Scientific paper

Preparation and Characterization of Ionic Liquid Supported on Fe_3O_4-Lignin and Investigation of Its Catalytic Activity in the Synthesis of Dihydropyrano[3,2-*c*] chromene Derivatives

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Abstract

To extend the use of supported ionic liquids as effective heterogeneous catalysts, in this research, the ionic liquid immobilized on magnetic lignin (Fe_3O_4-lignin-SO_3/IL) was used as an environmentally friendly, and recyclable catalyst for the synthesis of dihydropyrano[3,2-*c*]chromene derivatives via a one-pot reaction between aromatic aldehydes, malononitrile, and 4-hydroxycoumarin. This method offers the benefits of high yield, short reaction times, straightforward processing, and its potential for green applications in pharmaceutical and chemical sectors. Furthermore, the detailed role of Fe_3O_4-lignin-SO_3/IL as a catalyst in chemical reactions was examined, providing insights into its mechanism and potential uses in organic synthesis and other chemical processes.

Keywords: Lignin, Ionic liquid, Nanocatalyst, Dihydropyrano[3,2-*c*]chromene

1. Introduction

Catalysts are generally divided into two major classes: homogeneous and heterogeneous.[1] In the context of liquid-phase organic synthesis, homogeneous catalysts are widely used due to their high activity and well-defined active sites. However, they often pose challenges in separation and recycling, which can limit their practical applications, especially in sustainable and green chemistry approaches.[2] In contrast, heterogeneous catalysts offer the advantage of easy separation from reaction mixtures, typically via simple filtration or magnetic recovery (when applicable), making them highly attractive for reuse in organic transformations. Many heterogeneous catalytic systems have been developed by dispersing metal nanoparticles or organometallic complexes onto solid supports such as carbon, silica, metal oxides, polymers, reduced graphene oxide, or mesoporous materials through covalent or non-covalent interactions.[3–5] A common limitation of conventional heterogeneous catalysts is the loss of catalyst during recovery and the time-consuming separation processes, which can reduce their overall efficiency. To address these issues, magnetic nanocatalysts (particularly those based on magnetite (Fe_3O_4) have emerged as promising alternatives. Their superparamagnetic properties enable rapid and efficient separation using external magnetic fields, minimizing catalyst loss and eliminating the need for expensive and labor-intensive workup procedures. Fe_3O_4 nanoparticles also provide an excellent platform for further functionalization with biocompatible and biodegradable materials, enhancing catalytic performance, stability, and selectivity.[6,7] They are often coated with mesoporous silica, polymers, carbon-based materials (e.g., carbon nanotubes, graphene oxide, biochar), or boehmite to create core–shell nanostructures. These modifications extend their applicability in areas such as catalysis, biomedicine, and nanotechnology.[8,9]

Lignin, a complex aromatic compound, is abundant in plant biomass and exhibits unique physical properties that can enhance catalyst performance.[10] Also, lignin and its derivatives have been used in the manufacture of adsorbents, catalyst supports, flame retardants, adhesives, carbon fibers, bioplastics, dispersants, reinforcement, etc. Lignin as an amorphous polymer, has advantages such as low cost, biocompatibility, high thermal stability, and abundance.[11] Heterogeneous catalysts supported on lignin

as natural substrates offer an eco-friendly approach to catalysis, leveraging renewable biomass-derived materials as supports.[12] This biopolymer offers abundant functional groups (e.g., hydroxyl, carboxyl, and aromatic structures) that facilitate strong interactions with catalytic metal nanoparticles or active species, enhancing their dispersion and stability. By anchoring heterogeneous catalysts to this natural substrate, the surface area and accessibility for reactants are maximized, improving catalytic efficiency. The natural porous structures of lignin can increase the surface area available for catalysis, enhancing reaction rates and selectivity. Furthermore, their three-dimensional interpenetrating network architecture allows for the incorporation of a wide range of catalytic metals, including noble metals and transition metals, enabling various catalytic applications. Its unique physicochemical properties could synergize with metal complexes to enhance catalytic activity or improve the selectivity of the reaction.[13–15]

Ionic liquids (ILs) are salts that remain in liquid form at or near room temperature and have received significant attention due to their exceptional properties such as low vapor pressure, low toxicity, high chemical and thermal stability, and the ability to dissolve a wide range of organic, inorganic, and polymeric materials.[16] ILs have various applications in electrochemistry, water treatment, polymerization, engineering, and biological uses, and are applied as efficient solvents and catalysts in different organic reactions.[17] In the field of catalysis, ILs can be applied as homogeneous or heterogeneous catalysts. ILs can act as both catalysts and reaction media, enhancing reaction rates while minimizing side reactions.[18] Recently, several research teams have reported the ability of ILs immobilized on the surfaces of nanomaterials to catalyze many chemical reactions.[19,20] In such systems, the catalytic activity typically arises from Brønsted-acidic functional groups, such as sulfonic acid (–SO_3H). These groups release protons, which help to facilitate acid-catalyzed transformations. They play a crucial role in activating electrophilic centers, such as carbonyl or nitrile groups, thereby accelerating nucleophilic addition steps. Their ionic nature enables them to stabilize transition states and reactive intermediates, making them particularly useful in acid-base catalysis, enzymatic reactions, and metal-catalyzed processes. In heterogeneous IL-based systems, the IL is usually immobilized on a solid support to improve stability and reusability while maintaining its Brønsted or Lewis acidic properties. Consequently, the active sites primarily come from the acidic groups of the IL instead of the support itself. The integration of ILs with natural substrates, such as cellulose and lignin, offers a compelling approach to enhance the catalytic efficiency and sustainability of chemical processes.[21] Immobilizing ILs on natural substrates helps reduce the challenges of catalyst separation and recycling while maintaining or improving catalytic performance, especially in processes like biomass conversion, green chemistry, and renewable energy production. The interaction between ILs and these biopolymers can also enhance the dispersal of the IL, creating more active sites for catalysis and improving overall reaction efficiency.[22,23]

Pyrano[3,2-*c*]chromene derivatives are an important class of O-containing heterocyclic compounds that find widespread use in the pharmaceutical and agrochemical industries.[24] These heterocycles are known to possess a wide variety of biological activities, including spasmolytic, diuretic, anticoagulant, anti-cancer, and anti-anaphylactic effects.[25] Pyranochromenes also form components of many natural products such as calanolides, calophyllolide, and calanone.[26] Moreover, some pyrano[3,2-*c*]chromenes also serve as valuable photoactive agents. Many drugs contain the pyranochromene structure, including acetylcholinesterase[27] and Novobicin.[28] Although these compounds hold significant pharmacological, industrial, and synthetic value, there are relatively few methods available for synthesizing pyrano[3,2-*c*]chromene derivatives. The main method for their preparation is the one-pot three-component reaction of 4-hydroxycoumarin with aldehyde and malononitrile in the presence of a catalyst. Recent advances have focused on developing greener and more efficient synthetic routes to overcome limitations in traditional methods. Furthermore, exploring novel catalytic systems could enhance the yield and selectivity of pyrano[3,2-*c*]chromene derivatives in pharmaceutical applications.[29,30] Acid-catalyzed multicomponent reactions particularly benefit from catalysts that can activate carbonyl groups while stabilizing intermediates. Consequently, a Brønsted-acidic IL immobilized on a biopolymeric magnetic support is well-suited for these transformations.[31]

In continuation of our research on the introduction of recoverable catalysts in organic synthesis,[30–37] herein, lignin-based nanocomposite containing high contents of Fe_3O_4 nanoparticles (Fe_3O_4–Lignin-SO_3/IL) was used as a catalyst in the condensation reaction between aromatic aldehydes, malononitrile, and 4-hydroxycoumarin to prepare dihydropyrano[3,2-*c*]chromene derivatives in good to excellent yields. The main catalytic activity in this system is due to the sulfonic acid groups in the ionic liquid component, which act as Bronsted acid sites to facilitate the critical steps of the multicomponent reaction.

2. Experimental

All solvents, chemicals, and reagents were sourced from suppliers such as Fluka, Merck, and Sigma-Aldrich. Structural characterization of the samples was carried out using X-ray diffraction (XRD) on a Rigaku Ultima IV diffractometer. The magnetic properties of the synthesized materials were measured with a vibrating sample magnetometer (VSM) model MDK VSM. Additionally, Fourier-transform infrared (FT-IR) spectra covering the range of 400–4000 cm^{-1} were obtained using an FT-IR JASCO-Model 680 spectrometer.

2. 1. Preparation of Zwitterionic Salts [$(CH_2)_4SO_3TEA$]

The zwitterionic compound was synthesized through a simple one-step process by reacting 1 mmol of triethylamine with 1 mmol of 1,4-butane sultone, under solvent-free conditions, with continuous stirring at ambient temperature for 18 h. The produced solid salt was extensively washed with diethyl ether and then dried under vacuum at 75 °C to obtain the final product.[38]

2. 2. Synthesis of Fe_3O_4 Nanoparticles

Initially, $FeCl_2{\cdot}4H_2O$ (0.5 g, 2.5 mmol) and $FeCl_3{\cdot}6H_2O$ (1.35 g, 5 mmol) were dissolved in deionized water (30 mL) under a nitrogen atmosphere at 80 °C. Next, a sodium hydroxide solution (10 M, 5 mL) was gradually added dropwise over 60 min. After the reaction was completed, the magnetic solid was collected using a magnet and washed with water and ethanol. The obtained solid was then dried in an oven at 80 °C for 2 h to yield Fe_3O_4 nanoparticles.[39]

2. 3. Preparation of Fe_3O_4-Lignin Composite

To prepare the Fe_3O_4-lignin composite, lignin (0.5 g) was dissolved in deionized water (30 mL) with continuous stirring for 1 h until fully dissolved. The mixture was then filtered to remove any particulate impurities. Next, Fe_3O_4 nanoparticles (0.15 g) were added to the lignin solution and sonicated for 50 min. The mixture was stirred for 12 h at room temperature. The resultant Fe_3O_4-lignin composite was separated using a magnet, washed with ethanol, and dried.[40]

2. 4. Synthesis of Fe_3O_4-Lignin-SO_3H

In the following, Fe_3O_4-lignin (0.3 g) was dispersed in CH_2Cl_2 (10 mL) by sonication for 20 min. Then, chlorosulfonic acid (0.1 mL) was added dropwise to the reaction mixture for 20 min at room temperature and it was stirred for 2 h. The resulting solid was separated using an external magnet and dried in an oven at 90 °C for 2 h to obtain Fe_3O_4-lignin-SO_3H.[41]

2. 5. Preparation of Fe_3O_4-Lignin-SO_3/IL

In the final step, Fe_3O_4-lignin-SO_3H (1.5 g) was dispersed in toluene (30 mL) using sonication for 20 min. Subsequently, a solution of the zwitterionic salt [$(CH_2)_4SO_3TEA$] (0.8 g) in 1,4-dioxane (20 mL) was added to the mixture at room temperature. The reaction temperature was then raised to 85 °C and maintained for 3 h with continuous stirring. Following this, the solvent was removed under vacuum at 80 °C. The Fe_3O_4-lignin-SO_3/IL catalyst obtained was washed with ethanol and subsequently dried under vacuum at 70 °C.[42]

2. 6. General Procedure for the Synthesis of Dihydropyrano[3,2-*c*]chromene Derivatives

In a 25 mL round-bottom flask equipped with a magnetic stirrer and reflux condenser, a mixture of the desired aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), 4-hydroxycoumarin (1 mmol), and Fe_3O_4-lignin-SO_3H/IL nanocatalyst (0.025 g) was added to 4 mL of a 1:1 ethanol-water mixture. The reaction mixture was heated under reflux conditions with constant stirring. The progress of the reaction was monitored by thin-layer chromatography (TLC) using ethyl acetate/*n*-hexane (2:1) as the eluent. Reaction completion was confirmed by the disappearance of the aldehyde spot on TLC, usually within 30–90 minutes, depending on the substrate. After the reaction was complete, the mixture was cooled to room temperature, and the catalyst was separated using a magnet. The crude product was filtered, washed with cold ethanol, and recrystallized from methanol to obtain the pure dihydropyrano[3,2-*c*]chromene derivative.

2. 7. Catalyst Recovery and Reusability

To assess the reusability of the Fe_3O_4-lignin-SO_3H/IL nanocatalyst, the catalyst was magnetically separated from the reaction mixture after product isolation, thoroughly washed with methanol to remove any adsorbed organic residues, and dried at 70 °C under vacuum. The recovered catalyst was reused directly in subsequent runs of the model reaction (benzaldehyde, malononitrile, and 4-hydroxycoumarin under identical reaction conditions as described in Section 2.6). The catalytic activity remained consistent over five consecutive cycles with minimal loss in product yield, demonstrating the excellent stability and recyclability of the nanocatalyst.

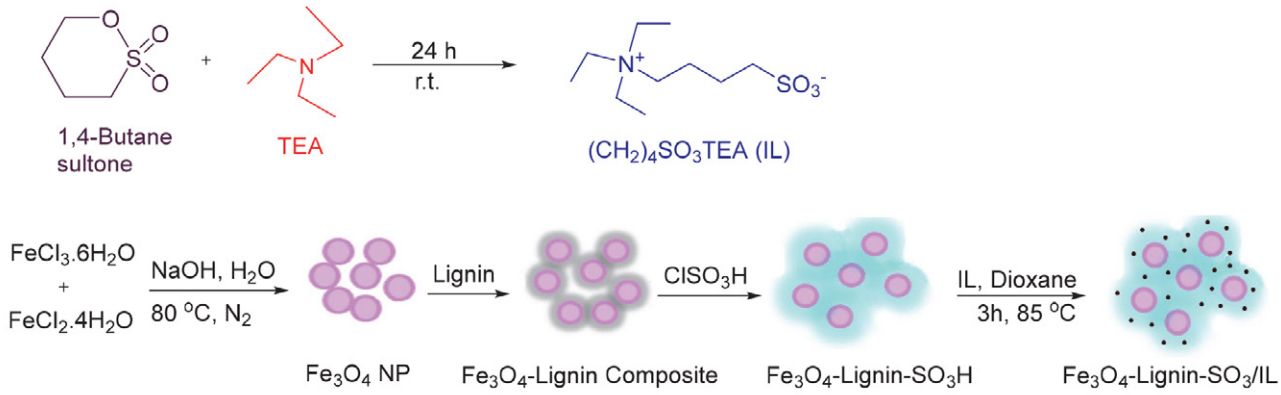
3. Results and Discussion

3.1. Synthesis of the Catalyst

This study describes the method for synthesizing Fe_3O_4-lignin-SO_3H/IL, with the steps illustrated in Scheme 1. The process began with the synthesis of Fe_3O_4 nanoparticles, which were then coated with lignin to produce Fe_3O_4-lignin. Next, Fe_3O_4-lignin reacted with chlorosulfonic acid to form Fe_3O_4-lignin-SO_3H. The ionic liquid (IL) was created by the reaction of triethylamine with 1,4-butane sultone. The final step was electrostatically stabilizing the IL onto Fe_3O_4-lignin-SO_3H to obtain the Fe_3O_4-lignin-SO_3H/IL nanocatalyst. This immobilization strategy ensured that the Brønsted-acidic –SO_3H functional groups of the ionic liquid (IL) were retained on the heterogeneous support, making them accessible as active sites during catalysis. The IL component introduces a strong proton-donating capacity to the composite, which is responsible for the acid-catalyzed activation of electrophilic centers, such as aldehydes, and for stabilizing reactive intermediates.

Meanwhile, the Fe_3O_4-lignin framework provides a high surface area and allows for magnetic recoverability without significantly contributing to catalytic activity. The synthesis and structural features of the catalyst were previously reported and characterized using XRD, FT-IR, FE-SEM, EDS, VSM, TGA, and TEM techniques [42].

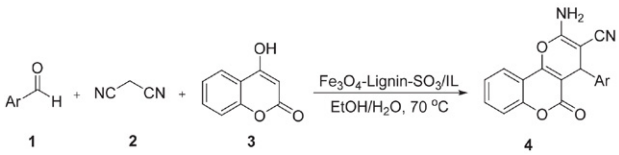
To determine the optimal reaction conditions, a one-pot reaction involving benzaldehyde, malononitrile, and 4-hydroxycoumarin was chosen as the model reaction. By screening loading of the catalyst and considering the effect of the solvent and temperature on the reaction, it was found that as little as 0.025 g of Fe_3O_4-lignin-SO_3/IL nanocatalyst was sufficient to produce the desired product **4a** at 70 °C in EtOH/H_2O as the solvent (Table 1). Following this, the various aryl aldehydes were used to synthesize dihydropyrano[3,2-*c*] chromene derivatives. As indicated in Table 2, the products were prepared in yields ranging from good to excellent. Subsequently, the effectiveness of the Fe_3O_4-lignin-SO_3/IL catalyst was compared with other catalysts reported for the synthesis of dihydropyrano[3,2-*c*] chromene derivatives. As illustrated in Table 3, the Fe_3O_4-lignin-SO_3/IL catalyst shows better performance than other catalysts in terms of catalyst amount, reaction temperature, reaction time, and yield.



Scheme 1. Preparation of Fe_3O_4-lignin-SO_3/IL nanocatalyst.

3.2. Synthesis of Dihydropyrano[3,2-*c*] chromenes Derivatives 4

Following the successful characterization of the Fe_3O_4-lignin-SO_3H/IL nanocatalyst, its catalytic potential was explored in the synthesis of dihydropyrano[3,2-*c*] chromenes through the reaction between aromatic aldehydes, malononitrile, and 4-hydroxycoumarin (Scheme 2).



Scheme 2. Synthesis of dihydropyrano[3,2-*c*]chromenes **4** using Fe_3O_4-lignin-SO_3/IL nanocatalyst.

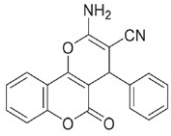
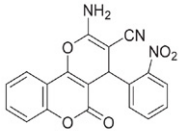
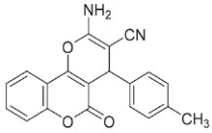
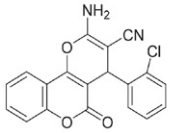
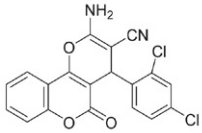
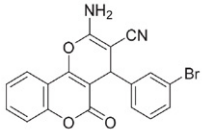
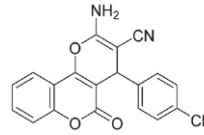
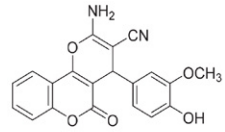
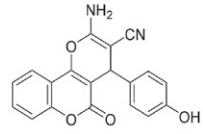
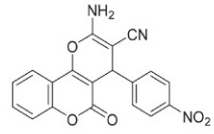
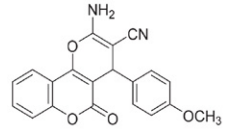
Scheme 3 illustrates the proposed mechanism for the formation of dihydropyrano[3,2-*c*]chromene derivatives in the presence of Fe_3O_4-lignin-SO_3/IL nanocatalyst. Initially, the carbonyl group of the aldehyde is activated by the acid catalyst, which accelerates the condensation step.

Table 1. Optimization of the reaction conditions for the synthesis of **4a**.[a]

Entry	Catalyst loading (g)	Solvent	Temp. (°C)	Yield (%)[b]
1	0.01	–	70	60
2	0.015	–	70	64
3	0.025	–	70	73
4	0.035	–	70	70
5	0.025	CH_3CN	70	75
6	0.025	EtOH	70	85
7	0.025	EtOH/H_2O (1:1)	70	92
8	0.025	MeOH	reflux	80
9	0.025	Toluene	70	70
10	0.025	EtOH/H_2O (1:1)	r.t.	40
11	0.025	EtOH/H_2O (1:1)	40	55
12	0.025	EtOH/H_2O (1:1)	60	85

[a] Reaction conditions: benzaldehyde (1 mmol), malononitrile (1.2 mmol), 4-hydroxycoumarin (1 mmol). time: 30 min. [b] Isolated yields.

Table 2. Synthesis of derivatives **4** using Fe_3O_4-lignin-SO_3/IL nanocatalyst.[a]

Entry	Product 4	M.p. (°C)	Yield (%)[b]
4a		252–254[43]	92
4b		258–260[44]	95
4c		258–260[45]	94
4d		267–269[46]	92
4e		257–259[47]	98
4f		249–251[48]	96
4g		256–258[47]	95
4h		255–257[49]	93
4i		259–261[47]	95
4j		260–262[47]	97
4k		246–248[47]	94

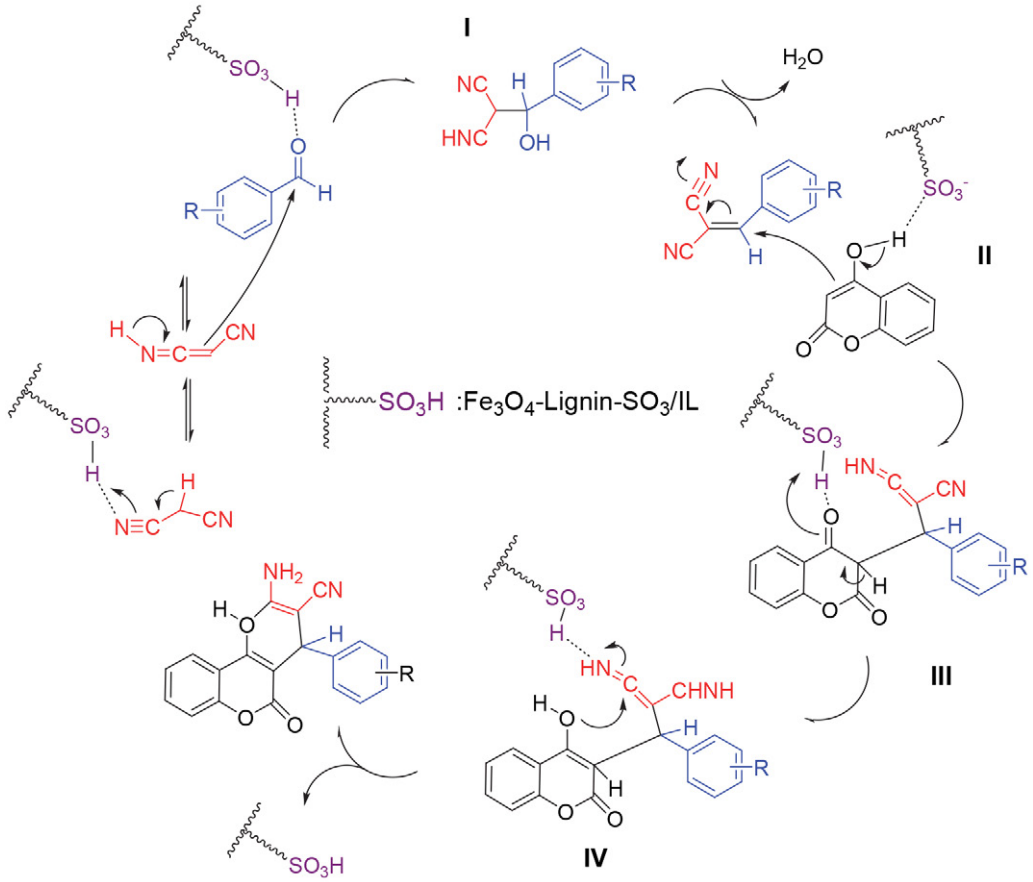
[a] Reaction conditions: Aldehyde (1 mmol), malononitrile (1.2 mmol), 4-hydroxycoumarin (1 mmol), Fe_3O_4-lignin-SO_3/IL (0.025 g), 70 °C, EtOH/H_2O (5 mL), time: 20–60 min. [b] Isolated yields.

Table 3. The comparison study between the efficiency of the present catalyst and that of other catalysts in the synthesis of **4a**.

Entry	Catalyst	Conditions	Time (min)	Yield (%)[a]
1	Zinc hydroxyapatite (0.1 g)	DMF, 120 °C	720	78 (ref. 50)
2	Amberlite IRA 400-Cl resin	H_2O/EtOH, 80 °C	180	95 (ref. 51)
3	Na_2SeO_4	EtOH/H_2O, Reflux	60	95 (ref. 52)
4	$Yb(PFO)_3$	DMF, 60 °C	300	92 (ref. 53)
5	Zn/Al hydrotalcite (0.1 g)	DMF, 120 °C	720	84 (ref. 54)
6	$H_3PW_{12}O_{40}$	EtOH/reflux	300	93 (ref. 55)
7	Fe_3O_4-lignin-SO_3/IL	Cat. (0.025 g), EtOH/H_2O, 85 °C	20	92[b]

[a] Isolated yields. [b] This work.

In this system, the Brønsted acid sites (coming from the sulfonic acid groups (-SO_3H) present in the ionic liquid) mainly protonate the carbonyl oxygen, making the aldehyde group more electrophilic. Subsequently, the activated aldehyde is attacked by the active methylene of malononitrile to give α,β-unsaturated intermediate **I** via the Knoevenagel condensation, and elimination of a water molecule. Next, a Michael addition reaction between 4-hydroxycoumarin and the activated intermediate **I** leads to the formation of intermediate **II**. Finally, the intramolecular cyclization of intermediate **II** to intermediate **III** and its tautomerization gives the corresponding products. Throughout this cascade process, the IL's acidic sites facilitate both the initial condensation and the subsequent cyclization steps, while the magnetic lignin support offering a stable, reusable heterogeneous platform that guarantees high catalyst dispersion and recoverability. Similar IL-functionalized systems have been shown in the literature to operate through analogous acid-catalyzed mechanisms in multicomponent transformations.[31]



Scheme 3. The suggested mechanism for the formation of compound **4**.

3. 3. Efficiency of the Catalyst

The leaching test was conducted to confirm the heterogeneous nature of the Fe_3O_4-lignin-SO_3/IL catalyst during the synthesis of dihydropyrano[3,2-*c*]chromene derivatives. Based on this, the model reaction was investigated using the optimized reaction conditions. After the progress of approximately 50%, the catalyst was removed from the reaction. Next, the residue of the reaction was stirred under optimal conditions without the presence of the catalyst. However, no significant increase in product conversion was observed, which confirms that the catalyst performance varies heterogeneously. The reusability of the catalyst was investigated in the model reaction under optimal reaction conditions. After completion of the reaction, the heterogeneous catalyst was magnetically separated, washed with MeOH, and dried for use in the next run. As shown in Figure 1, the recycled catalyst was used for five runs with no significant loss in performance.

The FT-IR spectrum of the recovered Fe_3O_4-lignin-SO_3/IL nanocatalyst is presented in Figure 2. This analysis demonstrates the high stability of the catalyst's struc-

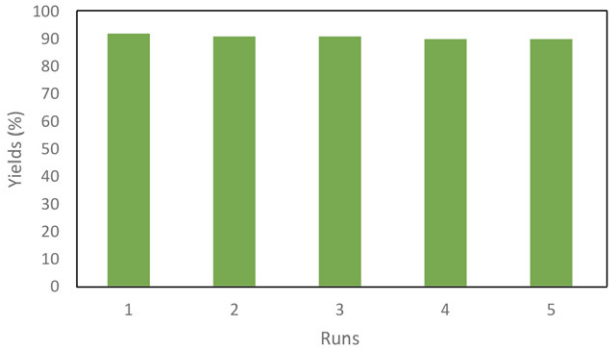


Figure 1. Reusability of Fe_3O_4-lignin-SO_3/IL in the synthesis of **4a**.

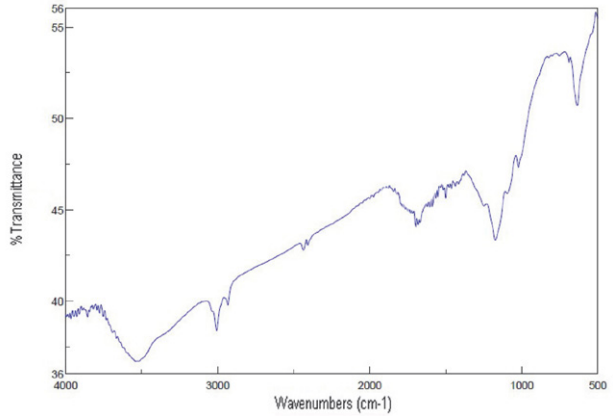


Figure 2. FT-IR spectrum of the recycled Fe_3O_4-lignin-SO_3/IL catalyst.

ture after reuse. In addition, the structural properties of the recovered catalyst have been examined using XRD diffraction patterns (Figure 3). As shown, the relative intensity and position of all the peaks confirm the stability of the catalyst. The VSM analysis of the reused catalyst was conducted, revealing that the magnetic properties of the catalyst remained consistent after multiple cycles (Figure 4).

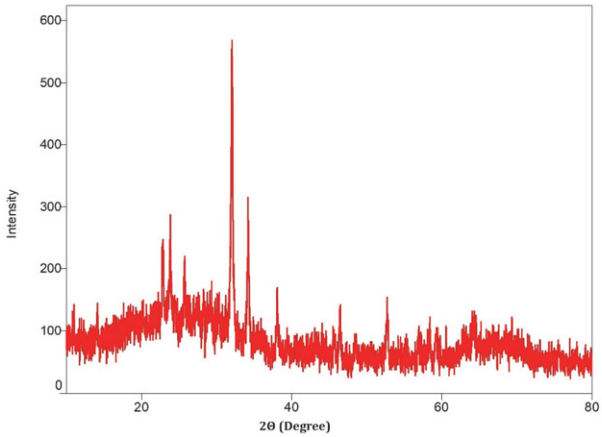


Figure 3. XRD pattern of the recycled Fe_3O_4-lignin-SO_3/IL catalyst.

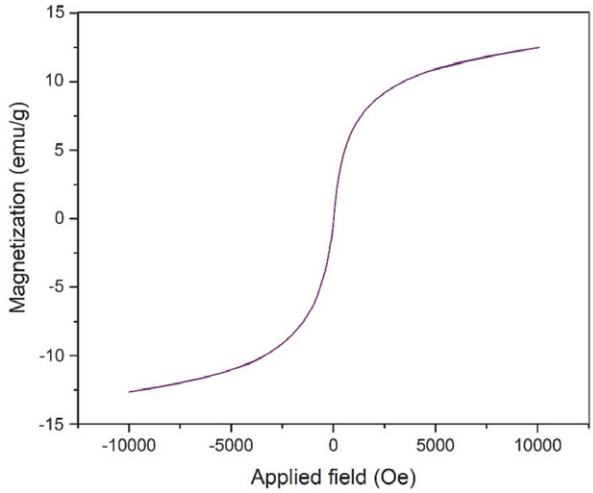


Figure 4. VSM curves of the recycled Fe_3O_4-lignin-SO_3/IL catalyst.

4. Conclusions

In this study, an ionic liquid was effectively immobilized on magnetic lignin to create a heterogeneous catalytic system (Fe_3O_4-lignin-SO_3/IL nanocatalyst), providing a green, efficient, and recyclable platform for chemical reactions. Its catalytic performance was tested in the synthesis of dihydropyrano[3,2-*c*]chromene derivatives, demonstrating excellent activity and selectivity. Notably, the catalyst's heterogeneous nature enabled easy magnetic recovery and reuse for at least five consecutive cycles with minimal activity loss, highlighting its potential for sustainable and practical use in organic synthesis.

5. References

1. D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem. Int. Ed.* **2005**, *44*, 7852–7872. **DOI:**10.1002/anie.200500766
2. I. Fechete, Y. Wang, J. C. Védrine, *Catal. Today,* **2012**, *189*, 2–27. **DOI:**10.1016/j.cattod.2012.04.003
3. V. I. Parvulescu, H. Garcia, *Catal. Sci. Technol.* **2018**, *8*, 4834–4857. **DOI:**10.1039/C8CY01295D
4. F. Zaera, *Chem. Rev.* **2022**, *122*, 8594–8757. **DOI:**10.1021/acs.chemrev.1c00905
5. C. A. McNamara, M. J. Dixon, M. Bradley, *Chem. Rev.* **2002**, *102*, 3275–3300. **DOI:**10.1021/cr0103571
6. M. B. Gawande, P. S. Brancoa, R. S. Varma, *Chem. Soc. Rev.* **2013**, *42*, 3371–3393. **DOI:**10.1039/c3cs35480f
7. M. Liu, Y. Ye, J. Ye, T. Gao, D. Wang, G. Chen, Z. Song, *Magnetochemistry* **2023**, *9*, 110. **DOI:**10.3390/magnetochemistry9040110
8. T. B. Mbuyazi, P. A. Ajibade, *Discover Nano* **2024**, *19*, 158. **DOI:**10.1186/s11671-024-04102-9
9. R. Dubadi, S. D. Huang, M. Jaroniec, *Materials* **2023**, *16*, 1460. **DOI:**10.3390/ma16041460
10. G. Haiwei, Q. I. Zaojuan, L. Yuxuan, X. Haian, L. Lin, H. Q. Huang, A. Wang, L. Changzhi, *Catal. Sci. Technol.* **2019**, *9*, 2144. **DOI:**10.1039/C9CY00251K
11. C. Vasile, M. Baican, *Polymers* **2023**, *15*, 3177. **DOI:**10.3390/polym15153177
12. P. K. Sarangi, A. K. Singh, S. V. Ganachari, D. P. G. Mohanakrishna, T. M. Aminabhavi, *Environ. Res.* **2024**, *261*, 119745. **DOI:**10.1016/j.envres.2024.119745
13. S. Laurichesse, L. Averous, *Prog. Polym. Sci.* **2014**, *39*, 1266–1290. **DOI:**10.1016/j.progpolymsci.2013.11.004
14. H. Zhang, S. Fu, X. Du, Y. Deng, *ChemSusChem* **2021**, *14*, 2268–2294. **DOI:**10.1002/cssc.202100067
15. A. Moreno, M. H. Sipponen, *Mater. Horiz.* **2020**, *7*, 2237. **DOI:**10.1039/D0MH00798F
16. S. K. Singh, A. W. Savoy, *J. Mol. Liq.* **2020**, *297*, 112038. **DOI:**10.1039/D0MH00798F
17. R. L. Vekariya, *J. Mol. Liq.* **2017**, *227*, 44–60. **DOI:**10.1016/j.molliq.2016.11.123
18. D. Xu, X. N. Wang, L. Wang, L. Dai, C. Yang, *Molecules* **2024**, *29*, 23. **DOI:**10.3390/molecules29235661
19. H. Liu, J. Lu, X. Zhao, T. Xu, *Synth. Commun.* **2021**, *51*, 2265–2286. **DOI:**10.1080/00397911.2021.1936057
20. B. Xin, J. Hao, *Chem. Soc. Rev.* **2014**, *43*, 7171–7187. **DOI:**10.1039/C4CS00172A
21. R. Liu, P. Zhang, S. Zhang, T. Yan, J. Xin, X. Zhang, *Rev. Chem. Eng.* **2016**, *32*, 587–609. **DOI:**10.1515/revce-2015-0078
22. M. G. Adsul, A. P. Terwadkar, A. J. Varma, D. V. Gokhale, *BioResources* **2009**, *4*, 1670–1681. **DOI:**10.15376/biores.4.4.1670-1681
23. I. A. Ansari, R. Gree, *Org. Lett.* **2002**, *4*, 1507–1509. **DOI:**10.1021/ol025721c

24. D. C. Mungra, M. P. Patel, D. P. Rajani, R. G. Patel, *Eur. J. Med. Chem*. **2011**, *46*, 4192–4200. **DOI:**10.1016/j.ejmech.2011.06.022
25. A. Rajmane, R. Bandal, S. Shirke, U. More, S. Patil, A. Kumbhar, *J. Mol. Liq*. **2023**, *391*, 123247. **DOI:**10.1016/j.molliq.2023.123247
26. M. Shunmughanathan, N. Madankumar, K. Pitchumani, *ChemistrySelect* **2018**, *48*, 13743–13750. **DOI:**10.1002/slct.201803483
27. J. Zheng, M. He, B. Xie, L. Yang, Z. Hu, H. B. Zhou, C. Dong, *Org. Biomol. Chem*. **2018**, *16*, 472–479. **DOI:**10.1039/C7OB02794J
28. K. Chand, A. N. Shirazi, P. Yadav, R. K. Tiwari, M. Kumari, K. Parang, S. K. Sharma, *Can. J. Chem*. **2013**, *91*, 741–754. **DOI:**10.1139/cjc-2013-0053
29. K. Tangdenpaisal, P. Songthammawat, K. Akkarasereenon, K. Chuayboonsong, S. Ruchirawat, P. Ploypradith, *J. Org. Chem*. **2019**, *84*, 13410–13429. **DOI:**10.1021/acs.joc.9b01596
30. S. Abdolmohammadi, S. Balalaie, *Tetrahedron Lett.* **2007**, *48*, 3299–3303. **DOI:**10.1016/j.tetlet.2007.02.135
31. A. Jahanbakhshi, M. Farahi, *RSC Adv*. **2024**, *14*, 16401–16410. **DOI:**10.1039/D4RA01381F
32. A. Jahanbakhshi, M. Farahi, *Arab. J. Chem*. **2022**, *15*, 104311. **DOI:**10.1016/j.arabjc.2022.104311
33. A. Jahanbakhshi, S. Eskandari, M. Farahi, *New J. Chem*. **2024**, *48*, 1381–1389. **DOI:**10.1039/D3NJ04796B
34. A. Jahanbakhshi, M. Farahi, *RSC Adv*. **2023**, *13*, 31252–31262. **DOI:**10.1039/D3RA04953A
35. M. Farahi, B. Karami, R. Keshavarz, F. Khosravian, *RSC Adv*. **2017**, *7*, 46644–46650. **DOI:**10.1039/C7RA08253C
36. S. Khodabakhshi, B. Karami, M. Baghernejad, *Monatsh. Chem*. **2014**, *145*, 1839–1843. **DOI:**10.1007/s00706-014-1240-7
37. I. Sedighimehr, B. Karami, M. Farahi, M. Keshavarz, *Mol. Divers*. **2022**, *26*, 3325–3336. **DOI:**10.1007/s11030-022-10393-w
38. J. E. Gholtash, M. Farahi, *RSC Adv*. **2018**, *8*, 40962–40967. **DOI:**10.1039/C8RA06886K
39. S. V. Salihov, Y. A. Ivanenkov, S. P. Krechetov, M. S. Veselov, N. V. Sviridenkova, A. G. Savchenko, A. G. Majouga, *J. Magn. Magn. Mater*. **2015**, *394*, 173–178. **DOI:**10.1016/j.jmmm.2015.06.012
40. T. A. Revathy, K. Dhanapal, S. Dhanavel, *J. Alloys Compd*. **2018**, *735*, 1703–1711. **DOI:**10.1016/j.jallcom.2017.11.264
41. S. Hashemi-Uderji, M. Abdollahi-Alibeik, R. Ranjbar-Karimi, *J. Porous Mater*. **2019**, *26*, 467–480. **DOI:**10.1007/s10934-018-0628-x
42. M. Gerami, M. Farahi, B. Karami, *J. Mol. Struct*. **2025**, *1328*, 141246. **DOI:**10.1016/j.molstruc.2024.141246
43. K. Niknam, A. Jamali, *Chin. J. Catal*. **2012**, 33, 1840–1849. **DOI:**10.1016/S1872-2067(11)60457-9
44. I. Clark, R. L. Gomes, C. Crawshaw, L. Neve, R. Lodge, M. Fay, C. Winkler, M. Hull, E. Lester, *React. Chem. Eng*. **2019**, *4*, 663–666. **DOI:**10.1039/C8RE00241J
45. J. Wang, D. Q. Shi, Q. Y. Zhuang, X. S. Wang, H. W. Hu, *J. Chem. Res*. **2004**, *12*, 818–820. **DOI:**10.3184/0308234043431221
46. M. Rostami, S. Momeni, R. Ghorbani, *J. Mol. Struct*. **2024**, *1312*, 138527. **DOI:**10.1016/j.molstruc.2024.138527
47. H. Mehrabi, H. Abusaidi, *J. Iran. Chem. Soc*. **2010**, *7*, 890–894. **DOI:**10.1007/BF03246084
48. M. G. Dekamin, M. Eslami, A. Maleki, *Tetrahedron* **2013**, *69*, 1074–1085. **DOI:**10.1016/j.tet.2012.11.068
49. M. Ahmadian, K. Rad-Moghadam, Z. Gholami, *J. Mol. Liq*. **2022**, *367*, 120501. **DOI:**10.1016/j.molliq.2022.120501
50. M. L. Kantam, V. Balasubrahmanyam, K. B. S. Kumar, *Synth. Commun*. **2006**, *36*, 1809–1814. **DOI:**10.1080/00397910600619630
51. I. Clark, R. L. Gomes, C. Crawshaw, L. Neve, R. Lodge, M. Fay, C. Winkler, M. Hull, E. Lester, *React. Chem. Eng*. **2019**, *4*, 663–666. **DOI:**10.1039/C8RE00241J
52. X. G. Si, Y. P. Zhao, Q. L. Song, J. P. Cao, R. Y. Wang, X. Y. Wei, *React. Chem. Eng*. **2020**, *5*, 886–895. **DOI:**10.1039/D0RE00071J
53. K. Nikoofar, H. Heidari, Y. Shahedi, *Res. Chem. Intermed*. **2018**, *44*, 4533–4546. **DOI:**10.1007/s11164-018-3402-4
54. M. L. Kantam, K. B. S. Kumar, K. P. Raja, *J. Mol. Catal. A Chem*. **2006**, *247*, 186–188. **DOI:**10.1016/j.molcata.2005.11.043
55. A. M. Alsalme, P. V. Wiper, Y. Z. Khimyak, E. F. Kozhevnikova, I. V. Kozhevnikov, *J. Catal*. **2010**, *276*, 181–189. **DOI:**10.1016/j.jcat.2010.09.014

Povzetek

Z namenom razširiti uporabnost imobiliziranih ionskih tekočin kot učinkovitih heterogenih katalizatorjev, smo ionsko tekočino imobilizirali na magnetni lignin (Fe_3O_4-lignin-SO_3/IL) ter tako pripravljeno snov uporabili kot okolju prijazen, obnovljiv katalizator v enolončni reakciji med aromatskimi aldehidi, malononitrilom in 4-hidroksikumarinom s katero smo sintetizirali serijo dihidropirano[3,2-*c*]kromenskih derivatov. Naš pristop se odlikuje z visokimi izkoristki, kratkimi reakcijskimi časi, enostavnostjo izolacije in je potencialno uporaben pri različnih okolju prijaznih procesih na področju farmacevtske kemije. Dodatno smo mehanistično razjasnili vlogo Fe_3O_4-lignin-SO_3/IL kot katalizatorja v izvedeni sintezi in s tem pokazali na njegovo potencialno uporabnost v organski sintezi in pri drugih kemijskih procesih.