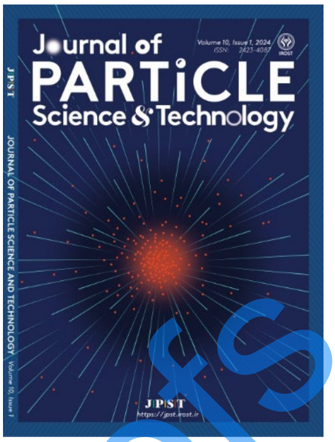

Engineered magnetic nanoparticles as recyclable Brønsted acid catalysts: Advances in particle design and applications in organic transformations

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Engineered magnetic nanoparticles as recyclable Brønsted acid catalysts: Advances in particle design and applications in organic transformations

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Abstract

The development of functionalized magnetic nanoparticles (MNPs) as heterogeneous catalysts represents a significant advancement in sustainable chemical synthesis. Among these, MNPs functionalized with Brønsted acid groups, particularly sulfonic acids, phosphonic acids, and acidic ionic liquids, have emerged as a versatile class of catalysts that combine the efficiency of homogeneous acids with the practical benefits of magnetic recoverability. These systems address critical challenges in traditional acid catalysis, including catalyst separation, waste generation, and energy-intensive recovery processes. By leveraging the unique properties of magnetic cores (e.g., Fe_3O_4, $CoFe_2O_4$) and tailored acid-functionalized shells, researchers have created robust catalytic platforms applicable to diverse organic transformations, from biomass valorization to pharmaceutical synthesis. This review aims to provide a comprehensive overview of recent developments in the synthesis, characterization, and catalytic applications of magnetic nanoparticles functionalized with Brønsted acid groups.

Keywords: Magnetic nanocatalysts; Brønsted acid catalysis; Sustainable chemistry; Heterogeneous acid-catalysis; Nanoparticles engineering

1. Introduction

The advancement of catalytic technologies plays a pivotal role in enabling sustainable chemical processes, particularly in the context of organic synthesis. Among this, Brønsted acid catalysis plays a pivotal role in modern organic synthesis, enabling the efficient and selective formation of carbon–heteroatom and carbon–carbon bonds [1]. As one of the most fundamental and versatile catalytic strategies, Brønsted acids (e.g., sulfuric acid, sulfonic acids, and acidic ionic liquids) facilitate a wide array of transformations, including esterification, hydrolysis, condensation, and rearrangement reactions. Their ability to protonate substrates, stabilize intermediates, and lower activation barriers makes them indispensable in both laboratory and industrial settings. The significance of Brønsted acid catalysis extends across multiple domains, from pharmaceuticals and agrochemicals to materials science and renewable energy [2]. For instance, acid-catalyzed esterification and transesterification are critical for biodiesel production, while Friedel–Crafts alkylations and acylations are key steps in fine chemical synthesis [3]. Additionally, Brønsted acids drive the conversion of biomass-derived platform molecules (e.g., 5-HMF, levulinic acid) into value-added chemicals, supporting sustainable biorefinery processes [4].

The application of homogeneous Brønsted acids such as sulfuric acid, *p*-toluenesulfonic acid, and trifluoroacetic acid has historically been favored due to their strong acidity, excellent solubility in organic media, and predictable reactivity profiles. However, their use is increasingly associated with critical drawbacks: corrosiveness, non-recyclability, tedious neutralization and product purification steps, and significant generation of acidic wastewater. These limitations not only reduce process efficiency but also raise serious concerns related to cost, safety, and regulatory compliance in industrial-scale operations. In contrast, *heterogenized acid catalysts* offer the potential for reusability, ease of separation, and minimal environmental footprint [5]. However, classical solid acid catalysts such as zeolites, silica-supported acids, and acidic resins often suffer from low surface accessibility, diffusion limitations, and irreversible deactivation during harsh reaction conditions. Moreover, the physical separation of such catalysts from complex reaction matrices typically requires filtration, centrifugation, or other energy-intensive methods that limit their practical utility.

To overcome these hurdles, magnetic nanoparticles functionalized with Brønsted acid groups have been engineered to integrate magnetic responsiveness, nanoscale dispersion, and acid functionality in a single platform. These materials, typically composed of iron oxide (Fe_3O_4 or γ-Fe_2O_3) cores, are coated or grafted with acidic organic or inorganic moieties (e.g., sulfonic acids, phosphonic acids, or carboxylic acids) to yield catalysts that are not only chemically robust and catalytically efficient, but also magnetically separable. This unique combination enables rapid and clean separation of the catalyst from the reaction mixture by simply applying an external magnetic field, eliminating the need for filtration or centrifugation, and preserving the integrity and reusability of the catalyst over multiple reaction cycles. Quantitative performance assessments reveal that these engineered systems often achieve yields exceeding 90% in key reactions like esterification and acetalization, rivaling their homogeneous counterparts, while demonstrating exceptional recyclability with minimal activity loss over dozens of cycles. These systems have demonstrated remarkable catalytic efficiency in a wide range of organic transformations, including but not limited to esterification, alkylation, acetalization, multicomponent reactions, and biomass valorization [6]. In many cases, these magnetic acid catalysts offer comparable or even superior activity to their homogeneous counterparts, while simultaneously enhancing sustainability and process economy. Additionally, the high surface area and functional tunability of MNPs allow for the design of task-specific catalysts that can be tailored to address mechanistic and kinetic requirements of specific transformations [7]. Beyond organic synthesis, the relevance of these functionalized nanomaterials spans several interdisciplinary domains such as biofuel production from renewable feedstocks, environmental remediation, pharmaceutical intermediate synthesis, green oxidation processes, and nanobiocatalysis. Their applications have grown in tandem with advances in materials science, surface engineering, and nanofabrication, opening new avenues for the development of intelligent, responsive, and multi-functional catalytic platforms.

This review aims to provide a comprehensive overview of recent developments in the synthesis, characterization, and catalytic applications of magnetic nanoparticles functionalized with Brønsted acid groups. First, we systematically examine synthetic strategies for surface functionalization with acid groups, including covalent grafting, polymer coating, and *in situ* incorporation of acidic moieties during nanoparticle synthesis. These methods are critically evaluated for their efficiency in controlling acid site density, stability, and accessibility. Second, we discuss advanced physicochemical characterization of nanocatalysts, highlighting techniques for acid site quantification, magnetic hysteresis measurements for recovery assessment, and porosimetry for textural analysis. These tools are essential for establishing structure–function relationships. Third, we analyze catalytic performance in key classes of organic transformations, including synthesis of heterocyclic compounds, biodiesel production, esterification, hydrolysis of cellulose and related compounds, 5-HMF production, acetalization and de-acetalization and Biginelli reaction. Case studies illustrate how acid strength, nanoparticle morphology, and support interactions influence activity and selectivity. Fourth, we evaluate recyclability, scalability, and environmental impact, emphasizing metrics like number of recycling, leaching resistance, and life-cycle analysis. Industrial scalability is assessed through continuous-flow applications and solvent-free protocols. Fifth, we present mechanistic insights and structure–activity correlations, linking catalyst design (e.g., core–shell architecture, acid group distribution) to reaction pathways. Spectroscopic and computational studies, if any, are highlighted to elucidate active-site dynamics. Finally, we address current limitations and future directions, such as stability under harsh conditions, cost-effective synthesis, and integration with circular economy principles. Through this synthesis, we seek to highlight both the transformative potential and the current bottlenecks of Brønsted acid-functionalized magnetic nanocatalysts, and to identify strategic opportunities for advancing the field toward industrially relevant and environmentally sustainable catalysis. By bridging fundamental research with practical applications, this review aims to inspire innovations in nanoparticle design, reactor engineering, and process optimization to unlock the full potential of these hybrid catalytic systems.

2. Application of magnetic nanoparticles as recyclable Brønsted acid catalysts

2.1. Synthesis of heterocyclic compounds

Brønsted acid-functionalized magnetic nanoparticles have emerged as versatile catalysts for the efficient synthesis of heterocyclic compounds, combining high activity with facile separation. These catalysts leverage tunable surface acidity and hydrophobicity to optimize reactivity and selectivity across diverse multicomponent reactions (MCRs).

Mobaraki *et al.* developed a hydrophobic magnetic nanocatalyst (Fe_3O_4@SiO_2@Me&Et-$PhSO_3H$) for efficient α-aminonitrile synthesis via a solvent-free Strecker reaction. The catalyst combined a silica-coated magnetite core with surface-bound methyl/ethyl phenyl sulfonic acid groups (0.78 mmol H^+/g), achieving >90% yield in the three-component condensation of aldehydes/ketones, amines, and TMSCN at 60°C (Fig. 1). The hydrophobic methyl groups prevented water-induced deactivation of acidic sites while enhancing substrate diffusion, resulting in a 3-fold rate increase over non-methylated analogues. The catalyst maintained 95% activity over 6 cycles, attributed to stable Si-O-C covalent bonding. The system was successfully applied to pharmaceutical precursors like N-benzyl-α-aminonitriles and sterically hindered dialkyl derivatives (85–88% yield). This work established critical design principles for magnetic Brønsted acid catalysts, emphasizing hydrophobic/hydrophilic balance and core-shell stability, and inspired later developments in sustainable heterocyclic synthesis [8].

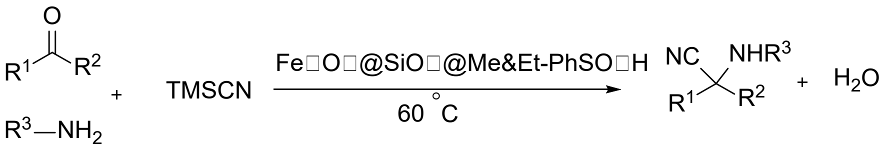

Fig. 1. Fe_3O_4@SiO_2@Me&Et-$PhSO_3H$ catalyst for α-aminonitrile synthesis.

Koukabi *et al.* developed a magnetically separable sulfonic acid catalyst through direct functionalization of magnetic particles (MPs) using chlorosulfonic acid (γ-Fe_2O_3-SO_3H). The catalyst was prepared via a rapid, room-temperature immobilization technique that achieved high functional group density while maintaining low production costs. The catalyst exhibited exceptional performance in Hantzsch reactions, synthesizing 1,4-dihydropyridines in 90-98% yields under solvent-free conditions (Fig. 2). The study highlighted how surface-engineered MPs combine homogeneous-like activity (TOF=32 h^{-1}) with heterogeneous recoverability, addressing longstanding challenges in catalyst recycling. The system demonstrated broad substrate scope, including electron-rich and sterically hindered aldehydes, with no observed leaching of acidic sites [9].

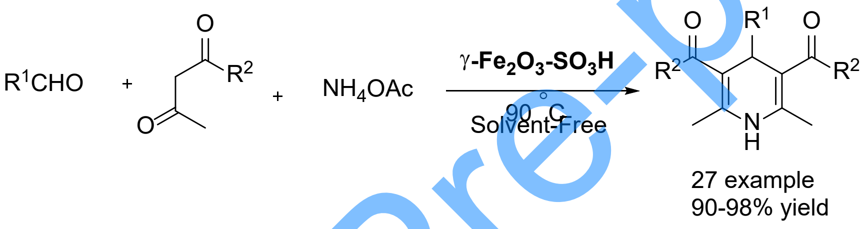

Fig. 2. γ-Fe_2O_3-SO_3H catalyst for Hantzsch reaction.

Kabiri Esfahani *et al.* developed a propylsulfonic acid-functionalized magnetic nanocatalyst (Fe_3O_4@SiO_2-$PrSO_3H$) for efficient β-amino carbonyl synthesis via three-component Mannich reactions. The catalyst was prepared through covalent anchoring of sulfonic groups to silica-coated nanoparticles using low-cost precursors. Under solvent-free conditions at room temperature, it achieved excellent yields of β-amino carbonyl compounds with broad substrate compatibility. The system demonstrated remarkable recyclability, maintaining consistent activity over 10 consecutive cycles with simple magnetic recovery. This work established an environmentally benign protocol for C-C bond formation, combining homogeneous-like efficiency with heterogeneous recoverability, particularly valuable for pharmaceutical intermediate synthesis [10]. In a separate study, the same catalyst exhibited exceptional performance in solvent-free Pechmann condensations, converting phenols and ethyl acetoacetate to coumarins at 130°C with >90% yields with 22-cycle reusability.

The system showed broad substrate scope, including electron-withdrawing substituted phenols typically challenging in coumarin synthesis. This work established a sustainable platform for oxygen heterocycle synthesis (Fig. 3) [11].

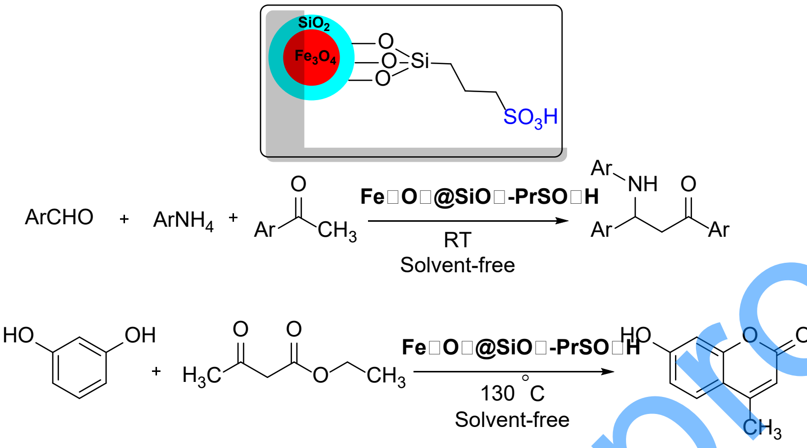

Fig. 3. $Fe_3O_4@SiO_2$-$PrSO_3H$ catalyst for Mannich and Pechmann reactions.

Awasthi and co-workers developed a magnetically recoverable cobalt ferrite nanocatalyst (CFNP@SO_3H) for efficient synthesis of 2-substituted benzimidazoles. The catalyst, characterized by FT-IR, XRD, and TEM (particle size: 12-18 nm), demonstrated exceptional activity in condensations of *o*-phenylenediamine with diverse aldehydes in ethanol, achieving up to 98% yields within 10-30 min at ambient conditions with low catalyst loading (1.5 mol%). The system exhibited broad functional group tolerance (aromatic, aliphatic, heterocyclic substrates) and maintained full activity over 7 cycles (Fig. 4) [12].

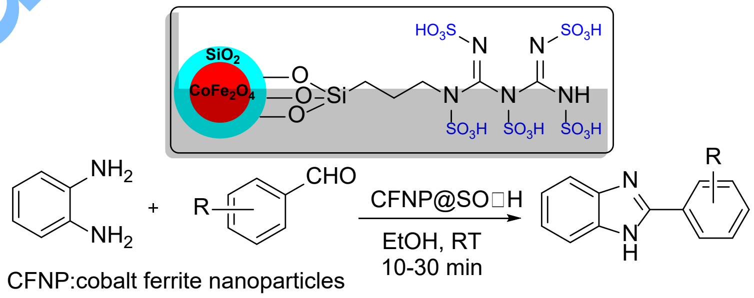

Fig. 4. CFNP@SO_3H catalyst for synthesis of 2-substituted benzimidazoles.

A recent work developed a relatively same nanocatalyst, just using magnetite core instead of cobalt ferrite, for sustainable synthesis of bioactive 2-substituted benzimidazoles and bis(indole)methanes. Comprehensive characterization confirmed successful sulfonic acid functionalization with strong magnetization (23 emu/g). The catalyst demonstrated exceptional performance in ethanol solvent, achieving >90% yields within 15-30 min under ambient conditions for both reaction types. Key advantages included broad substrate scope (30+ examples), low catalyst loading (2 mol%), rapid magnetic recovery (<1 min), and consistent activity over 6 cycles (<5% yield reduction). The system showed particular effectiveness for electron-deficient substrates, overcoming limitations of conventional acid catalysts. The bifunctional design (acidic -SO_3H and basic -NH_2 sites) enabled sequential transformations without intermediate purification. This work expands the toolbox of magnetically recoverable acidic catalysts for pharmaceutical building block synthesis [13].

Jahanbakhshi *et al*. developed a sustainable hybrid catalyst by immobilizing a sulfonic acid-functionalized ionic liquid (1-(propyl-3-sulfonate)vinyl imidazolium hydrogen sulfate) on magnetic cellulose (Fe_3O_4/MPC[IL], Fig. 5). Characterization revealed a mesoporous structure (surface area: 115 m^2/g) with strong magnetization (34 emu/g). The catalyst exhibited "quasi-homogeneous" behavior in one-pot synthesis of triazolo[4,3-a]pyrimidines from ethyl cyanoacetate, aminotriazole, and aldehydes, achieving 85-92% yields in water under mild conditions (50°C, 40-60 min). Using biocompatible cellulose support, low catalyst loading (3 mol%) and consistent performance over 6 cycles (5% activity loss) are the key advantages of this work. The system also showed exceptional functional group tolerance (28 substrates), including sensitive heteroaromatic aldehydes. The flexible imidazolium linker enhanced substrate accessibility while maintaining ionic liquid catalytic efficiency [14].

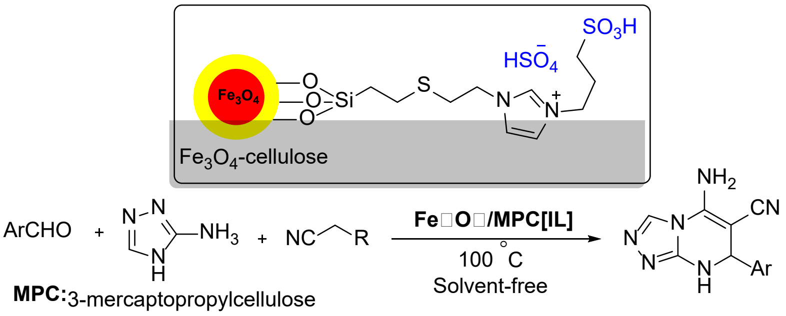

Fig. 5. Fe_3O_4/MPC[IL] catalyst for one-pot synthesis of triazolo[4,3-a]pyrimidines.

For the first time, researchers developed a sulfonated magnetic polyvinyl alcohol (Fe_3O_4@PVA-SO_3H) nanocomposite film for efficient dihydropyrimidine synthesis (Fig. 6). The catalyst was prepared via in situ precipitation and characterized by FE-SEM (particle size: 20-50 nm), BET (surface area: 68 m²/g), and VSM (magnetization: 39 emu/g). The system demonstrated excellent catalytic activity in the multi-component reaction of aldehydes, β-ketoesters, and urea/thiourea, achieving 85-94% yields under mild conditions (80°C, 1-2 h). The flexible PVA matrix prevented nanoparticle aggregation while maintaining acid site accessibility. This work presents a novel, sustainable approach to pharmaceutical building block synthesis using polymeric magnetic nanocomposites [15].

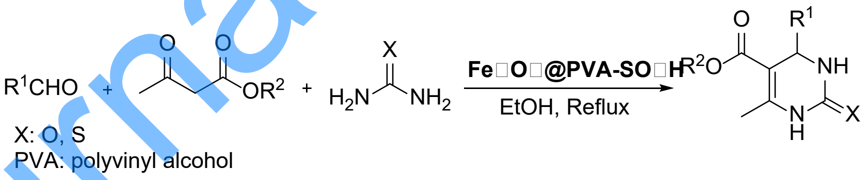

Fig. 6. Fe_3O_4@PVA-SO_3H nanocomposite for dihydropyrimidine synthesis.

Rostamizadeh *et al*. developed a novel bifunctional catalyst by grafting dual acidic ionic liquid (3-sulfobutyl-1-(3-propyltrimethoxysilane)imidazolium hydrogen sulfate) onto α-Fe_2O_3–MCM-41. Characterization revealed uniform mesochannels (3.8 nm pore size) with strong magnetization (28 emu/g). The hybrid material synergistically combined Brønsted (-SO_3H, 1.4 mmol/g) and Lewis (Fe^{3+}) acid sites, enabling efficient one-pot synthesis of pyrimido[4,5-d]pyrimidines from 6-

aminouracil, aldehydes, and urea/thiourea under solvent-free conditions (85-94% yields, 120°C). The high activity of the catalyst was attributed to the confined ionic environments in pores, cooperative acid activation, and enhanced mass transfer. This work pioneered the design of magnetically recoverable, dual-acid catalysts for N-heterocycle synthesis [16] (Fig. 7).

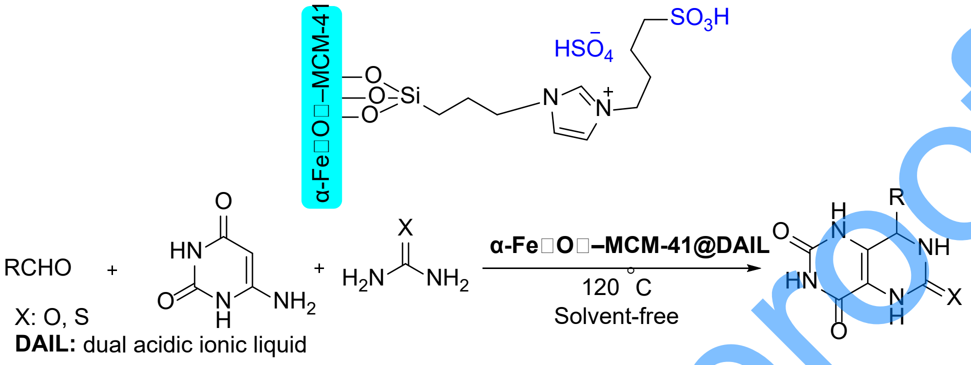

Fig. 7. α-Fe_2O_3–MCM-41@DAIL catalyst for one-pot synthesis of pyrimido[4,5-d]pyrimidines.

In 2022, Researchers developed a magnetic sulfonated melamine-formaldehyde resin (MSMF) by combining Fe_3O_4 nanoparticles with sulfonated polymer. Characterization revealed amorphous 40 nm particles with enhanced thermal stability (>300°C) and magnetization (32 emu/g). The catalyst efficiently promoted one-pot syntheses of: (1) benzyl pyrazolyl naphthoquinones (95% yield, 40 min, 50°C in water) and (2) indolyl-pyrazolones (87% yield, 80 min, 30°C in ethanol). The products exhibited notable bioactivity: 90% antioxidant capacity (DPPH assay) and antimicrobial effects against S. aureus (12 mm inhibition zone) [17].

In 2013, a core-shell magnetic catalyst (Fe_3O_4@γ-Fe_2O_3-SO_3H) was developed for efficient pyrrole synthesis. Characterization (TEM, XRD) revealed uniform 12-15 nm nanoparticles with a maghemite coating (shell thickness: 2-3 nm) and high magnetization (48 emu/g). The sulfonic acid-functionalized catalyst demonstrated excellent activity in pyrrole formation, benefiting from high surface area (125 m²/g), strong acidity (1.2 mmol H^+/g), and superparamagnetic properties. The system achieved >90% yields under mild conditions with: 9-cycle reusability and simple product purification. The protective maghemite layer prevented core corrosion while maintaining acid site accessibility [18].

A sulfonated poly(vinyl alcohol)-$CuFe_2O_4$ nanocomposite (SCPVA@$CuFe_2O_4$) was developed through crosslinking and sulfonation, creating a bifunctional catalyst (20-200 nm particles, 38 emu/g magnetization). The system demonstrated dual catalytic efficiency in: (1) imidazole synthesis (95% yield, 40 min, 80°C in ethanol) and (2) amino naphthoquinone formation (94% yield, 20 min, EtOH/H_2O). Key features included: (1) 5-cycle reusability with <8% activity loss, (2) rapid magnetic separation (<1 min), and (3) generation of bioactive products showing: 92% antioxidant activity (DPPH), 12 mm inhibition zones against S. aureus and Selective cytotoxicity against MCF-7 breast cancer cells (MTT assay). The crosslinked PVA matrix enhanced acid site stability while preventing nanoparticle aggregation. This work bridges nanocatalysis and medicinal chemistry by combining efficient heterocycle synthesis and direct production of therapeutic candidates through sustainable catalysis [19].

A sulfonated polyvinylamine (PVAm)-Fe_3O_4 nanocomposite was developed through in situ polymerization and Hofmann degradation, creating a high-loading acid catalyst (1.8 mmol H^+/g) without organosilane linkers. Characterization (TEM, TGA) confirmed uniform polymer grafting (25-40 nm particles) with excellent thermal stability (>280°C) and magnetization (41 emu/g). The catalyst demonstrated remarkable efficiency in solvent-free synthesis of 2,4,5-trisubstituted imidazoles (94% yield, 30 min) and 1,2,4,5-tetrasubstituted imidazoles (91% yield, 45 min). 8-cycle reusability (<5% activity loss), rapid magnetic separation, high functional group tolerance (28 substrates) and avoidance of toxic solvents/silanes are of key advantages of this work. The PVAm linker provided higher acid loading than conventional methods while preventing nanoparticle aggregation [20].

A breakthrough magnetic nanocatalyst was developed by functionalizing Fe_3O_4 nanoparticles with melamine-derived sulfonic acid groups, achieving a record acid density of 6.6 mmol H^+/g - the highest reported value for magnetic SO_3H catalysts. Through comprehensive characterization including FESEM, EDX, and VSM, the catalyst was shown to consist of uniform 15-20 nm particles with excellent thermal stability (>300°C) and strong magnetization (37 emu/g). The system demonstrated remarkable efficiency in the solvent-free, four-component synthesis of hexahydroquinolines from dimedone, aldehydes, ethyl acetoacetate, and ammonium acetate. Using design of experiments methodology, optimal conditions were established at 65°C with 0.04 g catalyst, achieving 92-97% yields in just 15-30 minutes (Fig. 8). The catalyst's unprecedented acidity enabled efficient conversion of sterically hindered substrates, including *ortho*-substituted aldehydes (85-90% yields). Practical advantages included simple magnetic recovery, eight reuses without significant activity loss, and avoidance of toxic metals or solvents. This work represents a significant advancement in high-density acid catalyst design for multicomponent heterocycle synthesis [21].

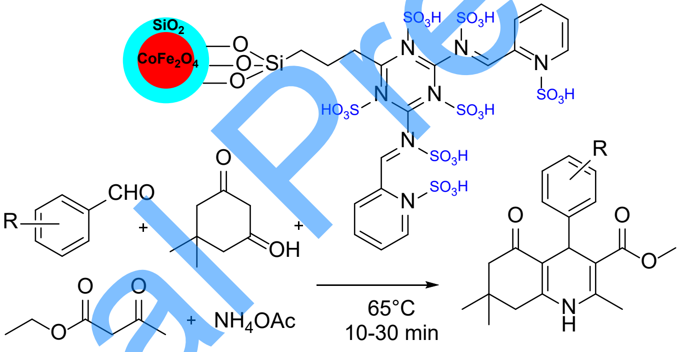

Fig. 8. magnetic melamine-derived sulfonic acid catalyst for synthesis of hexahydroquinolines.

A novel magnetic nanocatalyst (Fe_3O_4@Hal-Glu-SO_3H-IL) was developed through the functionalization of halloysite nanoclay with glutamine and sulfonic acid-containing ionic liquid. Comprehensive characterization confirmed the successful integration of components, revealing a nanocomposite with excellent thermal stability and magnetic properties (saturation magnetization of 32 emu/g). The catalyst demonstrated remarkable efficiency in the multicomponent synthesis of 4H-pyran derivatives, achieving 96% yield in water under reflux conditions within just 20 minutes using only 0.02 g of catalyst. The hybrid catalyst maintained consistent performance over six consecutive cycles with minimal activity loss, demonstrating excellent recyclability. The combination of halloysite's natural tubular structure with engineered functional groups created a robust catalytic system that synergistically enhanced both activity and stability [22].

A covalently sulfonated magnetic graphene oxide nanocomposite (Fe_3O_4@GO-Pr-SO_3H) was successfully developed through a multistep synthesis approach. The catalyst was prepared by first depositing Fe_3O_4 nanoparticles (8-12 nm) onto graphene oxide sheets via co-precipitation, followed by covalent grafting of propyl sulfonic acid groups. The hybrid material exhibited exceptional performance in three-component condensations of aromatic aldehydes, phthalhydrazide, and dimedone, achieving >90% yields within 2-3.5h under mild conditions (Fig. 9). Remarkably, the catalyst maintained full activity over 11 consecutive cycles, attributable to the robust covalent anchoring of functional groups. The system combined the advantages of graphene's high surface area (420 m^2/g), strong Brønsted acidity, and superparamagnetic properties (45 emu/g) for rapid separation. This work represents a significant advancement in designing stable, multifunctional carbon-based magnetic acid catalysts for complex heterocycle synthesis [23].

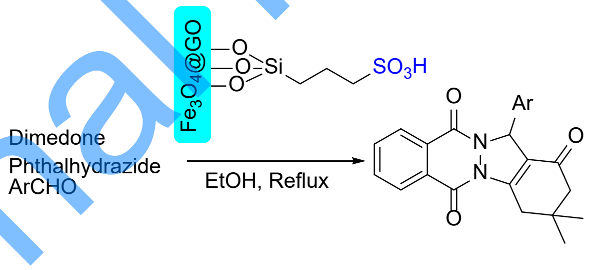

Fig. 9. Fe_3O_4@GO-Pr-SO_3H catalyst for three-component reaction of aromatic aldehydes, phthalhydrazide, and dimedone.

A core-shell magnetic nanocatalyst (Fe_3O_4@Ph-SO_3H) was successfully prepared through surface modification of magnetite nanoparticles with 1,4-bis(triethoxysilyl)benzene followed by aromatic ring sulfonation. The catalyst demonstrated remarkable efficiency in the ultrasound-assisted synthesis of tetrahydrobenzo[b]pyrans in aqueous media at room temperature, achieving yields of 90-96% within 15-30 minutes. The phenylsulfonic acid groups (1.2 mmol/g) provided enhanced lipophilicity that improved substrate diffusion while maintaining strong Brønsted acidity. The system exhibited exceptional recyclability, maintaining >95% of its initial activity after nine consecutive cycles with simple magnetic recovery [24].

A new class of magnetically recoverable Bronsted acidic ionic liquid (BAIL) catalysts was developed through the non-covalent immobilization of organosulfonate salts on Fe_3O_4@SiO_2-SO_3H nanoparticles. Two BAILs were synthesized from N-methylimidazole and 1-benzyl-4-phenyl-1H-1,2,3-triazole with 1,4-butanesultone, then supported on the magnetic carrier. The catalysts demonstrated exceptional performance in synthesizing pyrazolo[*b*]phthalazine diones and indazolo[*b*]phthalazine triones, achieving yields of 88-94% within 20-40 minutes. The non-covalent immobilization preserved the ionic liquid's flexibility while enabling simple magnetic recovery and 7-cycle reusability [25].

A novel bifunctional magnetic catalyst was developed through sequential modification of $NiFe_2O_4$@MCM-41 with phosphotungstic acid (PWA) and sulfate groups. Characterizations confirmed the inverse-cubic spinel structure ($NiFe_2O_4$ core) with excellent magnetic properties (45 emu/g) and uniform PWA/SO_4^{2-} dispersion within the mesopores (3.9 nm diameter). The dual-acid system demonstrated exceptional catalytic performance, achieving 93.9% yield for dibenzoxanthenes and 78.3% for 7-hydroxy-4-methylcoumarin under optimized conditions. The sulfate modification enhanced both acidity and activity compared to PWA alone, attributed to synergistic effects between Brønsted (SO_4^{2-}/PWA) and Lewis (Ni^{2+}/Fe^{3+}) acid sites. The catalyst exhibited remarkable stability over multiple cycles (>90% activity retention) with simple magnetic recovery [26].

A highly efficient magnetic nanocatalyst (Fe_3O_4@SiO_2-S-$BuSO_3H$) was developed for ultrasound-assisted benzothiazole synthesis, achieving exceptional yields (90-98%) in remarkably short reaction times (3-11 minutes). Characterization by FE-SEM, EDX, and VSM confirmed the successful functionalization of silica-coated magnetite nanoparticles (12-15 nm) with butyl sulfonic acid groups (1.4 mmol/g), exhibiting strong magnetization (38 emu/g) for rapid separation. The catalyst demonstrated outstanding performance in the condensation of o-aminothiophenol with diverse aldehydes under ultrasonic irradiation, with the combined Brønsted acidity and ultrasonic activation reducing reaction times (Fig. 10). The system maintained consistent activity over multiple cycles (>95% yield after 5 runs) with simple magnetic recovery. This work establishes a sustainable platform for sulfur heterocycle synthesis, combining the benefits of magnetic nanocatalysis with green process intensification through ultrasound, particularly valuable for pharmaceutical applications requiring rapid, scalable synthetic methods [27].

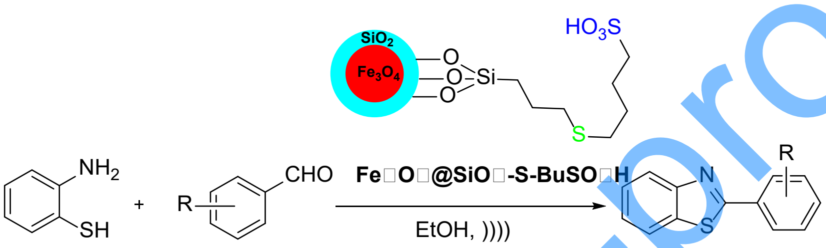

Fig. 10. $Fe_3O_4@SiO_2$-S-$BuSO_3H$ nanocatalyst for ultrasound-assisted benzothiazole synthesis.

A sulfonated polyvinyl alcohol-coated magnetic nanocatalyst ($Fe_3O_4@PVA$-SO_3H) was developed for efficient synthesis of 2,4,5-triarylimidazoles. The nanocomposite was prepared through in-situ synthesis and subsequent sulfonation, yielding spherical nanoparticles (23.5 nm average diameter) with strong acidity and superparamagnetic properties (42 emu/g). The catalyst demonstrated remarkable efficiency in one-pot, three-component condensations of ammonium acetate, benzyl/benzoin, and aromatic aldehydes, achieving 99% yield for 4-hydroxybenzaldehyde derivatives in ethanol under reflux. The system exhibited broad substrate compatibility and maintained consistent performance over 10 catalytic cycles. The robust PVA matrix prevented nanoparticle aggregation while providing abundant anchoring sites for sulfonic acid groups [28].

A sulfonic acid-functionalized nickel ferrite nanocatalyst ($NiFe_2O_4@SiO_2@SO_3H$) was developed for sustainable Hantzsch synthesis of 1,4-dihydropyridines. The catalyst demonstrated excellent performance in aqueous-phase reactions at 70°C, achieving >90% yields within 10-100 minutes for both ethyl acetoacetate and 4-hydroxycoumarin derivatives. The system showed remarkable versatility, accommodating diverse aromatic aldehydes including electron-withdrawing (NO_2, Cl) and electron-donating (OH, OMe) substituents with equal efficiency. Environmentally benign features included using water as sole solvent and 7-cycle reusability with <5% activity loss. The robust silica layer prevented nickel leaching while maintaining excellent acid site accessibility [29].

A novel photo-switchable magnetic catalyst was developed by functionalizing carbon quantum dots with both Fe_3O_4 nanoparticles and high-density sulfonic acid groups (9.6 mmol/g). Characterization (TEM, XPS, VSM) revealed 3-5 nm quantum dots with strong magnetization (28 emu/g) and unique photo-responsive properties. Under light irradiation, the catalyst exhibited enhanced proton generation through photoexcited charge separation, enabling efficient room-temperature synthesis of hexahydroquinolines (85-92% yields) via one-pot multicomponent reactions. The system demonstrated remarkable "on/off" switching capability, with reaction rates increasing under visible light compared to dark conditions. Comparative studies showed the sulfonated version outperformed non-sulfonated analogs by 40% in yield, highlighting the crucial role of Brønsted acidity. This work pioneers the development of stimuli-responsive nanocatalysts that combine magnetic separation with photo-modulated activity, offering new possibilities for sustainable organic synthesis controlled by external triggers [30].

A magnetic ionic liquid nanocatalyst ([HSO_3PMIM]OTf-SiO_2@MNPs) was developed by immobilizing 1-methyl-3-(propyl-3-sulfonic acid)imidazolium triflate on silica-coated Fe_3O_4 nanoparticles. The hybrid catalyst demonstrated excellent performance in both thermal and microwave-assisted synthesis of isobenzofuranones, achieving >90% yields under solvent-free conditions (Fig. 11). Microwave conditions reduced reaction times by 80% compared to thermal methods while maintaining excellent yields. The bifunctional nature of the catalyst (acidic -SO_3H and ionic liquid moieties) facilitated efficient activation of substrates [31].

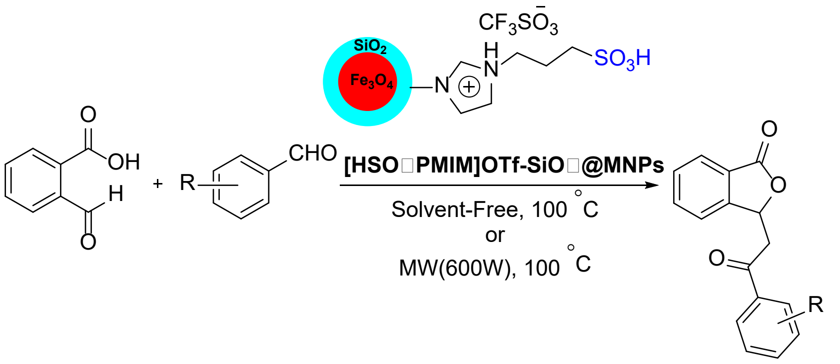

Fig. 11. [HSO$_3$PMIM]OTf-SiO$_2$@MNPs catalyst for synthesis of isobenzofuranones

A bio-inspired magnetic nanocatalyst was developed through functionalization of Fe$_3$O$_4$@SiO$_2$ core-shell nanoparticles with sulfonated gallic acid. The catalyst demonstrated excellent performance in aqueous-phase synthesis of acridine-1,8-diones via multicomponent reactions of dimedone with diverse aldehydes and amines, achieving 85-94% yields under mild conditions (Fig. 12). The gallic acid-derived sulfonic groups provided both strong Brønsted acidity (1.6 mmol H$^+$/g) and enhanced water compatibility, while the magnetic core enabled simple recovery, demonstrating 8-cycle reusability. Comparative studies showed 30% higher yields than conventional acid catalysts in water. This work exemplifies sustainable catalysis through the combination of bio-based modification, aqueous-phase reactivity, and energy-efficient magnetic separation, offering an eco-friendly platform for N-heterocycle synthesis [32].

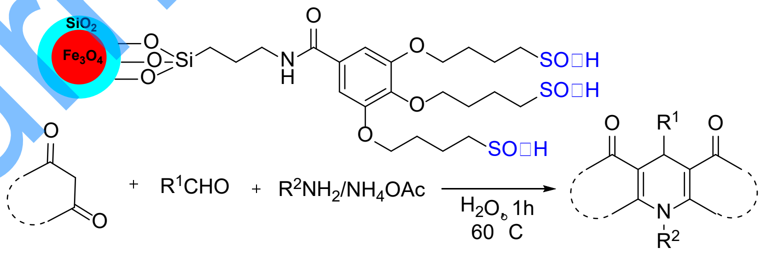

Fig. 12. Fe$_3$O$_4$@SiO$_2$ sulfonated gallic acid as catalyst for the synthesis of acridine-1,8-diones.

Recently, a magnetic graphene oxide nanocatalyst (GO/Fe$_3$O$_4$@BDSA@SO$_3$H, BDSA: 1,3-benzenedisulfonyl amide) was developed for the sustainable synthesis of pyrimido[4,5-b]quinolines. Functionalization with BDSA and chlorosulfonic acid created a high-density acidic surface (1.8 mmol H^+/g). The catalyst exhibited exceptional activity in solvent-free three-component reactions of benzaldehydes, dimedone, and 6-amino-1,3-dimethyluracil, achieving >90% yields at mild temperatures (60–80°C) with short reaction times (<1 h). The hybrid structure combined the high surface area of graphene oxide (420 m^2/g) with superparamagnetic properties (34 emu/g), enabling rapid separation and four reuse cycles with <10% activity loss [33].

A bio-derived magnetic nanocatalyst ($CoFe_2O_4$-Sp-SO_3H) was developed through sulfonation of Spirulina algae-functionalized cobalt ferrite nanoparticles. The catalyst demonstrated exceptional efficiency in aqueous-phase synthesis of dihydroquinazolinones via three-component condensation of isatoic anhydride, aldehydes and amines, achieving 85-96% yields at 60°C within 30-50 minutes. Unique features included the successful incorporation of challenging 2-furan substituents (90-92% yields) and excellent functional group tolerance. The Spirulina matrix provided enhanced stability and biodegradability while maintaining excellent acid site accessibility [34].

A sulfamic acid-functionalized magnetic nanocatalyst (SA-MNPs) was developed for ultrasound-assisted imidazole synthesis. The catalyst was prepared through silanization of Fe_3O_4 nanoparticles with APTES followed by chlorosulfuric acid grafting, yielding uniform 10-12 nm particles with strong magnetization (45 emu/g). The system demonstrated remarkable efficiency in three-component condensations of benzil, aldehydes and ammonium acetate, achieving 90-95% yields within 15-30 minutes under ultrasonic irradiation at room temperature. The ultrasound activation significantly improved mass transfer while the sulfamic acid groups provided optimal acidity for selective product formation [35].

A magnetically recoverable acidic ionic liquid catalyst (Mag@Morph-AIL) was developed through sequential functionalization of Fe_3O_4 nanoparticles with SiO_2, chloropropyltriethoxysilane, and morpholine sulfate (Fig. 13). The core-shell structured nanocatalyst demonstrated excellent performance in synthesizing 3,4-dihydropyrimidinones, achieving >92% conversion within 60 minutes at 78°C. Compared to conventional methods, this system eliminated toxic metal catalysts while improving recyclability and operational simplicity [36].

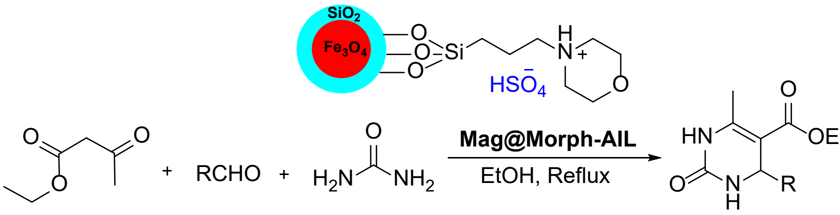

Fig. 13. Mag@Morph-AIL catalyst in synthesizing 3,4-dihydropyrimidinones.

2.2. Biodiesel production

Biodiesel, a renewable and biodegradable fuel derived from vegetable oils, animal fats, or waste feedstocks, offers a sustainable alternative to fossil diesel. It significantly reduces greenhouse gas emissions, enhances energy security, and supports circular economy principles by utilizing non-edible oils and waste materials. Biodiesel's compatibility with existing diesel engines and infrastructure facilitates its adoption without major modifications [37]. However, conventional production faces challenges, including high feedstock costs, slow reaction kinetics, and catalyst separation issues. The development of magnetically recoverable Brønsted acid catalysts has significantly advanced biodiesel production by enabling efficient conversion of low-cost feedstocks, including waste oils, non-edible plant oils, and high free fatty acid (FFA) sources. These catalysts combine the high activity of homogeneous acids with the ease of separation offered by magnetic nanoparticles, addressing key challenges in conventional biodiesel synthesis. Recent studies highlight various innovative designs, such as ionic liquid-functionalized magnetic silica composites, sulfonated biochar-derived catalysts, and dual-functional magnetic poly(ionic liquid) systems. These catalysts exhibit excellent reusability, tolerance to water and FFAs, and compatibility with diverse feedstocks, including microalgae, *Jatropha curcas* oil, and waste cooking oil. Their magnetic properties facilitate rapid separation, minimizing energy-intensive purification steps. Furthermore, their mesoporous structures enhance mass transfer, while strong Brønsted acidity ensures high catalytic efficiency under mild conditions. This section reviews key advancements in magnetically separable acid catalysts for sustainable biodiesel production, emphasizing their structural design, performance optimization, and industrial potential.

A magnetically recoverable ionic liquid catalyst was developed by grafting 3-sulfopropyl-1-(3-propyltrimethoxysilane) imidazolium hydrogensulfate onto mesoporous silica-coated Fe_3O_4 nanoparticles. Characterization revealed a core-shell structure with high surface area (420 m^2/g), uniform mesopores (3.8 nm), and strong magnetization (38 emu/g). The catalyst demonstrated excellent performance in biodiesel production via oleic acid esterification, achieving 93.5% conversion under mild conditions (70°C, 4 h) (Fig. 14). The system combined advantages of homogeneous ionic liquid catalysis with heterogeneous recovery, featuring complete magnetic separation, 8-cycle reusability, and clean product isolation without catalyst residues. The ordered mesochannels facilitated substrate diffusion to acidic sites, while the ionic liquid moiety enhanced both activity and stability. Compared to conventional acid catalysts, this catalyst showed 25% higher conversion and eliminated neutralization waste [38].

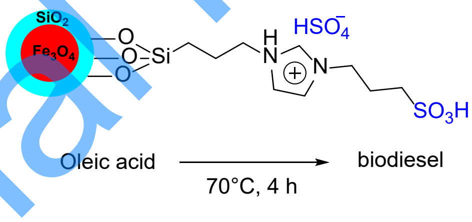

Fig. 14. magnetically recoverable 3-sulfopropyl-1-(3-propyltrimethoxysilane) imidazolium hydrogensulfate catalyst for biodiesel production.

A novel magnetic ionic liquid nanocomposite ([$NiFe_2O_4$@BMSI]HSO_4) was developed for efficient biodiesel production through palm oil transesterification. The catalyst was synthesized via ion exchange from its bromide precursor, with characterization confirming preserved mesoporosity (87 m^2/g surface area) and magnetic properties (32 emu/g) after functionalization (Fig. 15). The acidic nanocomposite demonstrated superior catalytic performance, achieving 86.4% biodiesel yield under optimized conditions (5 wt% catalyst, 1:12 oil:methanol ratio, 80°C, 8 h), a 16% improvement over the bromide analogue. The system exhibited excellent stability, maintaining 92.7% initial activity after six cycles with simple magnetic recovery. Comparative analysis revealed the critical role of HSO_4^- anions in enhancing both activity and stability [39].

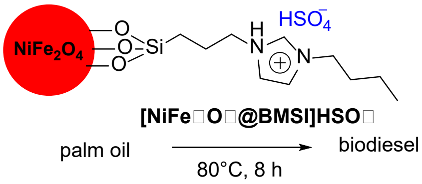

Fig. 15. [$NiFe_2O_4$@BMSI]HSO_4 catalyst for biodiesel production from palm oil.

Similarly, a magnetically recoverable ionic liquid catalyst (Fe_3O_4@SiO_2@[C_4mim]HSO_4) was developed for sustainable biodiesel production from Schisandra chinensis seed oil. The catalyst was synthesized through a three-step immobilization process, achieving 43.6% ionic liquid loading under optimized conditions. The system demonstrated excellent performance in methanolysis of extracted seed oil, achieving 89.2% biodiesel conversion under mild conditions (3 h, mechanical stirring). The resulting biodiesel showed significantly improved fuel properties, with a 19% increase in heating value (32.14 to 38.28 kJ/g). The catalyst exhibited remarkable recyclability, maintaining 87.6% activity after 4 cycles and 71.4% after 6 cycles, with simple magnetic separation. This system shows particular promise for scaling up biofuel production from underutilized plant sources [40].

A magnetically recoverable poly(ionic liquid) catalyst (Fe_3O_4@SiO_2@PIL) with sponge-like architecture was developed for efficient biodiesel production. The catalyst was constructed through grafting copolymerization of sulfonated vinylimidazolium ionic liquid onto silica-coated magnetite nanoparticles, creating a dual-acidic system with enhanced active site accessibility. The system demonstrated exceptional catalytic performance in oleic acid esterification, achieving 92.1% conversion and 92.1% methyl oleate yield under optimized conditions (80°C, 4 h, 5 wt% catalyst). The sponge-like PIL matrix provided higher surface area than conventional supports, while the dual-acid sites (SO_3H/HSO_4^-) enabled synergistic catalysis. This work presents a sustainable approach to biodiesel synthesis, combining the benefits of polymeric ionic liquid catalysis with energy-efficient magnetic recovery for potential industrial implementation [41].

A magnetically recoverable bifunctional catalyst (Zr-CMC-SO_3H@3Fe-C400, CMC: sodium carboxymethylcellulose) was developed for sustainable biodiesel production from low-grade feedstocks. The catalyst was synthesized through a four-step process involving iron/zirconium chelation and sulfonation, yielding a mesoporous carbon structure (BET: 85 m^2/g) with both Brønsted (1.6 mmol H^+/g) and Lewis acid sites. Characterization confirmed uniform zirconium dispersion (5-8 nm clusters) and strong magnetization (28 emu/g). The system demonstrated exceptional catalytic performance in esterification (97% oleic acid conversion) and transesterification (95% yield from high-acid soybean oil). This work presents an industrially viable solution for biodiesel production, combining dual acid functionality and waste oil processing capability with scalable synthesis protocol [42].

Yang and co-workers developed a magnetically recoverable poly(ionic liquid) catalyst for efficient biodiesel production from non-edible Euphorbia lathyris L. oil. The catalyst was synthesized with controlled hydrophobicity and acidity, exhibiting a core-shell structure with uniform mesopores (4.2 nm) and high surface area (128.1 m^2/g). Comprehensive characterization confirmed strong Brønsted acidity (2.14 mmol/g) and excellent hydrophobic properties (115.4° water contact angle). The system demonstrated high catalytic efficiency in both esterification of oleic acid (95.3% yield at 75°C for 3 h) and simultaneous esterification/transesterification of crude oil (91.7% yield), reducing the acid value from 24.59 to 0.8 mg KOH/g. Remarkably, the catalyst maintained >90% biodiesel yield even with 6 wt% water content in the feedstock. Kinetic studies revealed a pseudo-first-order reaction with activation energy of 39.2 kJ/mol. The produced biodiesel fully complied with EN 14214 and ASTM D6751 standards. The catalyst showed good reusability, retaining 87.5% activity after five cycles with simple magnetic separation. This work presents a viable approach for industrial biodiesel production from low-quality, non-edible oil feedstocks [43].

Sulfonated lignin-coated ferrite nanoparticles were developed as magnetically separable catalysts for biodiesel production from oleic acid. The catalysts were prepared by coating cobalt or manganese ferrite nanoparticles ($CoFe_2O_4$, $MnFe_2O_4$) with sulfonated lignin derived from sugarcane bagasse, achieving over 50% coating efficiency as confirmed by TGA. Characterization revealed successful sulfonic acid group incorporation (2.68% sulfur content) and preserved magnetic properties. The $CoFe_2O_4$-SL5 and $MnFe_2O_4$-SL7.5 catalysts (sulfuric acid volume: 5 and 7.5 ml, respectively) demonstrated optimal performance, achieving approximately 80% conversion to fatty acid methyl esters under optimized conditions (100°C, 6h, 10:1 methanol:oleic acid ratio). The reaction efficiency correlated with both acid site density and surface area accessibility. The magnetic properties enabled simple catalyst recovery, while the lignin coating provided thermal stability and acid site protection. This work presents a sustainable approach combining waste lignin valorization with efficient magnetic catalyst design, offering advantages over homogeneous systems through easier separation, reusability, and compatibility with high free fatty acid feedstocks [44].

In 2023, a sulfonated magnetic biochar catalyst was developed from rice husk pyrolysis for efficient biodiesel production via oleic acid esterification. The catalyst was synthesized through $ZnCl_2$/$FeCl_3$ activation followed by chlorosulfonic acid sulfonation, yielding a porous structure (BET: 285 m^2/g) with strong acidity (1.8 mmol H^+/g) and magnetization (32 emu/g). Process optimization via response surface methodology identified optimal conditions: 9.9 wt% catalyst loading, 16:1 methanol-to-oil ratio, 74.8°C, and 4.8 h reaction time, achieving 98.11% biodiesel yield. The catalyst exhibited excellent thermal stability (>300°C) and retained high activity over multiple cycles due to its robust magnetic core and sulfonic acid-functionalized biochar matrix [45].

A magnetic polymer-based solid acid catalyst was developed through reflux-precipitation polymerization of styrene/divinylbenzene on Fe_3O_4 clusters followed by chlorosulfonic acid treatment. The catalyst exhibited optimized physicochemical properties with 243 m²/g surface area, 2.113 mmol/g acid density, and 18 emu/g magnetization. In oleic acid esterification, the catalyst demonstrated superior performance (91% conversion) under mild conditions (Fig. 16), outperforming Amberlyst-15 and approaching concentrated H_2SO_4 activity. The catalyst maintained >95% initial activity over three cycles with simple magnetic recovery. The system also showed versatility in catalyzing fructose dehydration to 5-hydroxymethylfurfural [46].

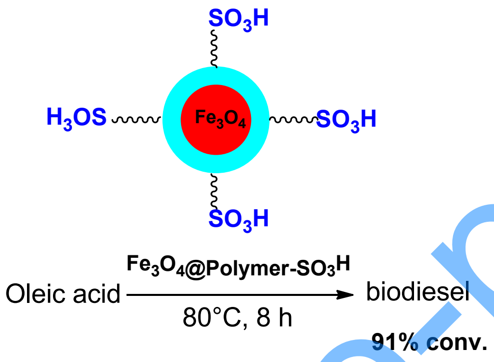

Fig. 16. Fe_3O_4@Polymer-SO_3H catalyst for biodiesel production from oleic acid.

A sustainable magnetic acid catalyst was developed from Amazonian waste materials (açaí seeds and red mud) for biodiesel production. The optimal catalyst, prepared through carbonization (400°C, 3h) and sulfonation (80°C, 3h) of a 1:1 biomass-red mud composite, demonstrated 88% conversion of oleic acid to methyl oleate under mild conditions (100°C, 1h, 5% catalyst loading, 1:12 methanol:oil ratio). Characterization revealed the catalyst possessed both Brønsted acid sites (1.4 mmol/g) and magnetic iron oxide phases (hematite/magnetite) derived from red mud, enabling simple magnetic separation. The system outperformed commercial Amberlyst-15 and maintained activity through three reaction cycles. This work presents the first reported use of red mud as a magnetic precursor in sulfonated carbon catalysts [47].

A microalgae-derived magnetic solid acid catalyst was synthesized through a three-step process of magnetization, carbonization (800°C), and H_2SO_4 sulfonation (150°C), utilizing lipid-extracted algal residue as a sustainable carbon source. The optimized catalyst, prepared with NaCl porogen (1:1

mass ratio), exhibited exceptional properties: high surface area (124.70 m²/g), strong acidity (3.64 mmol/g), and sufficient magnetization (1.042 emu/g) for separation. In microwave-assisted transesterification of wet microalgae at 90°C, the catalyst achieved 98.51% biodiesel conversion under optimal conditions (5 wt% loading, 6.25:1 methanol-to-biomass ratio). The system demonstrated remarkable stability, maintaining 85.5% average conversion over five consecutive cycles without regeneration [48]. Similarly, a magnetic sulfonated biochar catalyst was prepared from cassava peel waste through pyrolysis, sulfonation, and Fe_3O_4 nanoparticle incorporation. Characterization revealed a mesoporous structure (423.89 m²/g surface area, 108.77 nm pore diameter) with three acidic sites: -OH (weak), -COOH and $-SO_3H$ (strong), totaling 3.2 mmol/g acid density. The catalyst demonstrated exceptional performance in microwave-assisted biodiesel production from Millettia pinnata seed oil, achieving 98.7% yield under optimized conditions (65°C, 11:1 methanol:oil ratio, 3 wt% catalyst, 45 min). The high activity was attributed to the synergistic effect of accessible strong acid sites and the magnetic core's stability [49**].**

A core-shell magnetic catalyst was prepared by grafting dual-acidic ionic liquids onto silica-coated Fe_3O_4 nanoparticles for one-pot biodiesel production from low-quality oils. The catalyst combined 1-vinyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate monomers with 1,4-butanediyl-3,3′-bis-1-vinylimidazolium cross-linkers, creating a porous polymeric ionic liquid network (3.93 mmol H^+/g) around a magnetic core (27.5 emu/g). Characterization confirmed preservation of the core-shell structure after functionalization, with the system demonstrating exceptional dual functionality: 92% conversion in soybean oil transesterification and 94% esterification of free fatty acids simultaneously under optimized conditions. The catalyst exhibited remarkable stability, maintaining >90% activity over five cycles with simple magnetic recovery, and showed unique insensitivity to both moisture (up to 5 wt%) and high FFA content (up to 20 wt%) in feedstocks [50].

A simple core-shell magnetic catalyst ($Fe_3O_4@SiO_2-SO_3H$) was developed for biodiesel production from Jatropha curcas oil. The catalyst was synthesized through co-precipitation, silica coating, and sulfonation, yielding a structure with 30.94 emu/g magnetization, and 0.76 mmol/g acidity. The system demonstrated exceptional performance in simultaneous transesterification/esterification, achieving 98% fatty acid methyl ester conversion under optimized conditions (9:1 methanol:oil ratio, 8 wt% catalyst, 80°C, 3.5 h). The catalyst exhibited remarkable stability, maintaining identical performance between 1st and 10th cycles through simple one-pot regeneration (Fig. 17) [51].

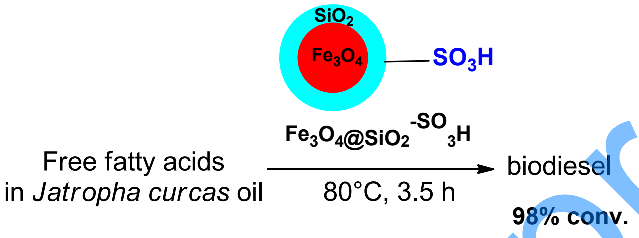

Fig. 17. $Fe_3O_4@SiO_2$-SO_3H catalyst for biodiesel production from Jatropha curcas oil.

In 2018, a chitosan-derived magnetic catalyst was reported for effective biodiesel production from high-acid feedstocks. The core-shell mesoporous material was synthesized through chitosan functionalization with sulfonic acid groups (-SO_3H) and iron oxide nanoparticles, creating a bifunctional catalyst with both Brønsted acid and ammonium (NH_3^+) sites. The catalyst demonstrated exceptional performance in oleic acid esterification, achieving 96.7% biodiesel yield under optimized conditions (80°C, 3 h, 4 wt% catalyst, 15:1 methanol:oil ratio). The system maintained >90% activity over five cycles with simple magnetic recovery [52].

A magnetically recoverable nanosized solid acid catalyst was reported for biodiesel production from high-FFA waste grease. The core-shell structured catalyst, comprising iron oxide nanoparticles (90 nm) coated with poly(glycidyl methacrylate) and surface sulfonic groups (2.3 mmol H^+/g), demonstrated exceptional performance in FFA esterification. The system achieved 96% conversion of 16 wt% FFA in grease within 2 hours (4 wt% catalyst loading, methanol:FFA ratio 20:1), outperforming both conventional Amberlyst 15 (40% lower activity) and other nanosized analogues. The poly(glycidyl methacrylate) shell's stability under mild sulfonation conditions (Na_2SO_3) proved crucial for maintaining both catalytic activity and superparamagnetic properties. This work presents a practical two-step process for waste grease valorization, combining the benefits of nanosized catalyst efficiency with robust magnetic recovery for sustainable biodiesel production [53].

A magnetically recoverable dual Brønsted acid catalyst (DAIL-Fe_3O_4@SiO_2) was prepared by immobilizing 1-(propyl-3-sulfonate)imidazolium hydrogen sulfate onto silica-coated iron oxide nanoparticles (Fig. 18). The catalyst demonstrated excellent performance in both esterification and transesterification, achieving 92.9% biodiesel yield from oleic acid/ethanol under optimized conditions. The system showed broad alcohol compatibility in esterification and effectively catalyzed soybean oil transesterification. Key advantages are 8-cycle reusability with <5% activity loss, and dual acid functionality from both sulfonic and HSO_4^- groups. Comparative studies revealed superior activity to conventional acid catalysts, attributed to enhanced substrate accessibility in the ionic liquid layer [54].

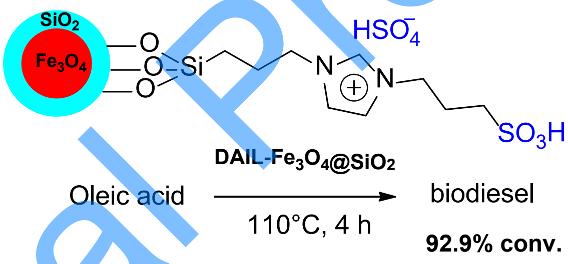

Fig. 18. DAIL-Fe_3O_4@SiO_2 catalyst for biodiesel production from oleic acid.

A novel magnetically separable Fe_3O_4@biochar@SO_3H catalyst was synthesized from *Mesua assamica* seed shell biochar via Fe_3O_4 impregnation and sulfonation. The catalyst exhibited a total acidity of 3.9 mmol.g^{-1} and –SO_3H density of 1.8 mmol.g^{-1}, enabling efficient transesterification of *Mesua assamica*, jatropha, and soybean oils into biodiesel with yields exceeding 95%. Kinetic studies indicated pseudo-first-order reaction kinetics with activation energy of 32.42 kJ.mol^{-1}. The catalyst demonstrated good reusability, maintaining over 75% yield after three cycles due to its magnetic separation capability. This study highlights the potential of *Mesua assamica* seed shells as a low-cost catalyst precursor and non-edible oil source, contributing to sustainable biodiesel production while utilizing agricultural waste [55].

Xie *et al.* developed a magnetically recyclable acid catalyst for biodiesel production from low-quality acidic oils by immobilizing polyoxometalate-based sulfonated ionic liquids (ILs) on an amino-functionalized metal-organic framework ($CoFe_2O_4$/MIL-88B(Fe)-NH_2). The catalyst, $CoFe_2O_4$/MIL-88B(Fe)-NH_2/(Py-Ps)PMo, (Fig. 19) combined Brønsted-Lewis acid sites from phosphomolybdic acid (HPMo)-modified ILs with the porous structure of the magnetic support. The catalyst demonstrated high activity in both esterification of free fatty acids (FFAs) and transesterification of soybean oil, enabling one-pot biodiesel production from acidic feedstocks. Its dual acid sites and porous framework enhanced catalytic performance, while magnetic separation facilitated easy recovery. The catalyst maintained stable activity over multiple cycles without significant deactivation [56].

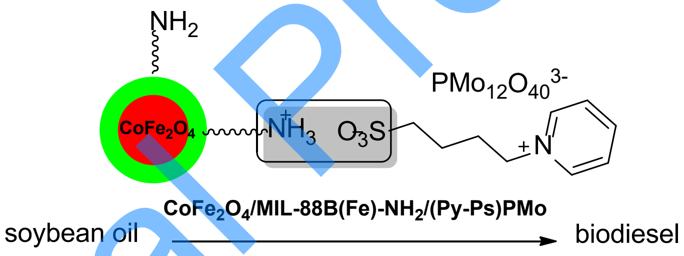

Fig. 19. $CoFe_2O_4$/MIL-88B(Fe)-NH_2/(Py-Ps)PMo, catalyst for biodiesel production from soybean oil.

Sulfonic acid-functionalized magnetic nanoparticles (MNPs) (Fe_3O_4-SO_3H) and silica-coated MNPs (Fe_3O_4@SiO_2-SO_3H) were synthesized through chlorosulfonic acid functionalization and developed as acid catalysts for biodiesel production via esterification. While both catalysts effectively converted palmitic acid to biodiesel, the silica-coated variant (Fe_3O_4@SiO_2-SO_3H) demonstrated superior performance due to its porous silica layer, which enhanced mass transport and acidic stability without significantly compromising magnetic separation. The silica coating also improved catalyst durability in harsh reaction conditions. Both catalysts could be magnetically recovered, eliminating the need for filtration or centrifugation. These findings highlight the potential of silica-modified magnetic nanocatalysts for efficient and recyclable biodiesel production [57].

Wang and co-workers synthesized sulfonated magnetic solid acid catalysts (ZrFe-SA-SO_3H) with both Brønsted and Lewis acid sites for biodiesel production via oleic acid esterification. The catalysts, prepared through a multi-step process involving chelation, calcination, and sulfonation, exhibited high acid density (4.4–8.4 mmol/g) and strong magnetization. The optimized catalyst, $Zr_{1.0}Fe_{1.0}$-SA-SO_3H, achieved 99.5% biodiesel yield in the first cycle (90°C, 4 h) and retained 90.3% yield after five cycles, demonstrating excellent reusability. Replacing starch-derived SA with sodium carboxymethylcellulose (CMC) yielded similar results, highlighting the versatility of the synthesis approach [58].

A magnetically recyclable solid acid catalyst was prepared by immobilizing a polymeric acidic ionic liquid (IL) on core-shell Fe_3O_4/SiO_2 nanoparticles for efficient biodiesel production from low-cost oils. The catalyst was synthesized via radical grafting copolymerization of a sulfonic acid-functionalized imidazolium IL onto the magnetic support, creating a heterogeneous Brønsted acid catalyst with strong covalent bonding. The catalyst demonstrated excellent performance in one-pot transesterification-esterification of high-FFA oils, achieving 93.3% biodiesel yield (120°C, 6 h, methanol-to-oil ratio 35:1, 9 wt% catalyst). The catalyst retained its activity over multiple cycles with minimal leaching [59].

A magnetic carbonaceous acid catalyst (JHC-12-600-$SO_3H@Fe/Fe_3O_4$) was synthesized from Jatropha hull hydrolysates through hydrothermal precipitation, pyrolytic carbonization, and sulfonation. The catalyst exhibited a total acid content of 2.69 mmol.g^{-1} and strong magnetization. Characterization confirmed the presence of $–SO_3H$, –COOH, and –OH groups on the carbon-coated Fe_3O_4 core (<20 nm). The catalyst achieved 95.9% biodiesel yield from high-acid-value Jatropha oil (17.2 mg KOH/g) under optimized conditions (180°C, 7.5 h, methanol-to-oil ratio 18:1, 7.5 wt%

catalyst). In a 5 L batch reactor, it maintained 94.3% recovery efficiency and stable performance over 5 cycles, demonstrating scalability [60].

A layered magnetic SO_4/Fe-Al-TiO_2 solid acid catalyst was developed for efficient biodiesel production from waste cooking oil (WCO). The catalyst was constructed through sequential functionalization of TiO_2 nanoparticles with alumina (buffer layer), hematite (magnetic component), and sulfonic groups (Brønsted acid sites). The catalyst demonstrated exceptional performance, achieving 96% FAME yield in 2.5 h at 90°C (3 wt% catalyst, 10:1 methanol:oil ratio). It showed remarkable versatility, processing feedstocks with ≤20% FFA content and maintaining stable performance over 10 cycles via magnetic separation and thermal regeneration. The unique layered design combined strong Brønsted acidity with superparamagnetic properties, enabling efficient transesterification of challenging waste oils while addressing catalyst recovery challenges in industrial applications [61].

Very recently, a heterogeneous magnetic nanocatalyst ($AlFe_2O_4$@n-Pr@Et-SO_3H) was synthesized and applied for biodiesel production via oleic acid esterification (Fig. 20) as well as sulfide oxidation. The catalyst demonstrated excellent activity in esterification, achieving high biodiesel yields under mild conditions, while also exhibiting dual functionality in sulfide oxidation. Its magnetic core enabled easy recovery using an external magnet, with reusability for at least four cycles without significant activity loss [62].

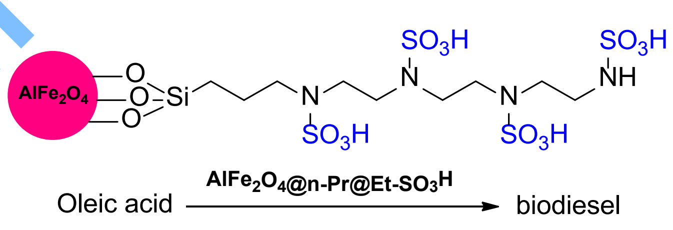

Fig. 20. $AlFe_2O_4$@n-Pr@Et-SO_3H catalyst for biodiesel production from oleic acid.

2.3. Esterification

Esterification is a fundamental organic transformation that forms ester bonds (–COOR) between carboxylic acids and alcohols, with applications spanning pharmaceuticals, polymers, fragrances, and biofuels. This reaction enables the synthesis of key intermediates, such as plasticizers, flavoring agents, and biodiesel precursors, while also serving as a model for studying acid catalysis. Industrially, esterification is vital for producing polyesters, surfactants, and solvent esters [63]. Despite its simplicity, challenges like equilibrium limitations, water sensitivity, and catalyst recovery persist. Recent advances in heterogeneous and magnetic acid catalysts have improved efficiency, selectivity, and sustainability, making esterification a cornerstone of green chemistry and industrial organic synthesis. This section reviews the latest developments in magnetically recoverable acid catalysts, emphasizing their structural diversity, reaction mechanisms, and industrial potential for sustainable ester synthesis.

Zeng and co-workers prepared sulfonated magnetic SiO_2 microsphere catalysts using Fe_3O_4 nanoparticles as magnetic cores, comparing impregnation and grafting functionalization methods. Characterization confirmed successful SiO_2 coating and sulfonic acid ($-SO_3H$) modification of the Fe_3O_4 cores. The impregnated catalyst demonstrated superior initial activity (99.00% esterification yield at 105°C with 2.95% catalyst loading) of n-butanol and adipic acid (Fig. 21), while the grafted version showed enhanced stability (85.61% vs 81.35% yield after six cycles). Both catalysts exhibited excellent magnetic separability, addressing a key challenge in heterogeneous catalysis. The work systematically compared synthetic approaches, revealing a trade-off between maximum activity and long-term stability. The findings provide practical insights for designing magnetic solid acid catalysts, particularly highlighting the impregnation method for high-activity applications and grafting for processes requiring extended catalyst reuse [64].

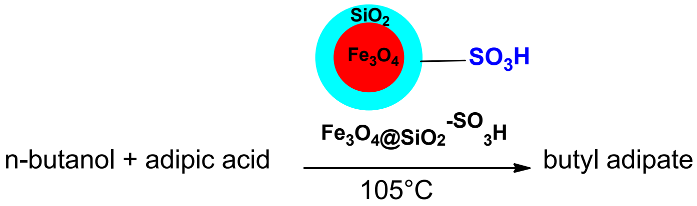

Fig. 21. sulfonated magnetic SiO_2 microsphere as catalyst for esterification of n-butanol and adipic acid.

A magnetic mesoporous silica-supported ionic liquid catalyst ([BsAIm][OTf]/SCF) was synthesized via reverse microemulsion-mediated sol-gel and thiol-ene click chemistry, incorporating cobalt ferrite nanoparticles for magnetic separation. Characterization by FT-IR, XRD, TEM, and N_2 adsorption-desorption confirmed the mesoporous structure and successful immobilization of the sulfonic acid-functionalized ionic liquid. The study revealed an inverse relationship between sulfhydryl (SH) group loading and pore diameter, impacting ionic liquid incorporation. Higher SH modification reduced pore size, limiting [BsAIm][OTf] diffusion and loading. In oleic acid esterification, catalytic efficiency decreased with longer alcohol carbon chains due to increased mass-transfer resistance, highlighting shape-selective behavior. The catalyst demonstrated potential for tailored applications, with performance dependent on substrate size and pore accessibility. This work underscores the importance of balancing functional group density and porosity in designing magnetic heterogeneous acid catalysts for esterification [65].

A magnetic sulfonated carbon/Fe_3O_4/palygorskite (SC-F-Plg) composite catalyst was developed via one-pot calcination-sulfonation of sucrose, *p*-toluenesulfonic acid (TsOH), and Fe_3O_4/Plg. The palygorskite (Plg) nanorods served as a low-cost, high-surface-area support, replacing conventional carbon sources and enhancing dispersion of Fe_3O_4 nanoparticles. The catalyst exhibited dual functionality: a sulfonated carbon layer provided Brønsted acid sites (88.69% oleic acid esterification in first cycle), while embedded Fe_3O_3 enabled magnetic recovery (70.31% yield after 5 cycles). The carbon coating stabilized the magnetic core, preventing leaching. This green synthesis leveraged clay mineral supports to improve surface area and acid density, addressing key limitations of sulfonated carbons [66].

A sulfonated single-walled carbon nanohorn (SO_3H/Fe-SWCNH) catalyst was synthesized via a gas-injected arc-in-water (GI-AIW) method, incorporating iron nanoparticles (6–13 wt%) to enhance both catalytic activity and magnetic properties. Functionalization with sulfuric acid and calcination yielded a solid super-acid catalyst with high acid density (5.6–8.5 mmol g^{-1}). XRD confirmed the transformation of Fe to α-Fe_2O_3, which improved magnetic recoverability without compromising catalytic performance. In palmitic acid esterification, higher Fe-loading significantly increased methyl palmitate yield, demonstrating a synergistic effect between acid sites and dispersed Fe_2O_3 nanoparticles. The catalyst maintained its activity and magnetic susceptibility over multiple cycles [67].

A magnetic sulfonated biochar catalyst was synthesized from oil palm empty fruit bunches via $FeCl_3$ pretreatment, pyrolysis (500°C), and sulfonation, yielding a mesoporous structure (53.77 m^2/g) with embedded Fe_3O_4 nanocrystals for magnetic separation. The catalyst exhibited dual acid sites (–SO_3H, –COOH, –OH; total acidity: 0.28 mmol/g) and soft ferromagnetism. In oleic acid esterification, the catalyst achieved 97.6% methyl oleate yield under optimized conditions (5 wt% catalyst, 1:8 oleic acid:methanol, 150°C, 90 min), outperforming commercial solid and homogeneous acid catalysts [68].

A facile synthesis route was developed for preparing magnetic carbonaceous solid acids (MCSAs) from waste banana peel through integrated fast pyrolysis of Fe(III) complexes and vapor-phase sulfonation. This method produced superparamagnetic catalysts with tunable textural properties (surface area: 156-1097 m^2/g, pore volume: 0.17-0.74 cm^3/g, mesopore size: 6.1-11.4 nm) by adjusting Fe(III) dosage. The MCSAs exhibited exceptional catalytic performance in oleic acid esterification, surpassing commercial Amberlyst-15, sulfonated activated carbon, and niobic acid, while rivaling homogeneous H_2SO_4. Their superior activity derived from high acid density, hydrophobic surfaces, and large mesopores facilitating reactant diffusion. The catalysts maintained excellent magnetic separability, enabling convenient recovery [69]. Similarly, a magnetic porous carbonaceous (MPC) solid acid catalyst was synthesized from sawdust biomass waste via an integrated fast pyrolysis–sulfonation process, leveraging the catalytic effect of Fe to achieve a high surface area (296.4 $m^2\ g^{-1}$) and mesoporous structure. The catalyst exhibited strong acidity (2.57 mmol g^{-1} total acid sites) and demonstrated excellent performance in esterification, dehydration, and hydrolysis reactions, typical acid-catalyzed transformations. Its porous carbon–sulfonic acid framework ensured stability, allowing five reuse cycles without significant activity loss [70].

Very recently, a cross-linked magnetic ionic network nanoparticle (HSO_4^-@MINN) (Fig. 22) was developed as a high-performance solid acid catalyst, combining core-shell silica-coated iron oxide nanoparticles with a 3D imidazolium-based poly(ionic liquid) (PIL) framework. Synthesized via microemulsion and radical polymerization, followed by sulfonic acid anion exchange, the catalyst featured well-distributed acidic sites, hydrophobic nanoreactors, and superparamagnetic properties. Characterization by TGA, FTIR, TEM, and N_2 adsorption confirmed its thermal stability, high ionic density, and mesoporous structure. In solvent-free esterification of diverse alcohols (primary, secondary, benzylic, aliphatic, cyclic) with acetic acid, the catalyst achieved 78–99% yields at 0.1 mol% loading (85°C). Its hydrophobic 3D PIL matrix enhanced water resistance and substrate diffusion, while magnetic separation enabled 10 recycles without activity loss [71].

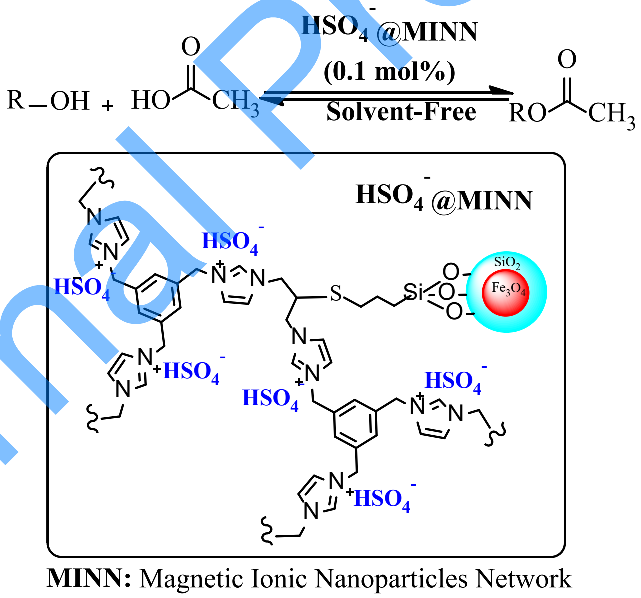

Fig. 22. HSO_4^-@MINN catalyst for esterification of diverse alcohols.

2.4. Hydrolysis of cellulose and other lignin-based polysaccharides

The hydrolysis of cellulose and other lignin-based polysaccharides is a critical step in valorizing lignocellulosic biomass into fermentable sugars, biofuels, and platform chemicals. As the most abundant renewable carbon source on Earth, plant biomass offers a sustainable alternative to fossil-derived feedstocks [72]. However, the recalcitrant structure of cellulose, caused by crystalline regions and lignin encapsulation, poses significant challenges for efficient depolymerization. Advances in catalytic, enzymatic, and hybrid hydrolysis systems aim to overcome these barriers while improving selectivity and energy efficiency. This section examines cutting-edge strategies using magnetically separable acid catalyst for breaking down lignocellulose (see Table 1).

A magnetically separable carbon-based solid acid catalyst was synthesized from sulfonated sucralose through Fe^{3+}-assisted incomplete carbonization, embedding γ-Fe_2O_3 nanoparticles for easy recovery. The catalyst exhibited dual functionality, combining cellulose-binding sites with Brønsted acid groups, enabling efficient hydrolysis of ball-milled microcrystalline cellulose to glucose (32% yield, 363 K, 30 h). Characterization confirmed its amorphous carbon structure with stable magnetic properties, allowing 90% activity retention over five cycles via magnetic separation. The synthesis route offered low-energy, scalable preparation while addressing challenges in biomass valorization [73].

A core–shell magnetic solid acid catalyst ($Fe_3O_4@SiO_2$-SO_3H) was synthesized via solvothermal preparation of Fe_3O_4 nanoparticles, silica encapsulation, and sulfonation. Characterization confirmed the nanostructured core–shell morphology, superparamagnetic properties (saturation magnetization: 9.81 emu g^{-1}), and high acid density (3.36 mmol g^{-1}). The catalyst demonstrated exceptional performance in cellulose hydrolysis, achieving 59.91% glucose yield under optimized conditions (150°C, 7 h). Its magnetic separability enabled easy recovery, with stable activity and magnetization over five cycles, highlighting its potential for sustainable biomass conversion [74].

Sulfonated magnetic carbon nanotube arrays (MCNAs) were developed as efficient solid acid catalysts for the hydrolysis of polysaccharides in crop stalks into sugars. Characterization via electron microscopy and microanalysis confirmed their structure, high acidity, and superparamagnetic properties. The catalysts demonstrated high activity, selectivity, and stability in converting corn stalk polysaccharides, with potential for sustainable biomass valorization [75].

A magnetic core-shell structured solid acid catalyst (Fe_3O_4@C-SO_3H) was synthesized for efficient cellulose hydrolysis, combining catalytic activity with facile magnetic separation. The catalyst features a sulfonated carbon shell providing Brønsted acid sites (SO_3H groups) and a magnetic Fe_3O_4 core enabling easy recovery. Under moderate conditions (140°C, 12 h), the catalyst achieved 48.6% cellulose conversion with 52.1% glucose selectivity, demonstrating competitive performance among solid acid catalysts. The carbon shell's sulfonic acid groups effectively catalyzed the hydrolysis while protecting the magnetic core from leaching. Importantly, the catalyst maintained both its catalytic activity and magnetization through multiple cycles, with simple magnetic separation between reactions. This design addresses two key challenges in biomass conversion: the need for active acid sites to break recalcitrant cellulose bonds and the practical requirement for catalyst recovery in continuous processes [76].

A magnetic sulfonated reduced graphene oxide (Fe_3O_4-RGO-SO_3H) catalyst was established for efficient cellulose hydrolysis, integrating Fe_3O_4 nanoparticles for magnetic separation and -$PhSO_3H$, -COOH, and -OH groups for enhanced catalytic activity. The crumpled layered structure improved cellulose accessibility to active sites, while -COOH groups provided acidic functionality and -OH groups facilitated substrate adsorption via hydrogen bonding with β-1,4-glycosidic bonds. The catalyst demonstrated high dispersion in water and superior stability, attributed to -COOH groups stabilizing the sulfonic acid sites. Its magnetic properties enabled easy recovery and reuse for ≥5 cycles without significant activity loss [77].

A magnetic carbonaceous acid catalyst (C-SO_3H@Fe_3O_4/C) was synthesized via a one-pot hydrothermal precipitation-sulfonation method using nano-Fe_3O_4, glucose, and hydroxyethyl-sulfonic acid, avoiding conventional concentrated sulfuric acid treatment. The catalyst exhibited both high acidity (1.23 mmol g^{-1}) and strong magnetization (12.85 emu/g), enabling efficient hydrolysis of NaOH-freeze pretreated sugarcane bagasse in a microwave reactor. Under optimized conditions (180°C), it achieved exceptional yields of 62.59% glucose and 73.01% total reducing sugars (TRS). The catalyst demonstrated remarkable recyclability, maintaining 93.18% recovery efficiency via magnetic separation and producing 54.47% glucose yield after five cycles [78].

A magnetic polystyrene-based solid acid catalyst (Fe_3O_4@PS-SO_3H) was prepared for efficient aqueous-phase cellulose hydrolysis. The catalyst was synthesized via oleic acid modification of Fe_3O_4 nanoparticles, followed by emulsion polymerization of polystyrene (PS) and sulfonation. Characterization confirmed a core-shell structure with 3.56 mmol g^{-1} acid density and 35.28 emu g^{-1} magnetization. In cellulose hydrolysis (140°C, 10 h, 1:1 catalyst-to-substrate ratio), it achieved 64.14% glucose yield. The catalyst maintained stable performance over 5 cycles with magnetic recovery, demonstrating exceptional durability in aqueous media [79].

A magnetically recoverable Brønsted acidic ionic liquid (BAIL) catalyst (BAIL–Fe_3O_4@SiO_2) was developed for lignin depolymerization into aromatic monomers. The core-shell structured catalyst (500–600 nm diameter) featured a mesoporous silica layer (185.7 m^2 g^{-1} surface area, 4.362 nm pore size) and 30 wt% BAIL loading, combining high acidity with superparamagnetic properties. Under optimized conditions (160°C, 3 h, 40 wt% catalyst), it achieved 54.0% lignin conversion and 33.0% aromatic monomer yield, with aryl aldehydes as the dominant product (19.2% yield). The catalyst retained >90% of initial activity after 3 cycles, demonstrating exceptional stability and easy magnetic separation. This work presents a sustainable alternative to fossil-derived aromatics, addressing challenges in lignin valorization through recyclable, multifunctional catalysis [80].

In 2024, a magnetic solid acid catalyst (Fe_3O_4/C–SiO_2) was synthesized via co-precipitation and sulfonation, utilizing rice husk ash-derived SiO_2 as a sustainable support. Characterization confirmed successful –SO_3H functionalization (0.96 mmol/g acid density) and a mesoporous structure (72 m^2/g surface area). Applied to corncob hydrolysis, the catalyst achieved optimal total reducing sugar yield at 90°C, with kinetics following Saeman's model (activation energy: 12.33 kJ/mol) and first-order reaction models (42.4 kJ/mol). Thermodynamic analysis revealed the process was enthalpically favorable, with glucose formation more stable than degradation products. The catalyst maintained its activity over 4 cycles, demonstrating robust recyclability via magnetic separation [81].

Table 1. Developed magnetically separable acid catalyst for hydrolysis of cellulose and other lignin-based polysaccharides.

Catalyst	**Substrate**	**Product**	**Reaction conditions**	**Recycle number**	**Ref.**
Magnetic Sucra-SO_3H^a	cellulose	Glucose (32%)	363 K, 30 h	5	[73]
$Fe_3O_4@SiO_2$-SO_3H	cellulose	glucose (59.91%)	150°C, 7 h	5	[74]
MCNAs[b]	crop stalks	Sugars (31%)	150°C, 2 h	4	[75]
$Fe_3O_4@C$-SO_3H	cellulose	glucose (52.1%)	140°C, 12 h	3	[76]
Fe_3O_4-RGO-SO_3H^c	carbohydrates	Glucose (12-96%)	150°C, 3-12 h	5	[77]
C-$SO_3H@Fe_3O_4$/C	pretreated sugarcane bagasse	glucose (62.59%)	MW, 180°C	5	[78]
Fe_3O_4@PS-SO_3H^d	cellulose	glucose (64.14%)	140°C, 10 h	5	[79]
BAIL–$Fe_3O_4@SiO_2^e$	lignin	aromatic monomers (33%)	160°C, 3 h	3	[80]
Fe_3O_4/C–SiO_2)	corncob	reducing sugar	90°C	4	[81]

[a] magnetically separable sucralose-based solid acid; [b] Sulfonated magnetic carbon nanotube arrays; [c] RGO: reduced graphene oxide; [d] PS: polystyrene; [e] BAIL: Brønsted acidic ionic liquid.

2.5. HMF production

5-hydroxymethylfurfural (5-HMF) stands as a pivotal bio-based platform molecule, bridging renewable carbohydrates with high-value chemicals, polymers, and biofuels. Derived from hexose dehydration, 5-HMF serves as a versatile precursor for furan dicarboxylic acid (FDCA, a PET alternative), liquid fuels (e.g., DMF), and pharmaceuticals. Its production aligns with sustainable biorefinery concepts, valorizing abundant biomass like cellulose and inedible sugars [82]. However, challenges including low yields, side reactions, and costly separation, hinder large-scale adoption. Advances in catalytic systems (e.g., acidic, biphasic, or enzymatic) aim to optimize selectivity and efficiency. This section explores innovative strategies in the field of magnetically separable acid-catalyzed 5-HMF production (Table 2).

Sulfonated magnetic carbon nanoparticles (SMCNs) were synthesized from eucalyptus oil via ferrocene-assisted co-pyrolysis and H_2SO_4 sulfonation, creating a sustainable catalyst for fructose dehydration to 5-HMF. Under optimized conditions (180°C, 30 min, catalyst-to-fructose ratio of 0.167), SMCNs achieved 84% fructose conversion and 51.6% 5-HMF yield, outperforming many conventional acid catalysts. The material's superparamagnetic properties enabled easy recovery, with >50% 5-HMF yield maintained over 3 cycles. Byproduct analysis confirmed selectivity against levulinic acid (LA) and humin formation [83].

A magnetically separable core-shell catalyst (Fe_3O_4@Si/Ph-SO_3H) was synthesized via reverse microemulsion, featuring a Fe_3O_4 core and a phenyl-modified silica shell with surface sulfonic acid groups. The catalyst demonstrated exceptional activity in fructose dehydration to 5-HMF, achieving 99% conversion and 82% HMF yield in dimethylsulfoxide at 110°C (3 h), surpassing conventional Amberlyst-15 and rivaling homogeneous acids. The nanocoating design ensured high exposure of acid sites, while the magnetic core enabled facile separation and reuse without activity loss [84].

Recently, a dendrimer-functionalized magnetic solid acid catalyst (G2-PAMAM@SMNPs-COOH) was developed through stepwise grafting of amine-terminated PAMAM dendrimers onto silica-coated magnetic nanoparticles, followed by carboxylation with bromoacetic acid. The catalyst exhibited dual acid-base functionality, enabling both fructose dehydration to 5-hydroxymethylfurfural (87% yield, 140°C, 3 h in DMSO/H_2O) and glucose isomerization to fructose, facilitating direct conversion of glucose-based feedstocks. Characterization confirmed the covalent immobilization of dendrimers and weak acidity (carboxylic groups), while the magnetic core allowed easy recovery and reuse for 6 cycles without efficiency loss. This work presents a sustainable, sulfur-free alternative to conventional acid catalysts, combining high selectivity, substrate versatility, and magnetic recyclability for biomass-derived platform chemical synthesis [85].

A magnetic sulfonated graphene oxide catalyst (Fe_3O_4/SGO) was synthesized via co-precipitation for furfural production from sugarcane bagasse. Characterization confirmed successful integration of Fe_3O_4 nanoparticles with sulfonated graphene oxide (SGO), yielding a high surface area (121.8 m^2/g) and superparamagnetic properties. The catalyst's aryl-SO_3H groups and oxygen functionalities facilitated direct biomass dehydration, achieving 14.07% furfural yield at 190°C in 90 min. The material demonstrated excellent recyclability, maintaining consistent activity over 5 cycles with magnetic recovery [86].

Magnetically separable sulfated zirconia (M-SZF) catalysts were synthesized via zirconia coating and chlorosulfonic acid sulfonation, optimizing acidity for the green synthesis of ethyl levulinate (EL) from furfuryl alcohol (FAL) and ethanol. The M-SZF catalyst demonstrated exceptional performance, achieving 96% EL yield with 100% FAL conversion (1:15 molar ratio, 2 h) [87].

Table 2. Developed magnetically separable acid catalyst for 5-HMF production.

Catalyst	**Substrate**	**Product**	**Reaction conditions**	**Recycle number**	**Ref.**
SMCNs [a]	fructose	5-HMF (51.6%)	180°C, 30 min	3	[83]
Fe_3O_4@Si/Ph-SO_3H	fructose	5-HMF (82%)	110°C, 3 h	3	[84]
G2-PAMAM@SMNPs-COOH	glucose	5-HMF (87%)	140°C, 3 h	6	[85]
Fe_3O_4/SGO[b]	sugarcane bagasse	furfural (140.07%)	190°C, 90 min	5	[86]
M-SZF[c]	furfuryl alcohol	ethyl levulinate (96%)	120°C, 2 h	8	[87]

[a] Sulfonated magnetic carbon nanoparticles; [b] sulfonated graphene oxide; [c] Magnetically separable sulfated zirconia

2.6. Acetalization and de-acetalization

Acetalization and deacetalization are fundamental transformations in organic chemistry, serving as versatile tools for carbonyl protection, controlled release of bioactive molecules, and synthesis of oxygenated scaffolds. These reactions enable selective masking of aldehydes and ketones as acetals, stable under basic/neutral conditions yet reversible under acidic or enzymatic triggers, making them indispensable in multistep syntheses of pharmaceuticals, fragrances, and polymers [88]. Recent advances in catalytic systems (e.g., Brønsted/Lewis acids, enzymes, and stimuli-responsive materials) have enhanced their efficiency and sustainability, particularly when using magnetically separable Bronsted acid catalysts.

Pourjavadi *et al*. reports the synthesis of an acidic poly(ionic liquid)-coated magnetic nanoparticle (Fe_3O_4@acidic-PIL) catalyst through distillation-precipitation polymerization of functionalized vinylimidazolium monomers on modified Fe_3O_4 nanoparticles (Fig. 23). The resulting heterogeneous catalyst efficiently promotes the formation of 1,1-diacetates (acylals) from aldehydes under solvent-free, room-temperature conditions, achieving high yields. Additionally, it facilitates the deprotection of acylals back to aldehydes. The catalyst design integrates the advantages of ionic liquids, such as high catalytic activity and tenability, with the magnetic properties of Fe_3O_4, enabling simple recovery using an external magnet. The polymeric ionic liquid (PIL) layer enhances stability, allowing multiple reaction cycles without significant loss in performance. The methodology eliminates the need for conventional filtration, streamlining catalyst separation. Given its operational simplicity, mild reaction conditions, and reusability, this system presents a practical and environmentally friendly approach for protecting and deprotecting aldehydes, with potential applications in organic synthesis and industrial processes [89].

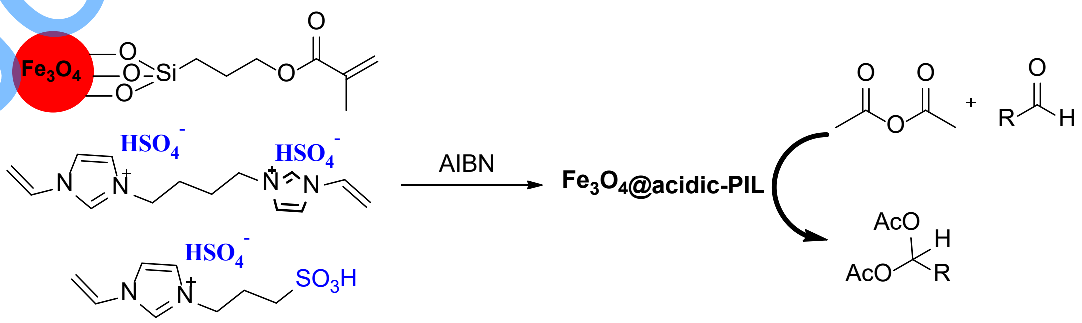

Fig. 23. Fe_3O_4@acidic-PIL as catalyst for the formation of 1,1-diacetates.

Wang *et al*. presents a two-step synthesis of a magnetic nano-solid acid catalyst (MNPsSi-PPh$_3$-SO$_3$H) by grafting an ionic liquid onto Fe$_3$O$_4$ nanoparticles, followed by sulfonation of the phenyl groups (Fig. 24). The catalyst demonstrates high efficiency in the acetalization of benzaldehyde with ethylene glycol, achieving a 97% yield under mild conditions. Its magnetic properties allow easy separation using an external magnet, and the catalyst retains its activity over multiple cycles without significant degradation [90].

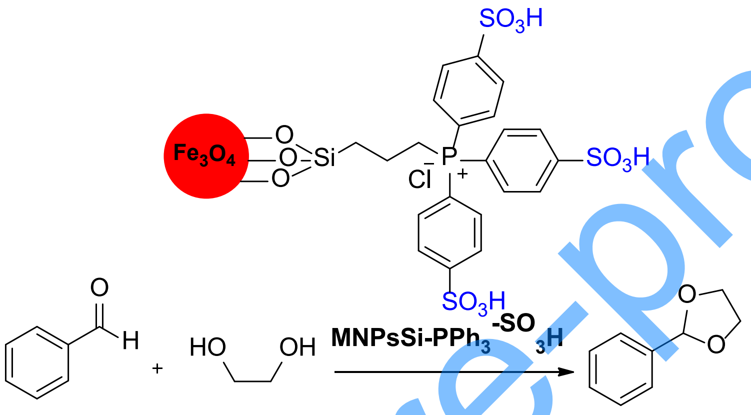

Fig. 24. MNPsSi-PPh$_3$-SO$_3$H catalyst for acetalization of benzaldehyde with ethylene glycol.

Masteri-Farahani and his co-worker reported the design of magnetically recoverable solid acid catalysts through the surface functionalization of silica-coated magnetite nanoparticles (SCMNPs) with sulfonic acid groups. The SCMNPs were first modified with 3-aminopropyl groups, followed by reaction with 1,4-butane sultone and acidification with phosphotungstic acid (HPW) or sulfuric acid to yield HPW-ampsul-SCMNPs and H-ampsul-SCMNPs, respectively. Comprehensive characterization confirmed the successful integration of acidic sites. The catalysts demonstrated excellent performance in the esterification of acetic acid with butanol and the acetalization of benzaldehyde with ethylene glycol, achieving high efficiencies. The presence of dual acidic sites enhanced catalytic activity. Both catalysts retained their activity over five consecutive cycles without significant degradation [91]. The same research group developed sulfonic acid-functionalized chitosan and chitosan-magnetite nanocomposites as efficient solid acid catalysts through a ring-opening nucleophilic reaction between chitosan's amine groups and 1,4-butane sultone.

Comprehensive characterization confirmed successful sulfonation and revealed increased surface area after nanocomposite formation. The chitosan-magnetite variant exhibited superparamagnetic properties, enabling convenient magnetic separation. Both catalysts demonstrated excellent performance in model acid-catalyzed reactions: esterification of acetic acid with n-butanol and acetalization of benzaldehyde with ethylene glycol [92].

Yuan *et al.* developed sulfonic acid-functionalized core-shell Fe_3O_4@carbon microspheres (Fe_3O_4@C-SO_3H) as efficient, recyclable solid acid catalysts. The synthesis involved interfacial polymerization of resorcinol-formaldehyde (RF) on magnetic Fe_3O_4 microspheres, followed by controlled carbonization and sulfonation to introduce acidic SO_3H groups (0.59-1.04 mmol/g). The resulting materials featured uniform core-shell structures, partially graphitized carbon frameworks, and strong superparamagnetism (10.6 emu/g saturation magnetization). When applied to the acetalization of benzaldehyde with ethylene glycol (Fig. 25), the catalyst demonstrated excellent performance (97% selectivity to benzaldehyde ethylene glycol acetal) and remarkable recyclability, maintaining activity over nine cycles with simple magnetic separation. The adjustable carbonization temperature allowed tuning of the carbon shell's graphitization degree, which in turn controlled the density of accessible acid sites [93].

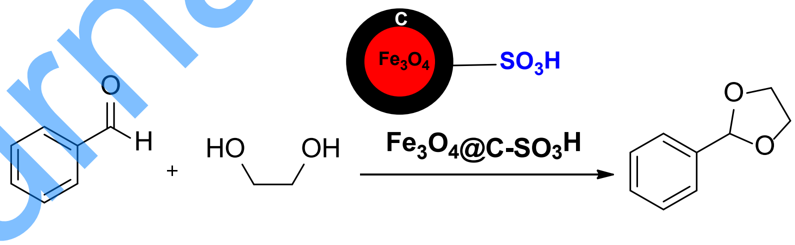

Fig. 25. Fe_3O_4@C-SO_3H catalyst for acetalization of benzaldehyde with ethylene glycol.

Using a relatively similar strategy, Zheng *et al.* reported a solvothermal synthesis of sulfonic acid-functionalized Fe_3O_4@C core-shell nanoparticles (Fe_3O_4@C-SO_3H) using ferrocene as a single precursor. The resulting magnetic nanoparticles (190 nm average size) feature a protective mesoporous carbon layer that prevents Fe_3O_4 core aggregation and oxidation while providing anchoring sites for Brønsted acid groups (0.2 mmol g^{-1} SO_3H loading). The catalyst demonstrated excellent performance in the model acetalization of benzaldehyde with ethylene glycol, achieving 88.3% conversion under mild conditions. Remarkably, the material maintained its catalytic activity through eight consecutive reaction cycles without significant degradation [94].

Veisi *et al.* presented a core-shell Fe_3O_4@PDA-SO_3H (PDA: polydopamine) nanocatalyst fabricated through sulfonic acid functionalization of polydopamine-coated magnetic nanoparticles. The material demonstrated exceptional catalytic performance in solvent-free acetylation reactions of diverse nucleophiles (alcohols, phenols, amines, thiols) with acetic anhydride at room temperature, achieving high yields across a broad substrate scope. The catalyst recovered during 12 consecutive reaction cycles without activity loss. The polydopamine shell serves as an effective platform for sulfonic acid group immobilization while protecting the magnetic core [95**]**. This research group reported an efficient N-formylation of various amines and alcohols using ethyl formate catalyzed by the same Fe_3O_4@PDA-SO_3H material under solvent-free conditions [96].

Jones and co-workers developed silica-coated magnetic nanoparticle (SiMNP) supported sulfonic acid catalysts through grafting four different sulfonic acids onto the silica surface. The hybrid organic-inorganic catalysts were thoroughly evaluated in the deprotection reaction of benzaldehyde dimethylacetaland compared with commercial acidic resins (Amberlyst A-15, Nafion) and homogeneous sulfonic acids. Characterization confirmed that three of the four catalysts maintained surface-bound acid functionalities while exhibiting comparable or superior activity to commercial alternatives. Interestingly, mesoporous SBA-15 supported versions (SBA1, SBA4) showed enhanced activity compared to nonporous SiMNPs, suggesting surface area optimization potential. While three catalysts functioned as true heterogeneous systems, one acted as a homogeneous source under these conditions, highlighting structure-performance relationships [97].

Hosseini *et al.* reports the synthesis of a novel dual-acid magnetic catalyst (HPW-SulPip-SCMNPs) by grafting sulfonic acid (–SO_3H) and phosphotungstic acid (HPW) groups onto silica-coated magnetite nanoparticles (SCMNPs) via a piperazine spacer (Fig. 26). Comprehensive characterization confirmed the successful integration of both Brønsted acid sites. The catalyst exhibited exceptional activity in the acetalization of benzaldehyde with ethylene glycol, achieving 97% conversion in a short reaction time, significantly outperforming the single-acid (sulfonic-only) variant, highlighting the synergistic effect of the dual-acid system. The piperazine spacer enhanced HPW immobilization and improved acid site distribution, boosting catalytic efficiency. Magnetic separation enabled easy recovery, and the catalyst retained full activity over four cycles without degradation. This work demonstrates the advantages of combining cooperative acid sites on a magnetically retrievable support, offering a sustainable and highly efficient alternative for acid-catalyzed reactions, with potential applications in fine chemical synthesis [98].

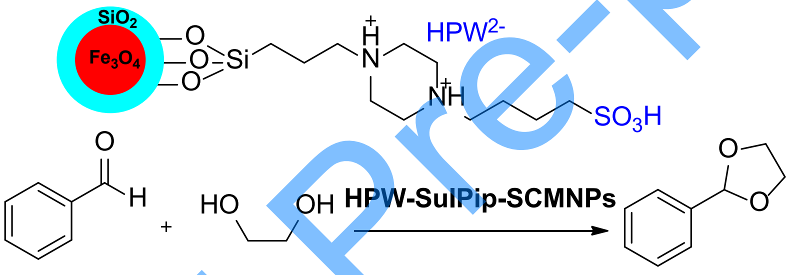

Fig. 26. HPW-SulPip-SCMNPs catalyst for acetalization of benzaldehyde with ethylene glycol.

2.7. Biginelli reaction

The Biginelli reaction represents one of the most efficient and atom-economical methods for constructing dihydropyrimidinones (DHPMs), privileged scaffolds in medicinal chemistry and drug discovery. These compounds exhibit diverse pharmacological activities, including antiviral, antihypertensive, and anticancer properties. The reaction's simplicity, a one-pot, three-component condensation of aldehydes, β-ketoesters, and urea/thiourea, aligns with green chemistry principles by minimizing waste and step count [99]. This section highlights recent advances in the application of magnetically recoverable acid catalysts for Biginelli reaction.

Mobaraki *et al.* developed two organosulfonic acid-functionalized silica-coated magnetic nanoparticle catalysts ($Fe_3O_4@SiO_2@Et\text{-}PhSO_3H$ and $Fe_3O_4@SiO_2@Me\&Et\text{-}PhSO_3H$) with tailored hydrophobicity for water-generating reactions. The last catalyst, featuring methyl groups, demonstrated superior water tolerance and activity in esterification of fatty alcohols, bis(indolyl)methane synthesis, and Biginelli reactions under solvent-free conditions. The hydrophobic methyl groups prevented water-induced deactivation of sulfonic acid sites, enabling efficient synthesis of 3,4-dihydropyrimidin-2-ones/thiones, pharmaceutically relevant DHPM derivatives. Comparative studies revealed that enhanced performance is due to improved mass transfer and water extrusion from active sites [100].

Zamani *et al*. presented a simple preparation of sulfonated-phenylacetic acid-coated Fe_3O_4 nanoparticles (Fe_3O_4/PAA-SO_3H) as a magnetically recoverable acid catalyst. The organic-inorganic hybrid material was successfully employed in the one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) via Biginelli reaction under mild, solvent-free conditions, yielding products in excellent yields (Fig. 27). The catalyst combines several advantageous features: (1) straightforward and cost-effective synthesis, (2) high catalytic activity under mild reaction conditions, and (3) convenient magnetic separation allowing multiple reuses without significant activity loss [101**]**. The same group presented a simple *in-situ* synthesis of a magnetic acid catalyst (Fe_3O_4/SMPA) through 3-mercaptopropanoic acid (MPA) coating followed by oxidation with H_2O_2/H_2SO_4. The resulting hybrid catalyst demonstrated excellent performance in the one-pot Biginelli reaction under almost same conditions, achieving high product yields [102**].**

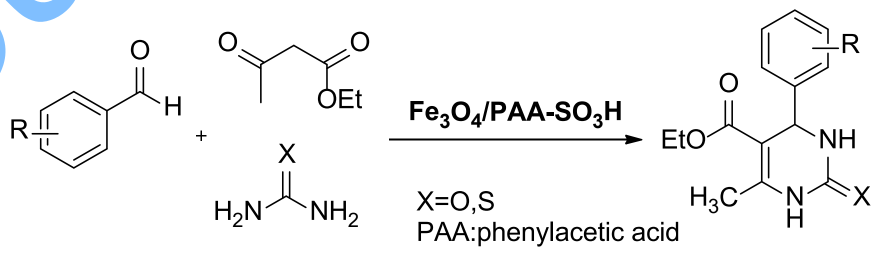

Fig. 27. Fe_3O_4/PAA-SO_3H catalyst for Biginelli reaction.

Recently, Jamshidifard *et al*. reported the development of novel magnetic nanocomposite catalysts through two distinct preparation methods: calcination and wet impregnation of TiO_2/ZnO nanoparticles on sulfonated melamine-formaldehyde (SMF)-coated Fe_3O_4. The resulting materials (Fe_3O_4/SMF/TiO_2/ZnO and SMF/Fe_3O_4/TiO_2/ZnO) were thoroughly characterized using FT-IR, XRD, BET, TGA, FESEM, TEM, EDX, and VSM techniques. These catalysts demonstrated exceptional performance in the Biginelli reaction, enabling rapid synthesis (30-45 min) of biologically active 3,4-dihydropyrimidinones with high yields (70-95%). The Fe_3O_4/SMF/TiO_2 variant showed particular effectiveness across diverse aldehydes, accommodating both electron-withdrawing and electron-donating substituents. The magnetic properties facilitated convenient catalyst recovery using an external magnet, with the materials maintaining activity over five consecutive cycles without significant performance loss. This work highlights the successful integration of multiple functional components (magnetic core, acidic SMF support, and metal oxide nanoparticles) to create efficient, reusable catalysts for pharmaceutically relevant multicomponent reactions [103].

2.8. Miscellaneous reactions

Zhu *et al*. reported the development of a novel class of magnetic solid acid catalysts (M@NC-SO_3H, M = Fe, Co, Ni) featuring sulfonated N-doped carbon nanotubes encapsulating transition metal nanoparticles. The catalysts were prepared through a simplified one-step calcination process that simultaneously formed the magnetic core and functionalized the carbon support. The Co@NC-SO_3H variant demonstrated exceptional catalytic performance in the condensation of levulinic acid with phenol to diphenolic acid (DPA), achieving 95% yield (Fig. 28). The unique encapsulated structure provided remarkable stability under acidic reaction conditions, as confirmed by recycling experiments and comprehensive characterization. The *in situ* formation of magnetic nanoparticles during calcination eliminated separate preparation steps while enabling efficient magnetic recovery.

Reaction optimization revealed temperature and additives as critical factors influencing conversion efficiency [104].

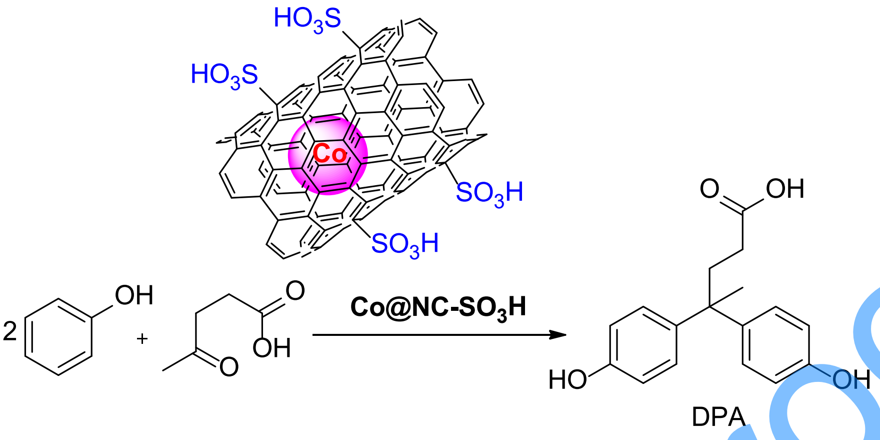

Fig. 28. Co@NC-SO_3H catalyst for diphenolic acid (DPA) synthesis.

Liang developed a magnetic carbon-based solid acid catalyst through hydrothermal carbonization of glucose on magnetic cores, followed by sulfonation with hydroxyethylsulfonic acid. The resulting core-shell structured material exhibited a high BET surface area with readily accessible acid sites on the carbon shell. The catalyst demonstrated exceptional performance in the hydrophobic alkylation of benzene with 1-dodecene, achieving complete conversion of dodecene and 74.4% selectivity for 2- or 3-dodecylbenzene, significantly outperforming conventional carbon-based acids (4.5–25.4% conversion) and homogeneous acids ($AlCl_3$, H_2SO_4). The hydrophilic surface groups (carbonyl, hydroxyl) suppressed double-bond migration, enhancing selectivity. Magnetic separation enabled simple recovery, and the catalyst maintained high activity over multiple cycles without degradation. With its high efficiency (100% conversion in 60 min), low catalyst loading (0.23 g), and stability in hydrophobic reactions, this system addresses key limitations of traditional solid acids while offering a sustainable alternative for industrial acid-catalyzed processes [105].

Wang *et al.* developed a magnetic sulfonated polystyrene brush catalyst (SG-Fe_3O_4@PS-PSH) through a multi-step synthesis involving surface-initiated atom transfer radical polymerization. The catalyst was fabricated by grafting sulfonated polystyrene chains onto 10 nm Fe_3O_4 nanoparticles, creating a core-shell structure with high sulfonic acid loading. When applied to ethyl N-phenylformimidate synthesis, the catalyst demonstrated superior performance compared to p-toluenesulfonic acid and commercial macroporous sulfonic acid resins, achieving faster reaction rates despite lower catalyst loading. The magnetic properties enabled simple recovery using an external field, reducing processing steps and minimizing catalyst loss. Remarkably, the catalyst maintained consistent activity over four reuse cycles without significant performance degradation. The brush-like architecture provided abundant accessible acid sites [106].

Very recently a magnetically separable Brønsted acid catalyst, [Fe_3O_4@SiO_2-$(Pr)_3$-N-Bu-SO_3H][HSO_4^-], was developed for the sustainable synthesis of Bisguaiacol-F (BGF), a safer alternative to Bisphenol-A (BPA) (Fig. 29). The catalyst enabled the condensation of aqueous formaldehyde and guaiacol with complete conversion of both reactants, eliminating the need for excess guaiacol. Remarkably, it achieved 99% guaiacol conversion with high selectivity for the *pp′*-BGF regioisomer (62%), alongside *mp′*-BGF (15%) and *op′*-BGF (6%). The pendant –SO_3H group on a flexible butyl chain enhanced catalytic accessibility, while the magnetic core allowed easy recovery and six reuses without activity loss. The method was extended to other aldehydes, demonstrating versatility for Bisguaiacol derivatives. This work presents an eco-friendly, industrially viable route to BGF, addressing health concerns associated with BPA while offering efficient catalysis, stoichiometric reactant use, and excellent recyclability [107].

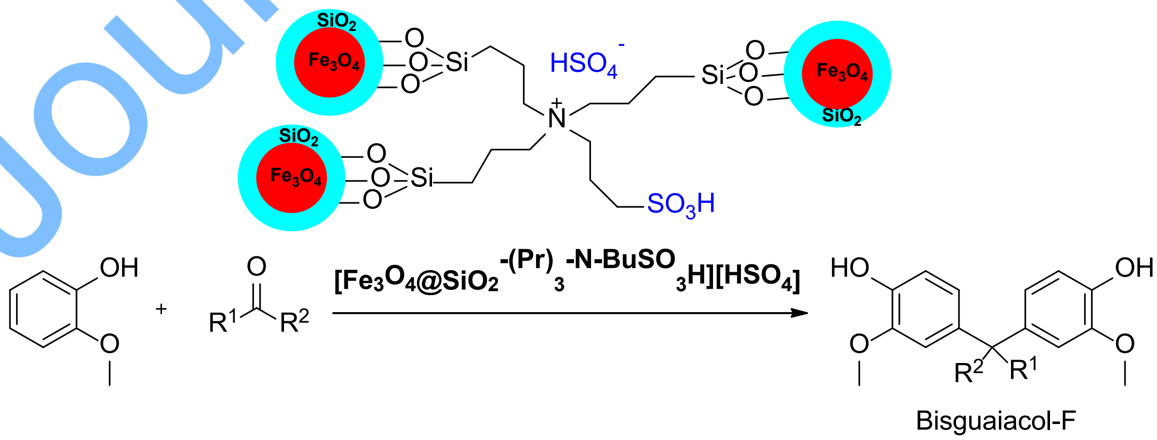

Fig. 29. [Fe_3O_4@SiO_2-$(Pr)_3$-N-Bu-SO_3H][HSO_4^-] catalyst for the synthesis of Bisguaiacol-F.

3. Summary and outlook

The development of magnetically separable Brønsted acid catalysts represents a transformative advancement in sustainable catalysis, addressing critical challenges in organic synthesis, biomass valorization, and industrial processes. These hybrid systems combine the high activity of homogeneous acids with the practical benefits of heterogeneous supports, enabling efficient recovery, recyclability, and reduced environmental impact. This review has comprehensively examined recent progress in their design, characterization, and applications across diverse reactions, including heterocycle synthesis, biodiesel production, esterification, hydrolysis of lignocellulosic biomass, 5-HMF production, acetalization/deacetalization, and multicomponent reactions like the Biginelli condensation.

Current research has focused on optimizing the design of these catalysts through various synthetic strategies. Core-shell architectures with carefully engineered interfaces have proven particularly effective, allowing for precise control over acid site distribution while protecting the magnetic core. Functionalization techniques such as covalent grafting, polymer coating, and ionic liquid immobilization have enabled the development of catalysts with tunable properties, including hydrophobicity, pore structure, and acid strength. These design innovations have translated into exceptional performance across multiple reaction types, with many systems achieving near-quantitative yields while maintaining excellent recyclability. The magnetic separation capability, often requiring less than a minute, represents a major advantage over conventional filtration or centrifugation methods.

The applications of these catalysts span diverse areas of chemical synthesis. In biodiesel production, they have enabled efficient processing of low-quality feedstocks with high free fatty acid content, overcoming limitations of traditional alkaline catalysts. For biomass conversion, their ability to hydrolyze recalcitrant cellulose and lignin structures under moderate conditions has opened new pathways for sustainable biorefineries. The synthesis of valuable platform chemicals like 5-HMF and pharmaceutical intermediates has benefited from their selective acid catalysis and easy recovery. Multicomponent reactions, including the Biginelli condensation, have been significantly improved through the use of these magnetically recoverable systems, offering both environmental and economic advantages over conventional methods.

Despite these advances, several challenges remain to be addressed. The stability of these catalysts under harsh reaction conditions, particularly at elevated temperatures or in strongly acidic environments, requires further improvement. Scalability of synthesis methods and cost-effectiveness of materials need optimization for industrial adoption. Performance with complex, real-world feedstocks often differ from model reactions, necessitating additional development. The balance between high acid site density and maintenance of strong magnetic properties continues to be an area of active research. Achieving acid strengths comparable to mineral acids, maintaining thermal and chemical stability under rigorous reaction conditions, ensuring leach-proof immobilization of active sites, and scaling up the synthesis of these catalysts while preserving their structural fidelity are areas that continue to require focused research. Furthermore, a deeper understanding of the structure–activity relationship (SAR), catalyst deactivation pathways, and reaction mechanism at the nanoscale is essential for rational design and application of next-generation magnetic Brønsted acid catalysts.

Looking forward, the field is moving toward more sophisticated catalyst designs and integrated process solutions. The development of multifunctional systems combining Brønsted acidity with other catalytic features shows particular promise. Biomass-derived supports and waste materials are being explored as sustainable alternatives for catalyst preparation. Process intensification through combination with alternative energy inputs like microwaves or ultrasound could further enhance efficiency. The integration of these catalysts into continuous flow systems represents another important direction for industrial implementation.

The broader implications of this technology extend to fundamental green chemistry principles and circular economy concepts. By reducing energy consumption in separation processes, minimizing waste generation, and enabling the use of renewable feedstocks, magnetic Brønsted acid catalysts align with global sustainability goals. Their potential to transform traditional chemical processes into more environmentally benign alternatives is particularly significant in the context of increasing environmental regulations and the push toward carbon neutrality.

As the field progresses, interdisciplinary collaboration will be essential to address remaining challenges and unlocks the full potential of these materials. The intersection of materials science, catalysis, and process engineering offers numerous opportunities for innovation. With continued development, magnetically separable Brønsted acid catalysts are poised to make substantial contributions to sustainable chemistry across academic and industrial settings, bridging the gap between fundamental research and practical applications in the chemical industry.

4. Challenges and future perspectives in particle design

Despite the significant progress in developing magnetic Brønsted acid nanocatalysts, several challenges in particle design remain to be fully addressed, presenting key avenues for future research.

A primary challenge lies in achieving precise control over the uniformity and reproducibility of the core-shell architecture. Inconsistent shell thickness or incomplete surface functionalization can lead to heterogeneous acid site distribution, directly impacting catalytic efficiency and reproducibility across batches. Furthermore, while magnetic separation is a major advantage, the long-term chemical and mechanical stability of the polymer or carbon shells under harsh reaction conditions (e.g., high temperatures, strong acidity, or in continuous flow systems) is not always guaranteed. Leaching of acidic species or degradation of the organic matrix can lead to a gradual decline in performance, limiting industrial applicability.

Another significant hurdle is the intricate and multi-step synthesis required for many of these sophisticated designs. Processes involving sequential polymerization, grafting, and functionalization, while effective on a laboratory scale, can be economically and technically challenging to scale up.

Simplifying synthesis protocols without compromising the catalyst's performance is crucial for broader adoption.

Looking forward, future research should focus on rational design strategies that target these challenges. The development of novel coating materials, such as more robust and inert ceramics or advanced porous organic frameworks, could enhance stability. Exploring single-pot synthesis methods that integrate magnetic core formation, shell growth, and acid functionalization in a single step would represent a significant advancement for scalability. Moreover, employing machine learning and computational modeling to predict the optimal combination of core, shell, and acid group for a specific reaction could accelerate the discovery of next-generation catalysts. Finally, more studies on the performance of these catalysts in continuous-flow reactors are essential to demonstrate their true potential for industrial-scale green chemical processes. By tackling these challenges, the field can move towards creating truly robust, efficient, and scalable magnetic acid catalysts.

Conflict of Interest

There are no competing interests to declare.

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