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N–H and S–H insertions over Cu(I)-zeolites as heterogeneous catalysts

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ABSTRACT

N–H and S–H insertion reactions of α-diazoesters into amines and thiols were conducted using various Cu(I)-zeolites, such as zeolite Y, Y USY, ZSM-5, and beta. All the Cu(I)-zeolites successfully catalyzed N–H insertion reactions with high product yields (70–82%) in aqueous solution at room temperature. Interestingly, Cu(I)-USY (Si/Al = 30) showed better activity for both N–H and S–H insertion reactions than Cu(I)-Y (Si/Al = 2.6), even though they have the same structure and the same +1 oxidation state for Cu. X-ray diffraction, transmission electron microscopy, and X-ray photoemission spectroscopy analysis of the fresh and used catalysts revealed that no noticeable change in the zeolite structure, oxidation state of Cu, or sintering of Cu occurred during the reactions. Furthermore, after being recycled four times, the catalysts showed only minor activity decreases, exhibiting conversion rates 70–80% of those of the fresh catalysts, demonstrating their stability under the current reaction conditions. Temperature programmed reduction experiments showed that reduction of Cu^+ to Cu° occurred at ca. 300 °C over Cu(I)-USY, while it occurred at ca. 800 °C over Cu(I)-Y. The significantly higher activity of Cu(I)-USY than Cu(I)-Y may be due to the more electrophilic Cu centers on Cu(I)-USY, which is highly favorable for ylide formation, and therefore facilitates N–H and S–H insertions.

1. Introduction

Carbon–heteroatom bond formation is an important challenge for synthetic chemists because such bonds are present in both natural and man-made molecules [1,2]. Recently, carbenoid-mediated carbon–heteroatom bond formation has become of great interest to the scientific community because carbenoid-based X–H insertions (XHIs), where X = N, O, S, Se, P, or a halogen, are applicable to both small molecules and biomolecules [3–7]. The N–H insertion of α-diazocarbonyl compounds into amines using transition metals (Rh, Cu, Fe, Ru, etc.) is very useful for the synthesis of α-amino acid derivatives, the basic building blocks of proteins [4,7,8]. Furthermore, transition-metal-catalyzed insertions of α-diazocarbonyl compounds into the S–H bonds of thiols is an efficient method for the construction of C—S bonds, which are present in various natural and synthetic molecules with important biological activities [8,9].

Much research effort has been focused on developing catalytic reactions based on Cu because it is an abundant and practical alternative to precious metal catalysts [7]. Furthermore, there have been extensive studies to develop immobilized, reusable Cu catalysts due to their economic and environmental benefits. Therefore, much effort has focused on developing immobilized Cu catalysts on solid-support materials, such as clay [10], silica or silica-alumina [11,12], metal-organic-frameworks [13,14], and polymers [15,16]. Many of these heterogeneous Cu catalysts exhibited similar or better reaction performances than those of homogeneous Cu catalysts.

Cu(I)-zeolite is a supported catalyst system that, when high-Si/Al-ratio zeolites are employed, exhibits highly stable Cu^+ [17–22] under aerobic conditions, and they have been employed in various Cu-catalyzed reactions. For example, Sommer and Pale have extensively studied azide-alkyne cycloadditions [23–25], azomethine imine cycloadditions [26], multicomponent condensations [27], homocoupling of alkynes [28], and coupling of alkynes with amides [29]. Furthermore, Zaccheria et al. have performed C–H insertion reactions using a heterogeneous Cu/SiO_2-Al_2O_3 catalyst [11,12].

Herein, we expand Cu(I)-zeolite-catalyzed reactions to N–H and S–H insertions with α-diazoesters (Scheme 1) with high yields

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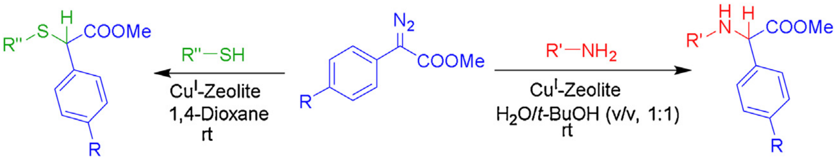


Scheme 1. Environmentally friendly catalytic N–H and S–H insertion reactions.

(70–82%) in aqueous solution at room temperature. Furthermore, these heterogeneous catalysts exhibit high stability, allowing them to be used several times.

2. Experimental

2.1. Preparation of the catalysts

USY (CBV 760, Si/Al = 30), Y (CBV 100, Si/Al = 2.6), ZSM-5 (CBV 3024E, Si/Al = 15), MOR (CBV 10A, Si/Al = 6.5) and zeolite beta (CP 814E, Si/Al = 12.5) were obtained from Zeolyst International Co. Cu(I)-zeolites were prepared by a previously reported two-step ion-exchange and thermal treatment method [21]. First, NH_4^+-zeolites were synthesized by solution ion exchange using an aqueous solution of NH_4NO_3 (0.1 M). Following ion exchange, the samples were filtered, washed, and dried at 100 °C overnight. All the catalyst samples were then calcined at 400 °C for 12 h under flowing He (flow rate = 1.0 mL/s) to decompose the NH_4^+ and form H-zeolites. Solid-state ion exchange of Cu(I) onto the H-zeolites was accomplished by physical mixing with CuCl in a glove box and subsequent thermal treatment at 400 °C for 2 h under flowing He (flow rate = 1.0 mL/s). The amount of CuCl were controlled for 3 wt% of Cu^+ of final products. The concentrations of Cu in the zeolites were confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian, 720-ES) after acid digestion using hydrofluoric acid. The obtained Cu(I)-zeolites were stored in an inert atmosphere prior to use.

2.2. Characterization of the catalysts

The crystalline structure of the Cu-zeolites before and after reaction was confirmed by X-ray diffraction (XRD). XRD patterns were obtained on a Bruker D8 Advance using CuKα radiation ($\lambda = 1.5406$ Å) in step mode with 2θ values between 5° and 50°, with a step size of 0.05°/s. Transmission electron microscopy (TEM) images of Cu(I)-zeolites before and after reaction were collected using a JEOL JEM-2100F microscope operated at 200 kV. TEM samples were prepared by dusting the gently grounded zeolites samples onto a carbon coated Ni grid. X-ray photoelectron spectroscopy (XPS) spectra were collected in order to ascertain the oxidation state of the Cu in the Cu-zeolites using an ESCALAB-250Xi XPS spectrometer equipped with an Al Kα radiation source ($h\nu = 1486.6$ eV) and using an analysis chamber pressure of ca. 5×10^{-10} mbar. The binding energy (BE) data were measured by normalizing to the C 1s transition at 284.6 eV.

H_2-temperature programmed reduction (TPR) measurements were performed to investigate the nature of the Cu species on the freshly prepared Cu(I)-zeolites. After solid-state ion exchange at 400 °C for 2 h under flowing He (1.0 ml/s), the samples were cooled to room temperature under continued He flow, and then purged with 2% H_2/Ar (1.0 ml/s) for 1 h at room temperature. After stabilization of the thermal conductivity detector (TCD) signal in a Hewlett-Packard 7820 gas chromatograph, TPR experiments were carried out under a flow of 2% H_2/Ar (1.0 ml/s) at a heating rate of 10 °C/min to 1000 °C. To avoid interference from water produced during the analysis, a dry ice/acetone trap was included prior to the detector.

2.3. General procedure for Cu(I)-zeolite catalyzed N–H insertion of amines with α-diazoesters (3a-o)

In an oven-dried round bottom flask, 1.0 mL of H_2O was added to the Cu(I)-zeolite (100 mg, 0.1 equiv). To this solution, a mixture of the amine (0.47 mmol, 1 equiv) and the α-diazoester (0.47 mmol, 1 equiv) in 1.0 mL *t*-BuOH was added dropwise, and the reaction mixture was stirred at room temperature for a specified time. The progress of the reaction was monitored using thin-layer chromatography (TLC) with ethyl acetate and hexane as eluents. After completion of the reaction, it was treated with ethyl acetate. The Cu(I)-zeolite was collected by centrifugation and washed successively with water and acetone. After drying under vacuum for 12 h at room temperature, the catalyst was reused in another reaction. The ethyl acetate layer was then washed with aqueous 0.3 M NaCl solution and water. The organic layer was dried over Na_2SO_4, filtered, and evaporated to leave the crude product, which was then purified using short-column silica gel chromatography to give the target compound.

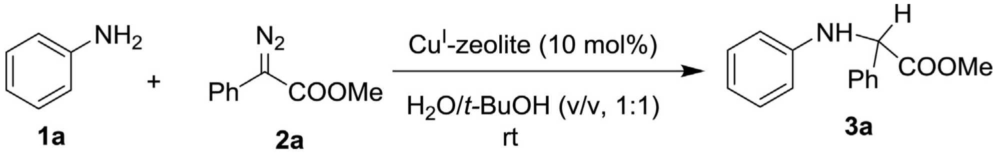
2.4. General procedure for Cu(I)-zeolite catalyzed S–H insertion of thiols with α-diazoesters (5a-i)

The Cu(I)-zeolite (100 mg, 0.1 equiv) was placed into an oven-dried round bottom flask, [1]and to it 1.0 mL 1,4-dioxane was added. A mixture of the thiol (0.47 mmol, 1 equiv) and α-diazoester (0.47 mmol, 1 equiv) in 1.0 ml 1,4-dioxane was then added dropwise and the reaction mixture was stirred at room temperature for a specified time. The progress of the reaction was monitored using TLC with ethyl acetate and hexane as eluents. After completion of the reaction it was treated with ethyl acetate. The Cu(I)-zeolite was collected by centrifugation and washed successively with water and acetone. After drying under vacuum for 12 h at room temperature, the catalyst was reused in another reaction. The ethyl acetate mixture layer was then washed with aqueous 0.3 M NaCl solution and water. The organic layer was dried over Na_2SO_4, filtered, and evaporated to leave the crude product, which was purified using short-column silica gel chromatography to give the target compound.

2.5. Recoverability testing of Cu(I)-USY

After the reaction between *p*-toluidine **1f** and methyl 2-diazo-2-(4-methoxyphenyl) acetate **2b**, the reaction mixture was treated with ethyl acetate. Cu(I)-USY was collected by centrifugation and washed successively with water and acetone. After drying under vacuum for 12 h at room temperature, the catalyst was reused for another reaction between fresh **1f** and **2b**. This process was repeated four times, with the product from each cycle being purified and the yield measured, and the recovered catalyst being characterized by XRD, ICP, TEM, and XPS.

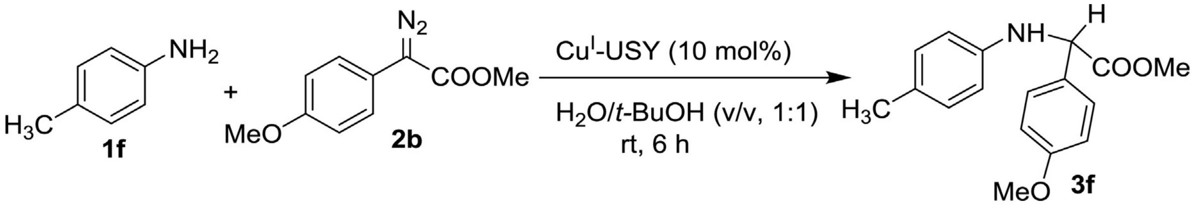
Table 1
N–H insertion of **1a** to **2a**[a] catalyzed by Cu(I)-zeolites..



Entry	Catalyst	Time (h)	yield (%)
1	Cu(I)-USY	6	82
2	Cu(I)-Y	6	68
3	Cu(I)-ZSM5	6	70
4	Cu(I)-MOR	6	62
5	Cu(I)-β	24	35

[a] Reaction conditions: aniline **1a** (1 equiv), methyl 2-diazo-2-phenylacetate **2a** (1 equiv), Cu(I)-zeolite (10 mol%) in 2.0 mL of H2O/t-BuOH (1:1 *v/v*). Yields refer to isolated yield. The compound was characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectroscopy.

Table 2
Recoverability of Cu(I)-USY.



Run	Catalyst recoverability (%)	Yield (%)[a,b]
1	>99	80
2[c]	>99	77
3[c]	99	75
4[c]	98	70

[a] Reaction conditions: *p*-Toluidine **1f** (1 equiv), methyl 2-diazo-2-(4-methoxyphenyl) acetate **2b** (1 equiv), Cu(I)-USY (10 mol%) in 2.0 mL of H_2O/*t*-BuOH (1:1 *v/v*) at rt for 6 h.

[b] Yields refer to isolated yield.

[c] Recovered catalyst used.

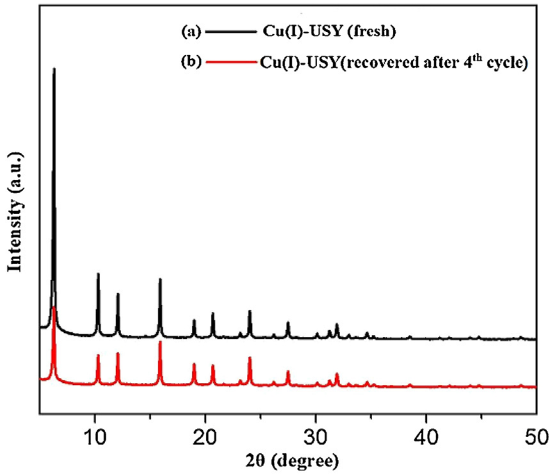


Fig. 1. Powder X-ray diffraction patterns of Cu(I)-USY. (a) Fresh and (b) recovered after four cycles.

3. Results and discussion

3.1. N–H insertion reactions over Cu-zeolites

To investigate the Cu(I)-zeolite-catalyzed XHIs, we prepared five representative Cu(I)-zeolites with[8] USY, Y, ZSM5, MOR, and beta to catalyze typical NH insertion reactions with α-diazoesters. Initially aniline **1a** (1.0 equiv) was reacted with methyl 2-diazo-2-phenylacetate **2a** (1.0 equiv) in H_2O/t-BuOH (1:1 *v/v*) over Cu(I)-USY (0.1 equiv) at room temperature, and the desired product **3a** was obtained in 82% yield. The reaction was also performed in the presence of other Cu(I)-zeolites, and the results are summarized in Table 1.

These results show that Cu(I)-USY is the best catalyst for this transformation. The reaction was also performed in organic solvents such as benzene, toluene, and dichloromethane. Although **3a** was formed in similar yields with all solvents assayed, H_2O/*t*-BuOH was considered the best solvent for this transformation due to its environmental benignity. Increasing the amount of Cu(I)-USY from 10 to 20 mol% did not increase the yield of **3a**, whereas a low yield of **3a** was obtained when the same reaction was performed using 5 mol% (0.05 equiv) of Cu(I)-USY. Therefore, 10 mol% Cu(I)-USY in H_2O/*t*-BuOH (1:1 *v/v*) was considered to be optimal for this reaction.

3.2. Recoverability of Cu(I)-USY

We found that Cu(I)-USY showed very robust reaction recoverability, affording the N–H insertion product **3f** in 70% yield, with >98% catalyst recovery over four reaction runs (Table 2). This recycling test indicates the stability of these Cu(I)-zeolite catalysts. To investigate the reason for their stability, both fresh and recovered catalysts were analyzed by XRD, TEM, XPS, and ICP.

We considered four types of modification that the catalysts could undergo during the test reactions. Firstly, we considered changes of the zeolite structures, which was investigated with XRD.

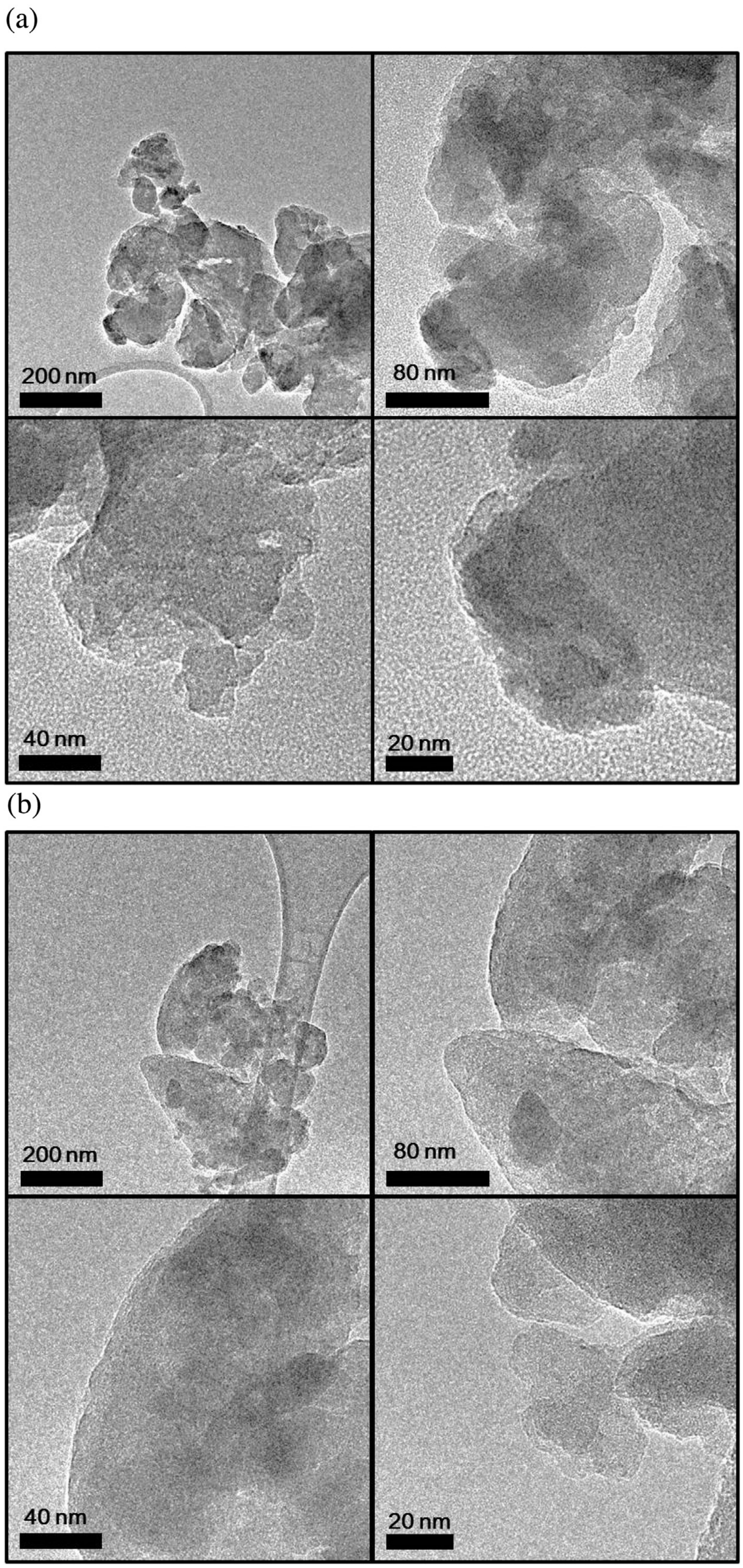


Fig. 2. High-resolution TEM images of Cu(I)-USY. (a) Fresh and (b) recovered.

As shown in Fig. 1, the XRD pattern of the recovered catalyst indicates that it has exactly the same crystalline phase as the freshly prepared catalyst.

Secondly, we considered Cu sintering, which reduces the number of catalytically active sites. The TEM images shown in Fig. 2a confirm the homogeneous distribution of Cu(I) species in the USY

Table 3
ICP analysis results of fresh and recovered Cu(I)-USY.

Cu(I)-USY	Cu/Al	Cu loading (wt%)
Fresh	0.8	2.6
Recovered	0.9	2.8

zeolite and show no evidence of sintered Cu clusters. TEM images of spent Cu(I)-USY indicate the same distribution of Cu on the zeolite. Therefore, we concluded that no Cu sintering occurs during test reactions.

Thirdly, we considered Cu(I) leaching during the reaction, which could lead to continuous loss of catalytic activity and, more seriously, allow the reaction to occur over the leached Cu^+ ions homogeneously. The results of ICP analysis (Table 3) confirm that there are no significant changes in Cu loading of the Cu(I)-USY catalyst during reaction. Thus, we concluded that there is no Cu leaching during the reactions.

Finally, we considered catalyst deactivation through changes in the oxidation state of the active Cu centers. It is well known that N–H or S–H insertion is only catalyzed by Cu^+, and not by Cu^{2+} or Cu^0. Therefore, if the Cu^+ in the zeolites are oxidized to Cu^{2+} or reduced to Cu^0, the catalysts lose their activities. To investigate the oxidation state of the Cu in the catalysts, we performed XPS analysis on fresh catalysts, recovered catalysts, and Cu(II)-USY as a standard. The XPS analysis results (Fig. 3) were used to identify the Cu ion oxidation state in the fresh and recovered zeolites. In the fresh Cu(I)-USY, the Cu $2p_{3/2}$ peak appears at 933.7 eV, which clearly indicates the presence of Cu^+ ions in the sample. Furthermore, the weak $2p_{1/2}$ peak at ca. 953 eV also indicates the presence of Cu^+. The recovered catalyst also exhibits a peak at 934 eV, which indicates the Cu^+ oxidation state. Cu^{2+} ions result in peaks at ca. 936 eV for $2p_{3/2}$ and ca. 956 eV for $2p_{1/2}$, and a small satellite peak at ca. 945 eV. The spectrum of Cu(II)-USY (Fig. 3c) exhibits these $2p_{3/2}$ and $2p_{1/2}$ peaks, and also some peaks from Cu^+ due to the auto-reduction of Cu^{2+} that is well known to occur in zeolites during XPS data collection. These results clearly indicate the presence of Cu^+ ions in both the fresh and recovered Cu(I)-USY.

The TEM, XRD, ICP, and XPS results are very similar for both the fresh and recovered Cu(I)-USY, which suggests that Cu(I)-USY does not undergo significant change, even over four reaction cycles. These results clearly demonstrate the high stability of Cu(I)-USY under the reaction conditions employed. Recyclability is one of the most important advantages of heterogeneous catalysts for practical applications. While homogeneous catalysts often show superior activity and selectivity to their heterogeneous analogues, their practical application is hindered by their cost, which is exacerbated by the inability to recycle them.

3.3. *Expansion of substrate scope*

The substrate scope of the current reaction system was investigated using different amines (Table 4). Aromatic amines give the corresponding mono-alkylated products **3a-m** in good yields without any side products, as determined from the ^{1}H NMR and ^{13}C NMR spectra of the crude products. Recrystallization of **3a** from chloroform produced single crystals whose structure was confirmed by X-ray analysis (Fig. 4) [12]. Of the aromatic amines, aniline gives a higher yield of its corresponding product than the substituted aromatic amines. The substituents on aromatic ring have an important effect on this reaction. Aromatic amines having electron-donating groups on the aromatic ring give higher yields compared to those having electron-withdrawing groups on the ring. Conversely, aliphatic amines such as *n*-butylamine **1n** and cyclohexylamine **1o**, do not afford any N–H insertion product under these reaction conditions, and the unreacted starting materials are recovered.

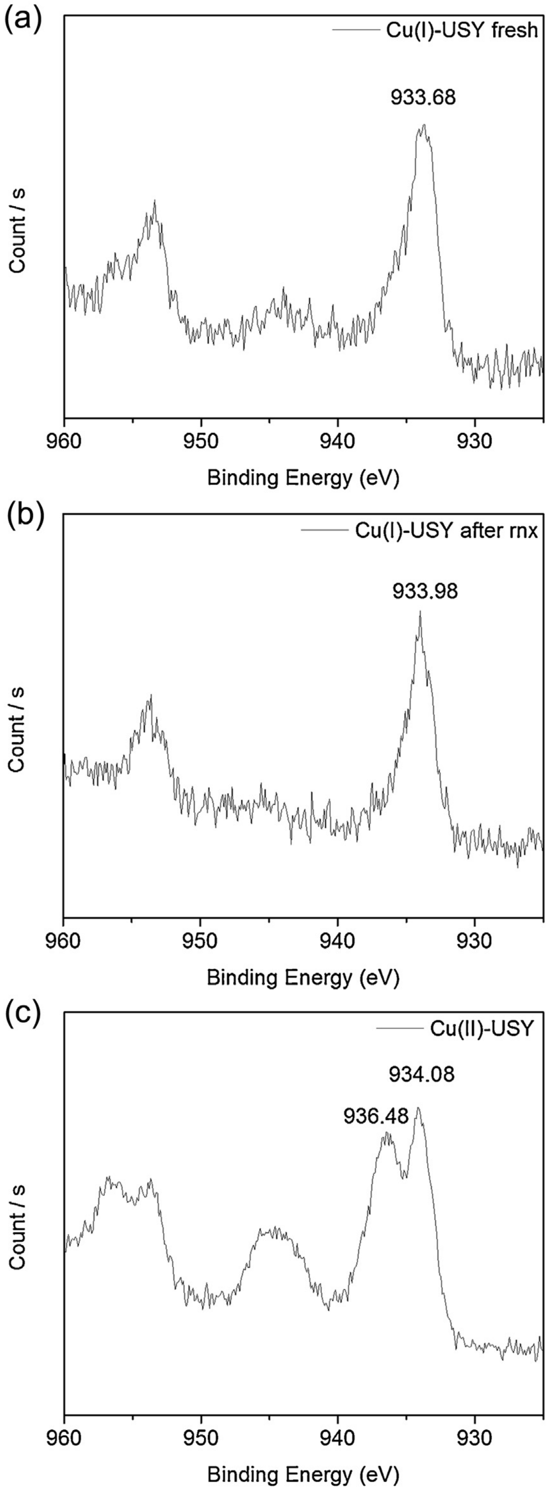
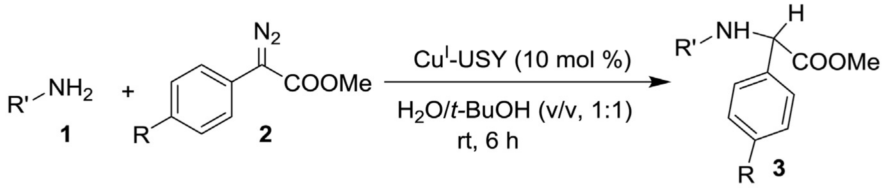
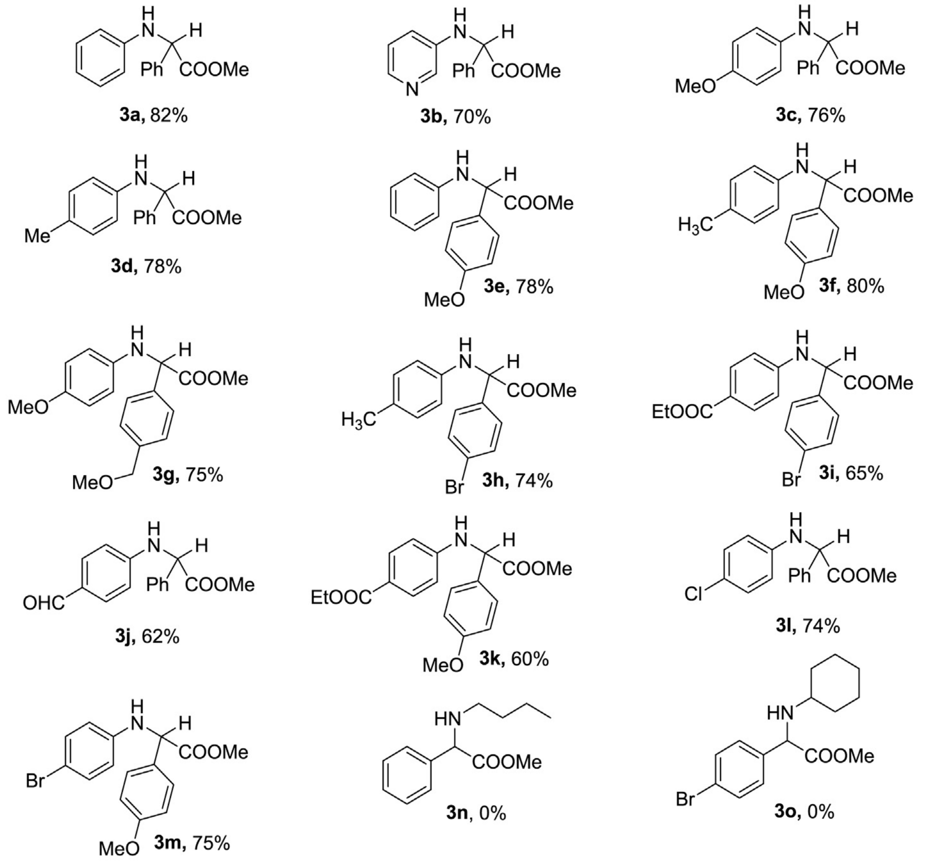


Fig. 3. Cu 2p XPS spectra of (a) fresh and (b) recovered Cu(I)-USY, and (c) Cu(II)-USY.

Encouraged by these results, the scope of the reaction was also investigated using various aliphatic and aromatic thiols. Initially, 4-methylbenzenethiol (**4a**, 1 equiv) was reacted with methyl 2-diazo-2-phenylacetate (**2a**, 1 equiv) in H_2O/t-BuOH (1:1 *v*/*v*) over Cu(I)-USY (0.1 equiv) at room temperature. However, only a trace amount of the S–H insertion product is detected in the ^{1}H NMR spectrum of the crude product. In contrast, when the same reaction

Table 4
N–H insertion reactions between different amines and α-diazoesters.[a]





3a, 82%
3b, 70%
3c, 76%
3d, 78%
3e, 78%
3f, 80%
3g, 75%
3h, 74%
3i, 65%
3j, 62%
3k, 60%
3l, 74%
3m, 75%
3n, 0%
3o, 0%

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[a] Reaction conditions: amines (1 equiv), α-diazoesters (1 equiv), Cu(I)-USY (10 mol%) in 2.0 mL of H_2O/t-BuOH (1:1 *v*/*v*) at rt for 6 h. Yields refer to isolated yield. The compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectroscopy.

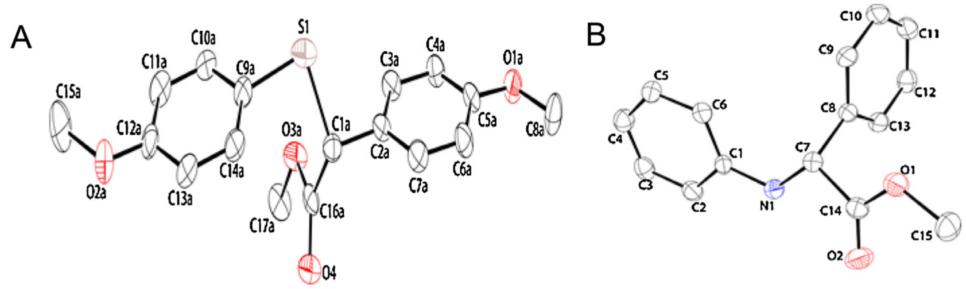
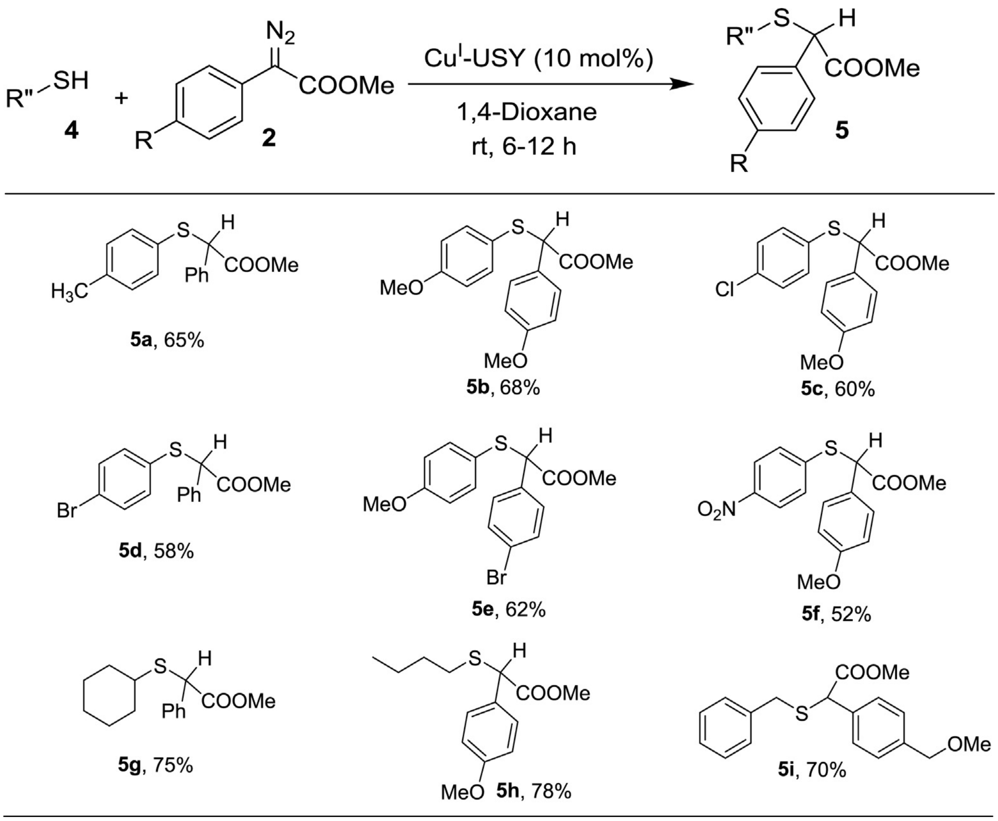


Fig. 4. X-ray crystal structure of inserted product. (A) ORTEP diagram of S–H insertion product **5b**. (B) ORTEP diagram of N–H insertion product **3a**.

is performed in an organic solvent such as 1,4-dioxane, the desired S–H insertion product **5a** is obtained in 65% yield (Table 5) at room temperature. Increasing the amount of Cu(I)-USY to 20 mol% (0.2 equiv) has no effect on yield.

Different aliphatic and aromatic thiols were reacted with α-diazoesters under these optimized reaction conditions, and the results are summarized in Table 5. Both aliphatic and aromatic thiols give the corresponding products in good yields. Aromatic thiols with electron-donating groups on the aromatic ring give higher yields than those having electron-withdrawing groups on the ring, and aliphatic thiols are better substrates than aromatic

Table 5
S–H insertion reactions between thiols and α-diazoesters.[a]



5a, 65%
5b, 68%
5c, 60%
5d, 58%
5e, 62%
5f, 52%
5g, 75%
5h, 78%
5i, 70%

[a] Reaction conditions: thiols (1 equiv), α-diazoesters (1 equiv), Cu(I)-USY (10 mol%) in 2.0 mL of 1,4-dioxane at rt. For aliphatic thiols the reaction time was 6 h, whereas for aromatic thiols the reaction time was 12 h. Yields refer to isolated yield. The compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectroscopy.

thiols. Recrystallization of **5b** from chloroform produced single crystals whose structure was confirmed by X-ray analysis (Fig. 4).

3.4. TPR measurement of Cu(I)-USY

Surprisingly, we found that when other zeolites are used to support the Cu(I), such as Y, ZSM5, MOR, and β, no S–H insertion product is formed, and in all cases, the unreacted starting materials are recovered. This is in contrast to the azide-alkyne cycloaddition results reported by Sommer et al. [11] and the N–H insertion reaction reported here, which is catalyzed by all the Cu(I)-zeolites. We performed TPR experiments with Cu(I)-USY, Cu(I)-Y, and Cu(II)-Y as a reference to identify the differences between these zeolites. As shown in Fig. 5, we found that Cu(I)-USY undergoes reduction at around 300 °C, whereas Cu(I)-Y undergoes reduction above 900 °C. The Cu^{2+} in Y zeolite shows two reduction peaks, one at 300–400 °C and one at ca. 900 °C, interpreted as Cu^{2+} to Cu^+ and Cu^+ to Cu^0 reductions, respectively. Therefore, the reduction peak at ca. 900 °C on Cu(I)-Y can be reasonably attributed to the Cu^+ to Cu^0 reduction. However, Cu(I)-USY shows two close reduction peaks at ca. 300 °C, which is much lower than the second reduction temperature observed with Cu(I)-Y, and is very close to the Cu^{2+} to Cu^+ reduction temperature observed in Cu(II)-Y. In contrast, the XPS data (Fig. 3) clearly indicate that the oxidation state of Cu in Cu(I)-USY is Cu^+ exclusively. Therefore, both the reduction peaks in Cu(I)-USY are interpreted as Cu^+ to Cu^0 reduction, with the small reduction temperature difference arising from the Cu being in different positions in the USY zeolite. It is noteworthy that Cu^+ ions in the same zeolite frameworks may exhibit different reduction temperatures.

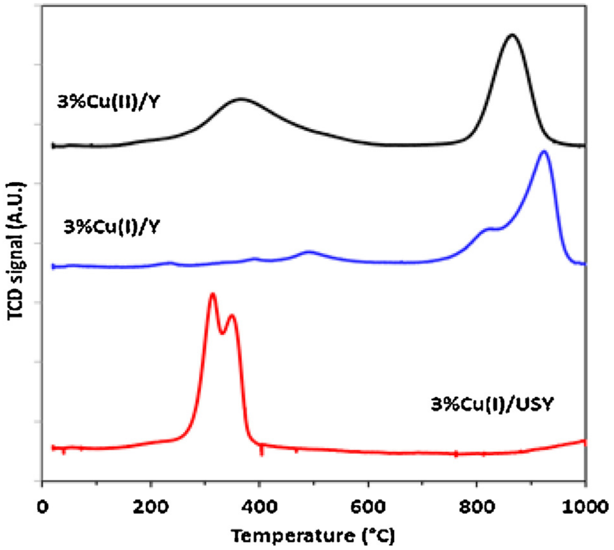
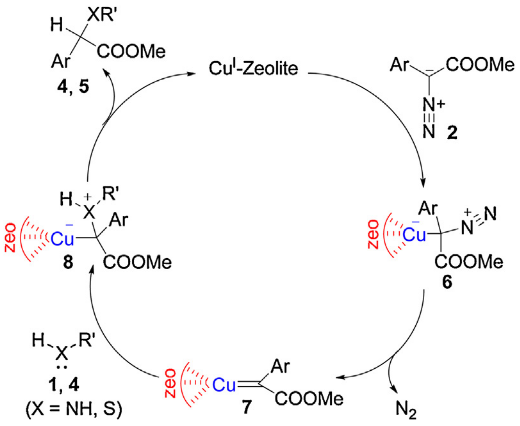


Fig. 5. TPR results for Cu(I)-USY (red), Cu(I)-Y (blue), and Cu(II)-Y (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

We considered that the reduction temperature of the Cu(I)-zeolites may yield information on the XHIs reaction mechanism. The reduction of Cu^+ to Cu^0 is an electron accepting process, so it is reasonable to assume that low-temperature reduction indicates superior electrophilicity of a catalyst. Thus, the TPR experiment indicates that the Cu(I)-USY catalyst is more electrophilic than Cu(I)-Y. As illustrated in Scheme 2, the XHI reaction proceeds via



Scheme 2. Proposed catalytic cycle for N–H and S–H insertions over the Cu(I)-USY catalyst.

the formation of an ylide intermediate. Therefore, it is assumed that Cu(I)-USY promotes the formation of a more stable sulfonium ylide intermediate, thereby facilitating the formation of the S–H insertion product. Conversely, due to their lower electrophilicity, the other Cu(I)-zeolites are unable to form this sulfonium ylide intermediate, and therefore no S–H insertion occurs with α-diazoesters over these catalysts.

It is noteworthy that our Cu(I)-zeolite affords the mono-alkylated aromatic amine product in higher yield with better selectivity than a previously reported homogeneous Cu catalyst, which produced mixtures of mono- and di-alkylated products [30]. Because of the limited pore size of the zeolite (diameter <10 Å) [31], only small molecules, such as aniline and the α-diazoesters, can access the reaction sites in the zeolite and couple with each other. Consequently, the branched mono-alkylated product may not re-react because it cannot access the catalytic sites. However, when a homogeneous catalyst is used, the initial reaction product can further react with another α-diazoester. Furthermore, the Cu$^+$ in homogeneous Cu-catalysts such as Cu(I)-THPTA and Cu(I)-TBTA is not perfectly stabilized; therefore, when homogeneous catalysts are used, exclusion of oxygen or a mild reducing agent (e.g. ascorbic acid, TCEP) may be required [32]. However, in our study, the Cu-zeolite reactions were performed under atmospheric conditions without the addition of any reducing reagents, as the local zeolite environment stabilizes the Cu$^+$ oxidation state. Thus, we found that Cu(I)-USY has several advantages over traditional catalysts, which could make it a practical alternative for N–H and S–H insertion reactions.

4. Conclusions

We have herein reported Cu(I)-zeolites as heterogeneous catalysts for Cu-carbenoid-mediated insertion reactions with α-diazoesters. All the Cu(I)-zeolites were prepared via a solid-state ion exchange method from H-zeolites and CuCl. The oxidation state of Cu in the catalysts was exclusively +1, as confirmed by XPS and H_2-TPR. Cu(I)-USY, Cu(I)-Y, Cu(I)-ZSM-5, and Cu(I)-MOR promoted the N–H insertion reaction with aniline, giving yields of 70–82% after 6 h at room temperature. Conversely, the use of Cu(I)-β promoted the same reaction with the relatively poor yield of ca. 35% after 24 h under the same conditions. Interestingly, only Cu(I)-USY catalyzed S–H insertion reactions. The superior catalytic activity of Cu(I)-USY for both N–H and S–H insertions is most likely related to its uniquely high Cu(I) electrophilicity, which was revealed by TPR experiments.

XRD, TEM, and XPS analyses of fresh and reclaimed catalysts did not reveal any noticeable differences between them in terms of the zeolite structure, oxidation state of Cu, and sintering of Cu. Catalyst recycled four times exhibited minor activity decreases (70 to 80% conversion rates). To the best of our knowledge, this is the first report of N–H and S–H insertions using zeolite chemistry. All these results suggest that Cu(I)-USY is a highly active and stable catalyst for N–H and S–H insertions.

Supporting information

General experimental procedures and spectroscopic data, NMR spectra (^{1}H and ^{13}C) of all compounds, single crystal X-ray data of **3a** and **5b**.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.02.031.

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