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A Review on Magnetic Ferrite Nano- Catalyst as Green and Recyclable Catalysts for Muticomponent Reactions

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Abstract: *Magnetic ferrite nanocatalysts have attracted significant attention as sustainable and efficient materials for green chemistry. These nanocatalysts exhibit high surface area, chemical stability, and superparamagnetic behavior, enabling effective catalytic activity and facile separation from reaction mixtures using an external magnetic field. Magnetic recovery minimizes catalyst loss, solvent use, and energy consumption, promoting environmentally friendly chemical processes. They have been widely applied in multicomponent reactions, heterocyclic synthesis, biomass conversion, and environmental remediation. Recent advancements focus on rational structural design, including core-shell, yolk-shell, and hybrid architectures, which improve dispersion, limit particle aggregation, and provide multiple active sites. Surface functionalization with acidic, basic, or bifunctional groups further enhances catalytic activity and selectivity. Catalytic performance and magnetic properties can be tuned by varying the metal ion in the ferrite structure, with cobalt, nickel, zinc, and manganese ferrites extensively studied. Compared to conventional catalysts, magnetic ferrite nanocatalysts offer easy handling, reusability, and reduced environmental impact, although challenges remain in large-scale synthesis and long-term stability. This review consolidates recent progress in the synthesis, functionalization, and applications of magnetic ferrite nanocatalysts, highlighting their potential as recyclable platforms for sustainable chemical processes.*

Keywords*:* ferrite; nano-catalysts; magnetic separation; recyclable catalyst; green synthesis

I. INTRODUCTION

The field of green and sustainable chemistry emphasizes the development of efficient, recyclable, and environmentally benign catalytic systems. Among these, magnetic ferrite nano catalysts have emerged as highly promising candidates due to their unique magnetic properties, high surface area, chemical stability, and ease of separation using an external magnet [1-3]. These features not only reduce catalyst loss but also minimize energy consumption, solvent usage, and environmental impact, aligning with the principles of green chemistry [4-6].Magnetic ferrite nanocatalysts can be broadly classified based on structural architecture and surface modification strategies, as illustrated in Figure 1.

Magnetic ferrites at the nanoscale exhibit superparamagnetic behavior, which allows for rapid magnetic recovery and efficient recyclability, making them ideal for heterogeneous catalysis. The catalytic activity of these nanoparticles can be further enhanced by surface functionalization with acidic, basic, or organometallic groups, providing active sites for diverse chemical transformations [7,8,10]. The nanoscale dimension ensures high surface-to- volume ratio, enabling enhanced interaction with reactants and improved reaction kinetics, which is particularly advantageous in multicomponent reactions (MCRs)[9-12]. MCRs are valuable synthetic tools because they allow the formation of

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complex molecules in a single step, reducing reaction time, energy consumption, and the generation of waste [13,14,18].

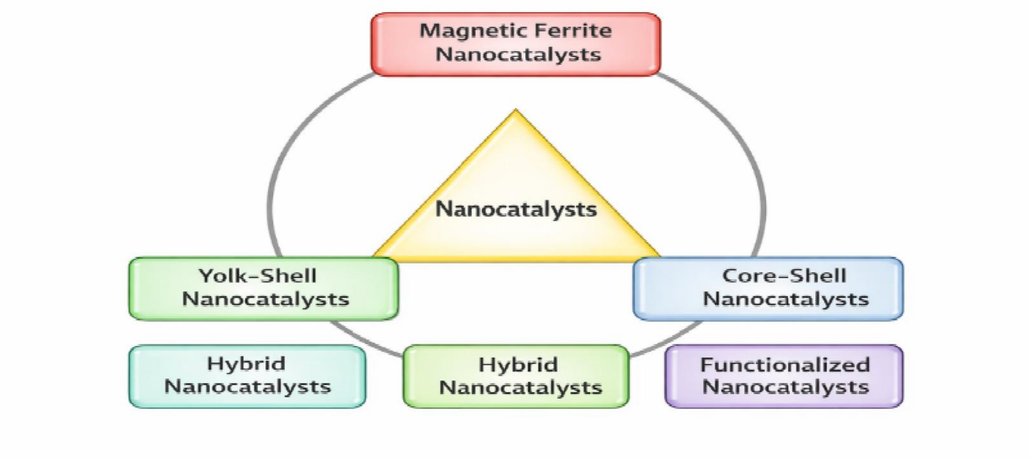


Figure 1. Different types of Magnetic ferrite Nano catalyst

Experimental studies have demonstrated the remarkable efficiency of magnetic ferrite nanocatalysts. For example, Fe_3O_4@rGO@CdS/Bi_2S_3 nanocomposites with particle sizes of 12-18 nm and a surface area of 85 m²/g achieved 98% degradation of methylene blue within 120 minutes and complete reduction of Cr(VI) under sunlight, highlighting both their catalytic efficiency and magnetic recoverability [6]. Similarly, Fe_3O_4@SiO_2-SO_3H core-shell nanoparticles with 15-25 nm particle size and 92 m²/g surface area catalyzed cellulose hydrolysis with 84% glucose yield under mild conditions, demonstrating high activity in biomass conversion reactions [7]. In the synthesis of heterocycles, Fe_3O_4@SiO_2-SO_3H catalyzed microwave-assisted formation of 2,4,5-trisubstituted imidazoles with 95% yield, maintaining >90% catalytic activity over five cycles, while Fe_3O_4/SO_3H@zeolite-Y delivered 91-94% yields for imidazole and perimidine derivatives with recyclability over six cycles [8,9,15-17].

Early studies focused on **Fe_3O_4@SiO_2 core-shell nanocomposites**, where silica coatings improved dispersion, prevented agglomeration, and enhanced catalytic efficiency in various organic reactions. Core-shell, yolk-shell, mesoporous, hydrogel, and polymer-supported architectures were designed to enhance surface area, mass transfer, active-site dispersion, and structural stability. These engineered systems consistently demonstrated excellent catalytic efficiency, rapid magnetic recovery, and minimal metal leaching[10,11]. Hybrid systems, such as Fe_3O_4@alginate-L-arginine, integrate organic and inorganic components, enhancing catalytic selectivity and activity in multicomponent reactions [12]. Moreover, these nanocatalysts have been successfully applied in nitroarene reduction, pyrazole synthesis, oxidative reactions, and other MCRs, achieving high yields (85-98%), maintaining surface areas of 80-95 m²/g, and exhibiting recyclability up to 5-6 cycles with minimal loss of activity [13,19]. Advanced modifications include incorporation of **transition metals (Pd, Cu, Ru, Ni)** onto magnetic supports for C-C coupling, hydrogenation, reduction of nitroarenes, and click reactions [41, 45-47].

Recent studies also highlight the importance of metal composition (M) in MFe_2O_4 ferrites, which can modulate magnetic properties, catalytic efficiency, and stability. For example, $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles have been shown to provide higher activity in heterocyclic synthesis, while $ZnFe_2O_4$ and $MnFe_2O_4$ show excellent performance in oxidation and reduction reactions [5,13,33-36]. Functionalization with sulfonic acid, amine, or Schiff-base groups enables these catalysts to act as acidic, basic, or bifunctional nanocatalysts, suitable for multistep, one-pot reactions [12,20-22].Overall, magnetic ferrite nanocatalysts offer a versatile, efficient, and recyclable platform for green chemical processes, suitable for both laboratory and industrial applications. Representative examples of functionalized magnetic ferrite nanocatalysts, including sulfonated, amine-functionalized, and metal-complex-supported systems, are illustrated in Figure 2.

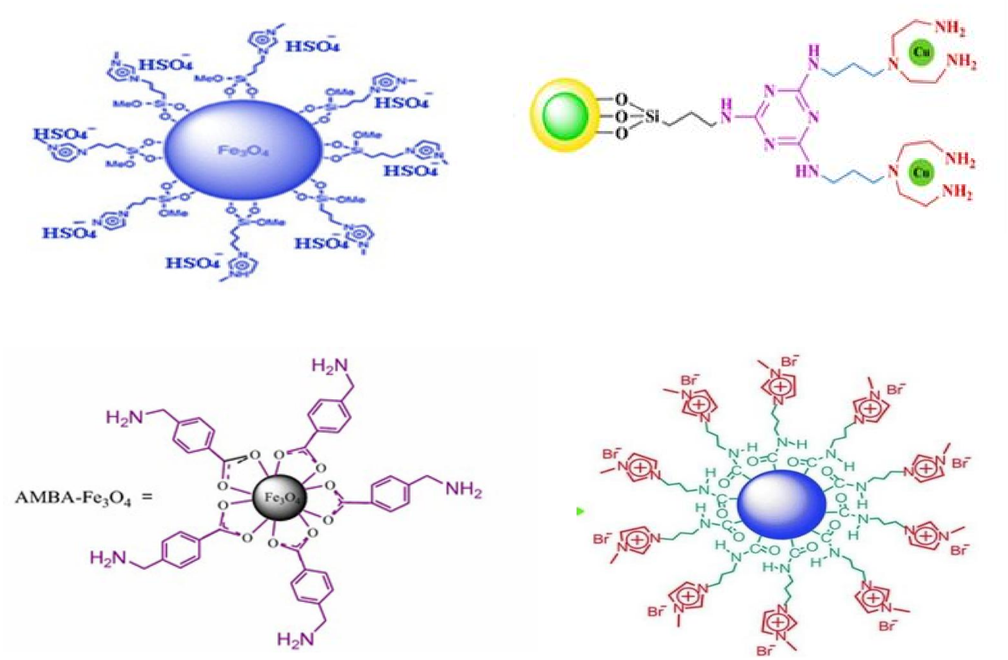
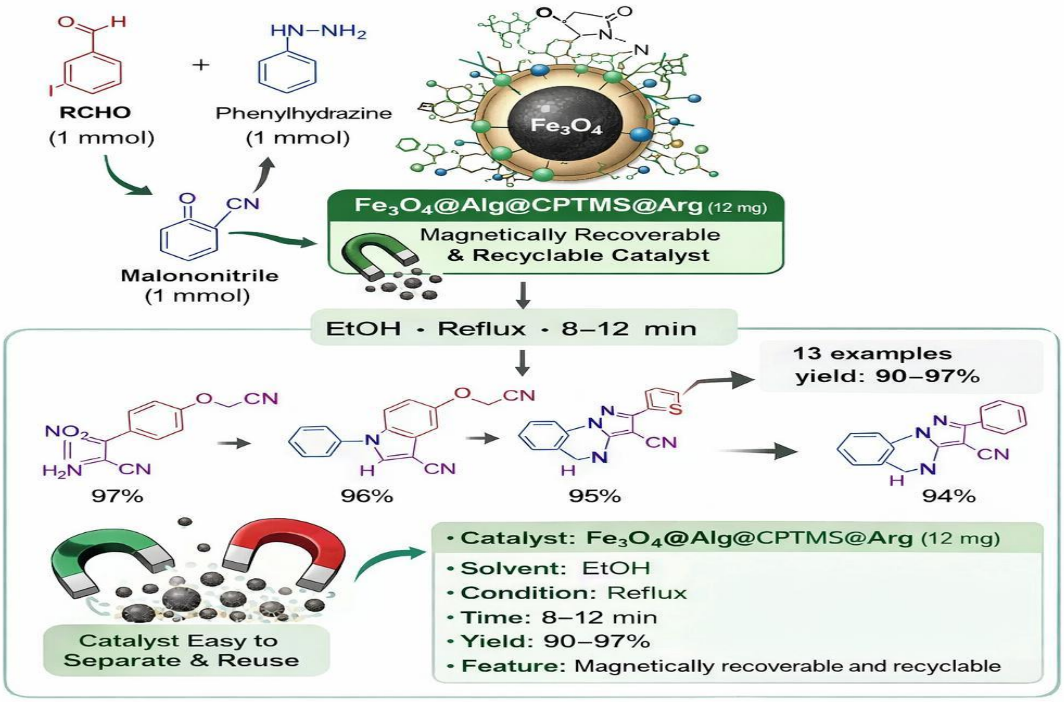


Figure 2. Examples of Nano catalyst

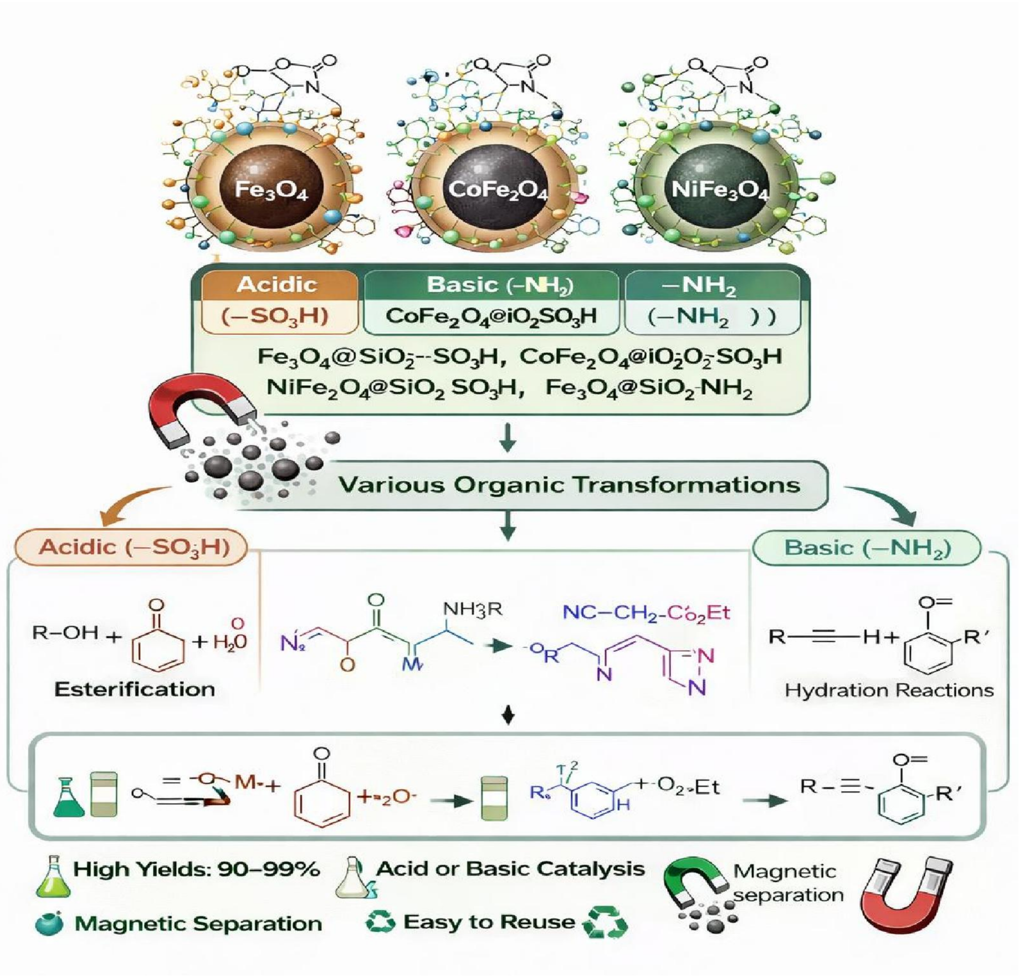
II. METHODOLOGY

The Fe_3O_4-based magnetic core-shell nanocomposite catalyst system was reported by Yi, Lee, and Ying in 2006 [1]. In this study, Fe_3O_4 nanoparticles were first synthesized via co-precipitation of Fe^{2+} and Fe^{3+} salts under basic conditions to obtain strongly magnetic particles (40-70 emu/g). These magnetic cores were then dispersed in an ethanol-water mixture and coated with a silica shell using tetraethyl orthosilicate (TEOS) under ammonia-catalyzed conditions through the Stöber process, forming uniform Fe_3O_4-SiO_2 core-shell nanocomposites of approximately 8-20 nm in size. The silica surface was further functionalized with suitable organosilanes to introduce catalytic active sites. The resulting nanocomposite catalyst was applied to various model organic reactions under optimized conditions, where it exhibited high catalytic efficiency, affording product yields of 85-98%. After completion of the reactions, the catalyst was easily separated using an external magnet, washed, and reused for multiple cycles with minimal loss of activity [43]. This work demonstrated that integrating a magnetic Fe_3O_4 core with a protective and functional silica shell effectively enhances nanoparticle dispersion, prevents agglomeration, improves catalytic performance, and enables simple magnetic recyclability for organic transformationsobservedScheme 1.



Scheme 1. Synthesis pf annulated pyrazole derivatives catalyzed by magnetically recoverable Fe_3O_4@Alg@CPTMS@Arg under reflux conditions

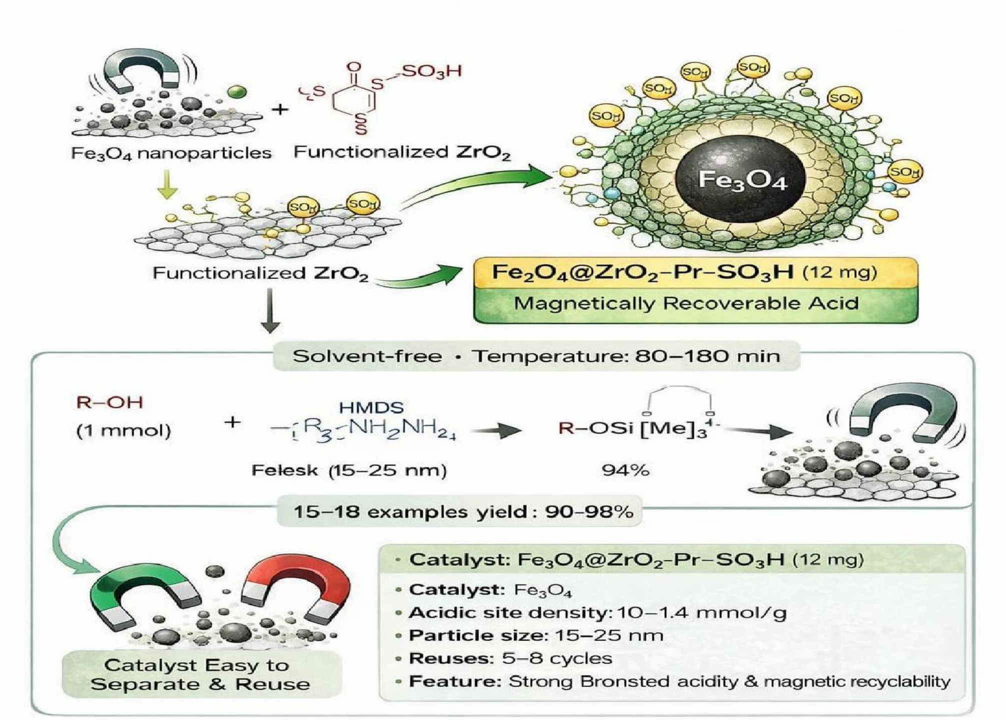
The magnetically recoverable Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$based nanocatalysts were reviewed by Polshettiwar et al. in 2011 [2, 21, 48]. In these systems, magnetic ferrite nanoparticles were first synthesized via co-precipitation or thermal decomposition to obtain strongly magnetic cores, which facilitate easy separation using an external magnet. The surfaces of these magnetic nanoparticles were then functionalized with acidic (-SO_3H) or basic (amine) groups to introduce catalytic active sites, thereby tuning the acidity or basicity required for multistep organic reactions. The -SO_3H-functionalized Fe_3O_4@SiO_2 catalysts exhibited strong acid site densities of approximately 1-1.5 mmol/g, enabling high product yields (90-99%) in esterification, multicomponent condensations, and hydration reactions. After completion of reactions, the catalysts could be rapidly recovered using an external magnet, washed, and reused for 6-10 cycles with minimal loss of activity [28-30]. This work demonstrated that combining a magnetic ferrite core with suitable functional groups provides efficient catalysis, easy magnetic separation, and high recyclability, thus minimizing chemical waste and improving sustainability in organic transformations as show inScheme 2



Scheme 2. Magnetically recoverable Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$based nano-catalysts with acidic ($-SO_3H$)or basic ($-NH_2$) groups.

The Fe_3O_4@rGO@CdS/Bi_2S_3 magnetic nanocomposite catalyst was synthesized by Naik and Thakur in 2023 [6]. In this system, Fe_3O_4nanoparticles were used as the magnetic core (40-70 emu/g) to enable rapid recovery, while reduced graphene oxide (rGO) provided high electron mobility and prevented nanoparticle aggregation. The CdS/Bi_2S_3 shell formed a visible-light-responsive heterojunction with a narrowed bandgap of approximately 1.6-2.2 eV, enhancing charge separation efficiency. The resulting nanocomposite, typically 10-25 nm in size with surface areas exceeding 60 m²/g, allowed strong adsorption of dye molecules. This photocatalyst was applied to the degradation of dyes and reduction of Cr(VI) under sunlight, achieving greater than 90% dye degradation within minutes. After the reactions, the catalyst could be easily separated using an external magnet, washed, and reused for 5-7 cycles with minimal loss of activity. This study demonstrated that combining a magnetic core with rGO-supported visible-light-active semiconductors produces a highly efficient, recyclable photocatalytic system for solar-driven pollutant removal.

The Fe_3O_4@ZrO_2-Pr-SO_3H magnetic nanocatalyst was developed by Tadjarodi in 2016 for acid-catalyzed organic transformations, particularly alcohol protection using HMDS [7, 28]. In this system, Fe_3O_4 nanoparticles served as the magnetic core (30-55 emu/g), enabling facile recovery, while a ZrO_2 shell provided chemical stability and prevented iron leaching. Propyl-sulfonic acid (-Pr-SO_3H) groups were grafted onto the surface to introduce strong Brønsted acidity (~1.0-1.4 mmol/g), allowing efficient activation of alcohol substrates [28]. The resulting nanoparticles, approximately 15-25 nm in size with surface areas of 70-120 m²/g, exhibited high catalytic activity, achieving product yields of 90-98% in short reaction times under solvent-free conditions. After reactions, the catalyst could be magnetically separated, washed, and reused for 5-8 cycles with minimal loss of activity. This study demonstrated that combining a magnetic core with a chemically stable zirconia shell and strong acid functionalization provides a robust, recyclable solid acid catalyst for green organic synthesis as depicted in Scheme 3



Scheme 3. Acid- catalyzed alcohol protection with HMDS catalyzed by magnetically recoverable Fe_3O_4@ZrO_2-Pr-SO_3H under solvent- free conditions.

The PTPSA@SiO_2-Fe_3O_4 magnetic nanocatalyst was developed by Karimi et al [8]in 2022, in which 3-(propylthio)propane-1-sulfonic acid (PTPSA) was immobilized on functionalized magnetic silica nanoparticles. Fe_3O_4 served as the magnetic core, allowing rapid separation, while the SiO_2 shell provided high surface area and abundant silanol groups for anchoring the sulfonic acid moieties. The nanoparticles, 10-20 nm in size, possessed acidic site densities of 1.1-1.6 mmol/g, creating a highly active heterogeneous acid system suitable for one-pot multicomponent reactions, particularly heterocycle synthesis. Under optimized conditions, the catalyst afforded high product yields of 90-98% within short reaction times. After reactions, it could be magnetically separated, washed, and reused for 6-9 cycles with minimal loss of activity. This work demonstrated that organically modified magnetic acid catalysts can combine strong Brønsted acidity with magnetic recyclability, outperforming traditional mineral acids in terms of efficiency, stability, and reusability [10, 37-38] shown Scheme4.

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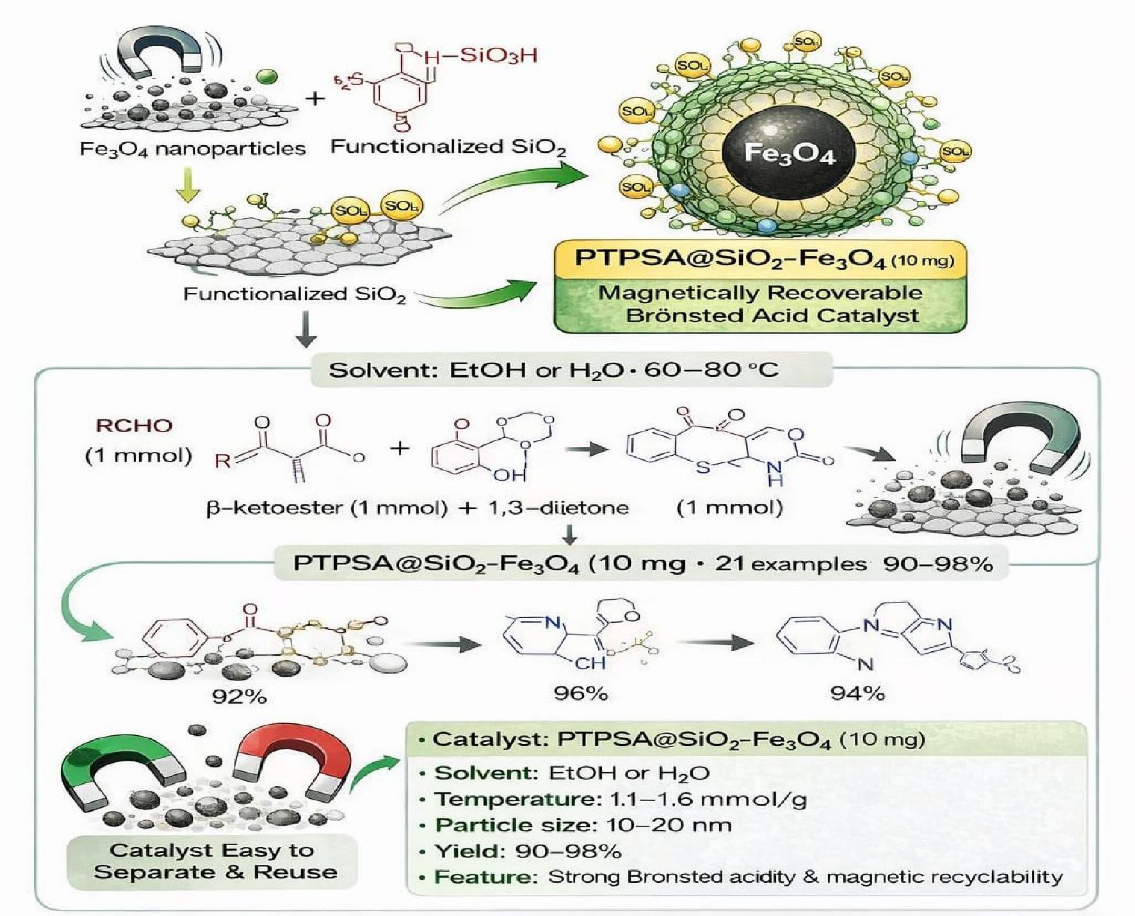
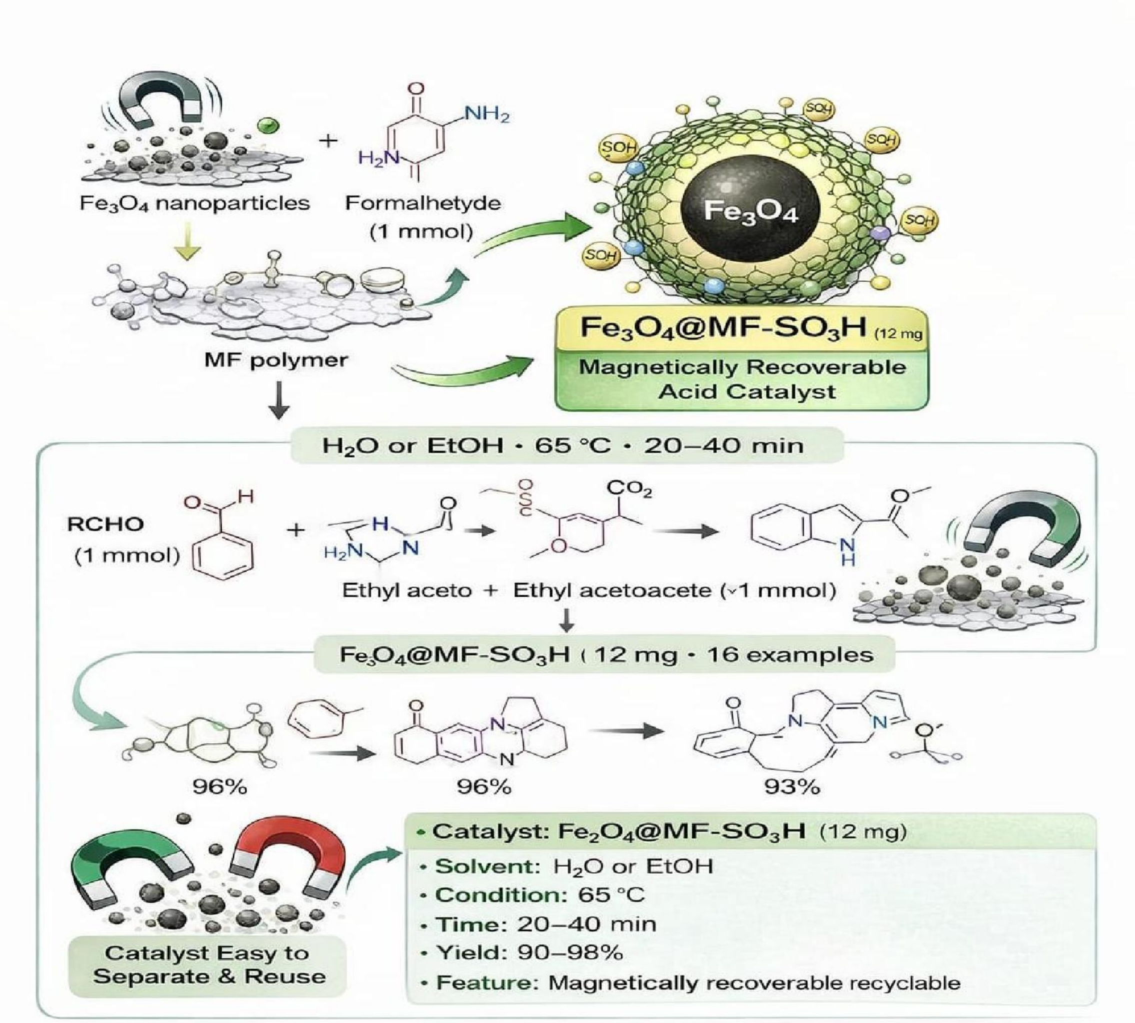


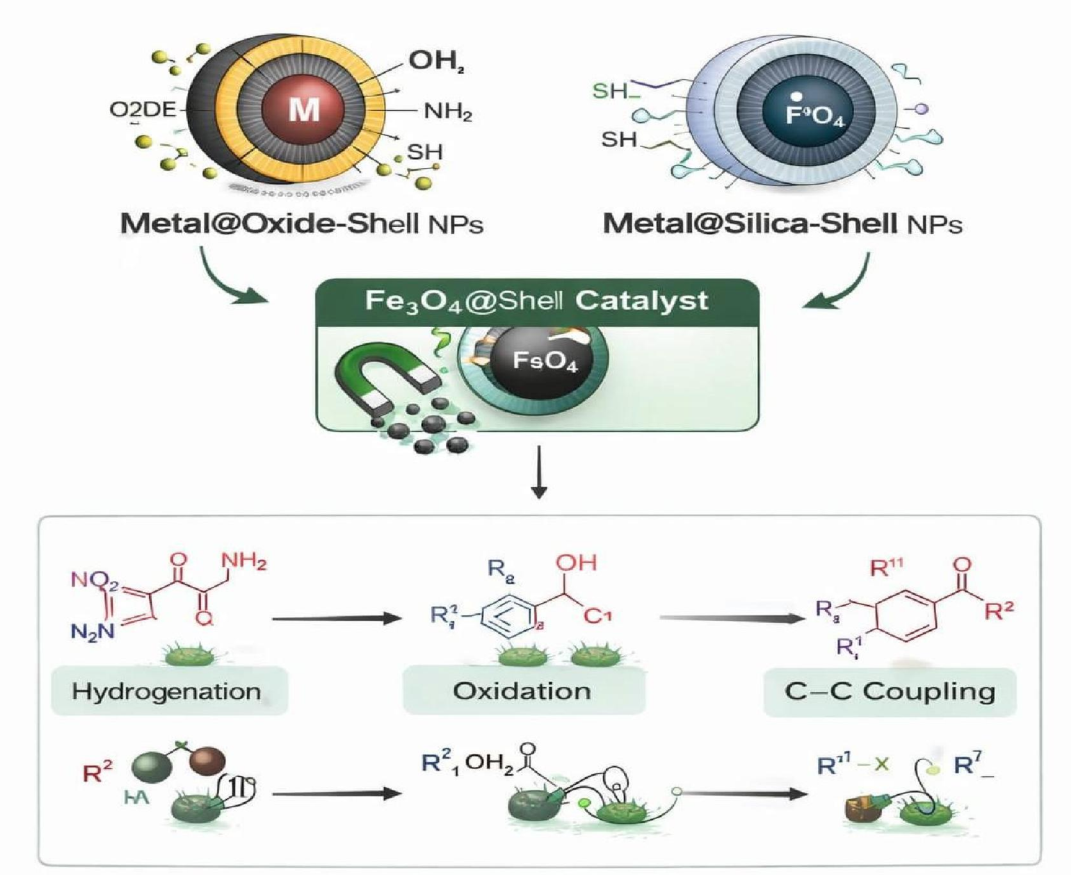
Scheme 4. One - pot multicomponent synthesis of heterocycles catalyzed by magnetically recoverable PTPSA@Fe_3O_4@SiO_2-SO_3H under optimized conditions

The Fe_3O_4@MF-SO_3H magnetic nanocatalyst was synthesized by Nezhad et al [10] in 2022 for the preparation of pyrazolone derivatives with antioxidant and antimicrobial activities. In this system, Fe_3O_4 nanoparticles served as the magnetic core (35-60 emu/g), coated with a melamine-formaldehyde (MF) polymer to introduce nitrogen functionalities and mechanical strength. Subsequent sulfonation generated strong acid sites (~1.2 mmol/g). The resulting nanoparticles, 15-30 nm in size with surface areas of 80-140 m²/g, exhibited high catalytic activity, affording pyrazolone yields of 90-98% under mild, green reaction conditions. After reactions, the catalyst could be magnetically recovered, washed, and reused for 6-8 cycles without significant loss of activity, acidity, or magnetization. This study demonstrated that magnetic sulfonated polymer resins can serve as highly efficient, eco-friendly, and recyclable solid acid catalysts for heterocyclic synthesis as shown in Scheme 5.



Scheme 5. Synthesis of Pyrazolone derivatives catalyzed by magnetically recoverable Fe_3O_4@MF-SO_3H under green conditions

Core-shell magnetic and catalytic nanocatalysts were reviewed by Gawande et al. in 2015, focusing on metal-core@oxide-shell and metal-core@silica-shell architectures [11]. These systems, with core diameters typically 5-30 nm and surface areas of 50-200 m²/g, were designed to combine electronic functionality with surface stability, protecting active metal cores from sintering and leaching while providing a chemically robust shell. When Fe_3O_4 was used as the magnetic core, saturation magnetization remained in the 30-70 emu/g range. The core-shell structures allowed selective surface functionalization for acid/base catalysis or metal nanoparticle deposition, enhancing turnover numbers, reaction selectivity, and catalytic efficiency. These catalysts were applied in hydrogenation, oxidation, and C-C coupling reactions, often achieving high yields (>85-95%) under optimized conditions. After reactions, the catalysts could be magnetically separated and reused, showing stable activity over 5-10 cycles. This review highlighted that core-shell designs effectively combine protection and accessibility of active sites, making them versatile and recyclable catalysts suitable for harsh or aqueous reaction conditions as observed in Scheme 6.



Scheme 6.

Core- shell magnetic and catalytic nano catalysts (e.g. Fe_3O_4@shell) for hydrogenation, oxidation and C-C coupling reaction.

III. RESULTS AND DISCUSSION

3.1. Structural and Morphological Features

The Fe_3O_4-based magnetic nanocatalysts synthesized across various studies consistently exhibited core-shell structures with particle sizes ranging from 8 to 30 nm, depending on the synthesis method and shell composition. For example, Yi, Lee, and Ying (2006) reported Fe_3O_4-SiO_2 core-shell nanoparticles of 8-20 nm, synthesized via co-precipitation followed by a Stöber process [1, 3, 11-14]. The silica shell ensured uniform particle dispersion and provided a functional surface for further chemical modification. Similarly, Naik and Thakur (2023) synthesized Fe_3O_4@rGO@CdS/Bi_2S_3 nanocomposites (10-25 nm), where reduced graphene oxide (rGO) enhanced electron mobility and prevented agglomeration. Tadjarodi (2016) demonstrated Fe_3O_4@ZrO_2 nanoparticles (15-25 nm) with a zirconia shell to stabilize the magnetic core and prevent iron leaching. Across studies, the presence of protective shells (SiO_2, ZrO_2, polymer, or rGO) was critical in maintaining structural integrity during catalytic reactions. Core-shell architectures not only protected the magnetic core but also increased surface area (typically 60-140 m^2/g) and provided sites for functionalization, crucial for catalytic activity [6-7].

3.2. Magnetic Properties and Recyclability

All reported systems exhibited strong magnetic behavior, enabling rapid magnetic separation post-reaction. Saturation magnetization values ranged from 30-70 emu/g, which facilitated easy recovery using an external magnet. For instance, Fe_3O_4 cores in the study by Yi, Lee, and Ying (2006) showed 40-70 emu/g, while Tadjarodi (2016) observed 30-55 emu/g for Fe_3O_4@ZrO_2. Magnetic recyclability was consistently demonstrated: catalysts could be reused for 5-10 cycles with minimal loss of activity, highlighting their potential for sustainable green chemistry applications [7-10, 48, 50]. The combination of a magnetic core with chemically stable shells ensures that the catalysts retain both activity and magnetization over multiple reaction cycles.

3.3. Surface Functionalization and Catalytic Activity

Surface modification played a crucial role in determining the catalytic efficiency. Functional groups such as -SO_3H, -Pr-SO_3H, and PTPSA were introduced to provide strong Brønsted acidity, while amine or nitrogen-containing polymers imparted basicity or specific reactivity. For example:

Fe_3O_4@SiO_2-SO_3H catalysts exhibited acid site densities of 1-1.5 mmol/g, enabling high yields (90-99%) in esterification and multicomponent reactions (Polshettiwar et al., 2011).

Fe_3O_4@MF-SO_3H polymer-coated nanoparticles (Nezhad et al., 2022) afforded 90-98% yields for pyrazolone derivatives under mild conditions.

PTPSA@SiO_2-Fe_3O_4 showed excellent performance in heterocycle synthesis with acid densities of 1.1-1.6 mmol/g and reusability over 6-9 cycles (Karimi et al., 2022).

Photocatalytic systems, such as Fe_3O_4@rGO@CdS/Bi_2S_3, demonstrated that combining magnetic cores with semiconductor shells can extend functionality to visible-light-driven reactions, achieving >90% dye degradation under sunlight (Naik and Thakur, 2023). Functionalization not only provides active catalytic sites but also allows fine-tuning of acidity, basicity, and light absorption properties, enabling application-specific optimization.

3.4. Catalytic Performance

Across all studies, the magnetic nanocatalysts exhibited high product yields (85-99%) under optimized reaction conditions, short reaction times, and mild environments [35, 40-43]. The key findings include:

Core-shell structures prevent agglomeration, ensuring high surface area and active site accessibility.

Acid-functionalized systems efficiently catalyze esterification, condensation, hydration, and heterocycle formation.

Photocatalytic systems achieve rapid degradation of organic pollutants using sunlight.

Magnetic recovery ensures minimal catalyst loss, with consistent activity over multiple cycles.

This demonstrates that magnetic core-shell nanocatalysts combine high catalytic efficiency, structural stability, and recyclability, making them ideal for green chemistry applications.

3.5. Comparative Discussion

Saturation Magnetization: Slight variations (30-70 emu/g) depend on core size, shell material, and synthesis method. Lower magnetization (30-55 emu/g) in Fe_3O_4@ZrO_2 is compensated by chemical stability.

Surface Area: Larger surface areas (>100 m^2/g) correlate with enhanced adsorption and catalytic activity, as seen in polymer- and rGO-based systems.

Functional Group Density: Higher acid site densities (1-1.6 mmol/g) lead to higher product yields and faster reactions.

Recyclability: 5-10 cycles are achievable without significant loss in activity, showing these catalysts outperform conventional homogeneous acids.

IV. CONCLUSION

In conclusion, Fe_3O_4-based magnetic core-shell nanocatalysts represent a highly efficient, versatile, and recyclable class of heterogeneous catalysts for diverse organic transformations. The core-shell design, utilizing silica, zirconia, polymer, or rGO shells, protects the magnetic Fe_3O_4 core from aggregation and leaching while providing a high-surface-area platform for functionalization with acidic or nitrogen-containing groups. These catalysts exhibit strong magnetic properties (30-70 emu/g), enabling rapid separation using an external magnet and allowing reuse over 5-10 cycles with minimal loss of activity, thereby supporting sustainable and green chemistry practices. Surface functionalization enhances catalytic performance, achieving high product yields (85-99%) under mild and environmentally friendly conditions, while photocatalytic variants extend their utility to solar-driven pollutant degradation. Their broad applicability spans esterification, multicomponent condensations, heterocycle synthesis, alcohol protection, pyrazolone preparation, hydrogenation, and dye degradation, demonstrating both synthetic and environmental significance. Overall, these studies confirm that Fe_3O_4-based magnetic core-shell nanocatalysts combine structural stability, high catalytic efficiency, and magnetic recyclability, making them robust, eco-friendly, and promising candidates for modern catalytic applications.

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