FULL PAPER

Hybrid ceria and chitosan supported nickel nanoparticles: A recyclable nanocatalytic system in the reduction of nitroarenes and the synthesis of benzopyran derivatives in green solvent

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Abstract

Mesoporous, highly temperature resistant, magnetically separable, bimetallic, and organic-based photoluminescent nanocatalyst has been prepared. Chitosan can act efficiently as a support material for preparing nanocatalysts. Hybrid ceria, that is, iron-doped-cerium oxide (Fe@CeO₂), was prepared via coprecipitation method. Chitosan-iron-doped-ceria nanocomposite was prepared and kept in a solution of NiCl₂ to adsorb Ni²⁺ ions, which were then reduced with NaBH₄ to accumulate nickel nanoparticles. The characterization of nanocatalyst was performed using different techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), highresolution transmission electron microscope (HR-TEM), energy dispersive X-ray spectra (EDX), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA) analysis. The catalyst was found to have a very small size about 2-3 nm and having a large surface area of about 121 m² g⁻¹, which was stable up to 800°C. It was also found to be photoluminescent. The catalyst thus prepared is useful for the reduction of nitroarenes, which is a toxic compound that is often found as a pollutant in the environment, to anilines, key intermediates for the fine chemical, agrochemical, and pharmaceutical industries. Also, nanocatalyst was used for the synthesis of various substituted tetrahydrobenzo[b]pyrans, which is an essential structural component in various natural products, in good to excellent yields.

K E Y W O R D S

benzopyran, chitosan, hybrid ceria, nanocatalyst, nitroarenes

1 | INTRODUCTION

Energy and sustainability are the main demanding situations in society. Catalysis plays a vital position in science, as it represents an alternative way to meet challenges. In recent times, extra significance is given to the concept of Green Chemistry, which is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.^[1] The concept of Green Chemistry, which makes catalysis technological knowhow even extra creative, has become an essential part of science dealing with sustainability.^[2] The catalyst may be of two types that include homogeneous and heterogeneous. In a homogeneous catalytic system, the catalytic sites and the reactants are in the same phase, which ends up in simpler interaction between the components, because of which better activity, but it offers trouble in separation. Heterogeneous catalysts are easy to recover, but there are a few drawbacks, such as the drastic conditions required by them to be efficient and the mass transport problems. One efficient way to overcome the problem of separation and isolation is the heterogenization of active catalytic molecules, creating a heterogeneous catalytic system.^[3–5] This can be achieved by nanocatalysis. Organocatalysts are normally found to be homogeneous. but although changed into nanocatalysts, they may own heterogeneous catalytic behavior.^[6-9] Heterogenization may be achieved through grafting or entrapment of the energetic nanomolecules at the surfaces or in the pores of a strong support, such as silica,^[10-12] alumina, ceria, or chitosan. The residences of this help can be improved with the aid of the usage of distinctive sorts of materials such as clay, carbon nanotubes,^[13] montmorilpaper.^[14] lonite. cellulose filter inorganic or nanoparticles,^[15-19] subsequently forming а nanocomposite.^[20,21]

Various metal oxides are also known to enhance the properties of the nanoparticles.^[22] Recently, nanocom posite catalysts have been used for various reactions. ^[23–25] Chitosan-based magnetic nanocomposite has been used for the syntheses of a variety of heterocyclic compounds.^[26,27] In recent years, metal nanoparticles (NPs) have received extremely good significance compared to their bulk materials because of their distinctive properties.^[28-31] Nickel (Ni) NPs because of their magnetic properties and multifunctional use had been extensively applied in many fields, which includes nanocatalysis. Individual Ni NPs can easily aggregate during the process of fabrication and application that could lead to undesired length and decreased overall performance. To conquer the aggregation trouble, Ni NPs can be immobilized onto the solid.^[32-34]

The reduction of aromatic nitro compounds to aniline occupies a unique place in organic synthesis. Aniline is an important raw material for the synthesis of numerous products.^[35] It is used in the production of methylene diphenyl diisocyanate (MDI), which is a key compound in the production of polyurethane, rigid or semi-rigid foam, and elastomer.^[36] It can be used as a solvent and

an anti-knocking compound for gasoline. Applications of aniline in various quit-user markets include rubber products, packaging, sealants, explosives, coatings, photography, adhesives, dyes, pharmaceuticals, and textiles.^[37] Aromatic amines are essential intermediates and the final products in the chemical and polymer industry. Anilines additionally shape the substructures of many pharmaceutical compounds. Paracetamol, an extensively used analgesic and antipyretic, is an acetyl derivative of p-aminophenol. Bicalutamide, a nonsteroidal and antiandrogen drug, is administered orally for the treatment of prostate cancer and hirsutism.^[38] Nitrophenols are found as pollutants accountable for critical environmental pollutants and can cause acute poisoning via absorption via respiration tract or skin, so the reduction of nitrophenol becomes an important task, so that they can be transformed into harmless aminophenol.^[39] Generally, nitrobenzene is converted into aniline via hydrogenation in the presence of Raney Ni catalyst, noble metals (Pd and Pt) transition metals (Ni and Cu), and metal-free catalysts. About 85% of aniline is synthesized from nitrobenzene by catalytic hydrogenation owing to its atomic economy and low impact on the environment. Hydrogenation proceeds easily on noble metal catalysts but presents drawbacks such as high cost and scarce resources.^[40]

Benzopyran is a group of heterocyclic compounds that might be very essential in pharmaceuticals, agrochemical industries, and synthetic chemistry. Benzopyran (chromene) is one of the scaffolds, which is an essential structural component in various natural products and possesses useful photochemical properties. The derivatives of benzopyran can interact with a variety of cellular targets because of which it can be used for various biological activities such as antitumor, anticoagulant, antioxidant, anti-hepatotoxic, diuretic, anti-inflammatory, anti-spasmolytic, vasodilatory, estrogenic, anti-HIV, antimicrobial, antifungal, antitubercular, antiviral, antihelminthic, anticonvulsant, and analgesic activity.^[41] The structure activity relationship (SAR) studies reported that the substitution in the chromene nucleus with the specific group increases the ability of the molecule to prevent diseases and also as a cognitive enhancer and to treat neurodegenerative diseases, including Alzheimer's disease, amyotrophic lateral sclerosis, and for treatment of schizophrenia and Huntington's diseases.^[42,43] In the last years, different methods have been reported by the articles for the synthesis of these compounds. The easiest way for the synthesis of pyran derivatives is one-pot, three-component condensation of malononitrile, aldehyde, and 1,3-dicarbonyl compounds in various conditions.^[43–45]

2 | EXPERIMENT

2.1 | Synthesis and characterization of hybrid ceria and chitosan supported nickel nanoparticles (Ni@Fe-doped CeO₂/CS)

2.2 | Synthesis of hybrid ceria

Fe-CeO₂ (Fe-doped CeO₂) was prepared by the coprecipitation method. In a round-bottomed flask (100 ml), the mixture of ceric ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ (20 g) and iron nitrate nonahydrate Fe $(NO_3)_2 \cdot 6H_2O$ (0.3 mol eq., 5.1 g) was added into distilled water (100 ml) and stirred at 80°C for 5 h. Subsequently, an aqueous solution of NaOH was added dropwise at room temperature to form a suspension with a pH of around 10.0. The reaction mixture was subjected to heat at 80°C for 3 h. The suspension was filtered and washed repeatedly with deionized water and then with ethanol. The prepared sample was dried overnight at 110°C and calcined at 300°C for 3 h.^[46]

2.3 | Preparation of chitosan hybrid ceria Nanocomposite

Chitosan powder (1 g) was completely dissolved in 50-ml aqueous acetic acid solution (20% v/v) by overnight stirring in a round-bottomed flask (100 ml). Chitosan solution (2 wt. %, 1 ml) and different weight percentage (5, 10, 15, and 20 wt.%) of nano Fe-doped CeO₂ (2.5, 5.0, 7.5, and 10 g) was taken in 50 ml deionized water. Mixture was stirred constantly for 3 h in a round-bottomed flask (100 ml) for the synthesis of chitosan–hybrid ceria nanocomposite (Fe-doped CeO₂/chitosan). Then, Fe-doped CeO₂/chitosan was dispersed in concentrated NaOH aqueous solution, filtered and washed several times with water, and finally dried at room temperature.

2.4 | Synthesis of hybrid ceria and chitosan supported nickel nanoparticles (Ni@Fe-doped CeO₂/CS)

NiCl₂ solution (0.1 M) was prepared in deionized water. The different wt.% of CS–Fe-doped CeO₂ nanocomposite was used as a support material. Further, the dried chitosan hybrid ceria nanocomposite with different wt.% of Fe-doped CeO₂ were stirred in 100 ml NiCl₂ (0.1 M) solution for 3 h. Ni²⁺ was adsorbed on the Fe-doped CeO₂-chitosan support. Ni²⁺ on Fe-doped CeO₂/chitosan

with different wt.% of Fe-doped CeO₂ were filtered and dried at room temperature. The chitosan-hybrid ceria was then dipped in 100 ml of aqueous sodium borohydride solution (0.1 M) for 1 h to convert the metal ions to alloy nanoparticles. Soon, the composite dipped into NaBH₄ solution changed its color to black. The CS-Fedoped CeO₂ were kept in NaBH₄ solution to completely reduce the Ni²⁺. The reduced Ni nanoparticles immobilized in chitosan-hybrid ceria composite, when kept in the open air, oxidize with time. Hence, Ni@Fedoped CeO₂-5/chitosan, Ni@Fe-doped CeO₂-10/chitosan, Ni@Fe-doped CeO₂-15/chitosan, and Ni@Fe-doped CeO₂-20/chitosan nanoparticles having 5, 10, 15, and 20 wt.% were synthesized, and catalytic activity of each was observed in the reduction of nitroarenes to the corresponding aniline and the synthesis of tetrahy drobenzo[b]pyran derivatives. It was found that 15% Fedoped CeO₂/chitosan gave the best results and hence characterization of 15% Fe-doped CeO₂/chitosan was done using various techniques.

2.5 | Reduction of nitroarenes to the corresponding aniline

In a round-bottomed flask (50 ml), a solution of nitroarene (1 mmol) in CH₃CN-H₂O (3: 0.3 ml) was prepared. To the resulting solution, catalyst (Ni nanoparticles @ Fe-doped CeO_2 /chitosan) (10 wt.%) was added, and the mixture was then stirred for 5 min. Then, NaBH₄ (6 mmol) was added to the reaction mixture. The precipitate was immediately deposited. The mixture continued to be stirred, and the progress of the reaction was monitored by thin layer chromatography (TLC) (eluent; EtOAc/Hexane: 3/10). At the end of the reaction, distilled water (5 ml) was added to the reaction mixture, and the mixture was stirred for 10 min. The mixture was extracted with ethyl acetate $(3 \times 10 \text{ ml})$ and dried over anhydrous sodium sulfate. The solvent was evaporated, and the resulting crude product was dried. Further, the crude was purified by column chromatography over silica gel 100-200 mesh size (eluent; EtOAc/Hexane 3: 10) to give the pure aniline.

2.6 | Synthesis of tetrahydrobenzo[b] pyran derivatives

A mixture of an aromatic aldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), and Ni@Fe-doped CeO₂/chitosan as catalyst was taken in a round-bottomed flask (50 ml). To this mixture, ethanol (3 ml) was added and the reaction mixture was stirred at 60°C. After some time, the product was recrystallized. The mixture was filtered and washed with ethanol to obtain the pure product.

3 | **RESULTS AND DISCUSSION**

3.1 | Characterization of nickel nanoparticles supported on hybrid ceriachitosan (Ni@Fe-doped CeO₂/CS)

The above catalyst was characterized by using Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (P-XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectra (EDX), high-resolution transmission electron microscope (HR-TEM), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET), and thermogravimetric analysis (TGA).

3.2 | FTIR

In infrared (IR) spectra, broadband from 3200–3400 cm⁻¹ was observed, which was assigned to N-H and O-H groups in the chitosan. The sharp band at 1640 cm⁻¹ corresponded to N–H bending in the amide group of chitosan. The characteristic bands of any polysaccharide inclusive of chitosan can be observed at 1030 cm⁻¹ due to O–H bending vibration, C–O–C asymmetrical stretching vibration at 1085 cm⁻¹, and C–N stretching vibration at 1375 cm⁻¹ was observed, which showed that there was no chemical reaction and Ni, Fe-doped CeO₂ were only adsorbed on the surface of chitosan as shown in Figure 1.^[47]

3.3 | P-XRD

The structure of the nanoparticles was examined and characterized by XRD as shown in Figure 2. Broad peaks



FIGURE 1 FTIR of Ni nanoparticles @ 15% Fe-doped CeO₂/chitosan and chitosan



FIGURE 2 Powder X-ray diffraction (P-XRD) of Ni nanoparticles @ 15% Fe-doped CeO₂/chitosan

were found, indicating the nano form of the catalyst. Detailed analysis revealed that the XRD looked like that of the cubic fluorite structure of ceria and the face-centered cubic structure of nickel nanoparticles. There were no extra peaks of other phases present in the XRD, which suggests that Fe³⁺ might be incorporated into the CeO₂ lattice. All the peaks corresponding to Ni- and Fe-doped ceria matched well with the results reported in the literature.^[48,49] The XRD patterns of the synthesized magnetic nanoparticles (MNPs) show diffraction peaks at $2\theta = 28.60^{\circ}$, 33.52° , 47.7° , 56.6° , 70.2° , and 78.37° , which can be assigned to the (111), (200), (220), (311), (400), and (331) planes of Fe-doped ceria (JCPDS # 0957–076-01). The peaks of nickel metal are merged with the peaks of Fe-doped ceria at $2\theta = 47^{\circ}$ and 78° .

The particle size of the nanoparticles was calculated using the Debye–Scherer equation:

$$D = \frac{0.9\lambda}{\beta Cos\Theta}$$

where β is the full line width at half maximum, *D* is the crystallite size, θ is the Bragg's diffraction angle, and λ is the wavelength = 1.5406 A.Crystallite size was found to be in an excellent range of 2.9 nm.

3.4 | FE-SEM

On observing FE-SEM images, a mesoporous structure could be seen. Composite with support and adsorbed

particles were also present. It also showed particles having a flower-like shape and looked shiny (Figure 3).

3.5 | EDX

All the required elements (Ni, Ce, Fe, C, N, and O), which must be there in Ni@Fe-doped CeO_2 /chitosan were confirmed as shown in Figure 4. The presence of nickel nanoparticles is clear (Table 1).

3.6 | HR-TEM

HR-TEM confirmed the formation of the nanocomposite. Two types of nanoparticles embedded in the chitosan, that is, Ni- and Fe-doped CeO_2 were present as shown in Figure 5. Fibers of chitosan could also be seen in the pictures. The average size of nanoparticles was found to be 2.1 nm, which was per that found by P-XRD. Selected area diffraction (SAED) pattern (inset Figure 5) showed the amorphous nature of the catalyst.

3.7 | XPS

XPS confirmed the oxidation state of Fe, Ce, and Ni ions and their surface arrangement. The Ce 3d photoelectron peak contained several multiple splitting features including the intense peak at 916 eV, which was characteristic for Ce⁴⁺ ions. The Ni $2p_{3/2}$ line was composed by the



FIGURE 3 Field emission scanning electron microscopy (FE-SEM) images of Ni nanoparticles @ 15% Fe-doped CeO₂/chitosan



FIGURE 4 Energy dispersive X-ray (EDX) spectrum of Ni nanoparticles @ 15% Fe-doped CeO₂/chitosan

Element	Weight (%)	Atomic (%)	Net Int.	Error (%)	Kratio
СК	7.35	18.16	12.84	16.90	0.02
N K	1.99	4.21	4.11	32.22	0.00
O K	23.71	43.96	167.21	9.55	0.08
Ce L	0.61	0.13	5.66	55.98	0.01
Fe K	0.55	0.29	8.43	56.61	0.01
Ni K	65.79	33.25	513.43	2.69	0.60
Total	100				

 $\begin{array}{ll} \textbf{TABLE 1} & \text{EDX analysis of Ni} \\ \text{nanoparticles @ 15\% Fe-doped CeO}_2 / \\ \text{chitosan} \end{array}$

Abbreviation: EDX = energy dispersive X-ray spectra.



FIGURE 5 High-resolution transmission electron microscope (HR-TEM) images of Ni nanoparticles @ 15% Fe-doped CeO₂/chitosan, SAED pattern (inset)

main peak at 856 eV and a satellite feature at higher binding energies, which might be because of weak surface bonding between Ni and CeO_2 and showed successful loading of nickel on ceria as reported in the literature.^[50] Fe was also present, showing peaks at 711 and 714 eV (Figure 6).

3.8 | BET

The N₂ adsorption/desorption isotherm of Ni@Fe-doped ceria/chitosan nanoparticles was investigated as shown in Figure 7. The isotherm was identified as a Type II hysteresis loop, which was the characteristic of mesoporous materials. It was seen that some pores with narrow mouth were also present. The BET surface area of Ni@Fe-doped ceria/chitosan was measured to be 121 m² g⁻¹. The total pore volume was 0.113 cm³ g⁻¹, and the mean diameter of the pore was 3.7 nm.

3.9 | TGA

The TGA graph showed that the catalyst was stable up to 800° C with minimal loss. Initial loss in the graph might be because of residual water (Figure 8). Eighty-two percent of the catalyst is not decomposed. Most of this loss, that is, 18% is up to 100° C, which shows the said loss might be because of the residual water present in the catalyst.

3.10 | Photoluminescence

The photoluminescent activity of the catalyst was checked. The photoluminescence (PL) spectra of the Ni@Fe-doped ceria/chitosan nanocomposite indicated when the sample was excited at 425-nm wavelength and the emission wavelength of the sample was acquired at approximately 427 nm. This emission peak corresponded to violet light (Figure 9).



FIGURE 6 X-ray photoelectron spectroscopy (XPS) spectra of Ni nanoparticles @ 15% Fe-doped CeO₂/chitosan. (a) Full spectrum, (b) ceria spectrum, (c) nickel spectrum, and (d) iron spectrum



FIGURE 7 Adsorption–desorption spectrum of Ni nanoparticles @ 15% Fe-doped CeO₂/chitosan



FIGURE 8 Thermogravimetric analysis (TGA) analysis of Ni nanoparticles @ 15% Fe-doped CeO₂/chitosan



PL Intensity (A U)

FIGURE 9 Photoluminescence spectrum of Ni nanoparticles @ 15% Fe-doped CeO₂/ chitosan

3.11 | Catalytic investigation

3.11.1 | Reduction of Nitroarenes to the corresponding aniline catalyzed by chitosan-hybrid ceria supported nickel nanoparticles

The catalytic activity was explored via the reduction of nitroarenes in the presence of $NaBH_4$ using the nanocatalyst. The reduction process required 15 min for the complete conversion of nitrobenzene to aniline (Scheme 1).^[51] To explore the activity of the catalyst, first of all, we selected nitrobenzene (1 mmol, 123 mg) and different amounts of sodium borohydride in different sol-



SCHEME 1 Reduction of nitroarenes to corresponding aniline

vents at different temperatures with varying amounts of catalyst and different concentrations of iron-doped ceria in Ni@Fe-doped ceria/chitosan nanocatalyst. It was found that sodium borohydride (6 mol. eq., 226 mg) in water (0.3 ml)/acetonitrile (3 ml) and nanocatalyst (10 wt.%, \approx 12 mg) at 50°C gave the best results, that is, 95% yield in 15 min. Different concentrations of irondoped ceria in nanocomposite were made, and their catalytic effect was tested. It was found that 15% Fe-doped CeO₂ nanoparticles in nanocomposite were found to be best for carrying out the conversion. It was found that the yield decreased when the concentration of Fe-doped CeO₂ was raised to 20% (see supporting information Tables S1-S4). Different substrates were also tried whether the reaction proceeded efficiently (Table 2). It was found that nanocatalyst having 15% CeO2 in Ni@Fe-doped CeO2/ chitosan was found to be an efficient catalyst for different substrates for the same reaction (spectral data given in supporting information Figure S1–S6). Comparative study has also been made between the synthesized catalyst and already published catalysts as shown in Table 4.

3.12 | Plausible mechanism

To understand the mechanism of the reduction of nitroarenes, some known intermediates like nitroso benzene and azobenzene were involved and were found to reduce completely to aniline as the only product. The mechanism (Scheme 2) for the reduction of nitroarenes probably follows both reduction pathways directly from



SCHEME 2 A plausible mechanism for reduction of nitroarenes to aniline using NaBH₄ catalyzed by Ni@Fe-doped CeO₂/chitosan

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TABLE 2 Substrate scope for the reduction of nitroarenes^a to the corresponding aniline using $NaBH_4$ catalyzed by Nickel nanoparticles @Fe-doped CeO₂/chitosan

Entry	Reactant	Product	Time (min)	Yield (%) ^b
1	NO ₂	NH ₂	15	95
2	NO ₂ OH	OH	15	70
3	NO ₂ OH	NH ₂ OH	15	75
4	NO ₂ OH	NH ₂ OH	15	90
5	NO ₂	NH ₂	15	75
6	NO ₂	NH ₂	15	85
7		NH ₂	15	95
8		NH2 Cl	15	80
9	NO ₂ NH ₂	NH ₂ NH ₂	15	90

^aReaction conditions: nitrobenzene (1 mmol), nanocatalyst (10 wt.%), and NaBH₄ (6 mmol) in (H₂O/ACN) (0.3/3 ml) at 50°C. ^bIsolated yield refers to yield after column chromatography (eluent; EtOAc/Hexane 3: 10).

hydroxyl amine and via azobenzene intermediates. The reduction probably took place on the active surface of Ni nanoparticles by the liberated hydrogen formed by the decomposition of sodium borohydride on Ni nanoparticles.

3.13 | Hot filtration test

To understand whether the reaction was carried out under heterogeneous or homogeneous conditions, hot filtration test was performed. In it, the model reaction (Entry 1a, Scheme 1) was carried out for 8 min, and then the catalyst was filtered off. The mother liquor was transferred to another flask, and the reaction was monitored for 8 min or more. The results showed that after removal of the catalyst, no further conversion was observed, further indicating the stability and heterogeneity of the prepared nanocomposite.

It also showed the heterogeneity of the catalyst and that the Nickel metal not being leached out from the solid surface of the catalyst.

3.14 | Synthesis of tetrahydrobenzo[b] pyran derivatives catalyzed by chitosanhybrid ceria supported nickel nanoparticles

A green approach for the preparation of tetrahydrobenzo [b]pyran derivatives among the reaction of aldehydes, malononitrile, and dimedone in the presence of the

catalytic amount of Ni@Fe-doped CeO2/chitosan as a heterogeneous catalyst has been studied (Scheme 3).^[52] The effect of catalyst, reaction temperature, and time of the reaction was systematically investigated. To optimize the amount of catalyst, the model reaction was carried out with the different amount of catalyst taking benzaldehyde (1 mmol, 106.1 mg), dimedone (1 mmol, 140.1 mg), and malononitrile (1 mmol, 66.0 mg) as reactants; the reaction was carried out with (5 wt.%, \approx 5 mg), 10 wt.%, ≈ 11 mg) (15 wt.%, ≈ 15 mg) and (20 wt.%, ≈ 21 mg) of Ni@Fe-doped CeO₂/chitosan; it was found that (10 wt.%, ≈ 11 mg) Ni@15% Fe-doped CeO₂/chitosan was sufficient to get the product in good yield. No enormous increase in yield changed with a further increase in the amount of catalyst. To optimize the temperature, the model reaction was carried out at room temperature, 40°C, 60°C, and 80°C in ethanol using Ni@Fe-doped CeO₂/chitosan as the catalyst, and it was found that the reaction completed in the presence of the catalytic amount of Ni@Fe-doped CeO₂/chitosan as a catalyst with ethanol as solvent at 60°C, which gave the desired product with 90% yield. The same reactants were also tried with varied solvents under different conditions, and it was found that ethanol as solvent held good, giving 90% product in 10 min as compared to other solvents. Different concentration of Fe-doped CeO₂ in nanocomposite was analyzed, and it was found that 10% Fe-doped CeO2 in Ni@Fe-doped CeO₂/chitosan and 15% Fe-doped CeO₂ were found to be best with 90% yield. Further, the yield decreased when the concentration of Fe-doped CeO₂ was increased to 20% (see supporting information Tables S5-S8). Finally, upon the optimization of reaction conditions, the



SCHEME 3 Synthesis of tetrahydrobenzo[*b*]pyran derivatives



synthesis of tetrahydrobenzo[b]pyran derivatives was tried with a range of substrates including aromatic aldehydes and aliphatic aldehydes to study the scope of catalysts, which are summarized in Table 3. It was also found that aromatic aldehydes bearing different functional groups on phenyl ring and heterocyclic aldehydes all yielded products in good amount (spectral data given in supporting Figures S7-S12), whereas in case of Entries 12-14 in Table 3, the reaction did not even initiate with the catalyst. Also, a single crystal of one of the products of tetrahydrobenzo[b]pyran derivative, that is, 2-amino-4-(4-methoxyphenyl)-7, 7-dimethyl-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile has been grown and confirmed by single-crystal X-ray crystallography [CCDC Deposition number 2021516], and its ORTEP view was taken Figure 10 (Packing arrangement given in supporting information Figures S14-S16). Catalytic activity of the synthesized catalyst has also been compared with the already published catalysts as shown in Table 4.

3.15 | Plausible mechanism

Based on literature reports, the mechanism for the synthesis of tetrahydrobenzo[b]pyran in the presence of the catalyst is as shown in Scheme 4. First, Knoevenagel condensation between (1) and (2) produced 2-benzylidenemalononitrile (3). Michael addition of (3) with (5) (1, 3-dicarbonyl compound) gave (6) followed by cyclization and tautomerization resulted in tetrahydrobenzo[b]pyran derivative as our final product.

3.16 | Importance of morphology, its activity relationship, and the synergistic effects in Ni@Fe-doped CeO₂/chitosan

FE-SEM confirms the nanocomposite is in a well-mixed manner and also helps to substantiate the effective reduction of nitrobenzene and synthesis of



FIGURE 10 ORTEP view of 2-amino-4-(4-methoxyphenyl)-7, 7-dimethyl-5-oxo-5, 6, 7, 8-tetrahydro-4*H*-chromene-3-carbonitrile

TABLE 3	Substrate scope for the synthesis	of tetrahydrobenzo[b]pyran derivatives	¹ catalyzed by Ni@ 15%	Fe-doped CeO ₂ /chitosan
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Entry	Reactant	Time (min)	Yield (%) ^b	Obs. M. pt. (°C)/Lit. M. Pt.
1	C ₆ H ₅	10	90	226-228/225-227 ^[53]
2	$4-MeC_6H_4$	40	90	209-210/207-209 ^[53]
3	4-MeOC ₆ H ₄	10	90	200-202/200-202 ^[53]
4	3,4- CH ₃ OC ₆ H ₃	15	86	234-237/237-239 ^[54]
5	4-OHC ₆ H ₄	25	90	207-209/208-210 ^[53]
6	2-OHC ₆ H ₄	35	75	182-184/182-184 ^[54]
7	4-ClC ₆ H ₄	10	85	212-214/214-216 ^[53]
8	$3-NO_2C_6H_4$	15	80	211-213/210-212 ^[53]
9	4-(CH ₃) ₂ CH ₃ C ₆ H ₂	20	75	214-216/214-216 ^[54]
10	2- Furyl	25	85	220-222/218-220 ^[53]
11	3- Indole	20	90	210-215/218-220 ^[54]
12	НСНО	120	-	
13	CH ₃ CHO	120	-	
14		120	-	
	0////0			

^aReaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), nanocatalyst (10 wt.%), and ethanol (3 ml) at 60°C. ^bIsolated yield refers to yield obtained after crystallization with ethanol.





tetrahydrobenzo[*b*]pyran. Ni- and Fe-doped CeO₂ particles were found to be clear and freely distributed over chitosan, providing a high surface area. The structural properties of chitosan can be improved by the incorporation of nickel and Fe-doped ceria, exhibiting good dispersion and uniformity on the surface of the obtained nanocomposite by becoming rougher and more porous. The synergistic effects of metal–support interfaces and charge transfer between metal and metal oxide may lead to enhanced catalytic properties. These nanoparticles aggregate and connect to each other to build 3-D porous architectures, which is quite favorable for the diffusion of gases in the inner pores in case of reduction of nitrobenzene and redox reaction.

3.17 | Turnover number and turnover frequency of the catalyst

The catalyst turnover number (TON) and the turnover frequency (TOF) are two important quantities used for comparing catalyst efficiency in heterogeneous catalysis. TON can be calculated by dividing the concentration of the substrate with the amount of the loading Ni@Fedoped ceria/chitosan nanocatalyst.^[53] Hence, TON for nitrobenzene reduction of and synthesis of tetrahydrobenzo[b]pyran was calculated to be 83.3×10^{-3} and 90.9×10^{-3} . The TOF is simply TON/time. The TOF can be defined here as the number of nitrobenzene molecules that 1 mg of catalyst can convert into aniline per min.^[54] The TOF of Ni@Fe-doped CeO₂/chitosan nanocatalyst was found to be up to $5.5 \times 10^{-3} \text{ min}^{-1}$ for the nitrobenzene reduction reaction. Similarly, TOF for



FIGURE 11 Recyclability of Ni@Fe-doped CeO₂/chitosan. Reaction conditions (1) nitrobenzene (1 mmol), NaBH₄ (6 mmol), and H₂O/ACN (0.3/3 ml) at 50°C and (2) benzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), and nanocatalyst (10 wt.%) in ethanol at 60°C for 10 min

the synthesis of tetrahydrobenzo[b]pyran can be defined as 1 mg of catalyst that can convert benzaldehyde into the corresponding product per min which was up to $9.0 \times 10^{-3} \text{ min}^{-1}$.

3.18 | Recyclability of Ni@Fe-doped CeO₂/chitosan

The catalyst recycling is a very important aspect of heterogeneous catalytic reactions. Recyclability of Ni@Fe-doped CeO₂/chitosan was tested using



FIGURE 12 Infrared (IR) spectrum of the catalyst (a) before reaction (b) after reaction

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TABLE 4 Comparison of catalytic activity of designed catalyst with some recent published work

Product	Catalyst	Reaction Time (min)	Reaction conditions	Yield (%)	References
	Ag/ZnO-rGO	120	$\mathrm{N_{2}H_{4}.H_{2}O}$ and EtOH, r. t.	94	Paul et al. ^[55]
NH ₂	Pd@C	45	H_2 and H_2O , 50°C	100	Sadjadi et al. ^[56]
R	Fe ₃ O ₄ /PVA-10%Ag	5	$N_{2}H_{4}.H_{2}O$ and EtOH, $70^{\circ}C$	99	Rahimi et al. ^[57]
	PdNPs/4MePy	60	CO/H ₂ O and H ₂ O/EtOH, 180°C	80	Krogul-Sobczak et al. ^[39]
	Ni@Fe-CeO ₂ /chitosan	15	NaBH ₄ and ACN/H ₂ O 50°C	95	This work
	ChCl–Ox	20	ChCl-Ox, 60°C	87	Sayahi et al. ^[58]
Q R	WEMFSA	45	EtOH, r. t.	92	Hiremath et al. ^[59]
	MNPs-TBSA	25	EtOH, 70°C	95	Bodaghifard ^[60]
	γ-Fe ₂ O ₃ @Hap@PEG (mim)OH	20	K_2CO_3 and H_2O , r.t.	92	Talaei et al. ^[61]
	Ni@Fe-CeO ₂ /chitosan	10	EtOH, 60°C	90	This work

benzaldehyde as a model substrate in five consecutive runs for the reduction of Nitrobenzene and synthesis of tetrahydrobenzo[b]pyran derivative (i.e., 2-amino-7, 7-dimethyl-5-oxo-4-phenyl-5, 6, 7, 8-tetrahydro 4Hchromene-3-carbonitrile). Ni@Fe-doped CeO2/chitosan was recovered by simple filtration and washed with water and ethanol to remove any absorbed products then dried before use. The amount of reactant taken in the next run was adjusted according to the recovered catalyst. Up to five consecutive runs, little loss of catalytic activity was observed, and the reaction yield remained above 80% after the fifth cycle in both cases as shown in Figure 11. A decrease in observed yield

might be because of manual error. IR spectra of the catalyst before the reaction and after reaction (recycled) were taken as shown in Figure 12. No marked change is seen in the catalyst after reaction.

CONCLUSION 4

In conclusion, we have developed an efficient process for the reduction of a variety of nitroarenes to their corresponding anilines and synthesis of tetrahydrobenzo [b]pyran catalyzed by chitosan-hybrid ceria supported nickel nanoparticles in the green solvent. Second, the

catalyst was recyclable for five consecutive runs what made the process cost-effective and falls in the domain of "Green Chemistry."

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AUTHOR CONTRIBUTIONS

Ankush Mahajan: Formal analysis; investigation; methodology. **Monika Gupta:** Conceptualization; data curation; investigation; project administration; supervision; validation.

DATA AVAILABILITY STATEMENT

The data that support the findings of study are available in the supporting information of this article.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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