degradation of organic pollutants," *Journal of Environmental Chemical Engineering*, vol. 3, no. 3, pp. 2042–2049, 2015.
- [128] T. Xiao, J. Huang, D. Wang, T. Meng, and X. Yang, "Au and Au-based nanomaterials: synthesis and recent progress in electrochemical sensor applications," *Talanta*, vol. 206, article 120210, 2019.
- [129] A. E. Shanahan, M. McNamara, J. A. Sullivan, and H. J. Byrne, "An insight into the superior performance of a gold

- nanocatalyst on single wall carbon nanotubes to that on titanium dioxide and amorphous carbon for the green aerobic oxidation of aromatic alcohols," *New Carbon Materials*, vol. 32, no. 3, pp. 242–251, 2017.
- [130] S. Chairam, W. Konkamdee, and R. Parakhun, "Starch-supported gold nanoparticles and their use in 4-nitrophenol reduction," *Journal of Saudi Chemical Society*, vol. 21, no. 6, pp. 656–663, 2015.
- [131] A. Shajkumar, B. Nandan, S. Sanwaria et al., "Silica-supported Au@ hollow-SiO<sub>2</sub> particles with outstanding catalytic activity prepared via block copolymer template approach," *Journal of Colloid and Interface Science*, vol. 491, pp. 246–254, 2017.
- [132] P. Sudarsanam, B. Mallesham, A. Rangaswamy, B. G. Rao, S. K. Bhargava, and B. M. Reddy, "Promising nanostructured gold/metal oxide catalysts for oxidative coupling of benzylamines under eco-friendly conditions," *Journal of Molecular Catalysis A: Chemical*, vol. 412, pp. 47–55, 2016.
- [133] D. Shah and H. Kaur, "Resin-trapped gold nanoparticles: an efficient catalyst for reduction of nitro compounds and Suzuki-Miyaura coupling," *Journal of Molecular Catalysis A: Chemical*, vol. 381, pp. 70–76, 2014.
- [134] C. Wang, H. Yin, S. Dai, and S. Sun, "A general approach to noble metal-metal oxide dumbbell nanoparticles and their catalytic application for CO oxidation," *Chemistry of Materials*, vol. 22, no. 10, pp. 3277–3282, 2010.
- [135] Y. Lee, M. A. Garcia, N. A. Frey Huls, and S. Sun, "Synthetic tuning of the catalytic properties of Au-Fe<sub>3</sub>O<sub>4</sub> nanoparticles," *Angewandte Chemie International Edition*, vol. 49, no. 7, pp. 1271–1274, 2010.
- [136] F. Lin and R. Doong, "Bifunctional Au-Fe<sub>3</sub>O<sub>4</sub> heterostructures for magnetically recyclable catalysis of nitrophenol reduction," *The Journal of Physical Chemistry C*, vol. 115, no. 14, pp. 6591–6598, 2011.
- [137] H. Veisi, N. Dadres, P. Mohammadi, and S. Hemmati, "Green synthesis of silver nanoparticles based on oil-water interface method with essential oil of orange peel and its application as nanocatalyst for A3 coupling," *Materials Science and Engineering: C*, vol. 105, article 110031, 2019.
- [138] R. Sedghi, S. Asadi, B. Heidari, and M. M. Heravi, "TiO<sub>2</sub>/polymeric supported silver nanoparticles applied as superior nanocatalyst in reduction reactions," *Materials Research Bulletin*, vol. 92, pp. 65–73, 2017.
- [139] P. Paul, P. Bhanja, N. Salam et al., "Silver nanoparticles supported over mesoporous alumina as an efficient nanocatalyst for N-alkylation of hetero (aromatic) amines and aromatic amines using alcohols as alkylating agent," *Journal of Colloid and Interface Science*, vol. 493, pp. 206–217, 2017.
- [140] Y. Junejo and M. Safdar, "Highly effective heterogeneous doxycycline stabilized silver nanocatalyst for the degradation of ibuprofen and paracetamol drugs," *Arabian Journal of Chemistry*, 2015.
- [141] Q. Yi, H. Chu, M. Tang, Z. Yang, Q. Chen, and X. Liu, "Carbon nanotube-supported binary silver-based nanocatalysts for oxygen reduction reaction in alkaline media," *Journal of Electroanalytical Chemistry*, vol. 739, pp. 178–186, 2015.
- [142] B. K. Ghosh, D. Moitra, M. Chandel, H. Lulla, and N. N. Ghosh, "Ag nanoparticle immobilized mesoporous TiO<sub>2</sub>-cobalt ferrite nanocatalyst: a highly active, versatile, magnetically separable and reusable catalyst," *Materials Research Bulletin*, vol. 94, pp. 361–370, 2017.
- [143] U. Mandi, A. S. Roy, S. K. Kundu, S. Roy, A. Bhaumik, and S. M. Islam, "Mesoporous polyacrylic acid supported silver nanoparticles as an efficient catalyst for reductive coupling of nitrobenzenes and alcohols using glycerol as hydrogen source," *Journal of Colloid and Interface Science*, vol. 472, pp. 202–209, 2016.
- [144] Z. Ye, L. Hu, J. Jiang, J. Tang, X. Cao, and H. Gu, "CuO@Ag as a highly active catalyst for the selective oxidation of *trans*-stilbene and alcohols," *Catalysis Science & Technology*, vol. 2, no. 6, pp. 1146–1149, 2012.
- [145] C. Chen, J. Qu, C. Cao, F. Niu, and W. Song, "CuO nanoclusters coated with mesoporous SiO<sub>2</sub> as highly active and stable catalysts for olefin epoxidation," *Journal of Materials Chemistry*, vol. 21, no. 15, pp. 5774–5779, 2011.
- [146] M. J. Borah, A. Devi, R. Borah, and D. Deka, "Synthesis and application of Co doped ZnO as heterogeneous nanocatalyst for biodiesel production from non-edible oil," *Renewable Energy*, vol. 133, pp. 512–519, 2019.
- [147] E. Vessally, M. Babazadeh, A. Hosseinian, S. Arshadi, and L. Edjlali, "Nanocatalysts for chemical transformation of carbon dioxide," *Journal of CO<sub>2</sub> Utilization*, vol. 21, pp. 491–502, 2017.
- [148] A. Esmaeili and S. Kakavand, "Nanocomposites with different metals as magnetically separable nanocatalysts for oxidation of aldehydes," *Comptes Rendus Chimie*, vol. 19, no. 8, pp. 936–941, 2016.
- [149] R. Madhuvilakku and S. Piraman, "Biodiesel synthesis by TiO<sub>2</sub>-ZnO mixed oxide nanocatalyst catalyzed palm oil transesterification process," *Bioresource Technology*, vol. 150, pp. 55–59, 2013.
- [150] R. Bharati and S. Suresh, "Biosynthesis of ZnO/SiO<sub>2</sub> nanocatalyst with palash leaves' powder for treatment of petroleum refinery effluent," *Resource-Efficient Technologies*, vol. 3, no. 4, pp. 528–541, 2017.
- [151] G. R. Andrade, C. C. Nascimento, E. C. Silva Júnior, D. T. S. L. Mendes, and I. F. Gimenez, "ZnO/Au nanocatalysts for enhanced decolorization of an azo dye under solar, UV-A and dark conditions," *Journal of Alloys and Compounds*, vol. 710, pp. 557–566, 2017.
- [152] J. Albadi, A. Alihosseinzadeh, and M. Mardani, "Efficient approach for the chemoselective acetylation of alcohols catalyzed by a novel metal oxide nanocatalyst CuO-ZnO," *Chinese Journal of Catalysis*, vol. 36, no. 3, pp. 308–313, 2015.
- [153] H. Ajamein, M. Haghghi, and S. Alaei, "The role of various fuels on microwave-enhanced combustion synthesis of CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> nanocatalyst used in hydrogen production via methanol steam reforming," *Energy Conversion and Management*, vol. 137, pp. 61–73, 2017.
- [154] S. Minaei, M. Haghghi, N. Jodeiri, H. Ajamein, and M. Abdollahifar, "Urea-nitrates combustion preparation of CeO<sub>2</sub>-promoted CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> nanocatalyst for fuel cell grade hydrogen production via methanol steam reforming," *Advanced Powder Technology*, vol. 28, no. 3, pp. 842–853, 2017.
- [155] K. Ranjith and R. R. Kumar, "Surfactant free, simple, morphological and defect engineered ZnO nanocatalyst: effective study on sunlight driven and reusable photocatalytic properties," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 329, pp. 35–45, 2016.
- [156] I. Saikia, M. Hazarika, and C. Tamuly, "Synthesis, characterization of bio-derived ZnO nanoparticles and its catalytic activity," *Materials Letters*, vol. 161, pp. 29–32, 2015.

