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Efficient and sustainable Co₃O₄ nanocages based nickel catalyst: A suitable platform for the synthesis of quinoxaline derivatives

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ABSTRACT

Engineered nanocages have emerged at the forefront of nanomaterial investigation as they possess tremendous potential to boost key chemical processes owing to their hollow architectures that can help in achieving high reactivity. With an intention to make profitable use of their morphological features guided chemical activity, we developed dispersable Co_3O_4 nanocages decorated with nickel nanoparticles for accessing a broad spectrum of pharmaceutically and biologically active N-heterocyclic quinoxaline nuclei using α -dicarbonyls and 1,2-diamines as precursor reagents. For designing Co_3O_4 nanocages, we employed a simple and scalable method involving Kirkendall effect in which thermal decomposition of $Co_3[Co(CN)_6]_2$ was carried out thereafter, nanocages were loaded with Ni nanoparticles to obtain the final Ni@Co_3O_4 catalyst. Results revealed that Ni@Co_3O_4 catalyst possesses immense potential to accelerate condensation of diamines and di-carbonyls in absence of any additives under mild reaction conditions. The superior catalytic efficiency has been attributed to the hollow architecture of the nanocatalyst comprising of abundant catalytic sites. This protocol exhibits several remarkable attributes such as mild reaction conditions outstanding functional group tolerance, high yield, immense durability and reusability for six subsequent runs.

1. Introduction

Currently, nanocatalysis has blossomed as an exciting and integral area of nanoscience as it allows prospects of alteration in the chemical composition, dimensions as well as morphology of materials while also enhancing chemical reactivity. The possibility of engineering the structure of nanocatalysts via the cooperative integration of discrete nano objects has particularly provided remarkable opportunities for designing new catalytic systems with remarkable efficacy [1,2]. Amongst the several accomplishments, the introduction of solid supported heterogeneous nanoscaled catalysts wherein homogeneous metal complexes are anchored onto the surface of suitable support matrices has proven to be highly promising especially in view of environmental cognizance and economic viability [3–8]. Until now most of the heterogenized catalysts documented in literature comprise of noble metals that are not only toxic but also expensive, which restrict their applications. This has necessitated the exploration of sustainable alternatives and sincere efforts in this regard have led to the emergence of

earth-abundant based catalytic materials such as transition-metal chalcogenides, oxides, carbides, nitrides and phosphide [9-12]. Recently, metallic cobalt oxide Co₃O₄ based three-dimensional (3D) hollow porous nanocages have emerged as a competent catalyst support for developing heterogeneous catalytic systems owing to their unique features such as low density, high surface area-to-volume ratio, nontoxicity, good accessibility, cost-effectiveness and recyclability which are also desirable properties of a green catalyst [13-15]. In addition, for designing versatile catalyst, Co₃O₄ nanocages permit the integration of multiple catalytic active sites owing to their hollow assembly, intensifying their role in various important organic reactions. However, the efficacy of cobalt oxide hybrid catalyst remains unexplored for obtaining quinoxalines that constitute an essential class of aromatic N-heterocycles. These important moieties have enticed significant enthusiasm of the scientists/material chemists by bestowing a broad range of antibacterial, antiviral, antituberculotic, anti-inflammatory agents, kinase inhibiting and other properties comprising more than 50% of all drug constituents in therapeutic use. [16-19] Moreover, these compounds

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Received 31 July 2020; Received in revised form 23 November 2020; Accepted 29 January 2021 Available online 26 February 2021 2468-8231/© 2021 Published by Elsevier B.V. have also carved out a unique niche in material science due to their widespread applicability in fabricating luminescent compounds, organic dyes and building blocks for obtaining organic semiconductors rigid subunits of macrocyclic receptors for molecular recognition and chemically controllable switches [20-26]. Owing to the exceptional profile of quinoxaline motifs, various research groups have paid huge attention towards developing a multitude of catalytic systems for their construction through oxidative cyclization of N-arylenamines heteroannulation of nitroketene N,S-arylaminoacetals and 1,2-diketones, reductive cyclization of 2-nitroanilines and 1,2-diketones, dehydrogenative coupling of 1,2-diaminobenzene, oxidation-condensation of reaction of vicinal diols or keto alcohols with diamines and 1,2-diols and coupling reactions of o-phenylenediamine with terminal alkynes [27-36]. Nevertheless, several inevitable drawbacks have been encountered in these conventional methodologies such as intricate reaction procedures, use of expensive and toxic reactants, high catalyst loading, long reaction time, unsatisfactory yields, use of precious metals and poor catalyst recyclability which pose detrimental environmental as well as economic issues [37-39]. Therefore, in search of improved synthetic methodologies, catalytic condensation of α -diketones and 1,2-diamines has appeared as an attractive strategy for already reported ones which often employ several transition metal catalysts including ZrCl₄, MnCl₂, TiO₂, Zn²⁺-K10-clay, MIL-101-Cr–NH–RSO₃H, H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂, InCl₃, ZrO₂-Al₂O₃ etc. [28,36,40-44]. Although, these aforementioned protocols unfold several remarkable features, but the intrinsic difficulties arising due to the separation of catalyst from reaction system and reusability of homogeneous catalysts, inescapably add to cost and even render its bleak commercial utility due to presence of these metal residues in product stream. Therefore, there is a need to design sustainable and cost-effective catalytic systems which can readily overcome the challenges associated with homogeneous catalysis and can be efficiently employed for the construction of quinoxaline moieties.

Our quest for designing sustainable nanocatalytic protocols [45–54] has led to the development of 3D Co_3O_4 nanocages which have been designed using kirkendall effect involving the thermal decomposition of precursor $Co_3[Co(CN)_6]_2$ nanocubes followed by its decoration with Ni nanoparticles. The developed 3D nanocatalyst prove beneficial for expediting the synthesis of quinoxalines which are potentially useful precursors for pharmaceutical and synthetic materials within a lesser time period with additional prospects of ready recovery and excellent

recyclability up to six cycles without significantly affecting the structure or the texture of the catalyst. The recyclability and leaching tests helped in ascertaining the durability of the Ni@Co₃O₄ nanocages signifying stable active sites that offered better steric control over reaction intermediates. It is envisioned that the obtained results from the present study would infuriate a spark of interest amongst the researchers for translation of small scale synthesis to industrial scale processes.

2. Results and discussion

Scheme 1 depicts the preparation of Ni@Co₃O₄ catalyst. Firstly, $Co_3[Co(CN)_6]_2$ was fabricated following the protocol already reported in literature by Chen and co-workers [55]. Thereafter, calcination of precursor nanocubes was carried out at 400 °C for 1 h. Further, nickel nanoparticles were prepared by the methodology reported by Bouremana [56] which were then loaded on Co₃O₄ nanocages via ultrasonication to get the final nanocatalyst.

Keeping in mind the importance of sustainable methods, ease of recoverability and reusability, we herein describe cobalt oxide nanocages supported nickel nanoparticles for accomplishing the successful synthesis of quinoxaline and its derivatives. The superb catalytic performance of the developed catalyst can be attributed to hollow assembly that offers nanoreactor confinement that resulted in good to excellent yield of the target products. The structure of resulting nanocatalyst is confirmed by various microscopic and spectroscopic techniques such as FT-IR, TEM, SEM, XPS, XRD, ED-XRF, AAS and EDS.

2.1. Catalyst characterizations

2.1.1. FT-IR spectroscopy

The FT-IR spectrum of $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ illustrates significant absorption peak at 2172 cm⁻¹ due to stretching vibrations of C=N bond, while emergence of absorption bands at 1608 and 459 cm⁻¹ can be attributed to O-H-O scissor bending of water molecules and Co-C stretching vibration mode respectively (Fig. 1) [57–59]. Thereafter, calcination of nanocubes can be validated by the presence of peak at 1389 cm⁻¹ which corresponds to the NO₃- and bands at 663 and 559 cm⁻¹ associated with the Co-O vibrations [60]. Further, anchoring of nickel nanoparticles onto the surface of nanocages is verified by the decrease in intensities of the absorption peaks [61].



Scheme 1. Synthetic procedure for the formation of Ni@Co₃O₄ nanocatalyst.



Fig. 1. FT-IR spectra of (a) $\rm Co_3[Co(CN)_6]_2$ (b) $\rm Co_3O_4$ and (c) $\rm Ni@Co_3O_4$ nanocatalyst.

2.1.2. X-ray diffraction studies

XRD pattern of Co₃[Co(CN)₆]₂ exhibits intense and sharp characteristic peaks at 17.35°, 24.65°, 35.05°, 39.35°, 43.3°, 50.45°, 53.78° 56.7°, 65.7° and 68.3° which correspond to (200), (220), (400), (420), (422), (440), (600), (620), (640) and (642) planes respectively (Fig. 1a). All perceived XRD peaks are in good agreement with pure face-centered cubic (fcc) phase of Co₃[Co(CN)₆]₂.nH₂O (JCPDS: 77-1161) with an Fm3m system (Fig. 2a). [62,63] Further, thermal decomposition of precursor of nanocubes results in the formation of Co₃O₄ nanocages which is well confirmed with the appearance of diffraction values at 18.57°, 31.34°, 36.87°, 38.31°, 44.84°, 55.82°, 59.36° and 65.28° assigned to the (111), (220), (311), (222), (400), (422), (511) and (440) planes of face-centred cubic (fcc) Co₃O₄; respectively [planes of spinel Co₃O₄ JCPDS Card no. 42-1467] (Fig. 2b) [64,65] whereas Ni doped Co_3O_4 showed additional peaks at 20 values of 44.6°, 51.7° and 76.5° that can be indexed to (111), (200) and (220) planes Ni@Co₃O₄ nanocomposite. New peaks confirm successful anchoring of nickel nanoparticles over Co₃O₄ nanocages (Fig. 2c). [66,67]



Fig. 2. Powder XRD of (a) $\rm Co_3[\rm Co(\rm CN)_6]_2$ (b) $\rm Co_3O_4$ (c) $\rm Ni@\rm Co_3O_4$ nanocatalyst.

2.1.3. SEM and TEM

The results obtained from SEM analysis clearly exhibit that Co3[Co (CN)₆]₂ has well defined cubic shape with smooth facets which indicate single crystal like feature of synthesized nanocubes. Further, negligible changes were observed in Co₃O₄ as compared to Co₃[Co(CN)₆]₂ after calcination suggesting that shape of these cages does not change and consistent with nanocubes, but surface conditions of Co₃O₄ became rougher than those of Co₃[Co(CN)₆]₂ (Fig. 3). Moreover, Ni@Co₃O₄ possesses hollow structures with loaded Ni nanoparticles (Fig. S1) providing catalytically active sites for concerned condensation reaction of α -diketones and o-phenylenediamines. A representative TEM micrograph of precursor Co₃[Co(CN)₆]₂ complex further verifies polyhedral morphology with an average size of about 65 nm. It is also noticed that the morphology is preserved even after post annealing treatment and surface modification via decoration of nickel nanoparticles onto cubes (Fig. 4) [68]. In addition, SAED (Selected area electron diffraction) pattern of nanocatalyst shows sharp white spotty diffraction rings indicating polycrystalline nature of particles (Fig. 4d).

2.1.4. XPS

XPS measurements further revealed the elemental compositions and valence states of Ni@Co₃O₄ nanocatalyst displayed in the Ni and Co 2p core-level XPS spectra (Fig. 5). Ni@Co₃O₄ nanocatalyst showed two typical primary peaks from Co with two spin-orbit doublets of Co 2p_{3/2} and 2p_{1/2} (Fig. 5b). The two peaks of Co 2p_{3/2} spectrum of Ni@Co₃O₄ appeared at 778.79 and 780.52 eV, which fitted to Co^{3+} (778.79 eV) and Co^{2+} (780.52 eV) [69–71]. Additionally, the two peaks of Co $2p_{1/2}$ spectrum of Ni@Co₃O₄ appeared at 794.08 and 795.81 eV, represented to Co^{3+} (794.08) and Co^{2+} (795.81) with a clear split spin-orbit component (Δ metal =15.29 eV). The Co 2p peaks of the Ni@Co₃O₄ exhibit two weak satellite peaks centred at about 785.36 and 802.39 eV, which indicated that the Co atoms were mostly in the 3+ state (Fig. 5b). The Ni 2p core-level spectrum shows two intense peaks at around \sim 854.93 and 872.63 eV binding energies, attributed to Ni $2p_{3/2}$ and Ni 2p_{1/2}, respectively, accompanied by those of their corresponding satellites at around ~ 860.15 and 879.88 eV (Fig. 5c). These peaks are attributed to Ni (2+) in the form of oxide and hydroxide phases. Additionally, a peak located at 852.32 eV in Ni $2p_{3/2}$ and 869.53 Ni $2p_{1/2}$ indicates that the metallic nickel (0) phase is present with split spin-orbit component (Δ metal =17.7 eV) [72–74] (Fig. 5c). In Fig. 3d, the peak at 528.75 eV belonged to (typical metal-oxygen bonds) the lattice O^{2-} in Ni doped Co₃O₄, whereas the peak at 530.73 eV demonstrates the existence of hydroxyl groups.

2.1.5. Elemental and compositional analysis

Chemical composition of Ni@Co₃O₄ nanocomposite was studied through EDS and ED-XRF spectroscopy. Ni@Co₃O₄ clearly shows presence of elements Co, O and Ni in elemental mapping images which provides evidence for successful decoration of nickel particles onto surface of cobalt oxide nanocages (**Fig. S2**). In addition, EDS survey spectra displays elements Co, Ni and O confirming high purity of Ni@Co₃O₄ catalyst (**Fig. S3**). Further, appearance of nickel peak in ED-XRF spectrum of Ni@Co₃O₄ also authenticates successful metalation of Co₃O₄ nanocages (Fig. S4). Consequently, amount of nickel present in nanocatalyst was estimated through AAS and it was found that 0.427 mmol/g of nickel is present in the catalyst.

2.2. Catalytic activity tests

2.2.1. Optimization of reaction parameters

To examine efficiency of newly fabricated $Ni@Co_3O_4$, investigative experiments with various catalytic conditions (catalyst loading, solvent and time period) were scrutinized for condensation of o-phenylenediamine with hexane-3,4-dione as test substrates to acquire optimized reaction parameters (Table S1). Initially, model reaction was carried out in absence of catalyst and it was noted that no desired product was



Fig. 3. SEM micrographs of (a) Co₃[Co(CN)₆]₂, (b) Co₃O₄ and (c) Ni@Co₃O₄ nanocatalyst.



Fig. 4. TEM micrographs of (a) Co₃[Co(CN)₆]₂, (b) Co₃O₄ (c) Ni@Co₃O₄ nanocatalyst and (d) SAED image of Ni@Co₃O₄ catalyst.

formed, confirming that the role of catalyst is imperative for concerned reaction. Moreover, support used in the current work is cobalt oxide nanocages and its interaction with nickel nanoparticles creates an environment that favors the condensation of test substrates. We observed that the nanoparticles supported on nanocages tend to produce desired product with high conversion percentage and isolated yield. Next, effect of amount of catalyst was tested by keeping other parameters constant for synthesis of quinoxaline. The amount of Ni@Co₃O₄ was increased from 2 mg to 6 mg. Results revealed that conversion percentage of desired quinoxaline increased exponentially. However, an increase in amount of Ni@Co₃O₄ nanocatalyst to 8 mg had no significant influence on conversion percentage of desired product. Afterwards, to study effect of solvent on reaction kinetics, test substrates were allowed to react in polar as well as non-polar solvents. The obtained results unveiled that poor conversion percentage of the desired product was attained in non-polar solvents (toluene, hexane), while in presence of polar solvents such as ethanol, methanol, H_2O improved conversion of desired product was achieved. Best results were noted in ethanol with highest conversion percentage. Subsequently, to scrutinize time interval, test substrates were stirred vigorously for different intervals of time. The best optimized time was noted to be 15 min.

2.2.2. Synthesis of quinoxalines using Ni@Co₃O₄ nanocatalyst

After optimizing the reaction conditions, numerous 1,2-diketones were allowed to react with 1,2-diamines to evaluate generality and versatility of this approach. As shown in Table 1, electronically diverse



Fig. 5. Full-range XPS spectra of (a) Ni@Co₃O₄ nanocatalyst and core-level spectra of (b) Co 2p, (c) Ni 2p, and (d) O 1s.

nucleophiles, including electron neutral, electron-deficient and electron-rich diketones as well as diamines underwent reaction smoothly as they delivered desired quinoxaline moieties with excellent conversion percentage. Nevertheless, substrates containing deactivating groups such as Cl, Br etc. required longer reaction time (entry 5–9). Moreover, aromatic and aliphatic 1,2-diketones also resulted in good conversion percentage and exhibited high turnover number (TON). Broad substrate scope and reaction devoid of unwanted products are some of the important features of the protocol.

2.2.3. Hot filtration test

Sometimes, during the course of reaction, there is a possibility of leaching of active catalytic species of a heterogeneous catalyst. Thus, in order to verify that the obtained catalytic performance is truly caused by newly designed Ni@Co₃O₄ nanocatalyst, following experiment was performed. Condensation of hexane-3,4-dione and o-phenylenediamine was carried out using nanocages supported nickel nanoparticles using ethanol as solvent at 30 °C. Once the reaction was allowed to proceed for 7.5 min, Ni@Co₃O₄ was recovered from the reaction system. The clear supernatant was then again stirred for subsequent 15 min; but no increase in conversion percentage was observed which demonstrated that reaction mixture did not contain any catalytically active homogeneous species.

2.2.4. Plausible mechanism

A plausible mechanism based on previous literature reports has been proposed and is outlined in Fig. 6a. Firstly, interaction of 1,2-diketone with nickel nanoparticles of Ni@Co₃O₄ (A) generates complex B. Thereafter, nucleophilic attack of one of amine group of 1,2-diamine resulted in formation of complex C. Afterwards, another amine group attacked on carbonyl group resulting in formation of amino-1,2-diol (E) with subsequent dehydration to afford desirable quinoxaline moiety

[75].

2.2.5. Catalyst reuse studies

Another key consideration in addition to high activity, for the practical application of high-performance catalysts is innate stability of catalyst. To validate if nanocages supported nickel catalyst can be reused and maintained its catalytic activity even after multiple runs, reusability experiments were conducted by using hexane-3,4-dione and o-phenylenediamine as representative substrates for the concerned reaction. Thereafter, catalyst was separated out from reaction mixture *via* centrifugation and supernatant was then analyzed by GC–MS. Afterwards, fresh mixture of test substrates was allowed to react in the presence of recovered catalyst for 15 min time duration. It was noted that newly synthesized nanocomposite Ni@Co₃O₄ could be reprocessed/recycled up to 6 times without any appreciable loss in its catalytic activity (Fig. 6b). Furthermore, FT-IR and SEM images of spent catalyst after 6th run exhibited that overall hierarchically structured cubic morphology and structure was preserved (Figs. S5 and S6).

2.2.6. Comparison with literature reports

The comparative studies of catalytic activity of the synthesized nickel decorated cobalt oxide nanocages was carried out with existing catalytic approaches for the condensation of α -diketones with diamines to afford biologically significant quinoxalines and comparative results are compiled (Table S2) [37,40,41,43,76]. To date, a number of catalytic systems have been employed for successful formation of quinoxalines which suffer from recyclability issues and have serious limitations. However, as-synthesized Ni@Co₃O₄ recyclable nanocatalyst revealed excellent activity under optimized reaction parameters as it could be reused for multiple runs without affecting its catalytic efficacy. Moreover, it is also noteworthy that present protocol with comparable reaction conditions proves its supremacy in comparison to those reported in

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Table 1

Synthesis of quinoxaline derivatives using $Ni@Co_3O_4$ as a catalyst.

$R^{1} + R^{2} + \frac{Ni@Co_{3}O_{4} \text{ nanocages}}{\text{ethanol, 15-20 min,}} R^{2} + \frac{Ni@Co_{3}O_{4} \text{ nanocages}}{\frac{NH_{2}}{30 °C}} R^{2} + \frac{N}{N} + \frac{N}{N$						
Entry	Reactant 1	Reactant 2	Product	Time (min)	^b Conversion (%)	^c TON
1.	NH ₂	~j ⁱ ~	CLL	15	100	390
2.	NH ₂ NH ₂			15	100	390
3.	NH ₂ NH ₂	H ₅ CO		15	85	332
4.	NH ₂			15	85	332
5.	NH ₂			20	95	371
6.	CI			20	100	390
7.	CINH2	H ₃ CO		20	97	379
8.	CI	H ₃ CO		20	100	390
9.	CI			20	100	390
10.	CI	$\mathbf{y}^{\mathbf{l}}$		20	100	390
11.	NH ₂			15	100	390
12.	NH ₂			15	99.5	388
13.			\sim	15	100	390

(continued on next page)

Table 1 (continued)



^aReaction Conditions: α-dicarbonyls (1 mmol), 1,2-diamines (1 mmol), ethanol (2 mL), catalyst (6 mg), 30 °C.

^b Conversion percentage was determined by NMR.

^c TON is the number of moles of product per mole of catalyst.



Fig. 6. (a) Plausible mechanism for the condensation of α -dicarbonyls with 1,2-diamines and (b) Recycle runs for the synthesis of quinoxalines [reaction conditions: hexane-3,4-dione (1 mmol), 1,2-diamines (1 mmol), ethanol (2 mL), catalyst (6 mg/ 0.061 mol%), 15 min, 30 °C].

literature, thus making it greener protocol for furnishing quinoxaline moieties.

3. Conclusion

We have successfully designed a new heterogeneous catalyst which is composed of cobalt oxide nanocages supported Ni nanoparticles for synthesis of pharmaceutically important quinoxalines. Fine nickel nanoparticles with narrow size distribution were utilized to decorate Co_3O_4 nanocages *via* a simple method. The remarkable efficiency of Ni@ Co_3O_4 for condensation reaction of α -dicarbonyls with 1,2-diamines could be attributed to nanometer size and unique architecture of nanocages. Moreover, no leaching of nickel metal or detrimental agglomeration of nanoparticles was noted in the recovered catalyst and also catalytic activity could be completely redeemed after recovery of the catalyst signifying excellent stability, durability, recoverability and recyclability of synthesized catalytic system. Adding to the interest, these nanocages can be engineered utilizing modern tools of nanotechnology to meet many of the future challenges.

CRediT authorship contribution statement

Aditi Sharma: Writing - original draft, Data curation, Methodology, Investigation. Ranjana Dixit: Conceptualization, Methodology, Formal analysis. Shivani Sharma: Visualization, Writing - review & editing. Sriparna Dutta: Formal analysis, Validation. Sneha Yadav: Software, Investigation. Bhavya Arora: Resources. Manoj B. Gawande: Supervision. Rakesh K. Sharma: Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111454.

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