CHAPTER 5

Catalytic activity of CuS Nanoparticles
5.1 Introduction

Nanomaterials have an extremely wide range of potential applications from electronics, optical communications, biological systems, etc. to promoting new materials properties. Many possible applications have been explored and many devices and systems have been studied. More potential applications and new devices are being proposed in literature. It is interesting to note that the applications of nanotechnology in different fields have noticeably different demands, and thus face very different challenges, which require different approaches. For example, for applications in medicine, or in nanomedicine, the major challenge is “miniaturization”: new instruments to analyze tissues literally down to the molecular level, sensors smaller than a cell allowing it to look into its functioning, and small machines that literally circulate within a human body pursuing pathogens and neutralizing chemical toxins [1].

Applications of nanostructures and nanomaterials are based on,

(i) The peculiar physical properties of nanosized materials, e.g. gold nanoparticles used as inorganic dye to introduce colours into glass and as low temperature catalyst.

(ii) The huge surface area, such as mesoporous titania for photoelectrochemical cells, and nanoparticles for various sensors.

(iii) The small size that offers extra possibilities for manipulation and room for accommodating multiple functionalities.

For many applications, new materials and new properties are introduced. For example, various organic molecules are incorporated into electronic devices, such as sensors [2].

In nanoscale, nanotechnological application depends on the different morphology of the nanomaterials. CuS has different morphologies in nanoscale [3-18] which exhibited potential application in various field such as catalyst [19], photocatalyst [20], ultrasensitive nanoenzymatic glucose sensor [21], electrocatalytic activity [22], nanoswitches [23], solar cell and electronic circuit [24], drug delivery system [25], environmental pollution control [26], photovoltaic application [27], DNA biosensor [28], optical recording materials [29], thermoelectric generator [30], lithium
ion battery [31]. Among them this chapter describes the catalytic application of CuS on cellulose (biomass) pyrolysis.

The controlled thermochemical conversion process is one of the key pathways in converting biomass into liquid or gaseous fuels. This conversion process is known as biomass gasification or biomass pyrolysis. It has gained worldwide attention in fuel technology. Biomass gasification occurs in the presence of an oxidizing atmosphere and the pyrolysis occurs in inert atmosphere. The biomass pyrolysis process consists of complex reaction sequence that gets influenced by many factors, such as heating rate, pyrolysis temperature, pressure, residence time, moisture content, particles size and constitution of biomass materials [32]. The biomass pyrolysis is attractive because solid biomass and wastes which are abundant, but difficult and costly to manage can readily be converted into liquid fuel products. These liquids, as crude bio-oil or charcoal or oil, have advantages in transportation, storage, combustion, retrofitting, etc. Till date, many researchers studied thermal decomposition of biomass by the thermogravimetric analysis (TGA) technique, because it is most common versatile technique used for kinetic analysis and determination of constants such as enthalpy, entropy, Gibbs free energy, etc. Literature shows, lots of work on thermal analysis of different materials like, derivatives of rubber [33], plastic [35, 36], natural fibres [37], various type of biomass [38, 39], etc. during their thermal degradation.

Dry biomass consists of 88% to 99.9% organic compounds having important constituents as cellulose, hemicellulose and lignin, with cellulose as the major constituent contributing about 40-45%. Thus in energy extraction by biomass gasification or pyrolysis, cellulose is the main constituent. To enhance gasification or pyrolysis process, catalysts are used. Catalysts in nano forms have been found to be more effective than bulk form [40, 41]. Getting motivation from the reported works on nanosize materials important role as a catalyst in the fuel generation from biomass [42], effort to study the catalytic effect of copper sulphide was thought.

This chapter cover the catalytic action of CuS micro-particles and nanoparticles on cellulose pyrolysis. The study was carried out by analysing the recorded simultaneous thermogravimetric (TGA), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves. The CuS microparticles were market procured and CuS nanoparticles were synthesized by simple wet chemical technique at ambient temperature for studying their catalytic effect on cellulose
prolysis. The micro-particles and as-synthesized CuS nanoparticles were comprehensively characterized for, stoichiometry, structure, surface morphology and thermal stability. After complete characterizations, the micro-particles and as-synthesized CuS nanoparticles were used as catalyst in cellulose pyrolysis. The obtained results are discussed in details.

5.2 Materials

To study the catalytic activity in cellulose pyrolysis, CuS micro-particles (99.8%, metals basis, Alfa Aesar) and cellulose (microcrystalline powder, approximate 20 μm, Sigma Aldrich) were directly market purchased and used. The CuS nanoparticles were synthesized at ambient temperature by simple wet chemical technique describe in previous Chapter 4, Section 4.2.

5.3 Characterizations

5.3.1 EDAX Analysis

The chemical composition of direct market procured CuS micro-particles and wet chemical technique synthesized CuS nanoparticles were determined by EDAX technique. The obtained spectra are shown in Figure 1, which reveals that CuS micro-particles and the synthesized CuS nanoparticles do not contain any other impurity elements other than Cu and S. Table 1 shows the atomic percentage data of the elements present. The CuS micro-particles and as-synthesized nanoparticles are near to perfect stoichiometry.

![Figure 1 EDAX spectrum of as-synthesized CuS micro-particles and nanoparticles.](image-url)
Table 1 Obtained EDAX data of CuS micro- and nanoparticles.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Standard CuS Nanoparticles</th>
<th>CuS Micro-particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>50</td>
<td>48.73</td>
<td>49.35</td>
</tr>
<tr>
<td>S</td>
<td>50</td>
<td>51.27</td>
<td>50.65</td>
</tr>
</tbody>
</table>

5.3.2 Structural Analysis

Figure 2 (a) X-ray diffraction patterns and (b) Hall-Williamson plots of micro-particles and as-synthesized CuS nanoparticles.

Figure 2(a) shows the XRD pattern of CuS micro-particles and as-synthesized CuS nanoparticles. All the peaks in the XRD patterns were readily indexed with Powder X software as that of hexagonal CuS. The determined lattice parameters, $a = 3.79 \, \text{Å}$ and $c = 16.34 \, \text{Å}$ were in good agreement with the reported standard data (JCPDS Card No. 06-0464). The broadening of XRD peaks in case of CuS nanoparticles compared to micro-particles indicates the nanocrystallinity of the sample. Also there were no traces of diffraction corresponding to any other phases of copper sulphide such as Cu$_2$S, Cu$_{1.8}$S and Cu$_{1.96}$S in both the XRD patterns. The average crystallite sizes of CuS micro-particles and CuS nanoparticles determined from X-ray line broadening using the Debye-Scherrer’s formula and Hall-Williamson plot [42] are tabulated in Table 2. The values of the residual strain obtained from...
Hall-Williamson plots, Figure 2(b), indicate presence of tensile strain in CuS micro-particles and compressive strain in CuS nanoparticles.

**Table 2** Evaluated parameters from XRD data.

<table>
<thead>
<tr>
<th>CuS</th>
<th>Lattice Parameters</th>
<th>Structure</th>
<th>Crystallite size (nm)</th>
<th>Strain ($\times 10^{-3}$)</th>
</tr>
</thead>
</table>
| Nanoparticles   | $a=b=3.79 \text{ Å},$  
|                 | $c=16.34 \text{ Å},$  
|                 | $\alpha=\beta=90^\circ,\gamma=120^\circ$ | Hexagonal             | 4.01                   | 3.77                      | -7.53                    |
| Micro-particles |                    | (Space group = P6$_3$/mmc)         | 22.32                 | 35.30                     | 1.44                      |

**5.3.3 SEM Analysis**

The SEM images of CuS micro-particles and as-synthesized CuS nanoparticles are shown in Figure 3. Figure 3(a) shows CuS micro-particles to be spherical in shape. Figure 3(b) clearly reveals that the CuS nanoparticles are spherical in shape and uniformly distributed.

![SEM images](image)

(a) (b)

**Figure 3** SEM images of CuS (a) micro-particles and (b) nanoparticles.

**5.3.4 TEM and SAED analysis**

The samples for the TEM and SAED analysis were prepared by ultrasonically dispersing CuS micro-particles and nanoparticles in methanol just prior to loading for analysis. The particles size determined from the TEM image of the CuS micro-particles, Figure 4(a), varied from 1.2 μm to 1.7 μm and nanoparticles average size,
Figure 5(a), came out to be 18.29 nm. The SAED patterns shown in Figure 4(b) for micro-particles and 5(b) for nanoparticles, clearly shows rings, substantiating polycrystallinity of the samples. The SAED of CuS micro-particles, Figure 4(b), have some spots on the rings stating more crystalline nature of micro-particles compared to nanoparticles. The rings could be indexed as (1 1 0), (1 0 8) and (2 1 2) for micro-particles, while (107), (203) and (300) for CuS nanoparticles, which are consistent with the obtained respective XRD results.

![Figure 4](image_url)  
(a) TEM images and (b) SAED patterns of CuS micro-particles.

![Figure 5](image_url)  
(a) TEM images and (b) SAED patterns of CuS nanoparticles.
5.3.5 Thermal analysis

![TGA Curve](image)

![DTG Curve](image)

![DTA Curve](image)

**Figure 6** (a) TGA (b) DTG and (c) DTA curves of CuS micro-particles and as synthesized nanoparticles.

Before studying the catalytic effect of CuS micro- and nanoparticles on cellulose pyrolysis, the thermal analysis of CuS micro-particles and nanoparticles were undertaken. The thermal curves, TGA, DTG and DTA were recorded for both CuS micro-particles and nanoparticles from ambient temperature to 900°C in inert N₂ atmosphere at heating rate of 10°C.min⁻¹ having flow rate of 100 mL.min⁻¹, Figure 6 (a-c), respectively. The TGA curve reveals that the total weight loss in case of CuS micro-particles is 29% and it decomposes by two steps. The CuS as-synthesized nanoparticles have total weight loss of 42% having five steps decomposition. Thus the
TGA curve reveals that the weight loss in case of as-synthesized CuS nanoparticles is more in comparison to CuS micro-particles. The curves clearly states that the weight loss starts early in case of CuS nanoparticles (~50°C) than CuS micro-particles (~300°C). Thus the TG analysis establishes that, the CuS micro-particles are more stable than CuS nanoparticles. The DTG curves show two sharp peaks in case of micro-particles and five sharp peaks in case of as-synthesized nanoparticles. The peak numbers are in complete agreement with the observed weight loss steps observed in TGA. The DTA curves show that the micro-particles and as-synthesized CuS nanoparticles has curves below zero level meaning endothermic decrease. Other than usual DTA decrease, there is one sharp endothermic peak at 425 °C in case of CuS micro-particles and three endothermic peaks at 125, 290 and 305 °C in case of CuS nanoparticles. These DTA endothermic peaks are observed at the temperature corresponding to the large weight loss observed in DTG. This may be due to sulphur getting dissociated from the respective CuS samples giving rise to endothermic peaks in DTA and weight loss observed in TGA curve. The activation energy values were calculated from TGA curves using two steps for micro-particles and five steps for CuS nanoparticles employing standard Coats-Redfern (C-R) method [43]. The C-R method was employed since it is easy and simple to use with data obtained from the TGA. Other thermal parameters such as, activation enthalpy ($\Delta H^*$), activation entropy ($\Delta S^*$) and Gibbs free energy change ($\Delta G^*$) for both CuS micro-particles and nanoparticles were evaluated using TGA data by below equations [44]. The evaluated parameters are tabulated in Table 3.

\[
\begin{align*}
\Delta H^* &= E_a - RT \quad (5.1) \\
\Delta S^* &= 2.303 \, R \log \left( \frac{Ah}{k_B T} \right) \quad (5.2) \\
\Delta G^* &= \Delta H^* - T \Delta S^* \quad (5.3)
\end{align*}
\]

Here, $E_a$ is the activation energy, $A$ is Arrhenius constant, $k_B$ is Boltzmann constant, $h$ is Planck’s constant and $T$ is temperatures of DTG peaks between decomposition steps.

According to Table 3, the positive values of $\Delta H^*$ in both CuS particles signify that heat is being absorbed by the samples leading to dissociation endorsed by the endothermic nature reflected in the DTA curves. In the temperature range 300 – 820 °C, the entropy values of CuS micro-particles are very high in comparison to the as-synthesized nanoparticles. This means the disorder in micro-particles is more than
nанопarticles. But increased disorder does not lead to decomposition of micro-particless, as less weight loss is noticed in this temperature range of TGA curve.

In case of CuS nanoparticles, the weight loss is in five steps. The entropy values in Step – 1 and 2 are negative whereas in Steps – 3 to 5 are positive. The negative entropy values in Step – 1 and 2, states that ordering in nanoparticles takes place in this temperature range of 90 – 300 °C. In Steps – 3 to 5, the entropy increases meaning decomposition is taking place, also corroborated by the observed weight loss in TGA curve.
Figure 7 C-R plots for the decomposition of the CuS (a) micro-particles and (b) nanoparticles.
Table 3 Kinetic and thermal parameters of CuS micro-particles and nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Step</th>
<th>Temp. range (°C)</th>
<th>DTG Peak (°C)</th>
<th>Mass Loss %</th>
<th>Activation energy (Eₐ) (kJ.mol⁻¹)</th>
<th>A (Sec⁻¹)</th>
<th>ΔH* (kJ.mol⁻¹)</th>
<th>ΔS* (J.K⁻¹.mol⁻¹)</th>
<th>ΔG* (kJ.mol⁻¹)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS Micro-particles</td>
<td>1</td>
<td>300-450</td>
<td>440</td>
<td>15.75</td>
<td>359.53</td>
<td>3.22×10⁷</td>
<td>353.60</td>
<td>657.51</td>
<td>-468.45</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>725-950</td>
<td>800</td>
<td>8.93</td>
<td>104.81</td>
<td>6.09×10⁶</td>
<td>95.89</td>
<td>640.08</td>
<td>-686.72</td>
<td>0.99</td>
</tr>
<tr>
<td>CuS Nano particles</td>
<td>1</td>
<td>90-140</td>
<td>120</td>
<td>2.31</td>
<td>102.89</td>
<td>7.88×10¹²</td>
<td>99.63</td>
<td>-0.32</td>
<td>0.25</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>225-300</td>
<td>280</td>
<td>12.47</td>
<td>131.71</td>
<td>4.58×10¹¹</td>
<td>127.11</td>
<td>-26.80</td>
<td>15.08</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>300-380</td>
<td>332</td>
<td>11.36</td>
<td>265.79</td>
<td>1.47×10²²</td>
<td>260.76</td>
<td>173.62</td>
<td>-104.69</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>420-490</td>
<td>458</td>
<td>2.76</td>
<td>352.17</td>
<td>2.42×10²⁴</td>
<td>346.09</td>
<td>214.49</td>
<td>-156.27</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>720-820</td>
<td>777</td>
<td>4.54</td>
<td>526.95</td>
<td>2.72×10²⁵</td>
<td>518.22</td>
<td>231.52</td>
<td>-243.04</td>
<td>0.99</td>
</tr>
</tbody>
</table>
5.4 Catalytic activity

The catalytic activity of market purchased CuS micro-particles and as-synthesized CuS nanoparticles on market procured cellulose pyrolysis was done by recording simultaneous TGA, DTG and DTA curves employing thermal analyzer. The TGA, DTG and DTA curves were recorded for pure cellulose and cellulose mixed with 3% of CuS micro-particles and CuS nanoparticles as catalysts. The cellulose samples containing catalyst were freshly prepared by rigorous physical mixing of 0.45 mg (3%) of micro-particles and as-synthesized nanoparticles of CuS with market procured 15 mg of cellulose. In all the thermal analysis the total sample loading weight was kept constant as 5 mg. The photographs of three samples are shown in Figure 8.

![Figure 8](image)

**Figure 8** Samples of (a) pure cellulose (b) cellulose containing 3% CuS nanoparticles and (c) cellulose containing 3% CuS micro-particles.

5.5 Catalytic effect of CuS in thermal decomposition of cellulose

The catalytic effect of CuS micro-particles and as-synthesized nanoparticles on cellulose pyrolysis was studied by recording the simultaneous TGA, DTG and DTA thermal curves. The CuS micro-particles and CuS nanoparticles were physically thorough mixed with cellulose and loaded for thermal analysis.

The TGA curves of pure cellulose and cellulose mixed with CuS micro-particles and nanoparticles is shown in Figure 9. The thermal curves are recorded from ambient temperature to 700 °C employing a heating rate of 10 °C.min\(^{-1}\) in inert
N₂ atmosphere having flow rate of 100 mL.min⁻¹. The curves clearly show that in case of pure cellulose the decomposition starts at 295 °C and continues still 360 °C. The weight loss in this temperature range is 88%. In case of cellulose mixed with CuS micro-particles, the decomposition starts at 270 °C and continues till 360 °C. The observed weight loss is 76%. The decomposition in case of cellulose mixed with CuS nanoparticles starts at 205 °C and continues till 350 °C having weight loss of 70%. This TG behaviour having decomposition temperature edges at 295 °C (pure cellulose), 270 °C (cellulose mixed with CuS microparticles) and 205 °C (cellulose mixed with CuS nanoparticles) is clearly reflected and corroborated in DTG and DTA curves at the same respective temperatures. The TGA curves clearly states that as the cellulose is mixed with catalyst CuS, the decomposition starting temperature decreases. It is observed that cellulose mixed with CuS micro-particles, the decomposition starts at 270 °C, whereas in case of cellulose mixed with CuS nanoparticles the decomposition starts at 205 °C. That means the decomposition starting temperature decreased by 65 °C in case of cellulose mixed with CuS nanoparticles compared to cellulose mixed with CuS micro-particles. This clearly states that CuS nanoparticles are better catalyst then CuS micro-particles in cellulose pyrolysis.
Figure 9 (a) TGA (b) DTG and (c) DTA curves of pure cellulose and with CuS catalysts.
Figure 10 C-R plots for the decomposition of cellulose with and without CuS catalysts.

The kinetic and thermal parameters determined from the thermal curves of Figure 9 employing Coats- Redfern (C-R) method are tabulated in Table 4. It is clearly seen that the activation energy and active enthalpy value is highest for cellulose decomposition and lowest for cellulose decomposition mixed with CuS nanoparticles. The activation energy and active enthalpy value for cellulose mixed with CuS micro-particles lies between the two values. The active enthalpy ($\Delta H^*$) value is positive in all the three thermal decomposition, stating the decomposition to be endothermic. This endothermic nature is also reflected in the DTA curves, in which the curves decreases below zero base line. The activation energy and active enthalpy values are lowest in case of CuS nanoparticles, stating it to be the best catalyst in comparison to CuS micro-particles for cellulose pyrolysis. This result supports the results obtained from the TGA analysis.
Table 4 Kinetic and thermal parameters obtained for cellulose pyrolysis without and with different CuS catalyst.

<table>
<thead>
<tr>
<th>Cellulose</th>
<th>Decomposition temperature range °C</th>
<th>DTG peak °C</th>
<th>Mass loss %</th>
<th>$E_a$ kJ.mol$^{-1}$</th>
<th>$A$ Sec$^{-1}$</th>
<th>$\Delta H^*$ kJ.mol$^{-1}$</th>
<th>$\Delta S^*$ J.K$^{-1}$.mol$^{-1}$</th>
<th>$\Delta G^*$ kJ.mol$^{-1}$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>295-360</td>
<td>340</td>
<td>88</td>
<td>299.21</td>
<td>1.38×10$^{17}$</td>
<td>294.11</td>
<td>417.98</td>
<td>-255.92</td>
<td>0.99</td>
</tr>
<tr>
<td>Mixed with 3% CuS micro-particles</td>
<td>270-360</td>
<td>332</td>
<td>76</td>
<td>171.5</td>
<td>5.51×10$^{16}$</td>
<td>166.47</td>
<td>643.91</td>
<td>-389.40</td>
<td>0.99</td>
</tr>
<tr>
<td>Mixed with 3% CuS nanoparticles</td>
<td>205-335</td>
<td>315</td>
<td>70</td>
<td>93.84</td>
<td>9.97×10$^{17}$</td>
<td>88.95</td>
<td>668.42</td>
<td>-392.94</td>
<td>0.99</td>
</tr>
</tbody>
</table>
The above cellulose pyrolysis mechanism with and without added CuS catalyst can be understood as follows. In the case of pure cellulose with increase in pyrolysis temperature, initially moisture inside the cellulose gets evaporated. Later on, the already dried portions of the particles, in the neighbourhood of the heated surface (heating vessel), undergo thermal degradation and devolatilization to form an active substance. When the pyrolysis temperature is further increased, the thermal decomposition of cellulose components begins to occur, and the volatile species gradually evolved out from the cellulose particle surface leading to absolute degradation.

In the presence of CuS micro- and nanoparticles catalysts, which promote the devolatilization of cellulose and also thermal degradation, through formation of weak bonds between volatiles and the catalyst which caused other bonds in the volatile molecules to be stretched and weakened, ultimately to enhance the release of final gas products. Therefore, addition of CuS catalysts decreases the activation energy for pyrolysis of cellulose by providing another pathway. At the same time, the catalyst accelerates primary and secondary decomposition reactions of cellulose leading to pyrolysis to occur at a lower temperature. In particular, CuS nanoparticles with a large external surface area to volume ratio than that of CuS micro-particles disperse better in the cellulose substrate for a closer and more uniform contact between cellulose and catalyst particles, which finally promote the overall decomposition of cellulose.

5.6 Conclusions

- Prior to pyrolysis study, the market procured CuS micro- and as-synthesized nanoparticles were comprehensively characterized.
- The EDAX analysis showed that the CuS micro-particles and as-synthesized nanoparticles are nearly stoichiometric. Both of the particles do not have impurity or contaminants.
- The XRD confirmed that the CuS micro-particles and as-synthesized nanoparticles possess hexagonal structure. The lattice parameters of both the particles were in good agreement with the reported data. The average crystallite sizes of CuS micro-particles and CuS nanoparticles determined from X-ray line broadening using the Debye-Scherrer’s formula and Hall-Williamson plots showed that the crystallite size of nanoparticles is very small.
compared to micro-particles. The values of the residual strain obtained from Hall-Williamson plots, indicates presence of tensile strain in CuS micro-particles and compressive strain in case of CuS nanoparticles.

✓ The SEM micrographs of CuS micro-particles and as-synthesized CuS nanoparticles showed the particles to be spherical in shape.

✓ The particles size determined from the TEM image of the CuS microparticles varied from 1.2 μm to 1.7 μm and nanoparticles average size came out to be 18.29 nm.

✓ The thermal analysis of CuS micro-particles and nanoparticles in the temperature range of room temperature to 900 °C exhibited that CuS micro-particles decomposes by two steps with 29% weight loss and nanoparticles decomposes by five steps with 42% weight loss. The thermal curves clearly showed that the weight loss starts early in case of CuS nanoparticles (~50°C) than CuS micro-particles (~300°C). Thus with less weight loss and high decomposition start temperature the CuS micro-particles are more stable than nanoparticles.

✓ The catalytic study of CuS micro-particles and nanoparticles in thermal decomposition of cellulose by pyrolysis was done in the temperature range of room temperature to 700°C. The catalytic study in cellulose pyrolysis showed that the decomposition commences at temperature 295°C for pure cellulose, 270°C for cellulose mixed with 3% CuS micro-particles and 205°C for cellulose mixed with 3% CuS nanoparticles. That means the decomposition starting temperature decreased by 65°C in case of cellulose mixed with CuS nanoparticles compared to cellulose mixed with CuS micro-particles. Thus, CuS nanoparticles act as better catalyst than CuS micro-particles in cellulose pyrolysis. This result is substantiated by the lowest values of the activation energy and active enthalpy obtained in case of 3% CuS nanoparticles mixed with cellulose.
5.7 References


