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## A Concise Review of Nanocomposites' Function in Organic Reactions to Synthesize Various Organic Nuclei

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**Abstract:** Given the high aspect ratio and larger surface area of nanostructured materials, nanocomposites are essential catalysts in organic processes. The rate and yield of the product are enhanced during the reaction due to the significant interfacial contact of the reactant with the surface of nanocomposites. A critical investigation of the role of nanocomposites in chemical reactions (Reduction, oxidation, epoxidation, Knoevenagel Michael condensation and coupling reactions) to synthesize different organic nuclei is shown in the current review. Different transition metal-based nanocomposites track organic reaction selectivity as well as changes in yields, reaction time, atom economy, and solvent influence. Numerous recognized green one-pot synthesis methods for organic nuclei. These methods also include the use of different nano catalysts. Therefore, the current study investigates novel approaches to the replacement of conventional catalysts and reagents in organic synthesis with transition metal-based nanostructured catalysts, adhering to green chemistry principles.

**Keywords:** Nanocomposites; Organic Reactions; Organic Nuclei; oxidation, Knoevenagel Michael

### 1. INTRODUCTION

One of the main objectives of organic synthesis is the creation of straightforward synthesis methods for commonly used organic molecules using easily available reagents. Researchers are currently paying close attention to the production of new heterocyclic compounds with high biological activity through the use of highly efficient nanoparticles. Recently, there has been an increasing interest in the search for affordable and efficient solid nano catalysts [1, 2]. According to a number of recent research, magnetic nanoparticles can be used to synthesize novel chemicals utilizing simpler, more affordable, and environmentally friendly methods, such as nanocrystalline TiO<sub>2</sub>-HClO<sub>4</sub> [3]. ZnCl<sub>2</sub> supported on nano Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> [4], SO<sub>3</sub>H-dendrimer (Fe<sub>3</sub>O<sub>4</sub>@D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H), [5] nanostructured diphosphate (Na<sub>2</sub>CaP<sub>2</sub>O<sub>7</sub>), [6] and MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H. [7] Sulfonic acid nanoporous silica (SBA-Pr-SO<sub>3</sub>H), [8] Fe<sub>3</sub>O<sub>4</sub>, [9] nano[2-bromophenylsalicylaldiminemethyl pyranopyrazole]Cl<sub>2</sub>, [10] nickel NPs-N-doped TiO<sub>2</sub> [11] and MGO-D-NH-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H are further attempts at creating new, superior nanocatalysts [12]. Furthermore, the presence of effective and recyclable nano-catalysts like Mn<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, and ZnO enforced the field [13]. Nanocomposites based on transition metals are a novel class of materials that have unique properties and are better than conventional doped type systems. Some of the drawbacks of conventional catalysts include their costly synthesis techniques and laborious separation processes. In many different synthesis methods, catalysts based on nanocomposites have gained a great deal of interest. More stability and selectivity result from the substantial alteration of transition metal nano catalysts in terms of size, shape, and composition [14, 15]. However, good interpretation of the reaction mechanisms and analysis of potential by-products are crucial for the synthesis of novel chemicals, more advanced processes, and

increased efficiency. The fundamental idea behind nano catalysis can be understood by examining the crucial role that intrinsic properties of nanomaterials play in catalytic activity. These properties can be directly related to (a) bond length, primarily atomic density, mean lattice constant, and binding energy; (b) cohesive energy per discrete atom, such as critical temperature for phase transformations, diffusion, nano-solid evaporation, and chemical reactions; and properties like (c) A Hamiltonian that aids in identifying the whole band structure, core level energy, band gap, photoemission, and photo absorption and is dependent on the binding energy density in the relaxed continuum region (d) mechanical strength, strain, stress, Young's modulus, surface energy, and magnetic behavior, all of which are influenced by the interaction of binding energy density and cohesive energy between atoms [16]. Because the precise mechanism underlying these catalytic activities is yet unknown, researchers are drawn to developing new approaches to the design and analysis of nanocatalysts. Catalysis is responsible for the production of almost 50% of all compounds used in most chemical processes [17]. Heterogeneous catalysts became an essential component of many industrialized processes, such as organic synthesis, pollution management, and oil refining [18, 19]. By monitoring the pore shape or changing views toward, say, nanotechnology and nanoscience, it was more likely to promote heterogeneous catalytic activity [20]. Several catalyst supports were used to constrain the particle in order to address the problem of catalyst recovery and separation from the reaction matrix on behalf of heterogeneous catalysis. gives the heterogeneous catalyst enough surface area [21] to prevent it from dissolving into the solution matrix [22-24]. Thus, heterogeneous catalysts, such as TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and ZnO, were based on their broad availability and reasonably priced synthesis methods.

In this review, we aim to delve into the fundamentals and mechanisms of different transition metal-based nanocomposites track organic reaction selectivity as well as changes in yields, reaction time, atom economy, and solvent influence. Numerous recognized green one-pot synthesis methods for organic nuclei are examined, including diazenyl benzoic acid derivatives, 1H-3-Indolyl derivatives, 1H-benzo[d]imidazole derivatives, pyrano[2,3] pyrimidine derivatives, and pyrimidine-5-carbonitrile.

This review critically examines the role of nanocomposites in various chemical reactions, including reduction, oxidation, epoxidation, Knoevenagel-Michael condensation, and coupling reactions, for synthesizing different organic compounds.

The review highlights how different transition metal-based nanocomposites affect organic reaction selectivity, as well as changes in yields, reaction times, atom economy, and solvent effects. It also covers established green one-pot synthesis methods for organic compounds, which often utilize various nano catalysts.

The study focuses on exploring innovative approaches to replace traditional catalysts and reagents with transition metal-based nanostructured catalysts, in line with green chemistry principles. The main objectives and novel aspects of this study should be emphasized clearly.

## 2. MECHANISM OF ROLE OF NANO CATALYST IN ORGANIC CHEMISTRY

Shehab et al. discussed mechanism of role of nano catalyst in organic chemistry, because of their higher surface area and high aspect ratio, nanostructured materials are essential catalysts in organic processes and play a significant role in nanocomposites. The rate and yield of the product are increased throughout the reaction due to the reactant's high interfacial contact with the nanocomposites' surface Fig 1 [25].

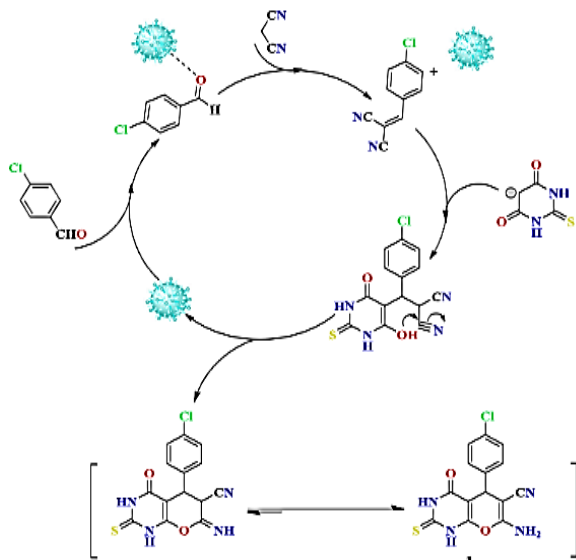


Fig. 1. The conceivable process for producing pyrano[2,3-d]pyrimidine-6-carbonitrile (1) [21]

## 3. APPLICATION OF TRANSITION METAL BASED NANOCOMPOSITE CATALYSTS FOR ORGANIC REACTIONS

The development of transition metal nanocomposites has been accelerated by their broad variety of synthesis

techniques, flexibility in modifying their characteristics and compositions, and extensive use in catalysis. A large number of novel and important materials synthesis processes in the industrial domain rely on catalysts derived from transition metal nanocomposites. With the exact control over the location, quantity, and kind of active sites as well as the hydrophilic and porosity characteristics of the catalyst, nanocomposite materials allow for wide catalyst creation. Many techniques for modifying the physical and chemical features of these composites are available to improve their catalytic effectiveness Fig 2 [26].

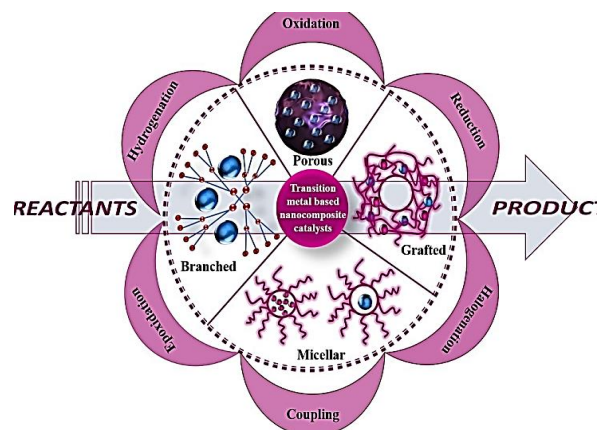


Fig. 2. Use of catalysts for organic processes based on transition metal nanocomposite materials [22].

### 3.1. Reduction reactions

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using transition metal-based nanocomposites as catalysts involves several mechanisms and catalyst designs to achieve efficient conversion.

#### 3.1.1. Catalyst Design and Mechanism:

**Metallic Species and Active Sites:** Transition metal-based nanocomposites are designed to have metallic species that provide active sites for adsorption of  $\text{NaBH}_4$ .  $\text{NaBH}_4$  acts as the source of hydride ions ( $\text{H}^-$ ) necessary for the reduction reaction.

**Formation of Metal-Hydride Complex:** The catalyst facilitates the adsorption of  $\text{NaBH}_4$ , which forms a metal-hydride complex on the catalyst surface. This complex is crucial as it generates active hydride species required for the reduction reaction.

#### 3.1.2.Reduction Mechanism:

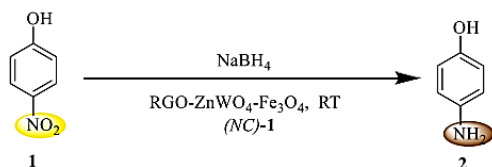
**Interaction with 4-Nitrophenol (4-NP):** 4-NP molecules diffuse onto the surface of the catalyst where they interact with the active hydrogen species generated from the  $\text{NaBH}_4$  reaction.

**Formation of 4-Aminophenol (4-AP):** The active hydrogen species from the metal-hydride complex react with the nitro group ( $-\text{NO}_2$ ) of 4-NP, leading to the reduction of the nitro group to an amino group ( $-\text{NH}_2$ ), thereby forming 4-aminophenol (4-AP).

#### 3.1.3. Examples of Catalysts and Their Efficiency:

Mohamed et al. (NC)-1 Catalyst: This catalyst,  $\text{RGO-ZnWO}_4\text{-Fe}_3\text{O}_4$ , demonstrates high efficiency in reducing

4-NP to 4-AP, completing the reaction in just 40 seconds compared to conventional methods [27] Fig 3.



Conventional Methods:	Method by Mohamed et al.:
● Longer time	● Reaction completion time 40 s
● Toxic Solvent	● Green solvent: Aqueous medium
● Temperature upto >200 °C	● Room Temperature reaction
● High amount of hazardous waste	● Minimum degradable waste

Fig. 3. Reduction of 4-Nitrophenol to 4-Aminophenol by RGO-ZnWO<sub>4</sub>-Fe<sub>3</sub>O<sub>4</sub> [32].

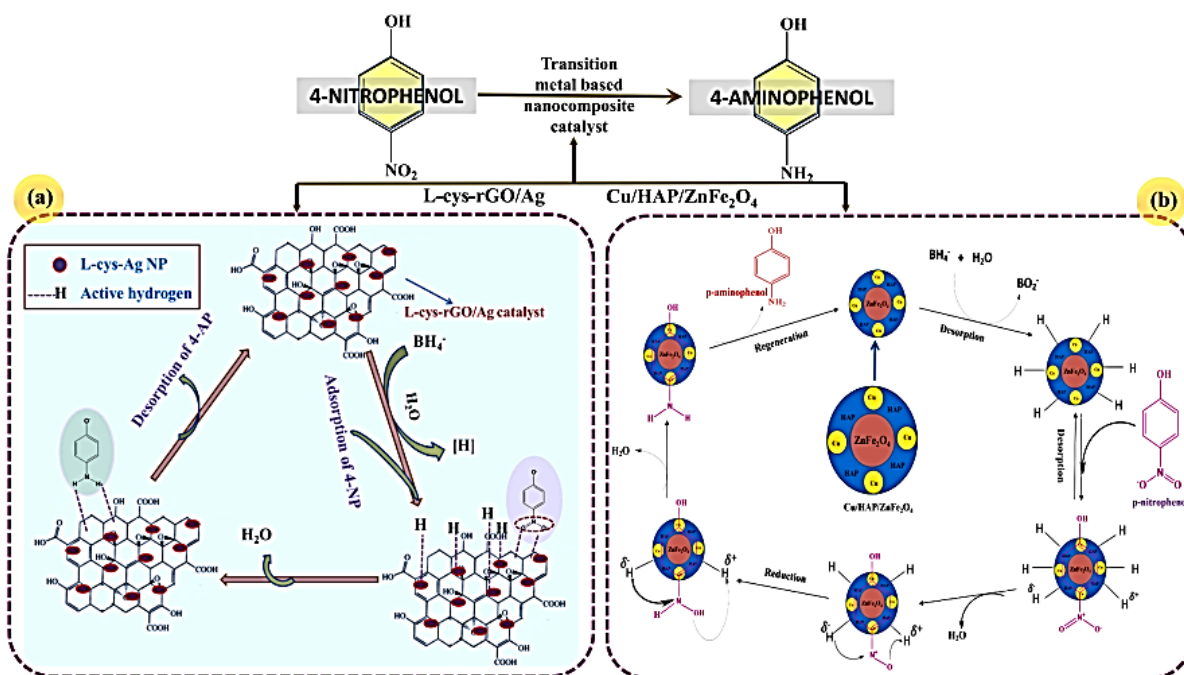


Fig. 4. (a) Reduction of 4-nitrophenol to 4-aminophenol by L-cys-rGO/Ag; (b) reduction of 4-nitrophenol to 4-aminophenol by Cu/HAP/ZnFe<sub>2</sub>O<sub>4</sub> [22].

### 3.2. Oxidation reactions

The oxidation mechanisms described by Shahriari et al. [26] and Mal et al. [28] illustrate different approaches in catalytic processes involving transition metal catalysts Fig 5.

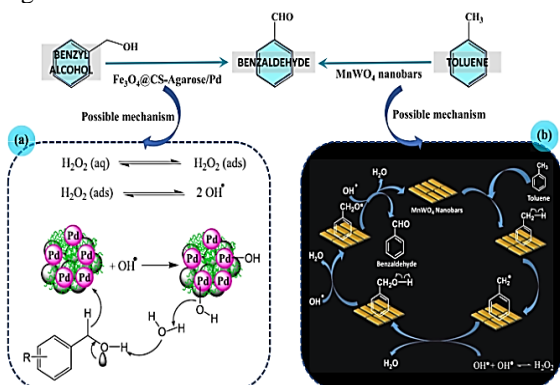
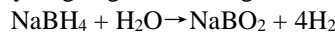


Fig. 5. Oxidation of (a) benzyl alcohol to benzaldehyde by Fe<sub>3</sub>O<sub>4</sub>@CS-Agarose/Pd [22];(b) toluene to

Sahu et al. L-cys-rGO/Ag Nanocomposite: This composite utilizes nano silver imprinted graphene oxide as a catalyst. L-cysteine present in the composite aids in stabilization and modification of the graphene oxide sheet, enhancing catalytic efficiency. This catalyst achieves rapid conversion of 4-NP to 4-AP within 6 to 7 minutes Fig 4a.

Das et al. Cu/HAP/ZnFe<sub>2</sub>O<sub>4</sub> catalyst: The NaBH<sub>4</sub> acts as a source of hydrogen. NaBH<sub>4</sub> reacts with water and produces hydrogen gas according to the equation below.



BH<sub>4</sub><sup>-</sup> ions are adsorbed and reacted with the surface of Cu/HAP/ZnFe<sub>2</sub>O<sub>4</sub> catalyst to produce active hydrogen species. At the same time, p-NP in the solution diffuses onto the surface of Cu/HAP/ZnFe<sub>2</sub>O<sub>4</sub> and reacts with the active hydrogen species to form p-AP Fig 4b [26].

benzaldehyde by MnWO<sub>4</sub> [24].

### 3.3. Knoevenagel Michael condensation

Shehab et al. used Mn<sub>2</sub>O<sub>3</sub> as a nano- and green solid acid catalyst for the synthesis of 7-amino-4-oxo-5-(thiophen-2-yl)2H-pyrano[2,3-d] pyrimidine-6-carbonitrile derivatives via the Knoevenagel Michael condensation. The process involves combining thiophene-2-carbaldehyde, barbituric acid derivatives, and malononitrile in ethanol. By examining how the amount of Mn<sub>2</sub>O<sub>3</sub> nano catalyst affects the reaction yield, optimization methods for Mn<sub>2</sub>O<sub>3</sub> catalysis and pyranopyrimidine heterocyclic synthesis have been established. It was discovered that 1 mmol of Mn<sub>2</sub>O<sub>3</sub> generated around 80% of pyranopyrimidine in 30 minutes, which is the optimal length of time to finish the reaction Fig 6 [29].

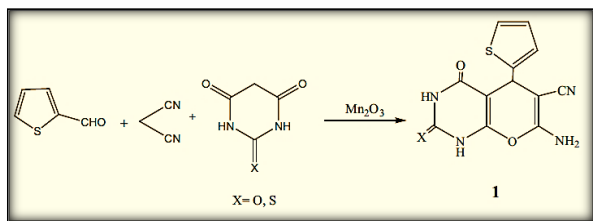


Fig. 6. synthesis of pyrano[2,3-d]pyrimidine Derivatives [25].

For the synthesis of 7-amino-5-(4-chlorophenyl)-4-oxo-2-thioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile, Abdel-Azim et al. used a one-pot multicomponent cyclocondensation process [25]. Refluxing conditions in ethanol facilitate the reaction of 4-chlorobenzaldehyde, thiobarbituric acid, and malononitrile with a catalytic quantity of Fe<sub>3</sub>O<sub>4</sub> (or Mn<sub>3</sub>O<sub>4</sub> or ZnO) nanoparticles as a catalyst. Various catalysts were employed to ascertain the ideal reaction conditions. First, this reaction using the methods mentioned in the literature [30] to determine the best kind of catalysts to utilize in this experiment: Fe<sub>3</sub>O<sub>4</sub>, ZnO, or Mn<sub>3</sub>O<sub>4</sub>. The use of Mn<sub>3</sub>O<sub>4</sub> in the reaction produced the best outcomes. The outcomes showed that Fe<sub>3</sub>O<sub>4</sub> had a low efficiency. The model reaction was conducted under refluxing conditions in ethanol in order to maximize the time. The findings show that after two hours, an 88% yield was achieved. On a carbon-coated copper grid, finely ground (Mn<sub>3</sub>O<sub>4</sub>, ZnO, and Fe<sub>3</sub>O<sub>4</sub>) nanocrystals were distributed in ethanol to produce high-resolution transmission electron microscopy pictures, as shown in Fig 7.

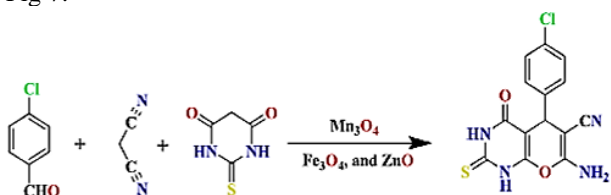


Fig. 7. synthesis of 7-amino-5-(4-chlorophenyl)-4-oxo-2-thioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile [21].

Elsayed et al. used TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub>-NPs) as a catalytic. It was discovered that when TiO<sub>2</sub>-NPs were added to the process, the greatest results were produced a 97% yield was reached after two hours Fig 8 [31].

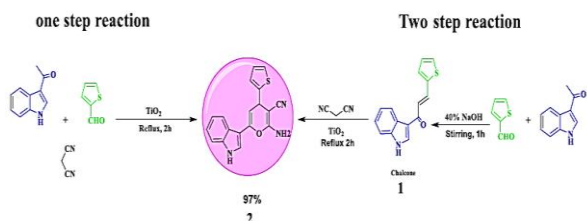


Fig. 8. The synthesis of 2-amino-6-(1H-indol-3-yl)-4-(thiophen-2-yl)-4H-pyran-3-carbonitrile [27].

The generation of CuO-NPs and sodium acetate (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>Na) were connected in order to obtain the best sort of catalysts [32]. It became clear that when the CuO-NPs were elaborated in the reaction, the best characteristics were obtained. The model reaction was carried out in stirring conditions in order to adjust the time. Organized findings confirmed that 4 minutes after ingesting the CuO-NPs as a catalyst, 99% yield was

attained. The tabulated data demonstrated that CuO-NPs produced the best outcomes in terms of yield and time Fig 9.

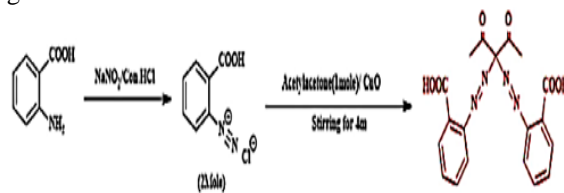


Fig. 9. The synthesis of diazenyl benzoic acid Derivatives [28].

Shehab et al. was created different new heterocyclic compounds based on the pyrimidine moiety. The starting material 4-(4-cyanophenyl)-6-oxo-2-thioxohexahydropyrimidine-5-carbonitrile was synthesized using two different methods [33]. The traditional method involves reacting 4-cyanobenzaldehyde with thiourea, also known as ethyl cyanoacetate, in ethanol under reflux circumstances while adding a small amount of triethylamine. The three components' reaction in the presence of Mn<sub>3</sub>O<sub>4</sub> nanoparticles (Mn<sub>3</sub>O<sub>4</sub>-NPs) as a catalytic quantity in ethanol under reflux was recorded in order to create pyrimidine-5-carbonitrile with ideal reaction conditions Fig 10.

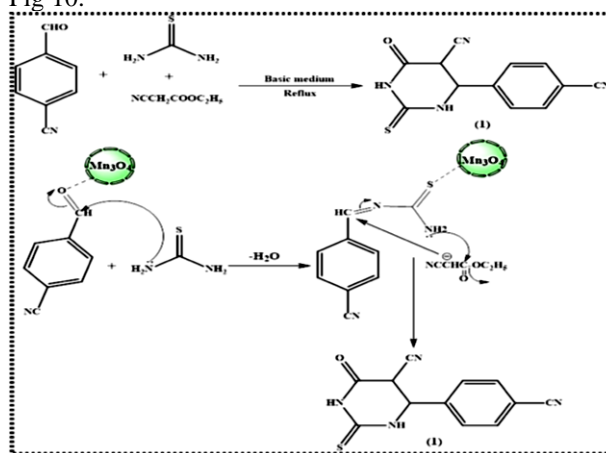


Fig. 10. The synthesis of 4-(4-cyanophenyl)-6-oxo-2-thioxohexahydropyrimidine-5-carbonitrile [29].

### 3.4. Epoxidation reactions

Mishra et al. [34] designed Ti-Co (NP)HT nano catalyst for oxidation of styrene-to-styrene oxide Fig. 11a.

According to Jiao et al. [35] there are two pathways to convert cyclohexene as given in Fig. 11b. Firstly, cyclohexene (1) is epoxidized to cyclohexene oxide (2), which can be hydrolysed to 1,2-cyclohexanediol (4) under acidic conditions. The other pathway is the allylic oxidation of cyclohexene to cyclohexen-1-one (3) and 2-cyclohexen-1-ol(5). the TPAOH modified samples have a comparable selectivity to cyclohexene oxide, while the TPAOH modified samples have higher selectivity of 1,2-cyclohexanediol and lower selectivity of cyclohexen-1-one and 2-cyclohexen-1-ol. This implies that more cyclohexene is oxidized to cyclohexene oxide and 1,2-cyclohexanediol via Pathway 1 over the as-prepared sample. These results clearly demonstrate the positive role of framework titanium in promoting Pathway 1 as the primary reaction route.

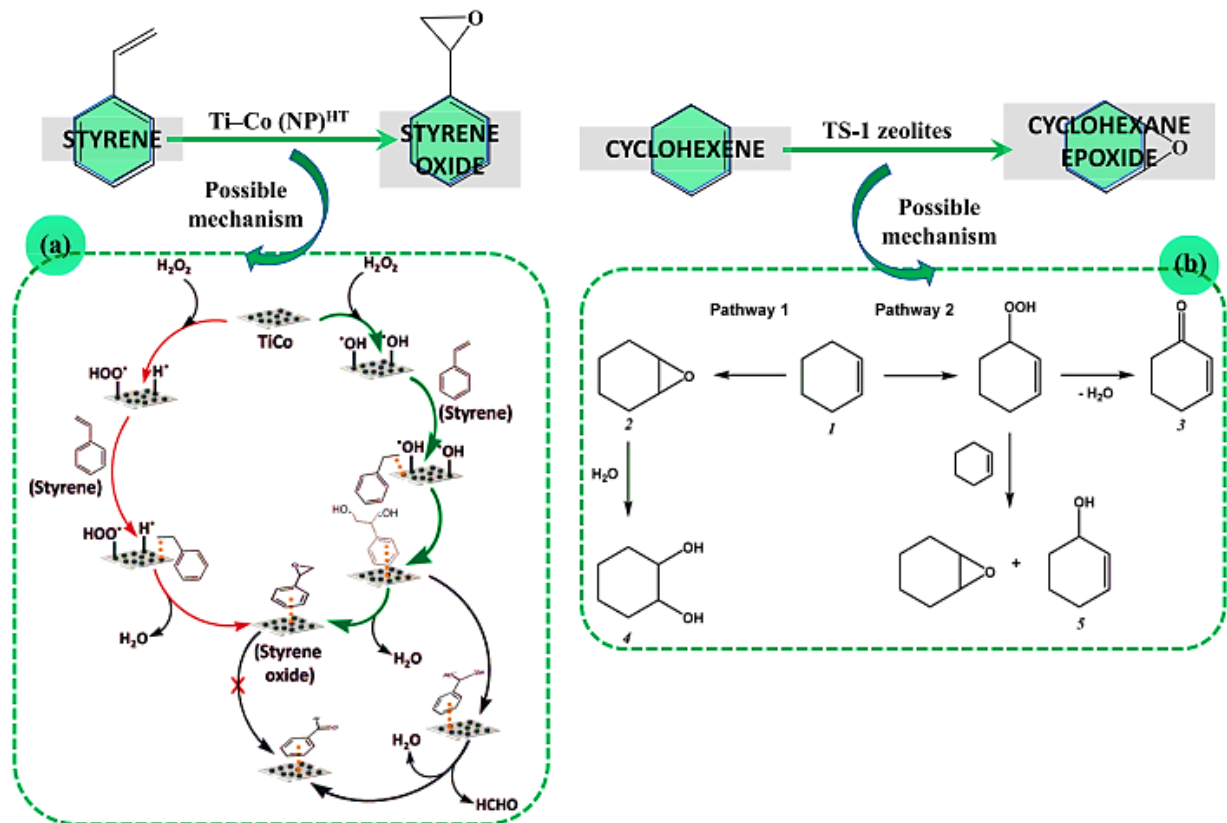
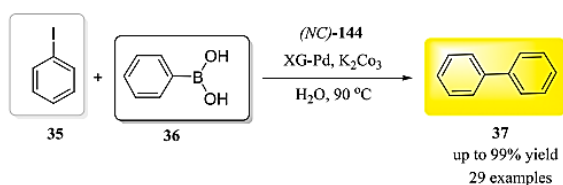


Fig. 11. Oxidation of styrene-to-styrene oxide by (a) Ti–Co (NP)HT [30]; (b) TS-1 zeolites [31].

### 3.5. Coupling reactions

Maity et al. synthesized a nanocomposite catalyst (*NC*-144, XG-Pd (Pd nanoparticle/ calcium-cholate (CaCh) xerogel) for Suzuki crosscoupling reaction of iodobenzene (**35**) and phenylboronic acid (**36**) Fig 12 [36]. This catalyst can be used 4 times efficiently to provide high yield of products.



Conventional Methods:	Method by Maity et. al.:
● Reusable but the activity decreases	● Easy recovery and reusable
● Toxic Solvent	● Green solvent: Aqueous medium
● Moderate-high yield	● High yield
● Slower reaction rate	● Faster reaction rate

Fig. 12. Suzuki cross-coupling reaction of iodobenzene and phenylboronic acid by using XG-Pd nanocomposite catalys [32].

Veisi et al. [37, 38] developed a nanohybrid material called  $\text{Fe}_3\text{O}_4/\text{DAG}/\text{Pd}$  ( $\text{Fe}_3\text{O}_4$  functionalized diaminoglyoxime nanocomposite supported by palladium nanoparticles) to catalyze the Mizoroki-Heck reaction between styrene and aryl halides. Fig 13a, the coupling of styrene and bromobenzene is optimized for various parameters, including solvent effects, base presence, and catalyst concentrations.  $\text{Et}_3\text{N}$  has a higher effect than other bases, and DMF is the best solvent option. Optimized circumstances result in efficient reactions between electron-donating and electron-withdrawing groups and styrene, providing high yields of trans-stilbene.

Heidari et al. [26] developed a  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{isoniazide}/\text{Pd}$  nanocatalyst for Suzuki coupling processes to produce biaryl compounds. Fig 13b illustrates the nanocatalyst's catalytic pathway. The first step involves the oxidative addition of an active palladium catalyst to an aryl halide to form Pd(II) intermediate (II). The second step involves exchanging the aryl moiety of phenyl boronic acid with halide on the catalyst's surface (III), followed by reductive elimination to produce the desired product. The magnetic catalyst is easily recovered and may be reused up to six times more efficiently.

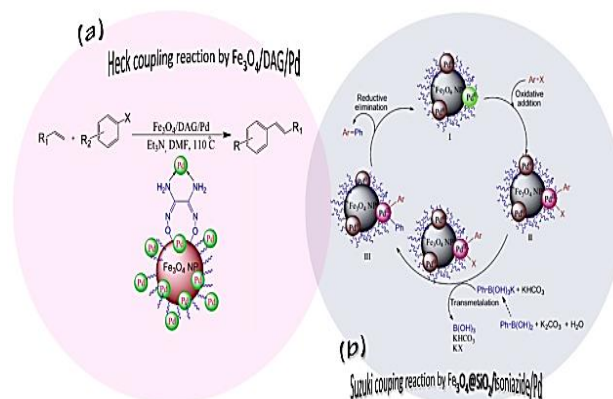


Fig. 13. Heck coupling reaction by  $\text{Fe}_3\text{O}_4/\text{DAG}/\text{Pd}$ . [33]; (b) Suzuki coupling reaction by  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{isoniazide}/\text{Pd}$ . [22].

## 4. CONCLUSION

This review comprehensively discusses the importance and advantages of nanocomposites in organic synthesis, emphasizing their role as catalysts. Nanocomposites, due to their high aspect ratio and large surface area, provide

enhanced interfacial contact between reactants and the catalyst surface, leading to increased reaction rates and yields. The review highlights several key points:

**Enhanced Catalytic Efficiency:** Nanocomposites improve the efficiency of organic reactions through their high surface area, which allows for greater interaction between reactants and the catalyst.

**Transition Metal-Based Nanocomposites:** These are particularly significant in tracking selectivity, yield, reaction time, atom economy, and solvent influence in organic reactions. They offer a promising alternative to traditional catalysts by providing better performance and adhering to green chemistry principles.

**Green One-Pot Synthesis Methods:** The review examines various green one-pot synthesis methods for organic nuclei such as diazenyl benzoic acid derivatives, 1H-3-Indolyl derivatives, 1H-benzo[d]imidazole derivatives, pyrano[2,3]pyrimidine derivatives, and pyrimidine-5-carbonitrile. These methods utilize different nanocatalysts to streamline synthesis processes, making them more environmentally friendly and efficient.

**Novel Approaches:** The study explores innovative approaches to replacing conventional catalysts and reagents in organic synthesis with transition metal-based nanostructured catalysts. This aligns with green chemistry principles by minimizing waste and the use of hazardous substances.

Overall, the review underscores the critical role of nanocomposites in advancing organic synthesis, providing a more sustainable and efficient alternative to traditional methods. The focus on green chemistry principles and the development of novel catalytic approaches highlights the potential for significant advancements in the field.

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