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# Heterogeneous CuS Flower Catalyzed Claisen Rearrangement and the Synthesis of Pyrazole



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## ABSTRACT

CuS flowers were prepared at room temp 303k to 365k through the chemical route. The equivalent and equimolar solutions of copper sulphate and sulphur were used for the synthesis of CuS. The surface of the catalyst has been studied using scanning electron microscopy (SEM), (X-ray diffraction XRD). The SEM image exhibited the cauliflower-like structure of the synthesized CuS. Claisen rearrangement and the synthesis of pyrazole derivative were carried out by using CuS flower as a catalyst. All the synthesized compounds were characterized by IR, <sup>1</sup>HNMR spectral techniques.



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## INTRODUCTION

Chalcogenides are an important class of materials that have found potential uses in catalysis, energy storage, conversion and optoelectronic devices<sup>1-5</sup>. Copper sulfide (CuS) is one of the chalcogenides that has received considerable attention in recent years owing to its wide stoichiometric composition [i.e., Cu<sub>2</sub>S, Cu<sub>1</sub>. S<sub>96</sub>, Cu<sub>1</sub>. S<sub>94</sub>, Cu<sub>1</sub>. S<sub>8</sub>, Cu<sub>1</sub>. S<sub>75</sub> and CuS] diverse morphology and non-linear optical property. In particular, the band gap of CuS can be varied in a wider range (1.2 to 2.5 eV) with stoichiometric composition ( $x = 1-2$ )<sup>6</sup>, making it a highly desirable material for solar cells<sup>7-9</sup>, nonvolatile memory devices<sup>10,11</sup> and gas sensing applications. Furthermore, CuxS is a potentially interesting material for cold cathodes and lithium ion batteries. Copper sulphides have gained extensive attention because of unique physical and chemical properties on account of various stoichiometric proportion of complex structures and valency state. The family of Claisen rearrangements has been particularly visible, in development as well as in application, over the past century<sup>12</sup>. Pyrazoles are chemical compounds of synthetic origin that have a five-membered heterocycle with two nitrogen atoms and three adjacent carbons. Pyrazole derivatives have shown good pharmacological effects and the potential biological activities, such as anti-inflammatory<sup>13</sup>, antiviral<sup>14</sup>, antimicrobial<sup>15</sup>, anticonvulsant<sup>16</sup>, antitumor<sup>17</sup>, fungicidal activities<sup>18</sup> and antihistaminic<sup>19</sup>. The pyrazolearylpyrazole derivatives have anti-HIV-1 activity<sup>20,21</sup> and some pyrazole-3-carboxamide moiety has anti-CB1 cannabinoid ability<sup>23</sup>, antiprolifere<sup>24,25</sup> agents. The prerequisite for improving catalytic systems and to design catalysts is the understanding of controlling the reaction kinetics i.e. the activation barrier in rate determining steps, by structural parameters of the catalyst and substrate, keeping above these aspects an experimental work on chemical synthesis of copper sulphide and its use in reaction as a catalyst has been undertaken in the present work.

## MATERIALS AND METHODS

All reactions were carried out in dry glassware. The catalyst was synthesized by using the Ultrasonication bath. The scanning electron microscope (SEM) measurement of catalyst was recorded on a JEOL Model JSM-6390V scanning electron microscope (SEM) Microscope. Merck, pre-coated Silica gel 60 F<sub>245</sub> (Aluminium sheet) plates were used for analytical TLC. The

melting point was determined in open capillary tubes using Prefit model. IR spectra of all the synthesized compounds were recorded on FTIR Spectrophotometer in  $^1\text{H}$ NMR spectra of all the synthesized compounds were recorded in  $(\text{CDCl}_3/\text{DMSO-d}_6)$  on BRUKER AVANCE- 2400 NMR Spectrophotometer.

### Experimental procedure:

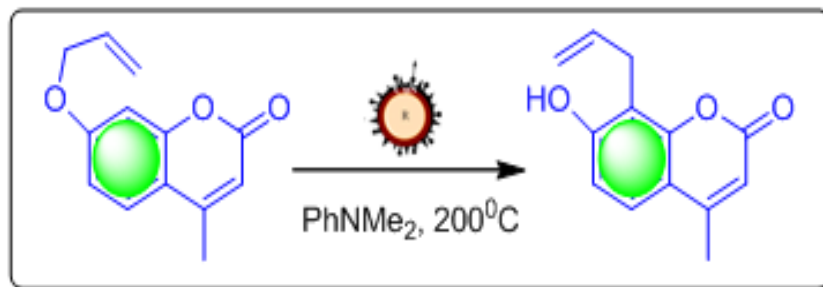
#### Synthesis of Catalyst:

For synthesis of catalyst, first  $\text{Cu}^{2+}$  is immobilized on a cation exchange resin surface. Then to the 0.05gm light blue coloured R-Cu beads an equivolume and equimolar solution of  $\text{S}_8$  taken in the beaker, add polyethylene glycol in it as a capping agent maintain the alkalinity of the solution by the addition of NaOH. Kept the above solution in the ultrasonication bath for 1 hour at  $80^\circ\text{C}$ . A distinct colour change of beads from light blue to black indicates, the formation of catalyst. Repetitive washing of the composite with water quantitatively removes NaOH and polyethylene glycol from the catalyst surface.

#### Claisen rearrangement reaction:

A Solution of 7-(allyloxy)-4-methyl-2H-chromen-2-one (2g), in N, N-diethylaniline (20ml) was heated at  $200^\circ\text{C}$  in presence of catalyst for 6 hours. The crude solid obtained was first washed with hexane and then dissolved in ether. The ether layer was washed with dilute HCl and then extracted with 2N NaOH. The aqueous layer was acidified with dilute HCl. White solid thus obtained was purified by column chromatography (hexane/acetone 9:1) to give 8-allyl-7-hydroxy-4-methyl-2H-chromen-2-one, (1.4, 70%), m.p.  $192-193^\circ\text{C}$ .

IR  $\text{cm}^{-1}$ : 3400 -OH, 2915 -Ar-H, 1703 -C=O, 1602 -C=C-, 1384 -C-O-; Mass: m/z - 217.08, 189.04, 161.05, 133.06, 105.06;  $^1\text{H}$ NMR(DMSO  $\text{d}_6$ ), 2.5 (s, 1H,  $\text{CH}_3$ ), 3.4 (d, 2H,  $\text{J}=6.3\text{Hz}$ , -C=C- $\text{CH}_2$ ), 4.91 (dd, 1H, C= $\text{CH}_2$ ), 4.96(dd, 1H, -C= $\text{CH}_2$ ), 5.90 (m, 1H,  $\text{J}=6.3\text{Hz}$ , -CH= $\text{CH}_2$ ), 6.13 (s, 1H, -C=CH), 6.87 (d, 1H,  $\text{J}=8.4\text{Hz}$ , Ar-H), 7.4 (d, 1H,  $\text{J}=8.7\text{ Hz}$ , Ar-H), 10.5 (s, 1H, Ar-OH)

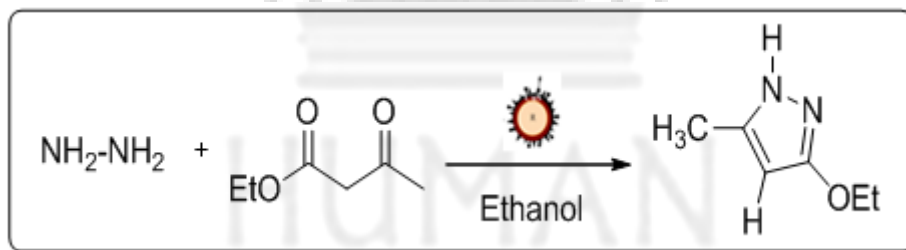


**Scheme: R-CuS catalyzed Claisen Rearrangement**

### Synthesis of pyrazole:

Ethyl acetoacetate (4 ml) is taken into the round bottom flask in ethanol, then add about 1.2784 gm of Hydrazine Hydrate to it dropwise, addition can be carried out in an ice bath because the reaction is too vigorous and then add heterogeneous catalyst and the reaction mixture for the reflux for an 1 Hr completion of the reaction was monitored by TLC (ethyl acetate: hexane = 70:30) pour the reaction mixture in ice cold water and extract the product with ethyl acetate.

<sup>1</sup>H NMR 400 MHz, DMSO:  $\delta$  1.3 (t, 3H, CH<sub>3</sub>),  $\delta$  4 (q, 2H, -O-CH<sub>2</sub>),  $\delta$  2.3 (s, 3H, CH<sub>3</sub>),  $\delta$  10.5 (s, 1H, -N-H), 6.0 (s, 1H, =CH-)



**Scheme: R-CuS catalyzed Synthesis of pyrazole**

## RESULTS AND DISCUSSION

The morphology of the prepared catalyst was examined with an Instrument JSM-6390 a scanning electron microscope (SEM) at different magnification. It clearly indicates the successful evolution of CuS nanoflower. It was found that the CuS nanostructures are composed of several tiny tips projecting outwardly with comparable length and having a common wider base.

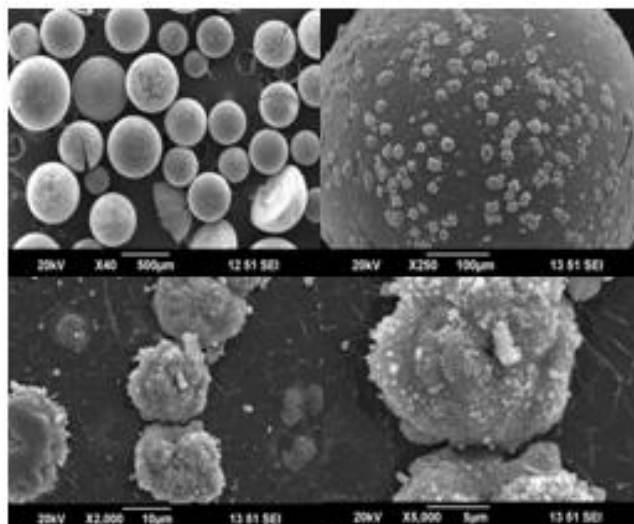


Figure 1: SEM of CuS

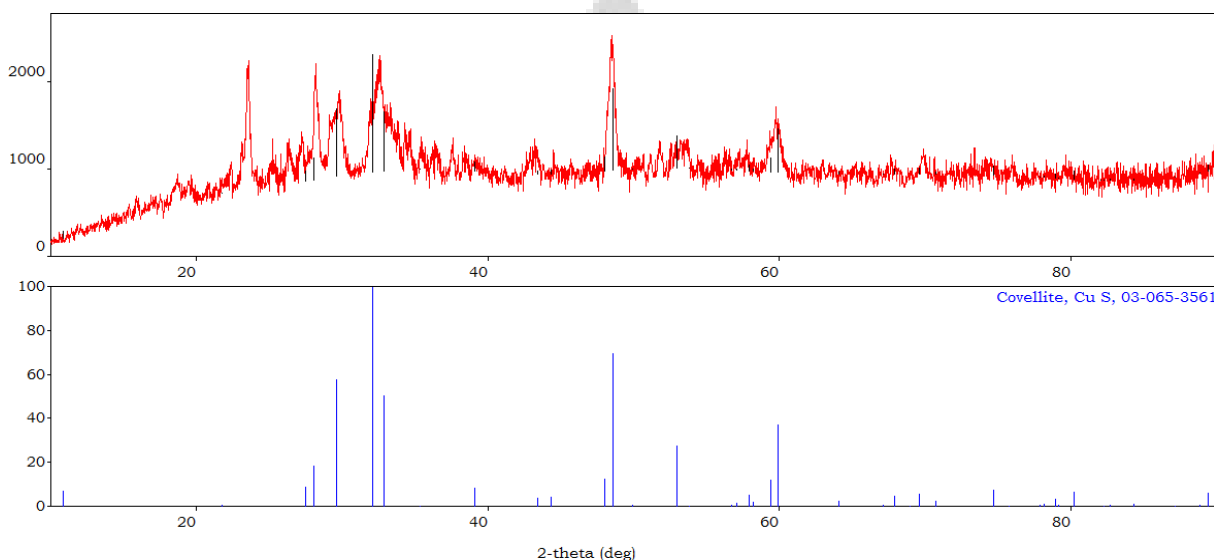


Figure 2: XRD of CuS

A Solution of 7-(allyloxy)-4-methyl-2H-chromen-2-one (2g), in presence of CuS Flower 5% as catalyst in the above reaction. This gives (1.6g) 80% yield in 4 Hr. m.p. 192-193<sup>0</sup>C i.e. there was increasing yield and decreasing time required to carry out the reaction by using CuS flower as a catalyst.

The synthesis of pyrazole can be carried out by means of various methods. Those including microwave assisted synthesis, using the flame temperature with distillation assembly etc. but in

present work, synthesis of pyrazole from the conventional heating method under the reflux condition which requires less time in the presence of the above catalyst and ethanol as a solvent.

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