



Cu-doped zeolitic imidazolate framework catalysed highly selective conversion of alkynes to β -keto and vinyl sulfones using sodium sulfinates

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Abstract. Cu²⁺-doped zeolitic imidazolate framework-8 (ZIF-8)-catalyzed one-pot procedure to synthesize β -keto and vinyl sulfones by the direct oxysulfonylation and hydrosulfonylation of alkynes *via* radical reaction under mild conditions has been described. The advantages of this protocol included broad substrate scope and excellent β -keto and E-stereoselectivity. The Cu/ZIF-8 catalyst not only exhibited excellent performance but also had a great stability in the reaction, successfully allowing its reuse up to five cycles. This efficient Cu/ZIF-8 heterogeneous catalyst is explored for the first time to generate β -keto and vinyl sulfones.

Keywords. Phenyl acetylenes; Cu/ZIF-8; β -Keto and vinyl sulfone.

1. Introduction

In recent years, there is a growing interest in the use of copper nanoparticles as a catalyst due to their significant physical and chemical properties as well as a broad range of applications.^{1–3} The capability of copper to attain various oxidation states makes it a suitable candidate for the synthesis of nanoparticles with varying composition. On the other hand, zeolitic imidazolate framework (ZIFs) materials constitute a new distinctive and rapidly developing subclass of metal-organic frameworks (MOFs). In particular, ZIF-8 is the most investigated ZIF material for a variety of applications including heterogeneous catalysis,^{7–12} gas sorption⁴ and sensing.^{5,6} Its application as an efficient heterogeneous catalyst support has been demonstrated recently for various reactions such as Knoevenagel reaction,^{13,14} 1,3-dipolar cycloadditions, Friedlander and Combes condensations.¹⁰ Based on these observations, we focused our efforts on the use of Cu²⁺-doped ZIF-8 as a heterogeneous catalyst for exploring new protocols for the synthesis of organic scaffolds. The presence of Cu²⁺ ions in the

ZIF-8 structure should enable its use as a reusable heterogeneous catalyst in organic reactions.¹⁰

Methods for the formation of C–S bonds are considered as an important tool in synthetic organic chemistry. These are used as versatile building blocks^{15–17} in biomedical research. Particularly, vinyl sulfones are a novel class of neuroprotective agents toward Parkinson's therapy,¹⁶ anti-trypanosomal agents¹⁸ and β -keto sulfones as inhibitors of 11 β -hydroxysteroid dehydrogenase type I.¹⁹ Over the years, a number of procedures were made available for the preparation of vinyl and β -keto sulfones.^{20–28} However, the major drawbacks of some of these methods include longer reaction periods, high temperatures and the formation of side products. Hence, the development of a new protocol for the synthesis of vinyl and β -keto sulfones using reusable heterogeneous catalyst is highly beneficial.

A literature survey revealed that homogeneous copper catalyzed sulfonylation of alkynes with sodium *p*-toluenesulfinate provides alkenyl sulfones with a trace amount of β -keto sulfones or β -hydroxyl sulfones

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as by-products.^{27,28} These reports not only encouraged us to initiate the heterogeneous catalysis but also directed us to investigate the oxysulfonylation and hydrosulfonylation of alkynes under mild conditions. Moreover, transition metals like Cu, Pd can transfer a single electron and are easily oxidized or reduced under certain conditions.^{22–28} Herein, we report Cu²⁺-doped nanoparticles supported on ZIF-8 as an efficient heterogeneous catalyst for hydrosulfonylation and oxysulfonylation of alkynes under relatively mild operating conditions. To the best of our knowledge, this is the first report on the formation of the C–S bond using heterogeneous Cu²⁺-doped ZIF-8 as a catalyst.

2. Experimental

2.1 Materials and physical measurements

All the reagents and solvents were purchased as commercial grade and used as received. IR spectra were recorded on a Nicolet-740 FT-IR spectrophotometer with KBr pellets. The NMR spectra were recorded with Bruker Avance (300/400/500 MHz) for ¹H, and 100/125 MHz for ¹³C NMR spectra in CDCl₃ with TMS as an internal standard. Coupling constants are given in Hz. The ESI MS data were recorded on an Agilent 1100 MSD with ESI SL Trap. The HR-ESIMS data were acquired on an Agilent 6510 Q-TOF and ESI probe. Scanning electron microscopy (SEM) pictures were prepared using a JEOL Scanning Electron Microscope JSM-6490 LV. The powder samples were placed on a silicon zero-background sample holder and the XRD patterns were recorded at room temperature using Cu K α radiation ($\lambda = 0.15418$ nm). The textural properties of the materials were investigated with a Micromeritics ASAP 2420 instrument using liquid nitrogen (-196 °C). Prior to the analyses, the samples were out-gassed overnight in vacuum at 40 °C on the degassing port followed by 4 h out-gassing on the analyse port. Diffuse reflectance UV-Vis spectra of the samples were measured using a Shimadzu UV-2101 PC spectrophotometer and spectra are recorded in a range of 200–700 nm.

2.2 Synthesis of β -keto sulfones

Phenyl acetylene **1a** (0.5 mmol, 1 equiv.), sodium 4-methylbenzenesulfinate **2a** (0.6 mmol, 1.2 equiv.), Cu_{25%}/ZIF-8 (0.05 mmol, 0.1 equiv.) and methanol were added to a 5 mL glass tube at room temperature and stirred for 12 h and monitored periodically by TLC. Then the reaction mixture was extracted with ethyl acetate (3 \times 5 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography using petroleum ether and ethyl acetate (8:2 v/v) as eluent to give the pure product **4a**.

2.3 Synthesis of (*E*)-Vinyl sulfones

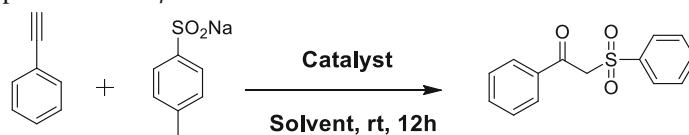
Phenyl acetylene **1a** (0.5 mmol, 1 equiv.), sodium 4-methylbenzenesulfinate **2a** (0.6 mmol, 1.2 equiv.), Cu_{25%}/ZIF-8 (0.05 mmol, 0.1 equiv.) and acetonitrile (2 mL) were added to a 5 mL glass tube at room temperature and stirred for 3 h and monitored periodically by TLC. Then the reaction mixture was extracted with ethyl acetate (3 \times 5 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography using petroleum ether and ethyl acetate (9:1 v/v) as eluent to give the pure product **3a**.

3. Results and Discussion

Cu²⁺-doped zeolitic imidazolate frameworks (ZIFs) crystals were synthesized following the same protocol reported in the literature.¹⁰ After preparation, these crystals were denoted as Cu_{1%}/ZIF-8, Cu_{7%}/ZIF-8, Cu_{15%}/ZIF-8, and Cu_{25%}/ZIF-8. The synthesized catalyst was characterized by FT-IR (Figure S1), UV (Figure S2), X-ray diffraction analysis (XRD) (Figure S3), scanning electron microscopy (SEM) (Figure S4), and also compared with reported data.¹⁰ The advantage of using ZIF-8 as the support is due to its ease of preparation, large surface area, and stability in acids, bases, water and even in the presence of methanol.

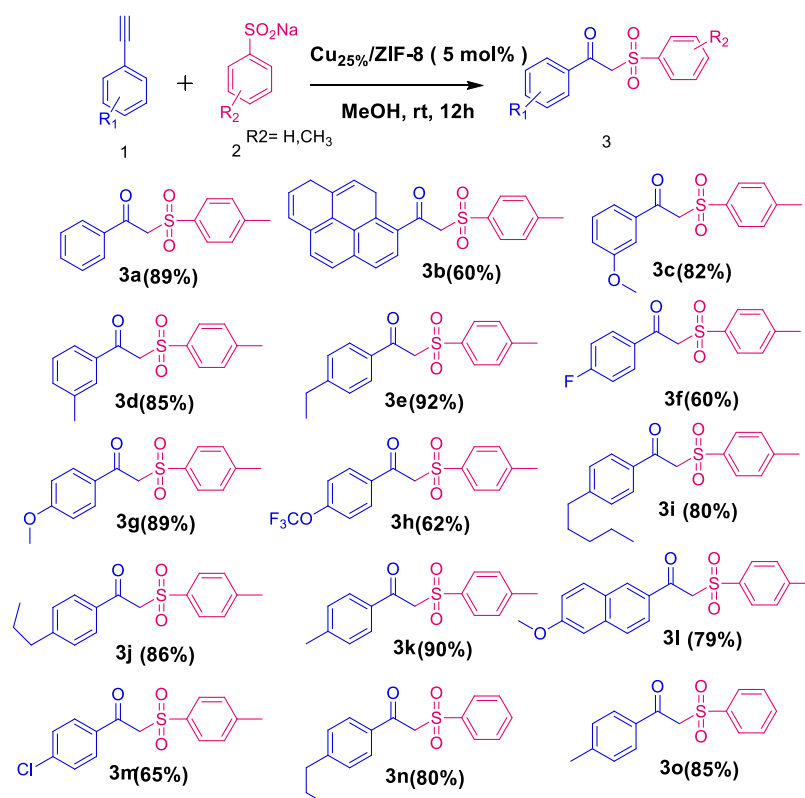
Initially, we performed the oxysulfonylation of phenylacetylene (**1**) with sodium *p*-toluenesulfinate (**2**) in the presence of Cu_{1%}/ZIF-8, Cu_{7%}/ZIF-8, Cu_{15%}/ZIF-8, Cu_{25%}/ZIF-8 in ethanol at room temperature for 12 h, the desired product **3a** was obtained in 65% yield with Cu_{25%}/ZIF-8 (Table 1, entry 5). Interestingly, the yield of **3a** was improved markedly to 89% when methanol was introduced into the Cu_{25%}/ZIF-8 catalyzed reaction system. These results indicated that methanol played a very significant role in the reaction. Methanol gives better yield compared to other solvents like ethanol, isopropanol, *tert*-butyl alcohol (Table 1, entry 4–8). A careful solvent survey indicated that methanol improved the yield compared to ethanol, isopropanol, *tert*-butyl alcohol, and water (Table 1, entry 4). Subsequently, various copper doping ZIF-8 catalysts Cu_{1%}/ZIF-8, Cu_{7%}/ZIF-8, Cu_{15%}/ZIF-8, Cu_{25%}/ZIF-8 were treated as the catalysts. Cu_{25%}/ZIF-8 was proved to be the best choice and the target product **3a** was obtained in 89% yield (Table 1, entry 4).

With optimized reaction conditions in hand, we next examined the substrate scope. Therefore, a range of substituted aromatic alkynes were chosen to react with Cu_{25%}/ZIF-8 and the results are summarized

Table 1. Optimization of β -ketosulfone reaction conditions^a.

Entry	Catalyst	Solvent	Yield ^b (%)
1	Cu ₁ %/ZIF-8	CH ₃ OH	Trace
2	Cu ₇ %/ZIF-8	CH ₃ OH	45
3	Cu ₁₅ %/ZIF-8	CH ₃ OH	65
4	Cu₂₅%/ZIF-8	CH₃OH	89
5	Cu ₂₅ %/ZIF-8	CH ₃ CH ₂ OH	65
6	Cu ₂₅ %/ZIF-8	(CH ₃) ₂ CHOH	Trace
7	Cu ₂₅ %/ZIF-8	(CH ₃) ₃ COH	0
8	Cu ₂₅ %/ZIF-8	H ₂ O	Trace
9	–	CH ₃ OH	0

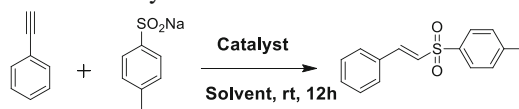
^aReaction conditions: Phenyl acetylene **1** (0.5 mmol, 1 equiv.), sodium 4-methylbenzenesulfinate **2** (0.6 mmol, 1.2 equiv.), Cu₂₅%/ZIF-8 (5 mol%) in methanol at room temperature. ^bIsolated yields. The bold letters signify the optimized and final reaction conditions.

Table 2. Scope of the β -ketosulfone reaction of various alkynes with sodiumsulfinate^{a,b}.

^aReaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), Cu₂₅%/ZIF-8 (5 mol%), MeOH (3 mL), 12 h. ^bIsolated yields based on **1**.

in Table 2. Halo groups such as (Br, F and OCF₃) were well-tolerated in the reaction system to provide β -keto sulfones in excellent yields (Table 2). Bulky

aromatic rings such as pyren-1-yl and 6-methoxy naphthalene-2-yl alkynes afforded the corresponding products in good yields (Table 2). Next, we turned

Table 3. Optimization of the vinyl sulfone reaction conditions^a.

Entry	Catalyst	Solvent	Yield ^b (%)
1	Cu _{25%} /ZIF-8	THF	0
2	Cu_{25%}/ZIF-8	CH₃CN	88
3	Cu _{25%} /ZIF-8	DME	80
4	Cu _{25%} /ZIF-8	DMF	78
5	Cu _{25%} /ZIF-8	DMSO	69
6	Cu _{25%} /ZIF-8	DCM	0
7	Cu _{25%} /ZIF-8	1,4-Dioxane	58
8	Cu _{25%} /ZIF-8	EtOAc	76
9	Cu _{25%} /ZIF-8	H ₂ O	0
10	Cu _{1%} /ZIF-8	CH ₃ CN	Trace
11	Cu _{7%} /ZIF-8	CH ₃ CN	45
12	Cu _{15%} /ZIF-8	CH ₃ CN	74
13	—	CH ₃ CN	0
14	Cu _{25%} /ZIF-8	CH ₃ CN	88 ^c

^aReaction conditions: Phenyl acetylene **1** (0.5 mmol, 1 equiv.), Sodium 4-methylbenzenesulfinate **2** (0.6 mmol, 1.2 equiv.), Cu_{25%}/ZIF-8 (5 mol%) in acetonitrile (3 mL) at room temperature. ^bIsolated yields. ^cReaction carried at 50 °C, 80 °C, 100 °C. The bold letters signify the optimized and final reaction conditions.

our focus towards hydrosulfonylation, in order to check the generality of the transformation in the presence of Cu_{15%}/ZIF-8 (5 mol%) in CH₃CN at room temperature for 12 h to afford (Table 3, entry 12) vinyl sulfone (**4a**) in 74% yield. A variety of other copper doped catalysts Cu_{1%}/ZIF-8, Cu_{7%}/ZIF-8, Cu_{15%}/ZIF-8, Cu_{25%}/ZIF-8 were investigated in CH₃CN (Table 3, entry 2, 10–12). Cu_{25%}/ZIF-8 accomplished **4a** in 88% yield (Table 3, entry 2). To check the effect of temperature on the reaction, the test reaction was carried out at different temperatures (Table 3, entry 14). It was observed that the maximum conversion occurred at room temperature in 12 h, providing the desired product **4a** in 88% yield (Table 3, entry 2). A higher temperature didn't improve the yield.

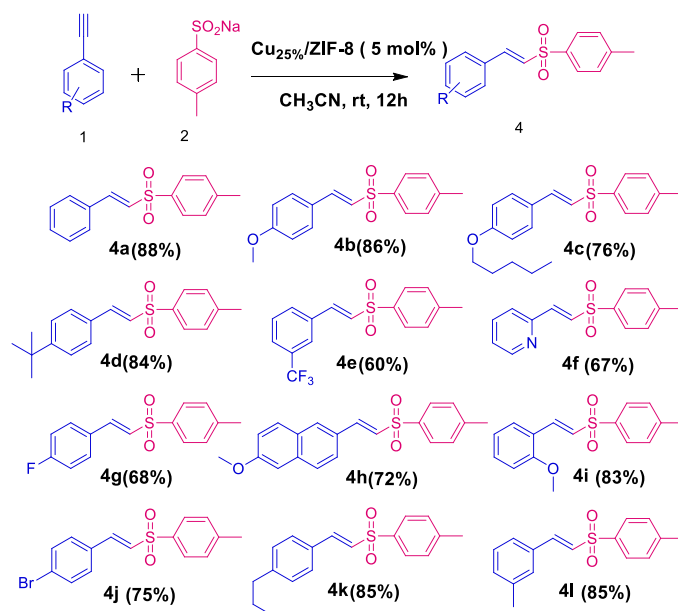
With optimized reaction conditions in hand, we next examined the substrate scope (Table 4) on substituents bearing either an electron donating or electron withdrawing groups on the aromatic ring. All reacted smoothly to furnish the desired vinyl sulfones with excellent *E*-stereo selectivity in good to excellent yields (Table 4), a number of functional groups (OMe, Br, F, CF₃, and CH₃) were tolerated under optimized conditions. Heterocyclic alkyne was also suitable for this transformation and corresponding vinyl sulfone was obtained in 67% yield (**4f**). When 6-methoxy naphthalene-2-yl substituted alkyne was treated with sodium *p*-toluenesulfinate under standard conditions,

the desired product (12 h) was obtained in 72% yield (Table 4).

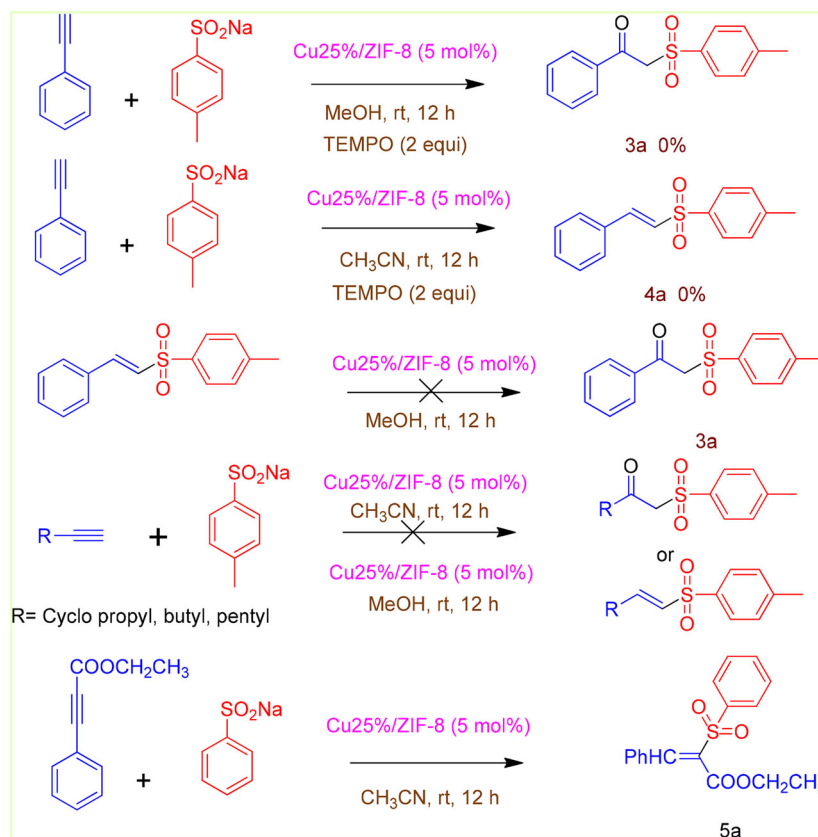
After completion of the reaction, the catalyst was separated by centrifugation and washed thoroughly with methanol, dried overnight at 100 °C and used directly for the next round of reaction. We noticed that catalyst was reused five cycles without any significant loss of activity.

To gain a better understanding of the reaction mechanism, a series of control experiments related to radicals were performed (Scheme 1). When the radical scavenger reagent TEMPO (2,2,6,6-tetramethyl piperadinyloxy, a well-known radical-capturing species) and DPE (1,1-diphenylethylene) were introduced into the standard reaction system, no products (**3a** and **4a**) were detected in both cases and the starting materials were recycled, indicating that the reactions were completely inhibited by TEMPO/DPE (Scheme 1). This strongly suggests that both the reactions have been preceded through a radical mechanism. When aliphatic terminal alkynes were introduced into the standard conditions, no product was observed whereas internal alkyne yielded the product **5a** (Scheme 1).

A plausible reaction mechanism for oxysulfonylation and hydrosulfonylation from these results and relevant literature^{29–38} is illustrated in Scheme 2. In the first step, sodium *p*-toluene sulfinate is oxidized in the presence of Cu(II) catalyst and sulfonyl radical A is

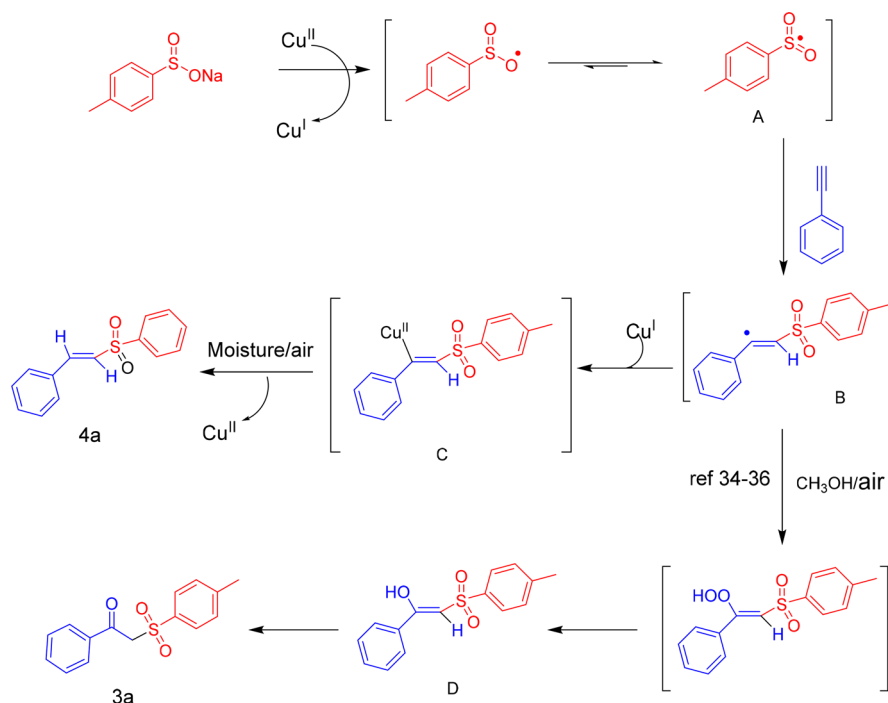
Table 4. Scope of the vinyl sulfone reaction of various alkynes with sodium sulfinate^{a,b}.

^aReaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), Cu₂₅%/ZIF-8(5 mol%), CH₃CN (3 mL), 12 h. ^bIsolated yields based on **1**.

**Scheme 1.** Control experiments.

generated, which reacts with an alkyne to give a radical intermediate B. In the next step, radical B is trapped with oxygen forming peroxy radical. Sequentially, after

abstraction of a hydrogen atom, the peroxy radical transforms into hydro peroxide,^{39–41} which transforms to D (Scheme 2), and gives the main product **3a** after



Scheme 2. A plausible oxysulfonylation and hydrosulfonylation mechanism using the example of the reaction of phenyl acetylene **1a** and sodium *p*-toluenesulfonate **2a**.

reduction followed by tautomerization. Further, reactive vinyl radical B interacted with Cu(I) species to yield vinyl copper(II) complex C. Finally, the protonation of C produced the desired product **4a**⁴² and regenerated Cu(II) catalyst.

4. Conclusions

In summary, we have demonstrated Cu_{25%}/ZIF-8 heterogeneous catalyst for oxysulfonylation, hydrosulfonylation reactions for the facile construction of various β -ketosulfones and vinylsulfones in moderate to good yields. Both the transformations feature mild reaction conditions, cost-effectiveness, and operational simplicity. The catalyst can be recycled at least five times without significant activity loss.

Supplementary Information (SI)

Characterization data and copies of ¹H, ¹³C NMR spectra are reported, and available free of charge. Supplementary Information is available at www.ias.ac.in/chemsci.

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