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Exploring Magnetic Chitosan Functionalized with POCl2-x as a Nanocatalyst for Amino Alcohol Synthesis from Azido Alcohol

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ABSTRACT

β-Amino alcohols play a crucial role in natural product synthesis, especially in the pharmaceutical industry, serving as important intermediates in advancing of medicinal chemistry and drug discovery. This study presents a new method for synthesizing β-amino alcohols using an eco-friendly nanocomposite Fe3O4@SiO2@CS@POCl2-x with an average size of 157nm, achieving rapid efficiency through the aminolysis of an azide compound in the presence of CH3CN-H2O (9:1) and heat (80°C), resulting in yields of 77-90%. The presence of chitosan enhances the catalyst's environmental friendliness and promotes the smooth conversion of azides into amino alcohols. This conversion process involves mechanisms such as water incorporation and proton transfer, facilitated by the surface hydroxyl and amine groups on the nanocomposite. The catalyst demonstrates exceptional performance under mild conditions, promising high yields and highlighting its significance in organic synthesis. Furthermore, the catalyst's magnetic recoverability, diverse composition, and ability to facilitate efficient and clean reactions underscore its indispensable role in amino alcohol synthesis.

INTRODUCTION

Amino alcohols, especially β-amino alcohols, play crucial roles in the synthesis of numerous natural products and bioactive compounds, particularly within the pharmaceutical sector (1). They offer significant utility in carbohydrate and nucleoside chemistry, expanding chemical diversity and facilitating the creation of innovative molecules with promising implications in medicinal chemistry (2), drug discovery (3, 4) , and related biological fields (5). These compounds are indispensable in chemistry and drug development, serving as versatile intermediates for synthesizing various molecules and contributing significantly to the advancement of medicinal chemistry and drug discovery (6).

Numerous catalysts have been developed for the production of β-amino alcohols, offering efficient and sustainable pathways to these valuable compounds. Transition metal complexes (7), such as ruthenium (8), palladium(9), and copper catalysts (10, 11), have exhibited remarkable activity in catalyzing the synthesis of amino alcohols through various reactions, including hydrogenation, amination, and reductive amination processes (5, 7). While reactions catalyzed by metal Lewis acids have shown the capability to produce β-amino alcohols in good to excellent yields, they frequently require the use of toxic metal salts, which can present challenges during separation processes. Separating, recovering, and recycling expensive or air-sensitive catalysts can be difficult. Currently, there is a growing interest in developing safer and more straightforward methods for synthesizing β-amino alcohols. Some reports suggest using sulfonated substrates with epoxides (12, 13), hydroxy methylation of imines with α-silyl ethers (14), silica gel (15), zeolite(16), modified montmorillonite clay (17), ionic liquids like 1-ethylpyridinium trifluoroacetate, (18) and solid acids in the presence or absence of a solvent. Organocatalysts, such as proline derivatives (19), amine catalysts, phosphonate catalysts (20, 21) and organic Lewis acids like organobismuth triflate (22) or presence of enzyme such as lipase from Thermomyces lanuginosus (23), have emerged as potent tools for promoting asymmetric transformations, enabling the synthesis of enantioenriched β-amino alcohols. Moreover, heterogeneous catalysts such as supported nanoparticles and metal-organic frameworks (24) offer benefits in terms of recyclability and ease of separation, making them attractive for large-scale synthesis(25, 26). Addressing the challenges related to synthesizing catalysts and conducting operations is crucial in this field. Therefore, there is

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considerable interest in introducing new catalysts, as they play pivotal roles in enabling the efficient and selective production of β-amino alcohols.

In this study, we introduce a novel catalyst, Fe_3O_4@SiO_2@CS@$POCl_{2-x}$ (NCP@ $POCl_{2-x}$), designed for the efficient conversion of β-azido alcohols to β-amino alcohols with high yields and minimal byproducts. By leveraging the magnetic properties of the catalyst, separation is made easy, streamlining the purification process. Moreover, the reaction conditions are straightforward, further enhancing the practicality of the methodology.

MATERIALS AND METHODS

All chemical materials from Merck or Fluka were utilized in the reactions. The reaction progress was monitored using thin-layer chromatography (TLC) on silica gel SILG-UV 254 plates. Column chromatography with silica gel 60 was used for further purification. Product identification was achieved by comparing physical and spectral characteristics with data from literature. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Advance DPX 250MHz instrument.

Preparation of NCP@$POCl_{2-x}$ (Fe_3O_4@SiO_2@CS@$POCl_{2-x}$) nanocomposite as a heterogeneous magnetic catalyst

The synthesis of the Fe_3O_4@SiO_2@CS@$POCl_{2-x}$ nanocomposite, previously reported (27), is briefly outlined here. Initially, Fe_3O_4 nanoparticles were synthesized by mixing $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}4H_2O$ in an ammonia solution under an argon atmosphere at 80˚C for 3 hours, followed by coating with SiO_2 using tetraethyl orthosilicate (TEOS) in absolute ethanol. Subsequently, this composite was combined with a mixture of chitosan and glutaraldehyde to form the final nanocomposite. Then, dried Fe_3O_4@SiO_2@CS (1.0 g, 0.4 mmol) in an argon-protected environment reacted with PCl_3 (15 mL, 0.1 mol) for 1 hour at 60°C and was maintained for 24 hours to promote the reaction between Fe_3O_4@SiO_2@CS and PCl_3. The resulting mixture was washed multiple times with dry CH_2Cl_2 (dichloromethane) to eliminate impurities or by-products, followed by drying under vacuum pressure to remove residual solvent. The obtained Fe_3O_4@SiO_2@CS@$POCl_{2-x}$ appeared as a green-gray solid, stored in a capped bottle to prevent exposure to air or moisture, and proved stable for several months without significant changes.

General procedure for the transformation of azidoalcohol to amino alcohol

A mixture of 2-azido alcohol (1 mmol) in CH_3CN (9 mL) was stirred, followed by the addition of NCP@$POCl_{2-x}$ (0.5g, 0.3 mmol). The mixture was then stirred for 1 hour under reflux conditions. After that, H_2O (1mL) was added to the reaction mixture, which was stirred for an additional 24 hours under reflux conditions. Once the reaction was complete, the mixture was filtered to remove the catalyst using an external magnetic force. CH_2Cl_2 was added, and the organic phase was washed with brine (10 mL) and water (2 × 10 mL). The filtrate was then dried with anhydrous Na_2SO_4. After evaporating of the solvent with a rotary evaporator, the resulting pure product was collected. The products were characterized by comparing their ^{1}H-NMR spectra with authentic samples. Additionally, we are providing identification data for the pure product below:

Table 2, entry 1, 1-amino-3-phenoxypropan-2-ol: brown crystal, m.p:94-96°C, FTIR(υ/cm^{-1}) (KBr): 3385(OH), 3200(N-H), 3100(=C-H), 2920 (C-H), 2876, 1735(C=O), 1587(C=C),1430 (N-H), 1022(C-O) cm^{-1}, ^{1}H-NMR (in $CDCl_3$, 250 MHz), Chemical shifts (δ ppm): 7.27-6.93 (m, 6H, C_6H_5, CH=C),5.37(s, 1H, OH), 4.20 - 3.95(m, 2H, CH_2),2.9-2.6(d, 2H), 1.82 (s, 2H, NH_2). ^{13}CNMR Chemical shifts (δ ppm): 154.63 (1C),132.97 (1C, C=C), 123.41 (2C, C=C), 73.9 (1C, CH_2), 72.4 (1C, CH_2-OH), 46.3 (1C, CH_2-NH_2). Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65%; H, 7.84%, N, 8.38%; Found: C, 66.45%; H, 8.12%, N, 8.42%.

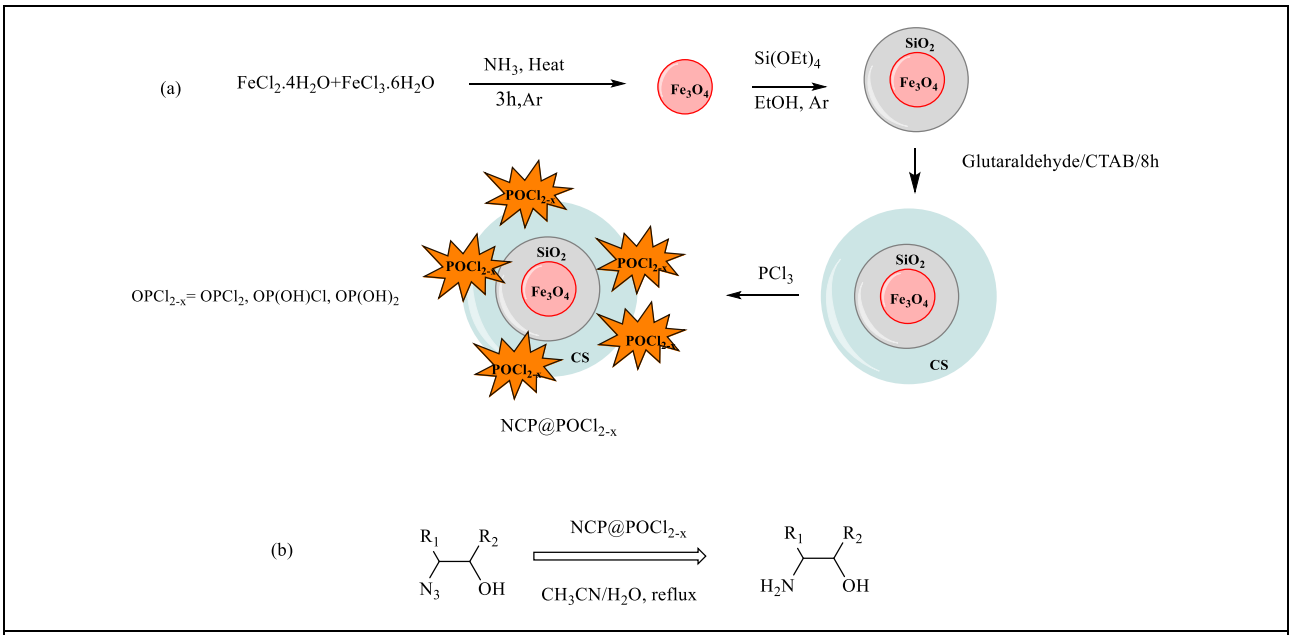
Table 2, entry 2, 3-amino-2-hydroxypropyl methacrylate: dark yellow crystal, m.p:56-60°C, FTIR (υ/cm^{-1})(KBr): 3359(OH),3214 (N-H), 3076(=C-H), , 2854(C-H), 1745(C=O),1640 (C=C), 1413(N-H), 1120(C-O) cm^{-1} ,^{1}H-NMR (in $CDCl_3$, 250 MHz), Chemical shifts (δ ppm): 6.760-6.676 (d, J=2.45 Hz, CH=C, 2H), 5.83 (s, 1H, OH), 4.6-4.45(m, CH_2), 2.65-2.43 (m, CH_2), 2.11 (s, 3H, CH3), 1.65 (s, NH_2). ^{13}CNMR Chemical shifts (δ ppm): 167. 95 (1C, C=O), 137.261 (1C, C=C),125. 63 (1C, C=C), 70.16(1C, C-OH),68.2(1C, CH_2), 49.21 (1C, CH_2-NH_2), 18.23 (1C, CH_3). Anal. Calcd for $C_7H_{13}NO_3$: C, 52.82%; H, 8.23%, N, 8.80%; Found: C, 53.38%; H, 9.34%, N, 8.22%.

Table 2, entry 3, 1-amino-3-isopropoxypropan-2-ol: dark yellow liquid, b.p:243-246°C, ^{13}C-NMR ($CDCl_3$), δ (ppm): 76.78(1C, CH), 72.684 (1C, CH_2) ,71. 42 (1C, CH_2-OH),46.3(1C, CH_2-NH_2) 22.34 (2C, CH3). Anal. Calcd for $C_6H_{15}NO_2$: C, 54.11%; H, 11.35%, N, 10.52%; Found: C, 55.33%; H, 12.55%, N, 10.88%.

Table 2, entry 4, 2-aminocyclooctan-1-ol: brown crystal, m.p:63-78°C, FTIR (υ/cm^{-1}): 3522, 3254 (N-H), 3080(=C-H), 2974(C-H), 1413(N-H), 1089(C-O) cm^{-1}, ^{13}C-NMR ($CDCl_3$), δ (ppm): 78.81(1C, CH_2-OH), 58.43 (1C, CH_2-NH_2), 28.979-27.104 (5C, CH_2). Anal. Calcd for $C_8H_{17}NO$: C, 67.09%; H, 11.96%, N, 9.78%; Found: C, 68.21%; H, 12.75%, N, 9.83%.

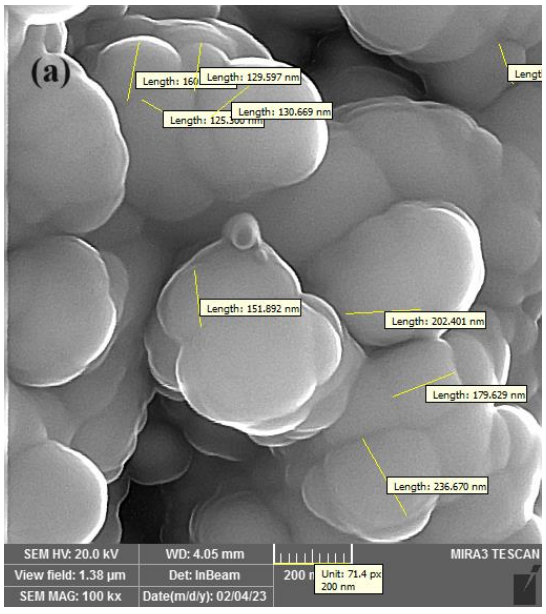
RESULTS AND DISCUSSION

We have recently demonstrated the remarkable versatility of Fe_3O_4@SiO_2@CS@$POCl_{2-x}$ (NCP@ $POCl_{2-x}$) in various organic transformations, including the conversion of alcohols to alkyl halides (27) and amines (11, 21) and as well as epoxides to amines (28). The steps for preparing the catalyst are briefly outlined in Scheme 1a. Building upon these accomplishments, our focus is to highlight the unique capability of this complex in activating 2-azido alcohols and subsequently advancing β-amino alcohol synthesis in a one-pot manner, as illustrated in Scheme 1b.



Scheme 1. (a) Steps in the preparation of the NCP@$POCl_{2-x}$ catalyst (b) Schematic for the synthesis of β-amino alcohols using NCP@$POCl_{2-x}$

The FESEM analysis of NCP@$POCl_{2-x}$, as shown in Figure 1, reveals significant differences compared to Fe_3O_4@SiO_2@CS. Specifically, the addition of the $POCl_{2-x}$ group to the catalyst's surface leads to a noticeable increase in size to 157nm, as demonstrated by comparative analysis. Additionally, the functionalization with the $POCl_{2-x}$ group causes increased separation between particles, suggesting partial functionalization of the chitosan surface rather than complete functionalization. Furthermore, the resulting morphology exhibits spherical particles with uniform characteristics, indicating a well-defined core-shell structure in NCP@$POCl_{2-x}$. These observations highlight the complex relationship between surface chemistry and particle morphology, providing insights into the intricacies of functionalized nano catalysts.



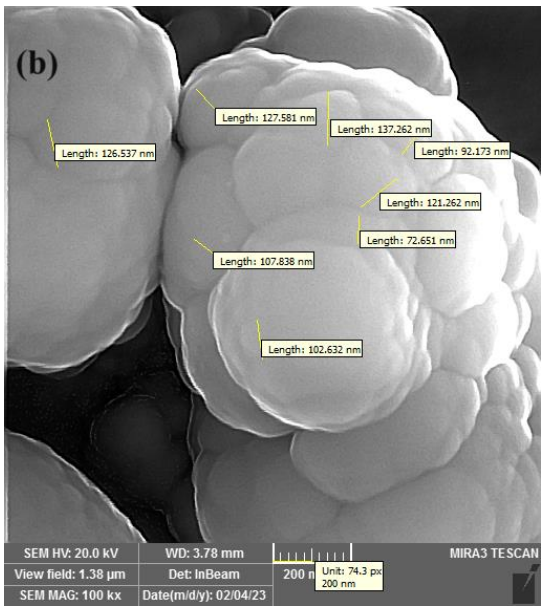


Fig. 1, FESEM image of (a) NCP@$POCl_{2-x}$(b) Fe_3O_4@SiO_2@CS

The analysis of the VSM curve in Figure 2a reveals that the NCP@$POCl_{2-x}$ composite exhibits sufficient magnetic properties. Further examination of the catalyst via FTIR spectroscopy confirms the presence of phosphorus-chlorine (P-Cl) bonds at wavenumbers of 566 cm^{-1} and 798 cm^{-1}. Additionally, phosphorus-oxygen (P-O) bonds were identified at cm^{-1} and 1225 cm^{-1}, with the latter indicative of phosphorus double-bonded to oxygen (P=O), as illustrated in Figure 2b (27).

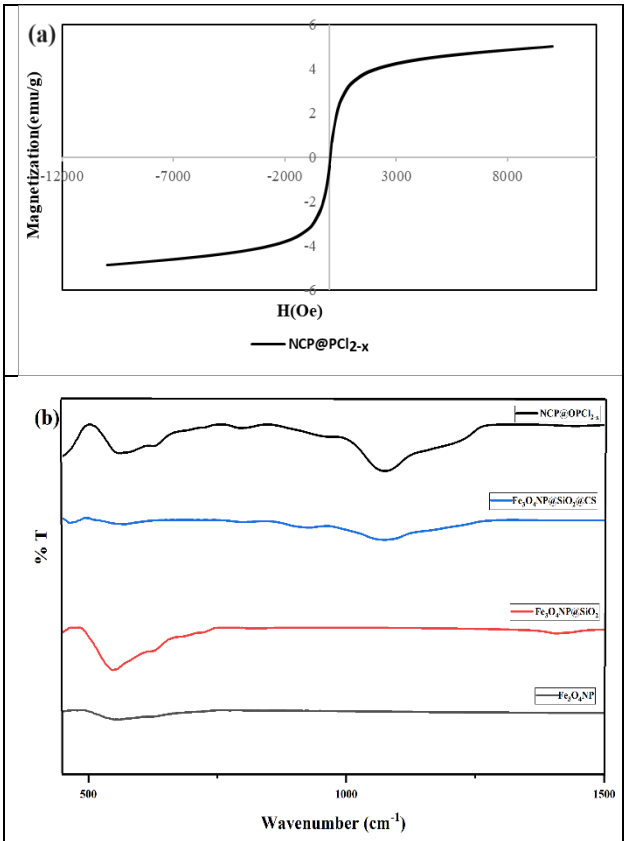


Fig. 2. (a) VSM Curve and (b) FTIR Spectroscopy Analysis of NCP@$POCl_{2-x}$ comparison with Fe_3O_4@SiO_2@CS, Fe_3O_4@SiO_2, and Fe_3O_4

A comprehensive series of experiments was undertaken to optimize reaction parameters and explore the effects of catalyst quantity, solvent choice, and temperature variation. The principal objective centered on the synthesis of 1-amino-3-phenoxypropan-2-ol from 1-azido-3-phenoxypropan-2-ol, chosen as a representative reaction, with detailed outcomes delineated in Table 1. In these experiments, 1 mmol of 1-azido-3-phenoxypropan-2-ol underwent reaction with 0.3-1.5 mmol of the catalyst (NCP@$POCl_{2-x}$) under diverse conditions, encompassing ambient temperature or reflux. A spectrum of solvents including $CHCl_3$, CH_2Cl_2, THF, EtOAc, H_2O, CH_3CN, and a CH_3CN-H_2O mixture (90:10) was systematically evaluated to comprehend their impact on reaction performance and selectivity.

Table 1
Optimization synthesis of 1-amino-3-phenoxypropan-2-ol form 1 mmol of 1-azido-3-phenoxypropan-2-ol with NCP@$OPCl_{2-x}$

Entry	Solvent	Amount of catalyst (mmol)	Reaction temperature	Time (h)	Conversion of product (%)[a]
1	$CHCl_3$	1.5	rt	24	15
2	CH_2Cl_2	1.5	rt	24	23
3	THF	1.5	rt	24	25
4	THF	1.5	reflux	7	35
5	EtOAc	1.5	rt	24	35
6	EtOAc	1.5	reflux	24	42
7	CH_3CN	1.5	rt	24	45
8	CH_3CN	1.5	reflux	24	56
9	H_2O	1.5	reflux	24	83
10	CH_3CN -H_2O	1.5	reflux	5	95
11	H_2O	0.5	reflux	24	84
12	CH_3CN -H_2O	0.5	reflux	5	93
13	CH_3CN -H_2O	0.3	reflux	5	93

According to the findings presented in Table 1, the optimal conditions for the conversion of 1-azido-3-phenoxypropan-2-ol to 1-amino-3-phenoxypropan-2-ol involved the use of 0.3 mmol of catalyst in the presence of a H_2O-CH_3CN solvent mixture under reflux conditions. Various factors, including the specific architecture of NCP@PCl_{2-x}, reaction parameters such as temperature and concentration, as well as the presence of additives or co-catalysts like H_2O, can exert significant influence on the outcome and efficiency of this chemical transformation.

To investigate the versatility of the catalyst across different substrates, we explored compounds with diverse functional groups. Subsequently, we applied the optimized conditions established earlier to these substrates containing electron-donating or electron-withdrawing groups.

Tables 2 present detailed results on amination of various substituted azido alcohols to amino alcohols using NCP@$POCl_{2-x}$, providing insights into the regioselective nature of the reaction across a wide range of substrate structures.

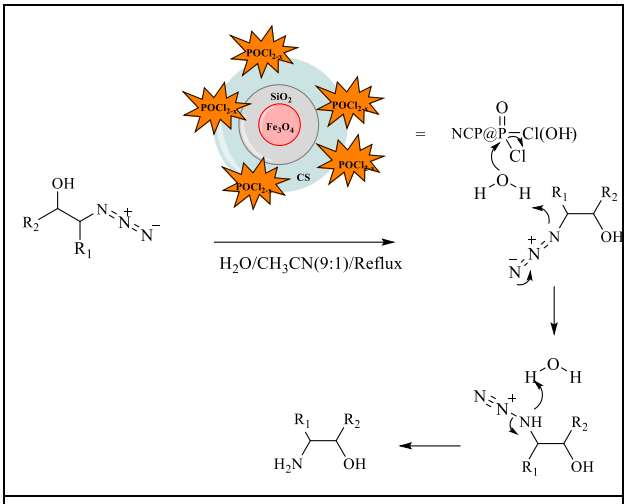
Notably, our observations reveal that functional groups such as simple esters, alkyl groups, and alkenes exhibit stability throughout the reaction. Furthermore, the magnetic catalyst's ease of separation simplifies the workup process, thereby enhancing the practicality of the synthetic procedure.

Table 2
Transformation β-azidoalcohol to β-aminoalcohol with NCP@$OPCl_{2-x}$

Entry	Substrate	Product	Time(h)	Yield (%)
1	1-azido-3-phenoxypropan-2-ol	1-amino-3-phenoxypropan-2-ol	5	90
2	3-azido-2-hydroxypropyl methacrylate	3-amino-2-hydroxypropyl methacrylate	3	86
3	2-azido-1-phenylethan-1-ol	2-amino-1-phenylethan-1-ol	2	88
4	1-azido-3-isopropoxypropan-2-ol	1-amino-3-isopropoxypropan-2-ol	2	89
5	2-azidocyclooctanol	2-aminocyclooctanol	3	77

Upon subjecting the reaction mixture to prolonged heating with the introduction of water, the azido alcohol undergoes a series of complex molecular rearrangements, ultimately yielding an amino alcohol. The core-shell structure of NCP@$POCl_{2-x}$ plays a critical role in mediating the formation of an intermediate complex with the β-azido alcohol through hydrogen bonding

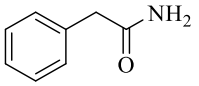
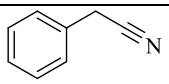
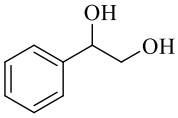
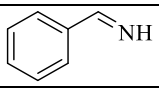
interactions, thus initiating the activation of the substrate for subsequent reactions. Importantly, in the presence of water, electron transfer processes are facilitated within the azide compound. Moreover, the combination of chitosan enhances the catalyst's environmental friendliness and improves its performance by creating a favorable environment for catalytic activity. Furthermore, the presence of a hydroxyl and amine moiety, which act as basic sites within the chitosan layer of the catalyst, aids in the transfer of hydrogen from the oxygen atom in water to the nitrogen atom in the azide group, resulting in the formation of an intermediate species (Intermediate I, Scheme 2). This intricate mechanism is accompanied by the simultaneous release of nitrogen gas (N_2), leading to the synthesis of the desired β-amino alcohol. A detailed depiction of this mechanistic pathway is presented in Scheme 2, providing a comprehensive insight into the complex molecular events underlying the reaction progression and elucidating the underlying reaction mechanism.



Scheme 2. Proposed mechanism for the preparation of amino alcohols

This work demonstrates that NCP@$POCl_{2-x}$ exhibits comparable generality and yield to other catalysts listed in Table 3 for the production of amino alcohols. Moreover, it offers distinct advantages over both homogeneous and other heterogeneous catalysts due to its ease of separation and ability to achieve high yields and availability and low price of catalyst.

Table 3
Comparison of Catalysts for Amino Alcohol Production to produce 2-amino-1-phenylethan-1-ol

Entry	Substrate	Catalyst	Conditions	Yield (%)
1		sodium bis(2-methoxyethoxy) aluminum hydride	SMEAH in MePh, THF/O_2 $H_2C_2O_4$ in Et_2O/MeOH (5:1)	28% (29)
2		sodium bis(2-methoxyethoxy) aluminum hydride	SMEAH in MePh, THF/O_2 $H_2C_2O_4$ in Et_2O/MeOH (5:1)	40% (29)
3		Linear and Divergent Enzymatic Cascades	Aa-ADH with At-ωTA or Bm-ωTA/$HCOONH_4$,30°C/ 48 hours.	90% (30)
4	Styrene	Iron-Catalyzed Intermolecular	HFIP as solvent	80% (31)
5		$TMSCH_2OPMP$	PC, water/ air	95% (14)
6	Styrene oxide	Silicagel (10%)	Neat, RT,3h, N_2	20% (32)
7	2-azido-1-phenylethan-1-ol	NCP@$POCl_{2-x}$	CH_3CN-H_2O/ Reflux condition, 2h	88 (this work)

The absence of NCP@$POCl_{2-x}$ significantly impacts the conversion process, resulting in a less favorable yield. This emphasizes the pivotal role of NCP@$POCl_{2-x}$ as a catalyst in facilitating the transformation of azido alcohols into amino alcohols. The catalytic activity of NCP@$POCl_{2-x}$ is essential for promoting the desired reaction, ultimately leading to improved yields and the specific formation of amino alcohols. Its ability to work in mild conditions and consistently produce high yields makes it suitable for many fields, like pharmaceuticals and materials science. Given these findings, NCP@$POCl_{2-x}$ emerges as a promising candidate for catalyzing a diverse array of reactions, offering not only enhanced efficiency and selectivity but also improved sustainability and environmental compatibility.

CONCLUSION

In conclusion, the study highlights the significant role of NCP@$POCl_{2-x}$ as a catalyst in promoting efficient and selective amino alcohol synthesis. The optimized

conditions and mechanistic insights provided lay the groundwork for this synthesis, promising further advancements in the field. Additionally, the regioselective nature of the reaction across diverse substrate structures underscores the versatility and potential of NCP@$POCl_{2-x}$ in facilitating complex molecular transformations. Its distinctive features, such as eco-friendly, easy separability, magnetic properties, and improved environmental compatibility due to chitosan integration, make it a highly advantageous tool in organic synthesis. With the ability to operate under mild reaction conditions and consistently yield high product yields, NCP@$POCl_{2-x}$ shows significant potential for use in various fields, including pharmaceuticals and materials science.

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CONFLICTS OF INTEREST

The author declares no conflict of interest.

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