Core-shell structured Fe₃O₄@MgO: magnetically recyclable nanocatalyst for one-pot synthesis of polyhydroquinoline derivatives under solvent-free conditions

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Abstract. Core-shell nanostructured Fe₃O₄@MgO catalyst was synthesized using a two-fold co-precipitation technique. High-resolution transmission electron microscopy (HR-TEM) images demonstrated that the catalyst had a core-shell framework with spherical morphology. In present study, Fe₃O₄@MgO is successfully used as an effective, novel, and recoverable nanocatalyst in an easy-to-follow, affordable, environment-friendly, and productive process for the synthesis of polyhydroquinoline derivatives via one-pot four-component Hantzsch condensation reaction. Importantly, magnetically retrievable Fe₃O₄@MgO nanoparticles provides high catalytic efficiency in solvent-free condition and can be used repeatedly up to six cycles without significant loss of catalytic activity. The study provides a greener route to yield 82-94% of polyhydroquinoline in a short reaction time under ultrasonication.

Keywords. Fe₃O₄@MgO; core-shell nanostructures; magnetically separable; polyhydroquinoline; green approach.

1. Introduction

Heterocyclic chemistry is recognized as one of the most significant and beneficial subfields of chemistry. The majority of pharmaceutical molecules and natural chemicals that mimic pharmaceutical compounds with biological activity are heterocyclic.¹ These molecules form the basis for most pharmaceuticals and antibiotics.² In this regard, it has been demonstrated that N-containing heterocyclic compounds, or more specifically quinoline derivatives, possess advantageous biological properties such as antimalarial, antibacterial, antiasthmatic, antihypertensive, and anti-inflammatory properties.³

Synthesis of polyhydroquinoline and its derivatives has acquired a great interest in the domain of synthesizing various medicinal products due to their pharmacological and biological properties such as analgesic, diuretics, vasodilators, bronchodilators, anti-HIV, antiatherosclerotics, anticancer, hepatoprotective and anti-diabetic properties.⁴⁻¹⁰ Polyhydroquinoline derivatives are also another possible class of calcium channel antagonists.¹¹ These compounds share structural similarities with physiologically active 1,4-dihydropyridines.¹²

Multi-component reactions (MCRs) have proven to be extremely potent and efficient reaction tools in organic, combinatorial, and medicinal chemistry over the past decade.¹³,¹⁴ The nature of the catalyst plays a very significant role in determining yield, selectivity, and general applicability in MCRs.¹⁵ Consequently, the development of a cheap, highly active, selective, reusable, mild, and heterogeneous catalyst for MCRs has become the most attractive research area in organic chemistry.¹⁶,¹⁷

The current scenario recommends a green approach in the organic transformation which encourages simple protocol, easy recovery of the catalyst, minimal or zero use of volatile organic solvents, toxic reagents, harsh conditions, etc.¹⁸ In this context, magnetic nanocatalysts have garnered substantial attention from researchers. They offer many size-related properties
such as large surface area, fine-tuning of the features, enhanced loading capacity, good dispersion, remarkable stability, and simple catalytic recycling, improving the efficiency of heterogeneous catalysis in MCRs.\textsuperscript{19–22} In contrast to cross-flow filtering and centrifugation, magnetic separation facilitates the recovery of catalysts from liquid-phase processes. Additionally, the magnetic characteristics of the particles are sufficiently robust to withstand most chemical conditions.

Previous reports have shown that combining magnetic nanostructures with other potentially reactive phases enhances catalytic performance.\textsuperscript{23} Specifically, core-shell structured nanomaterials provide benefits of enhanced catalytic performance due to the shell’s nanointerface (in terms of porosity, surface area, etc.) and the core’s support function\textsuperscript{24} synergy between the shell and the core that allows for greater efficiency, yield, and selectivity in catalytic applications.\textsuperscript{25}

Nowadays application of ultrasonication has become very common and a powerful tool for a variety of organic transformations. It this method, cavitation bubbles are created in the reaction media, allowed to expand, and then violently burst under the influence of ultrasonic waves, which speeds up the chemical processes. Compared to conventional approaches, the ultrasound-assisted approach has numerous benefits, including higher reaction rates, more favourable reaction conditions, and improved yields. Additionally, this approach is more cost-effective and less harmful to the environment.\textsuperscript{26}

Synthesis of physiologically active chemicals now frequently employs solvent-free and solid-state processes. Reducing the reaction time, simplifying the workup method, increasing product yields, and eliminating the requirement for an organic solvent are just some of the benefits of conducting the reaction without using hazardous and volatile organic solvents. Environmentally friendly processes are further advanced when solvent-free reactions are combined with different supporting catalysts. The employment of solvent-free conditions and methods, such as grinding, high-speed ball mills, and ultrasound irradiation, further improves the advantages and environmental friendliness over conventional methods.\textsuperscript{27}

Size-dependant properties, core-shell structure, and magnetic nature of Fe$_3$O$_4$@MgO make it an attractive candidate as a catalyst in organic transformations. Though these bifunctional Fe$_3$O$_4$@MgO nanoparticles have the potential to act as a catalyst, they remained unexplored. Very few studies were conducted using Fe$_3$O$_4$@MgO nanoparticles.

Previously, Fe$_3$O$_4$@MgO nanocomposite was utilized for the synthesis of phosphoramidites via the Atherton–Todd reaction,\textsuperscript{28} it was also used for selective adsorption of amaranth dye\textsuperscript{29} and rapid removal of polycyclic aromatic hydrocarbons and cadmium ions from water.\textsuperscript{30}

The present study focuses on developing Fe$_3$O$_4$@MgO, a magnetic core-shell structured nanocatalyst for synthesizing polyhydroquinoline derivatives under solvent-free conditions. The catalyst is comprised of a magnetic core of Fe$_3$O$_4$ nanoparticles and a thin shell of MgO. Fe$_3$O$_4$ core provides magnetic separability and strong support to the shell. Bare MgO itself is a versatile catalyst used in heterocyclic reactions. However, the combination of MgO and Fe$_3$O$_4$ provides diverse merits in catalysis such as facile preparation, greater surface-to-volume ratio, wide availability, economically viable, eco-friendly, easy separation, low catalyst loading which makes the synthetic protocol simple, one-pot, low-cost and green. This study introduced the successful utilization of Fe$_3$O$_4$@MgO core-shell for the synthesis of polyhydroquinoline derivatives via one-pot condensation of substituted aromatic aldehydes, ethyl acetocetate, dimedone, and ammonium acetate, respectively under solvent-free conditions (Figure 1).

2. Materials and methods

The reagents and chemicals used for the research work are of AR grades and were purchased from SD Fine Chemicals and used without any extra purification.

2.1 Synthesis of Fe$_3$O$_4$@MgO core-shell nanoparticles

In two-step synthesis, magnetic Fe$_3$O$_4$ nanoparticles were synthesized by using the simple co-precipitation method. Further, magnetic Fe$_3$O$_4$ nanoparticles were coated with MgO through direct precipitation. Typically, 0.5 g of as-prepared Fe$_3$O$_4$ nanoparticles were dispersed in 100 mL of CTAB (1 g) solution which

![Figure 1. Fe$_3$O$_4$@MgO Catalysed synthesis of polyhydroquinoline derivatives.](image-url)
helps to increase the stability of MNP’s. After 30 min of sonication, 50 mL of a 0.5 mol L⁻¹ MgCl₂ solution was added, and the mixture was stirred for 1 hour at room temperature. Further, the temperature was raised to 70 °C and ammonia solution was added with constant stirring for four hours. The mixture was allowed to cool to room temperature. The resulting product was washed multiple times with ethanol before being dried for six hours at 50 °C. The product was calcined at different temperatures, such as 450 °C, 550 °C, and 650 °C for three hours. The resulting brown-colored powder was further characterized to study their structural and morphological properties.

2.2 Characterisation of catalyst

Powder X-ray diffraction pattern was recorded using Bruker D8 Advance using CuKα radiation (wavelength λ = 0.15406 nm) over diffraction angles 2θ = 20 – 80°. The surface morphology of the nanoparticles was studied by using a High-Resolution Transmission electron microscope (HRTEM) (FEI, Tecnai G2, F30, 300 kV) and EDAX analysis is carried out using JEOL 6390 LA/OXFORD XMX N. The Zeta potential Fe₃O₄@MgO was determined using Malvern Zeta Sizer. The surface area was determined by single point dynamic N₂ BET method at -196 °C with N₂ purging for one hour on Micromeritics, ASAP 2010.

2.3 General procedure for the synthesis of polyhydroquinoline derivatives

A mixture of aldehyde (1 mmol), dimedone (1 mmol), ammonium acetate (1.5 mmol), ethyl acetoacetate (1 mmol), and 20 mg of Fe₃O₄@MgO nanoparticles (10 mol%) were taken in a round bottom flask and sonicated for the required time. The progress of the reaction was monitored by TLC (n-Hexane: EtOAc, 10:4). The final product was heated in ethanol and poured into water. The catalyst was magnetically removed and washed with ethanol for reuse. The residue was then poured into crushed ice and stirred. The pure product was obtained by recrystallization from hot aqueous alcohol. The magnetically separated catalyst was washed with chloroform and reused six times. Fe₃O₄@MgO core-shell nanoparticles were found to be a more rapid and effective catalyst for the synthesis of polyhydroquinoline derivatives with excellent yields.

The melting points of synthesized compounds were determined by the open capillary method and were reported without any further correction. The products’ Fourier Transform Infrared (FT-IR) spectrum was recorded using 3000 Hyperion Microscope with Vertex 80 FTIR System (Bruker, Germany) to determine the presence of specific functional groups in the molecule. ¹H NMR spectra were performed in CDCl₃ using TMS as an internal Standard on 400 MHz liquid state NMR spectrometer instrument. All Proton chemical shifts (δ) are relative to tetramethyl silane (TMS, δ = 0.00) as an internal standard, and coupling constants (J) are given in Hz.

2.4 Selected spectral data

2.4a Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 1, Entry 2): IR (KBr) 3295, 2959, 1699, 1605, 1517, 1482, 1345, 1218, 1073, 836, 694 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.92 (s, 3H), 1.10 (s, 3H), 1.12 (t, 3H), 1.57 (d, 1H), 2.36 (d, 1H), 2.43 (m, 4H), 3.51 (d, 1H), 4.06 (q, 2H), 5.16 (s, 1H), 7.47 (d, 2H), 8.09 (d, 2H), 9.18 (s, 1H, NH). ¹³C NMR (101 MHz, CDCl₃) δ 200.44, 166.43, 153.78, 151.68, 149.30, 145.88, 133.75, 128.50, 123.48, 109.26, 102.13, 82.21, 55.78, 46.31, 37.89, 32.32, 29.16, 24.67, 19.41.

2.4b Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 1, Entry 5): IR (KBr) 3275, 2958, 1706, 1604, 1488, 1381, 1214, 1200, 1071, 844, 534 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.92 (s, 3H), 1.06 (s, 3H), 1.20 (t, 3H), 1.78 (d, 1H), 2.16 (d, 1H), 2.20–2.28 (m, 4H), 2.35 (d, 1H), 4.05 (q, 2H), 5.02 (s, 1H), 6.49 (d, 2H), 7.25 (d, 2H), 9.04 (s, 1H, NH). ¹³C NMR (101 MHz, CDCl₃) δ 200.56, 171.38, 153.57, 150.84, 148.54, 136.86, 134.91, 133.35, 117.03, 110.78, 110.78, 65.75, 56.05, 45.99, 41.33, 37.86, 34.61, 32.38, 24.51, 19.13.

2.4c Ethyl 4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 1, Entry 9): IR (KBr): 3488, 3277, 3073, 2958, 2930, 1683, 1491, 1590, 1480, 1194 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.94 (s, 3H), 1.00 (s, 3H), 1.20 (t, 3H), 1.62–2.49 (m, 4H), 2.59 (s, 3H), 4.40 (q, 2H), 4.98 (1H, s, CH), 6.61–6.97 (d, 2H), 7.27 (d, 2H), 8.74 (s, 1H), 9.04 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.96, 159.72, 148.07, 134.55, 120.07, 65.38, 56.06, 52.99, 40.88, 37.79, 33.48, 32.38, 28.83, 24.17, 19.51.
Table 1. Fe₃O₄@MgO catalyzed direct synthesis of polyhydroquinoline derivatives.

<table>
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<td>13</td>
<td>![Product 13]</td>
<td>8</td>
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<td>266-268</td>
</tr>
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</table>

aReaction conditions: aldehyde (1 mmol), dimedone (1 mmol), ammonium acetate (1.5 mmol), ethyl acetoacetate (1 mmol), and 20 mg of Fe₃O₄@MgO.

bYield of pure isolated products.

cMelting points of isolated pure products.

2.4d Ethyl 4-(4-fluorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 1, Entry 11): IR (KBr) 3180, 2958, 1706, 1604, 1488, 1381, 1200, 1214, 1071, 844, 534 cm⁻¹. 

¹H NMR (400 MHz, CDCl₃) δ 0.97 (s, 3H), 1.08 (s, 3H), 1.22 (t, 3H), 1.57 (d, 1H), 2.21 (d, 1H), 2.31–2.37 (m, 4H), 2.89 (d, 1H), 4.96 (q, 2H), 5.60 (s, 1H), 7.27 (d, 2H), 7.52 (d, 2H), 9.09 (s, NH). 

¹³C NMR (101 MHz, CDCl₃) δ 200.57, 166.36, 153.94, 148.08,
IR (KBr) 3175, 2958, 1756, 1604, 1381, 1219, 1171, 884, 634 cm$^{-1}$. 1H NMR (400 MHz, CDCl$_3$) $\delta$ 1.11 (s, 6H), 1.58 (s, 3H), 2.24 (s, 3H), 2.31 (d, 2H), 3.80 (s, 9H), 4.12 (s, 2H), 5.03 (s, 3H), 5.72 (s, 1H), 6.54 (s, 1H), 7.27 (s, 1H) 9.28 (s, 1H), 13C NMR (101 MHz, CDCl$_3$) $\delta$ 157.90, 110.55, 82.74, 82.00, 81.88, 65.92, 65.05, 61.25, 55.92, 46.53, 41.77, 37.91, 34.74, 32.27, 24.73, 19.53.

2.4f 4-(4-Dimethylamino-phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-quinoline-3-carboxylic acid ethyl ester (Table 1, Entry 13): IR (KBr) 3278, 2858, 1716, 1600, 1478, 1318, 1215, 1204, 1171, 854, 543 cm$^{-1}$. 1H NMR (400 MHz, CDCl$_3$) $\delta$ 9.06 (s, NH), 7.27 (s, 2H), 6.72 (s, 1H), 6.53 (s, 1H), 5.04 (s, 1H), 4.07 (q, 2H), 2.64 (s, 8H), 1.95 (s, 5H), 1.56 (s, 3H), 1.30 (s, 6H). 13C NMR (101 MHz, CDCl$_3$) $\delta$ 200.53, 195.32, 177.98, 153.16, 148.22, 134.92, 119.31, 65.04, 56.07, 46.49, 41.01, 37.86, 34.70, 32.35, 24.86, 19.37.

3. Results and Discussion

3.1 Characterization of catalyst

The XRD analysis of Fe$_3$O$_4$@MgO powder exhibited the characteristic peaks of the crystalline phase of Fe$_3$O$_4$ with MgO (Figure 2). X-ray diffraction (XRD) patterns of the Fe$_3$O$_4$ and Fe$_3$O$_4$@MgO catalyst annealed at three different temperatures (450 °C, 550 °C, and 650 °C), are shown in the figure. The effect of temperature on Fe$_3$O$_4$@MgO was studied by annealing at different temperatures. XRD patterns reveals there is no effect of temperature on nanoparticles.

The HRTEM images (Figure 3a and b) reveal the spherical-shaped core-shell particles of Fe$_3$O$_4$@MgO. The clear lattice fringes reveal the crystalline nature of the Fe$_3$O$_4$ core however; the shell structure is amorphous and less dense than the core structure. The shell diameter is measured ~ 5 nm for almost all particles. The average core size found is ~ 12 nm, and some crystal planes are visible in the core structure calculated using ImageJ software. The Interlayer d-spacing was measured with ImageJ software, as illustrated in Figure 3b. The d-spacing values of Fe$_3$O$_4$@MgO were calculated as 2.06, 2.12 Å assigned to the (200) plane of MgO and 2.53, 2.49 Å assigned to the (311) plane of Fe$_3$O$_4$ as synchronized with XRD results.

Elemental composition/distribution provided by EDAX analysis as shown in Figure 3d. The strong peaks around 1.3 keV, 0.6 keV, and 6.5 keV represent the presence of elemental magnesium, oxygen, and iron as the main component of the nanocatalyst. By weight percent composition, Fe, O and Mg were found to be 9.86%, 42.99%, and 47.21%.

The simple and efficient recovery of the catalyst is illustrated in Figure 4 by the application of an external magnetic field. The BET surface area analysis showed that the surface area of the particles was 19.341 m$^2$/gm. The Zeta potential was found to be ~24.4 mV.
indicating nanocatalysts’ high colloidal stability in heterogeneous catalytic reactions.

3.2 Catalytic performance of nanocrystalline Fe₃O₄@MgO core-shell nanoparticles in the synthesis of polyhydroquinoline derivatives

The catalytic efficiency of Fe₃O₄@MgO core-shell nanoparticles in the synthesis of polyhydroquinolone derivatives was investigated at various operational conditions. The proposed method was applied to a model reaction involving benzaldehyde, dimedone, ethyl acetoacetate, and ammonium acetate to optimize a variety of reaction conditions, including catalyst loading, reaction time, temperature, and solvent effect (Table 1, Entry 1).

The model reaction was monitored in various solvents like C₂H₅OH, CHCl₃, CH₃CN, CH₃OH, DMF, and CH₂Cl₂ (Table 2, Entry 3-9). Other solvents were found to be substantially less successful than solvent-free ultrasonication for producing polyhydroquinolines (Table 2, Entry 10). This sequence of reactions was carried out with varying amounts of the Fe₃O₄@MgO catalyst (Table 2, Entry 11-13). In the absence of sonication, the reaction under solvent-free conditions produced a relatively low yield of the product (Table 2, Entry 1). In the absence of a catalyst, the product yield obtained was extremely low at room temperature and even under ultrasonication (Table 2, Entry 2-3).

Figure 3. (a) TEM image; (b) High-resolution TEM image; (c) SAED pattern; (d) EDAX analysis of Fe₃O₄@MgO core-shell nanoparticles.
The catalytic amount of 0.020 g was sufficient to obtain a remarkable yield (Table 2, Entry 10). Further increase in catalyst load did not show a noticeable effect on reaction time as well as product yield. The versatility of the proposed method was investigated by using different aromatic aldehydes. The aromatic aldehydes containing electron-donating and electron-drawing functional groups successfully produced the polyhydroquinoline derivatives that were expected to a significant extent (82-94%), as shown in Table 1 (Entry 1-13). Table 1 shows that aldehydes with electron-withdrawing groups responded more quickly than those with electron-releasing groups, as would be predicted. Longer reaction periods were needed for aromatic aldehydes that were sterically inhibited.

### Table 2. Optimization of reaction parameters for polyhydroquinoline derivative synthesis by using Fe₃O₄@MgO catalyst® (Table 1, Entry 1®).

<table>
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<th>Entry</th>
<th>Fe₃O₄@MgO (mg)</th>
<th>Solvent</th>
<th>Time (Min)</th>
<th>Temp</th>
<th>Yield (%)</th>
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<td>RT</td>
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*®Reaction conditions: The reactions were performed with Benzaldehyde (1.0 mmole), diamonide 2 (1 mmol), ammonium acetate 3 (1.5 mmol), ethyl acetoacetate 4 (1 mmol).®Yield of isolated pure products.
Electron-poor groups like fluoro and chloro, in ortho- or para-substituted benzaldehydes, showed less activity than benzaldehyde. The yields were good for those having electron-rich groups at the para position, such as methyl, methoxy, and tertiary amine. This is attributed to the better ability of the catalyst to coordinate with these compounds.

3.3 Reusability of the catalyst

Nanocatalyst Fe$_3$O$_4$@MgO is robust enough to retrieve magnetically without any loss. Therefore, the model reaction was studied for a total of six runs without suffering a significant reduction in its catalytic activity (Figure 5). After each use, the catalyst was washed with ethanol, and then the subsequent run was carried out with a brand-new reaction setup.

The peaks around 1.3 keV, 0.6 keV, and 6.5 keV indicate the presence of elemental magnesium, oxygen, and iron in the nanocatalyst following a six-fold reusability assessment shown in Figure 6. The weight percent composition of Fe, O, and Mg was determined to be 7.96%, 41.87%, and 27.13%, respectively. However, some additional peaks indicating the breakdown of the catalyst were identified.

Based on the results mentioned, a possible mechanism for the synthesis of polyhydroquinoline is illustrated in Figure 7. It depicts a potential synthesis mechanism for polyhydroquinoline derivatives. Aldehydes are coupled with active methylene compounds (dimedone and ethyl acetoacetate) in a Knoevenagel reaction. Additionally, the desired products can be obtained via a Michael addition of the intermediates.
Comparison of catalytic activity of \( \text{Fe}_3\text{O}_4@\text{MgO} \) with reported nanocatalysts

To synthesize a polyhydroquinoline derivative, the catalytic activity of magnetic \( \text{Fe}_3\text{O}_4@\text{MgO} \) was studied and compared to that of nanocatalysts that had been reported previously. This unequivocally demonstrates that nanocrystalline magnetic \( \text{Fe}_3\text{O}_4@\text{MgO} \) is an easy-to-use, highly efficient, and cost-effective catalyst that, under typical reaction conditions, can produce very high yields of polyhydroquinoline derivatives.

Table 3 demonstrates that \( \text{Fe}_3\text{O}_4@\text{MgO} \) nanocatalyst is rapid and efficient in synthesizing polyhydroquinoline derivatives under solvent-free conditions compared to the previously reported catalysts. An extraordinary yield of products is produced through rapid reactions. Further, magnesium oxide’s (MgO) low specific weight, high melting point, and negligible lattice mismatch with magnetite make it a promising magnetic core coating material.

4. Conclusions

Coprecipitation was used to prepare magnetically separable \( \text{Fe}_3\text{O}_4@\text{MgO} \) core-shell nanoparticles, which were subsequently utilized as a heterogeneous catalyst for the one-pot synthesis of polyhydroquinoline derivatives. With a maximum yield of 94%, a variety of aldehydes were transformed under solvent-free conditions using ultrasonication into their corresponding polyhydroquinoline derivatives. Notable features of this study include a new catalyst, green methodology, simple technique, rapid reaction time, a high product yield, and a catalyst that can be used repeatedly without degrading.

Supplementary Information (SI)

Supplementary information related to this article is available at http://www.ias.ac.in/chemsci.

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Declarations

Conflicts of interest The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

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