



Selective Utilization of N-acetyl Groups in Chitin for Transamidation of Amines

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The selective transformation of chitin into various renewable N-containing chemicals and medicines has attracted increasing attention. However, the N-acetyl groups in chitin construct strong hydrogen bond networks, which restricts its depolymerization and transformation. The selective conversion of robust chitin commonly requires considerable base catalysts to remove the N-acetyl group as a byproduct in advance, which is non-compliance with the principle of atomic economy. Herein, for the first time we demonstrate a novel approach to achieve the selective utilization of the N-acetyl group in chitin for transamidation of chitin with amines. A series of amine derivatives, mainly including aliphatic amine, cyclic amine and functionalized aromatic amine, could be selectively converted into the corresponding amide products frequently found in pharmaceuticals. Furthermore, the solid residue after removing the acetyl group (denoted as De-chitin) with the sufficient exposure of -NH₂ groups as a solid base catalyst shows excellent performance in the aldol condensation reaction of furfural and acetone to produce fuel precursors. Our process provides a strategy that exploiting every functional group adequately in substrates to obtain value-added chemicals.

Keywords: chitin, N-acetyl group, transamidation, amine, amide

OPEN ACCESS

Edited by:

Yanqin Wang,
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Reviewed by:

Hu Li,
Guizhou University, China
Heng Zhang,
Guizhou University, China

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Specialty section:

This article was submitted to
Catalytic Engineering,
a section of the journal
Frontiers in Chemical Engineering

Received: 29 November 2020

Accepted: 28 December 2020

Published: 29 January 2021

Citation:

Xin Y, Shen X, Liu H and Han B (2021)
Selective Utilization of N-acetyl Groups
in Chitin for Transamidation of Amines.
2:634983.
doi: 10.3389/fceng.2020.634983

INTRODUCTION

Chitin, the second most abundant biopolymer on the earth after cellulose, consists of N-acetylglucosamine units with β -1,4-glycosidic linkages. (Yabushita et al., 2015; Yan and Chen et al., 2015). Chitin is considered as the most promising biomass sources for the production of renewable N-containing chemicals and materials due to its high nitrogen content of around 7% by weight. (Omari et al., 2012; Chen et al., 2014; Chen et al., 2017; Kobayashi et al., 2017, 2019; Osada et al., 2019; Pham et al., 2019; Dai et al., 2020). In spite of the enormous economic and environmental interests, the existence of acetyl groups is the main challenge for the exploitation of chitin biomass, which seriously hampers its transformation into fuels and fine chemicals (Fang and Fan et al., 2019). It has been reported that deacetylation is commonly inevitable for the valorization of chitin. However, deacetylation is notorious due to the use of plenty of concentrated, corrosive basic solutions (Chen et al., 2017). Moreover, acetyl groups in chitin are removed as a byproduct, which results in low atomic utilization and is contrary to the theme of Green Chemistry.

Amides are enormously important building blocks in organic synthesis, and they serve as precursors for many value-added compounds, mainly including agrochemicals, pharmaceuticals,

organic materials and polymers (Pattabiraman and Bode et al., 2011; Lundberg et al., 2014; Kniss, 2017). Hitherto, several synthetic measures have been achieved. Generally, the preparation of amide involves hydroamination of alkynes (Uenoyama et al., 2005; Valeur and Bradley et al., 2009), hydration of nitriles (Goto et al., 2008; Raman et al., 2009; Williams et al., 2011) and the coupling of carboxylic acids, aldehydes and alcohols with amines (Srinivas and Das, 2003; Hosseini-Sarvari and Sharghi et al., 2006; Gunanathan and Milstein, 2007, Milstein, 2011; Nordstrom et al., 2008; Arnold et al., 2008; Zweifel et al., 2009; Watson et al., 2009; Soule et al., 2011; Lundberg et al., 2012; Gosh et al., 2012; Yamaguchi et al., 2012). Additionally, transamidation is a convenient and straightforward method for exchanging the constituents of two different amide groups and some significant progress has been achieved in recent years (Eldred et al., 2003; Eldred et al., 2008; Nguyen et al., 2012, Allen et al., 2012; Zhang et al., 2012; Nageswara et al., 2014; Becerra-Figueroa et al. 2014; Garg et al. 2017; Yin et al., 2019; Ghosh et al., 2019). Chitin possesses enormous N-acetyl groups and can be recognized as a kind of renewable amide compounds. Selective deacetylation of N-acetyl groups with additional amine source through transamidation not only generated high-value amide products, but benefited to its further valorization. To the best of our knowledge, transamidation reaction regarding renewable chitin as amide source has never been reported.

Aldol condensation is known as an important C-C bond forming reaction and a cornerstone of synthetic chemistry (Yutthalekha et al., 2017; Xu et al., 2017; Ngo et al., 2019). Generally, aldol reaction proceeds in the presence of acid, base or acid-base bifunctional catalysts. Among those catalysts, base catalysts gave remarkable catalytic performance owing to its strong ability to abstract α -protons and active substrate (Ngo et al., 2019). Homogeneous base catalysts, such as NaOH and KOH, were widely employed in the aldol reaction, but showed some disadvantages, mainly involving equipment corrosion, non-recyclability and complex separation (West et al., 2008; Fakhfakh et al., 2008; Xing et al., 2010; Ramirez-Barria et al., 2016; Gu et al., 2017). To overcome these drawbacks, heterogeneous base catalysts (MgAl-hydrotalcite and MgO et al.) were considered as suitable alternatives, while the challenge of catalyst stability existed in the presence of water generated in the process of aldol condensation (Yang et al., 2013; Shen et al., 2016; Bing et al., 2017; Ngo et al., 2018). Therefore, exploring a solid base catalyst with outstanding water-resistance to enhance aldol reaction is very urgent. Chitosan is the partially deacetylated form of chitin. Chitosan with considerable $-\text{NH}_2$ groups, as a promising renewable solid base catalyst, emerged to promote the aldol condensation reaction, due to its water resistance and recyclability (Sakthivel and Dhakshinamoorthy et al., 2017; Rani et al., 2018; Meninno, 2020; Anbu et al., 2020).

We report here a novel catalytic system where the deacetylation of C2-acetamido groups to C2-amido groups selectively occurred through a transamidation process with amines. The amine sources mainly include aliphatic amine, cyclic amine and functionalized aromatic amine, generating the corresponding amide as the desired product with excellent

yield. FT-IR spectra and XRD pattern demonstrated that the transamidation reaction proceeded mainly on the surface of chitin. Additionally, the solid residue after transamidation reaction (De-chitin), as a solid base catalyst with exposure of lots of $-\text{NH}_2$ groups, exhibited outstanding catalytic activity on aldol condensation of furfural with acetone to produce fuel precursor. Our work offers a strategy to sufficiently use every functional groups in the substrate for the production of value-added chemicals from an atomic economy perspective.

EXPERIMENTAL SECTION

Chemicals and Materials

Furfural (98%), acetone (99.9%), N, N-dimethylformamide (98%), chitin and chitosan were purchased from TCI. Aniline (99%), propylamine (99%), butylamine (99%), cyclopentamine (99%), cyclohexylamine (99%), benzylamine (99%), *p*-toluidine (99%), *p*-anisidine (99%), *p*-chloroaniline (98%), *p*-bromoaniline (99%) were purchased from Aladdin. NaOH (99%), $\text{Fe}(\text{OAc})_2$ (95%), $\text{Co}(\text{OAc})_2$ (98%), $\text{Ni}(\text{OAc})_2$ (97%), $\text{Cu}(\text{OAc})_2$ (99%), AlCl_3 (99%), CoCl_2 (97%), CuCl_2 (98%) were purchased from Alfa Aesar.

Catalytic Reactions

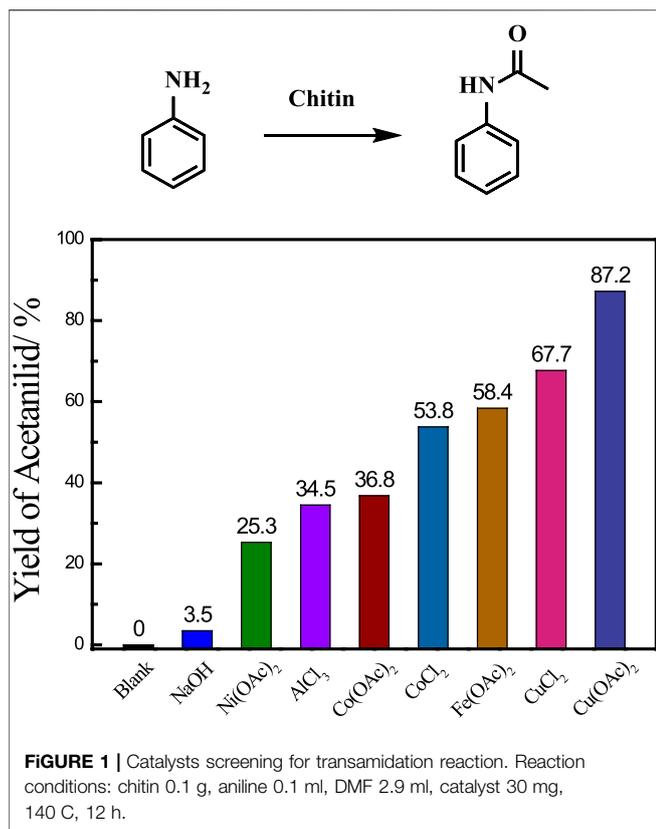
The transamidation reaction was performed in a 50 ml flask at ambient pressure. Typically, chitin (0.10 g), catalyst (0.03 g), amine and DMF (3 ml) were placed into the flask. The reactor was purged with N_2 three times. The reaction was then performed at 140°C under magnetic stirring for 12 h. The liquid solution was separated from the solid residual by centrifugation and analyzed qualitatively by GC-MS (Agilent 5977A) and quantitatively by GC equipped with a flame ionization detector (FID, Agilent 4890D) using dodecane as the internal standard. The experimental section of transamidation reaction involving other molecules is the same as the above process. Additionally, the solid residue (De-chitin) was collected, washed with ethanol and then dried in an oven for the next step.

The yield of amide product was calculated by using the equation: amide yield = (the actual moles of amide)/(the theoretical moles of amide). The theoretical moles of amide were obtained according to the degree of acetylation (DA) of chitin which was calculated based on elemental analysis (EA) (Chen et al., 2014).

$$\text{DA} = [(\text{C}/\text{N} - 5.14) / 1.72] \times 100\%$$

C/N means the ratio of carbon to nitrogen (w/w).

The aldol condensation of furfural with acetone was conducted in a 10 ml Teflon-lined stainless-steel autoclave. Furfural (0.48 g, 5 mmol), acetone (1.16 g, 20 mmol) and De-chitin catalyst (0.10 g) were transferred into the autoclave. The reactor was charged to 1 MPa N_2 pressure. The reaction was then performed at 140°C under magnetic stirring for 12 h. After the aldol condensation reaction, the autoclave was quenched in an ice-water bath to room temperature. The liquid solution was separated from the solid residual by centrifugation and analyzed qualitatively by GC-MS (Agilent, 5977A) and quantitatively by GC equipped with a flame ionization detector (FID, Agilent, 4890D) using dodecane as the



internal standard. Conversion of furfural and yield of products were calculated by using the equation:

$$\text{Furfural conversion} = \frac{(\text{moles of reacted furfural})}{(\text{moles of starting furfural})} \times 100\%.$$

$$\text{C8 yield} = \frac{(\text{moles of C8 product})}{(\text{moles of starting furfural})} \times 100\%$$

$$\text{C13 yield} = \frac{(\text{moles of C13 product})}{(\text{moles of starting furfural} / 2)} \times 100\%$$

Characterization

Powder X-ray diffraction (XRD) patterns were obtained by Rigaku D/max-2500X-ray diffractometer (excitation source: Cu K α radiation, $\lambda = 0.15406$ nm; tube voltage: 40 kV; tube current: 200 mA).

FT-IR spectra of commercially available chitin, chitosan and De-chitin were recorded with a TENSOR 27 spectrometer. The samples were blended with KBr for IR characterization.

RESULTS AND DISCUSSION

Initially, aniline was employed as an amine source to investigate the transamidation reaction between chitin and aniline, and various catalysts were screened for the production of acetanilid at 140°C (Figure 1). The degree of acetylation (DA) in chitin is 95.4% based on the elemental analysis and the theoretical moles of acetanilid

were calculated to 58.5 mg when the amount of chitin substrate is 100 mg (Supplementary Table S1) (Chen et al., 2014). The transamidation reaction did not occur without catalyst and homogeneous base catalyst (NaOH) showed poor performance with only 3.5% yield of acetanilid as the desired product. Lewis acid catalysts are known to be effective for this reaction. We evaluated lots of Lewis acid catalysts, mainly including Ni(OAc)₂, AlCl₃, Co(OAc)₂, CoCl₂, Fe(OAc)₂, CuCl₂ and Cu(OAc)₂, and found that all those catalysts could produce target molecular. Among them, Cu(OAc)₂ provided the best performance with 87.2% yield of acetanilid after 12 h at 140°C. Those results obviously indicated that metal core played a significant role in the transamidation reaction and the excellent catalytic activity of Cu catalyst may be attributed to the proper combination between acetyl groups in chitin and it.

With this promising result, the factors of reaction were further optimized, including solvents, reaction time, reaction temperature and the amount of Cu catalyst. The use of solvents involving tetrahydrofuran, acetonitrile, *p*-xylene, isopropanol and cyclohexane, did not provide the desired product, which demonstrates the critical role of DMF in promoting transamidation reaction (Figure 2A). Figure 2B illustrated the influence of reaction time on the transamidation reaction and the yield of acetanilid increased before 12 h. Prolonging the reaction time, the yield of the target product showed little change. In addition, the influence of reaction temperature on the yield of acetanilid was also investigated (Figure 2C) and the results showed that the reaction temperature played an important role in the transamidation reaction. The most suitable reaction temperature is 140°C and decreasing the reaction temperature proved to be unfavorable for the transamidation reaction. Moreover, the effect of the amounts of Cu catalyst on the yield of acetanilid was also studied. The yield of the target product increased continuously with the increasing amount of Cu(OAc)₂ at the beginning and reached a plateau when the amount of Cu(OAc)₂ was above 30 mg, revealing that Cu(OAc)₂ catalyzed the reaction during the reaction process (Figure 2D). A moderate yield of 55.3% was still achieved when the amount of Cu catalyst was decreased to 15 mg.

Based on the previous literature report (Ma and Gong, 2018) and our results, a reasonable reaction mechanism has been proposed (Scheme 1). Initially, the carbonyl group of chitin is activated by Cu(OAc)₂ catalyst through coordination. The activated chitin then undergoes nucleophilic attack by amine, which results in the formation of tetrahedral intermediate 1) With a proton transfer, the sterically congested intermediate 1 breaks down to generate intermediate 2) Finally, the target molecular, corresponding amide, is produced to finish the catalytic cycle.

Infrared spectroscopy is an important tool to acquire information on surface functional groups and all samples were analyzed by FT-IR (Supplementary Figure S1). The bands ranging from 2,800 to 3,500 cm⁻¹ are assigned to the vibrations of -CH, -NH and -OH groups, and the peaks between 1500 and 1670 cm⁻¹ represent amide bands. Commercial available chitosan and chitin gave remarkably different FT-IR spectra from 1,000–4,000 cm⁻¹. Three obvious peaks at 1,115, 1,550, and 3,250 cm⁻¹ in the chitin spectrum are absent in that of chitosan. Most importantly, the FT-IR spectrum

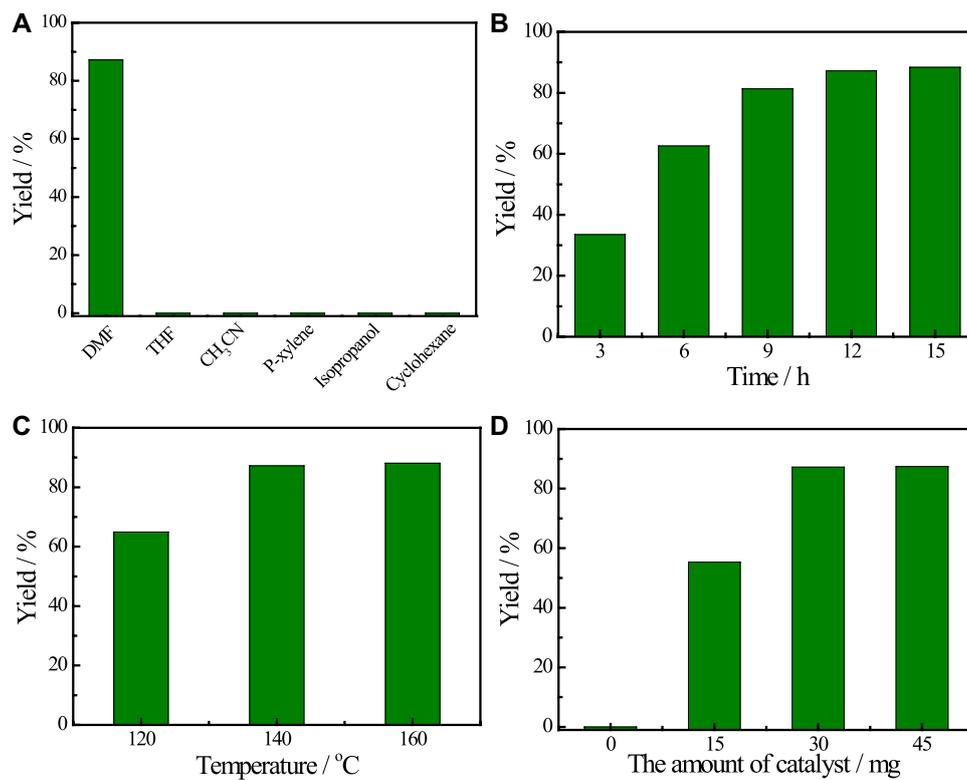
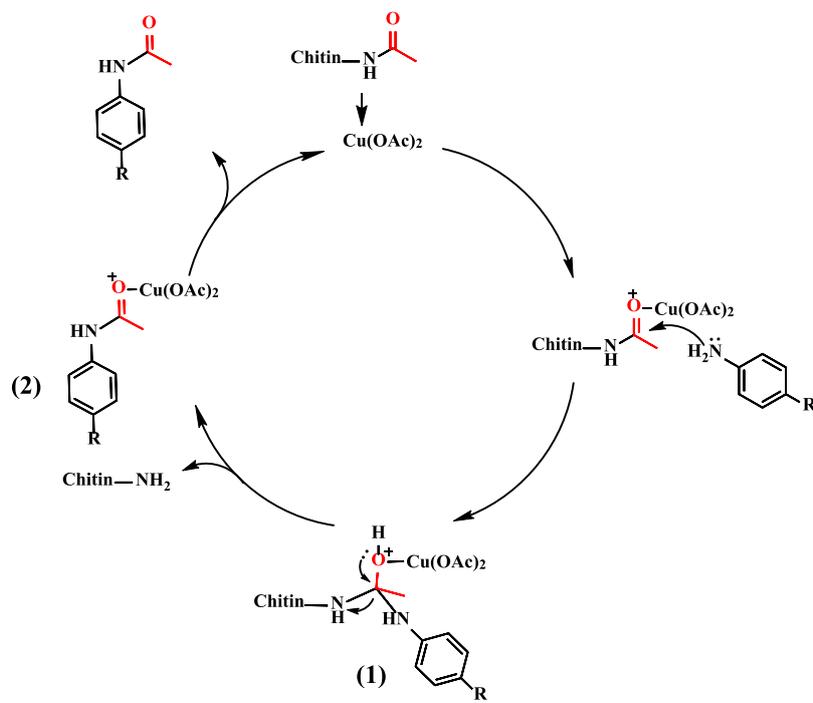
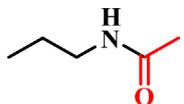
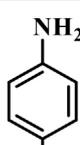
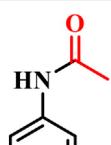
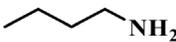
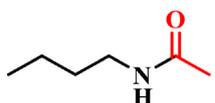
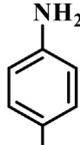
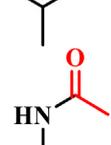
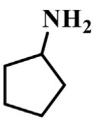
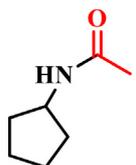
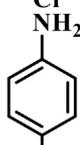
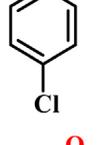
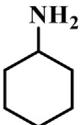
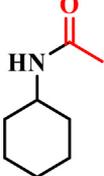
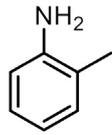
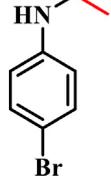
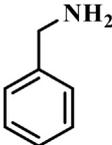
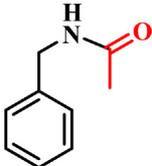
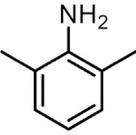
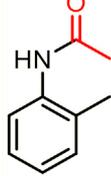
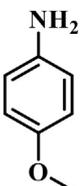
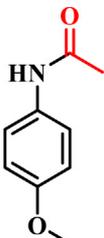
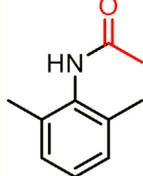
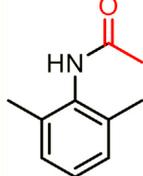


FIGURE 2 | The optimization of reaction factors. **(A)** solvents screening. **(B)** reaction time. **(C)** reaction temperature. **(D)** the amount of catalyst. Reaction conditions: chitin 0.1 g, aniline 0.1 ml, DMF 2.9 ml, catalyst 30 mg, 140°C, 12 h.



SCHEME 1 | Possible reaction mechanism.

TABLE 1 | Substrate scope in terms of amines.

Substrate	Product	Yield/%	Substrate	Product	Yield/%
		93.5			88.6
		92.1			79.5
		85.2			77.8
		83.9			83.7
		81.4			51.4
		89.1			

Reaction conditions: chitin 0.1 g, amine 0.1 ml, DMF 2.9 ml, catalyst 30 mg, 140°C, 12 h.

of De-chitin highly resembles that of chitosan, indicating effective deacetylation of N-acetyl groups in the catalytic system.

The XRD patterns of the three samples are depicted in **Supplementary Figure S2** to investigate their bulk phase structure. Chitin exhibits characteristic diffraction peaks centered at 9.6 and 19.6 of diffraction angle 2θ , representing the (020) and (110) planes of crystalline chitin, respectively. While chitosan has no obvious diffraction peaks, indicating its amorphous structure. Notably, the XRD pattern of De-chitin is similar with that of commercially available chitin. Namely, the original chitin structure is maintained during the $\text{Cu}(\text{OAc})_2$ -catalyzed process. FT-IR and XRD characterizations indicated the

deacetylation of C2-acetamido groups to C2-amido groups selectively occurred on the surface of chitin.

With the optimized conditions in hand, the amine scope of the $\text{Cu}(\text{OAc})_2$ -catalyzed transamidation reaction was examined (**Table 1**). The results revealed broad applicability of this reaction to various amines, mainly including aliphatic amines, cyclic amines and functionalized aromatic amines, generating the corresponding amide products. Particularly noteworthy is that aliphatic amine, such as propylamine and butylamine, can undergo transamidation with chitin even without catalyst and the yields of corresponding amides are up to 93.5 and 92.1%, respectively. The promising result is mostly ascribed to the

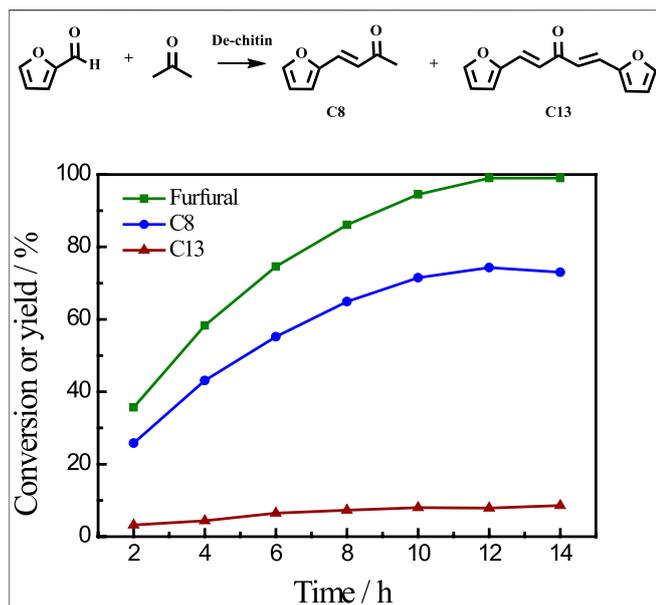


FIGURE 3 | Time conversion plot for the reaction of furfural with acetone over De-chitin as solid base catalyst. Reaction conditions: furfural 0.48 g, acetone 1.16 g, catalyst 0.1 g, 140°C.

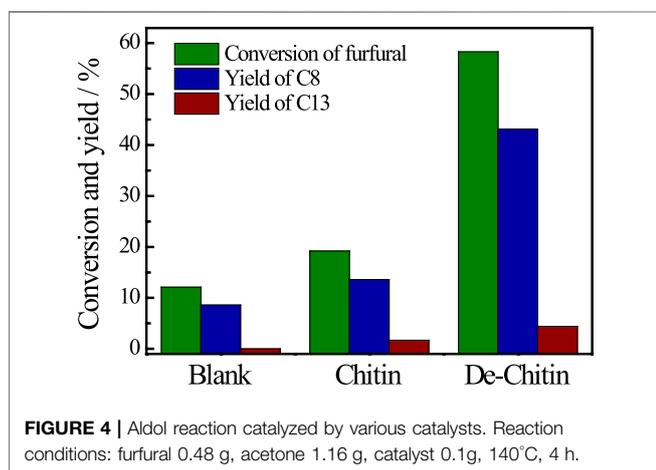


FIGURE 4 | Aldol reaction catalyzed by various catalysts. Reaction conditions: furfural 0.48 g, acetone 1.16 g, catalyst 0.1g, 140°C, 4 h.

stronger nucleophilic capability of aliphatic amine than others. When cyclopentamine and cyclohexylamine were employed as amine sources, excellent yields of corresponding amide products were achieved (85.2 and 83.9%, respectively). For functionalized aromatic amines, different functional groups on the benzene ring were compatible with the reaction, including methyl, methoxy, bromide and chlorine groups. The reaction proceeded well with *p*-methyl or *p*-methoxy aniline as substrate. However, the chlorine and bromine groups were found to have a negative influence on the transamidation reaction, giving the corresponding amines 79.5 and 77.8% yield, respectively. Furthermore, to investigate the effect of steric hindrance on the reaction, *o*-toluidine and 2,6-dimethylaniline were employed to conduct the transamidation reaction. Notably, the yield of corresponding amide decreased to 83.7 and 51.4% with

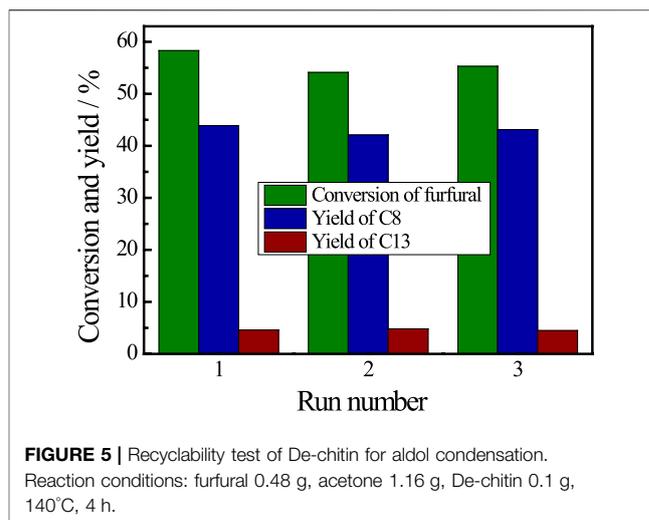


FIGURE 5 | Recyclability test of De-chitin for aldol condensation. Reaction conditions: furfural 0.48 g, acetone 1.16 g, De-chitin 0.1 g, 140°C, 4 h.

o-toluidine and 2,6-dimethylaniline as amine source as compared to that yield (87.2%) with aniline as amine source. The result demonstrated that the reaction was influenced by the steric effect of substrate, apart from nucleophilicity of the amine source.

After reaction, the solid residue (denoted as De-chitin) was separated by centrifugation, washed with ethanol and dried in an oven for the next step utilization. The initial Cu content is 9.54% based on the weight of chitin in catalytic system. We tested the Cu content in solid residue after reaction and found that only 0.07% Cu metal exist in the deacetylated chitin after centrifugation (**Supplementary Table S2**). The aldol condensation of furfural with acetone was employed as a model reaction to evaluate the catalytic performance of De-chitin. **Figure 3** illustrated the influence of reaction time on the aldol reaction. The conversion of furfural increased continuously with the prolongation of reaction time in the beginning and reached a plateau at 12 h. De-chitin catalyst showed remarkable catalytic performance and furfural was completely converted over De-chitin catalyst after 12 h at 140°C, with 74.3% C8 yield and 7.9% C13 yield. **Figure 4** revealed that the conversion of furfural was 12.1% even without catalyst under solvent-free condition. However, the conversion of furfural and yields of condensed products just increased slightly over chitin catalyst, mainly due to the existence of C2-acetamido groups and inadequate exposure of -NH₂ groups. Notably, De-chitin catalyst exhibited excellent catalytic performance for aldol condensation reaction, with the furfural conversion up to 58.3%, which is much higher than that with chitin as catalyst. The deacetylation of C2-acetamido groups to C2-amido groups, namely the adequate exposure of surface -NH₂ groups in the De-chitin sample, is responsible for the enhanced reaction activity.

The recyclability of the De-chitin catalyst for aldol condensation of furfural with acetone was investigated by reusing the catalyst in consecutive catalytic run. The catalyst was separated by simple filtration, washed with ethanol and oven dried for five hours. It can be seen from **Figure 5** that no obvious change was observed in the catalytic activity and product selectivity even after three runs. The recyclability test reveals

the potential application of De-chitin as a heterogeneous catalyst for aldol condensation.

CONCLUSION

In summary, N-acetyl groups in chitin were removed with additional amine sources through transamidation to generate corresponding amide products. The amine sources mainly involved aliphatic amines, cyclic amines and functionalized aromatic amines and the yields of corresponding amides commonly exceed 75%. Notably, aliphatic amines, such as propylamine and butylamine, can undergo transamidation with chitin even without catalyst and the yields of corresponding amides are up to 93.5 and 92.1%, respectively. The promising result is mostly ascribed to the stronger nucleophilic capability of aliphatic amine than others. Additionally, FT-IR and XRD results demonstrated that deacetylation reaction only occurred on the surface of chitin. Furthermore, the solid residue after transamidation reaction (De-chitin) was applied as a heterogeneous base catalyst for aldol condensation of furfural with acetone under mild reaction conditions and showed excellent catalytic activity. The catalyst was recovered and reused for three runs without any drop in its activity and selectivity. This work provides a measure to sufficiently use functional groups in the substrate to produce high-value chemicals from an atomic economy perspective.

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DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

YX, HL, and BH conceived the projects. YX carried out the experiments, analyzed data in the assist of XS and wrote the manuscript in the guidance of HL and BH.

FUNDING

The work was supported financially by National Natural Science Foundation of China (21871277) and Beijing Municipal Science & Technology Commission (Z191100007219009).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fceng.2020.634983/full#supplementary-material>.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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