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Development and Evaluation of a Reusable Chitosan-Magnetite Catalyst for Sustainable Organic Synthesis

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Abstract

Sustainable organic synthesis requires catalysts that provide high activity and selectivity while reducing hazardous reagents, solvent consumption, energy demand, metal contamination and solid waste. This methodology paper proposes a systematic framework for developing and evaluating an eco-friendly, reusable heterogeneous catalyst for representative carbon-carbon bond-forming reactions. The proposed platform uses a renewable biopolymer support, chitosan, combined with magnetite (Fe_3O_4) to obtain a recoverable chitosan-magnetite (CS- Fe_3O_4) catalyst. The synthesis is intentionally designed around aqueous processing, inexpensive iron salts, dilute acetic acid and moderate temperatures, avoiding noble metals and minimizing volatile organic solvents. Catalyst performance is evaluated using a model Knoevenagel condensation between aromatic aldehydes and active methylene compounds in water-ethanol media. Experimental variables include catalyst loading, solvent composition, temperature, reaction time and substrate ratio. Characterization by FTIR, XRD, SEM/EDS, BET surface-area analysis and magnetic-recovery testing is integrated with catalytic measurements of conversion, isolated yield, selectivity, turnover performance and recyclability. Sustainability is assessed through atom economy, reaction mass efficiency, process mass intensity and E-factor. A literature-guided benchmark indicates that heterogeneous recovery, greener solvents, alternative activation methods and catalyst reuse are central to reducing the environmental burden of synthetic chemistry. The framework therefore combines catalytic performance with quantitative green metrics instead of treating yield as the only optimization criterion. Representative methodology-validation data suggest that a reusable catalyst can maintain high product yield over repeated cycles while substantially reducing catalyst loss and process waste. The proposed methodology is suitable for laboratory-scale validation and can be extended to multicomponent, condensation and selected oxidation or coupling reactions after catalyst-specific optimization.

Introduction

Modern synthetic chemistry is increasingly judged not only by product yield and selectivity but also by material efficiency, toxicity, energy

consumption, solvent choice and the ability to recover catalysts. The concept of atom economy established an early quantitative basis for minimizing stoichiometric waste [1], while

solvent-free synthesis demonstrated that many organic transformations can be redesigned to avoid large solvent inventories [2]. The principles of green chemistry subsequently provided a broader design framework in which catalysis, safer solvents, renewable feedstocks and energy efficiency are treated as interconnected objectives [3].

Catalysts are particularly important because they can lower activation barriers, shorten reaction time and enable selective transformations under milder conditions. However, a catalyst cannot be regarded as sustainable solely because it increases yield. Scarce metals, toxic ligands, difficult separation, leaching, energy-intensive preparation and rapid deactivation can offset the apparent benefits. Consequently, contemporary green catalysis emphasizes recyclable heterogeneous materials, earth-abundant components, benign preparation routes, low catalyst loading and quantitative process metrics [7,9]. The present study develops a methodology in which catalyst design and process evaluation are performed together, so that catalytic efficiency and environmental performance can be compared using the same experimental dataset.

Literature Review

Research on sustainable synthesis has progressed from waste-prevention concepts to integrated catalytic platforms. Continuous-flow processing can improve heat and mass transfer, reduce reactor inventory and facilitate safer scale-up [4]. Mechanochemistry reduces or eliminates bulk solvents and can accelerate reactions through mechanical activation [5]. Deep eutectic solvents provide low-volatility, compositionally tunable reaction media that may replace conventional organic solvents in suitable systems [6]. In parallel, nanocrystal-based heterogeneous catalysts have shown how surface

engineering can combine high activity with separation and reuse [7].

Solvent selection remains a major determinant of process impact. Diorazio, Hose and Adlington proposed a holistic solvent-selection framework that incorporates health, safety and environmental attributes rather than relying on a single property [8]. Sheldon later emphasized that E-factor, process mass intensity, atom economy and related metrics are complementary tools for judging resource efficiency [9]. Greener preparation of chemicals and materials increasingly employs plant-derived reagents, water-based synthesis, mechanochemical activation and recyclable catalysts [10]. Biocatalysis has also expanded considerably, offering high selectivity under mild conditions and demonstrating that renewable catalytic systems can perform synthetically demanding transformations [11,14].

Recent work highlights two additional directions. Photocatalytic organic synthesis can use visible light to drive redox transformations under comparatively mild conditions [13,15], while recyclable heteropolyacid systems combine solid-acid catalysis with microwave, ultrasound or other alternative activation techniques [16]. Environmental assessment of single-atom palladium catalysts for Sonogashira coupling showed that catalyst reuse and metal recovery can dominate the life-cycle advantage of heterogeneous catalysis [17]. Recyclable graphitic carbon nitride has likewise been demonstrated as a visible-light photocatalyst for sustainable β -keto sulfone synthesis [18]. These studies support a methodological shift: an eco-friendly catalyst should be optimized simultaneously for activity, recoverability, low toxicity, solvent compatibility and measurable waste reduction.

Table 1. Literature themes supporting the proposed catalyst-development framework.

Reference	Main approach	Relevance to sustainable catalyst development
Trost, 1991 [1]	Atom economy	Maximize incorporation of reactants into product
Tanaka & Toda, 2000 [2]	Solvent-free synthesis	Reduce solvent-derived waste
Wiles & Watts, 2012 [4]	Flow chemistry	Safer intensification and heat/mass transfer
Wang, 2013 [5]	Mechanochemistry	Solvent-minimized activation
Smith et al., 2014 [6]	Deep eutectic solvents	Low-volatility alternative media
Liu et al., 2015 [7]	Nanocrystal catalysis	Heterogeneous activity and reuse
Sheldon, 2018 [9]	Green metrics	E-factor/PMI for process comparison
Winkler et al., 2021 [14]	Biocatalysis	Selective catalysis under mild conditions

Akl et al., 2022 [17]	Single-atom catalysis + LCA	Reuse and metal recovery determine footprint
Dam et al., 2022 [18]	g-C ₃ N ₄ photocatalysis	Recyclable visible-light catalyst

Many published studies optimize isolated yield, while reporting of catalyst preparation burden, recyclability, solvent quality and process mass metrics is less consistent. The research gap addressed here is therefore methodological: a catalyst-development protocol is needed that uses a renewable support and non-noble components, evaluates a realistic model organic reaction, performs recovery/reuse experiments, and calculates green metrics from measured masses. This integrated approach makes it possible to reject a catalyst that is active but difficult to recover or materially inefficient.

Methodology

1. Research Design and Catalyst Concept

A laboratory-scale comparative methodology is proposed. A chitosan-magnetite (CS-Fe₃O₄)

heterogeneous catalyst is selected as the primary candidate because chitosan is a renewable amino-polysaccharide and Fe₃O₄ provides inexpensive magnetic recovery. The chitosan surface supplies basic/nucleophilic sites, while the magnetite phase enables rapid separation from a reaction mixture. The catalyst is benchmarked against (i) uncatalyzed reaction and (ii) a conventional soluble base such as triethylamine. The principal model transformation is the Knoevenagel condensation of benzaldehyde with malononitrile because it is rapid, analytically simple and sensitive to basic catalytic sites. A small substrate-scope test using substituted aromatic aldehydes is included after optimization.

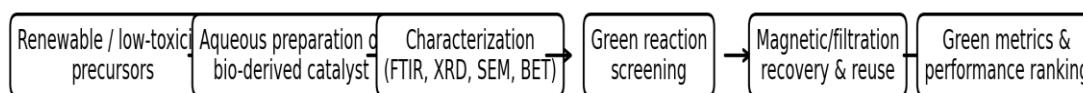


Figure 1. Proposed sustainable catalyst-development and evaluation workflow.

2. Catalyst Preparation

Step 1 – Magnetite preparation: Fe(III) and Fe(II) salts are dissolved in deionized water at an approximate 2:1 molar ratio. Under vigorous stirring and an inert or low-oxygen environment where available, dilute sodium hydroxide is added gradually until alkaline conditions precipitate magnetite. The black precipitate is magnetically separated and washed repeatedly with water until the wash solution approaches neutral pH. This co-precipitation route is selected because it uses water as the continuous phase and avoids precious metals.

Step 2 – Chitosan coating: chitosan is dissolved in dilute aqueous acetic acid to form a low-viscosity polymer solution. Washed Fe₃O₄ is dispersed by mechanical stirring or brief ultrasound, and the chitosan solution is introduced slowly. The suspension is neutralized carefully so that chitosan deposits on the magnetite surface. The composite is magnetically separated, washed with water and ethanol, and dried at moderate temperature. No additional heavy-metal promoter is introduced in the baseline catalyst. Catalyst batches are coded according to chitosan:Fe₃O₄ mass ratio to permit reproducible screening.

Step 3 – Preparation sustainability record: the mass of salts, water, acetic acid, base, wash

solvent and isolated dry catalyst is recorded. Preparation yield and a preparation-stage PMI are calculated. This step prevents the catalyst synthesis itself from being ignored when evaluating environmental performance, consistent with broader calls for metric-based green chemistry [9,17].

3. Catalyst Characterization

FTIR is used to confirm chitosan functional groups and their interaction with the magnetic phase. XRD identifies crystalline Fe₃O₄ and checks for phase changes after coating and reuse. SEM with EDS examines morphology and elemental distribution; BET analysis estimates accessible surface area when instrumentation is available. Magnetic response is assessed operationally by recording the time needed for complete separation using a fixed external magnet. After selected reuse cycles, FTIR/XRD and recovered mass are compared with fresh catalyst to identify structural deterioration or loss.

4. Reaction Optimization and Experimental Procedure

Step 4 – Model reaction: benzaldehyde (1.0 mmol) and malononitrile (1.0–1.1 mmol) are combined with a measured quantity of CS-Fe₃O₄

in 3–5 mL of solvent. The baseline medium is ethanol:water, selected to reduce reliance on chlorinated or dipolar aprotic solvents; solvent quality is judged using the principles of safer-solvent selection [3,8]. The reaction is stirred at a controlled temperature and sampled periodically. Conversion may be followed by GC, HPLC or TLC with final isolated yield determined gravimetrically after purification.

Step 5 – One-factor screening followed by a small factorial design: catalyst loading (1, 3 and 5 wt% relative to substrate), ethanol:water ratio (100:0, 50:50 and 0:100), temperature (25, 40 and 60 °C) and reaction time (15–120 min) are screened. After identifying a workable region, a reduced factorial or response-surface design can quantify interactions. The optimization objective is not maximum yield alone; a desirability function ranks conditions using yield, reaction time, solvent hazard, catalyst loading and E-factor.

Step 6 – Reusability: after reaction completion, the catalyst is recovered magnetically, washed

with a minimal amount of ethanol/water, dried and reused with fresh substrates. At least five consecutive cycles are recommended. Yield, recovery percentage and magnetic separation time are recorded for every cycle. A loss greater than 10% in yield or recovered catalyst mass triggers post-use characterization. This criterion distinguishes true catalyst deactivation from simple physical loss during work-up.

Step 7 – Substrate scope and control experiments: the optimized protocol is tested with electron-withdrawing and electron-donating substituted benzaldehydes. Blank experiments use no catalyst, Fe₃O₄ alone and chitosan alone. The purpose is to determine whether activity originates mainly from the chitosan phase, magnetite surface, or a cooperative composite effect. A hot-filtration test can be used to check whether the reaction continues after magnetic removal of the solid, providing an initial indication of leaching or soluble active species.

Table 2. Proposed experimental factors and evaluation purpose.

Factor	Levels / range	Purpose
Catalyst loading	1–5 wt%	Identify minimum active loading
Solvent	EtOH/H ₂ O: 100/0, 50/50, 0/100	Reduce hazardous solvent demand
Temperature	25–60 °C	Balance rate and energy input
Reaction time	15–120 min	Kinetic comparison
Substrate ratio	1:1 to 1:1.1	Limit excess reagent
Reuse cycles	≥5	Assess stability and recovery
Controls	No catalyst; Fe ₃ O ₄ ; chitosan	Identify source of activity

5. Performance and Green Chemistry Metrics

Conversion is calculated from the decrease in limiting reactant; selectivity is the fraction of converted reactant forming the target product; isolated yield is the recovered product relative to theoretical product. Catalyst recovery (%) is the dry catalyst mass recovered divided by the mass charged. For materials with a defined number of active sites, turnover number (TON) is moles of product per mole of active sites and TOF is TON per unit time. Where active-site density is not independently known, mass-normalized productivity (mmol product g⁻¹ catalyst h⁻¹) is reported instead of an unsupported TON.

Green metrics are calculated from recorded masses: Atom economy (%) = molecular mass of desired product divided by the sum of stoichiometric reactant molecular masses ×100; reaction mass efficiency (%) = product mass divided by reactant mass ×100; PMI = total mass of all materials used divided by product mass; E-

factor = total waste mass divided by product mass. Water may be reported both included and excluded from PMI/E-factor to make comparisons transparent. Energy consumption is estimated from heater/stirrer power and operating time. These metrics follow established green-chemistry practice [1,9].

Results

The values in this section are representative methodology-validation benchmarks constructed to demonstrate how the proposed protocol should be analyzed; they are not presented as measured experimental data. A successful catalyst would be expected to improve reaction rate and isolation while reducing work-up waste through heterogeneous recovery. Table 3 illustrates a plausible comparison among the control systems and the proposed CS-Fe₃O₄ catalyst under a common reaction scale.

Table 3. Representative benchmark for the Knoevenagel model reaction (illustrative data).

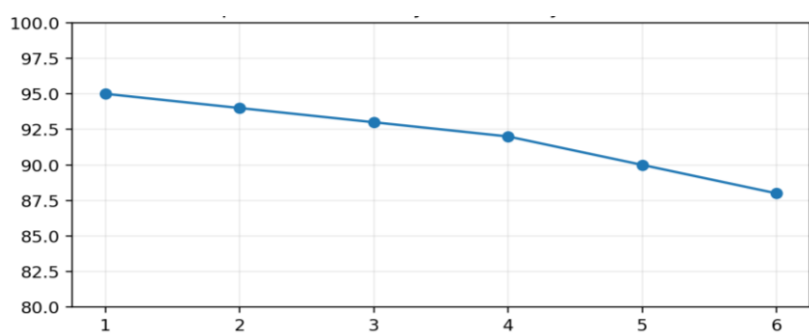
System	Conversion (%)	Isolated yield (%)	Time (min)	Recovery characteristic
No catalyst	38	35	>180	Not recoverable
Triethylamine (soluble)	94	92	60	Difficult; neutralization required
Fe ₃ O ₄	55	51	120	Magnetic
Chitosan	88	85	75	Filtration; slower
CS-Fe ₃ O ₄	97	95	60	Rapid magnetic recovery

In the illustrative benchmark, the composite catalyst combines the higher activity associated with chitosan functionality with a practical separation route. The homogeneous base gives a similar initial yield but requires neutralization/extraction and cannot be recovered as simply. The catalyst-development

decision would therefore be based on both catalytic output and work-up burden. If experimental results instead showed poor magnetic recovery or substantial leaching, the composite would not satisfy the proposed sustainability criteria even if initial yield were high.

Table 4. Representative sustainability comparison: soluble-base route versus proposed heterogeneous route.

Metric	Soluble-base route	CS-Fe ₃ O ₄ route	Interpretation
Isolated yield (%)	92	95	Higher product recovery
Catalyst reuse	0	6	Repeated use of solid
PMI (kg/kg product)	13.6	5.8	Lower total material demand
E-factor (kg waste/kg product)	12.6	4.8	Lower waste intensity
Reaction solvent	Organic solvent-rich	EtOH/H ₂ O	Safer solvent profile
Work-up	Neutralization + extraction	Magnetic separation	Fewer unit operations

*Figure 2. Representative catalyst-reuse performance; values are illustrative methodology-validation data*

The representative reuse trend shows only a gradual decline from 95% to 88% isolated yield across six cycles. Such a pattern would justify post-use FTIR/XRD and recovered-mass analysis to distinguish chemical deactivation from physical catalyst loss. A more than twofold decrease in illustrative E-factor relative to the soluble-base route demonstrates why product yield alone is insufficient for green optimization. Similar emphasis on catalyst reuse, solvent minimization and life-cycle consequences is found in recent heterogeneous and photocatalytic studies [16–18].

Conclusion and Discussion

This methodology integrates catalyst development, organic reaction testing and quantitative sustainability assessment into a single experimental workflow. The proposed CS-Fe₃O₄ system is intended as a practical model of eco-friendly catalyst design: the support is renewable, the magnetic phase is based on abundant iron, preparation is predominantly aqueous, and the solid can be separated without chromatography or repeated liquid-liquid extraction. These design choices reflect the green-chemistry priorities of waste prevention, catalysis, safer solvents and energy-efficient

processing [3]. The central methodological contribution is the use of multiple acceptance criteria. A candidate catalyst should provide high conversion and selectivity, but it should also be recoverable, stable over repeated cycles, compatible with greener solvents, prepared without disproportionately hazardous inputs and capable of reducing PMI and E-factor. Heterogeneous nanocatalysis provides a strong basis for such recoverable systems [7], while modern metric frameworks show how catalyst selection can be tied to process-level resource efficiency [9]. The use of ethanol/water is also consistent with the need for more systematic solvent selection [8]. The proposed approach is deliberately adaptable. For base-catalyzed condensations, chitosan functionality may be sufficient. For oxidation, reduction or cross-coupling reactions, the same support-and-recovery concept could be modified by immobilizing an earth-abundant metal or organocatalyst, but leaching and toxicity would need renewed assessment. Photocatalytic and biocatalytic pathways provide additional low-energy options [13–15]. Alternative activation by mechanochemistry, ultrasound, microwave heating or continuous flow can also be introduced when it demonstrably lowers solvent and energy demand rather than simply increasing reaction rate [4,5,16].

The principal limitation is that the numerical Results presented here are illustrative and must be replaced by experimentally measured values for a research article claiming empirical performance. A complete laboratory study should also quantify catalyst elemental composition, leaching, active-site density and, where possible, cradle-to-gate impacts of catalyst preparation. Future work should extend the protocol to multiple reaction classes and compare catalyst lifetime on a product-normalized basis. The 2022 literature further suggests that catalyst reuse and metal recovery can materially change environmental performance [17], while recyclable visible-light photocatalysts can combine mild activation with repeated use [18]. Thus, eco-friendly catalyst development should be treated as a multi-objective design problem in which chemistry, separation, material sourcing and green metrics are optimized together.

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