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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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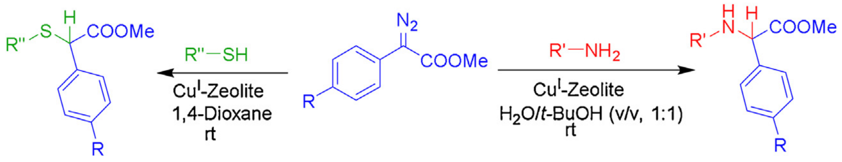

Scheme 1. Environmentally friendly catalytic N–H and S–H insertion reactions.

(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.