Preparation and characterization of chromium-copper supported biogenic catalyst from rice husk

A Sahoo¹, G V V Gowthami and S S Mohapatra

1 Chemical Engg. Dept., National Institute of Technology, Rourkela, India
E-mail: asahu@nitrkl.ac.in

Abstract. Attempt was made to prepare the biogenic catalyst from waste biomass with the support of chromium and copper metals. Metal modified silica catalysts were prepared by incorporating the metals like chromium and copper into silica matrix. In the present work the rice husk samples were pre-treated with different acids and then the samples were subjected to pyrolysis under controlled burning conditions. Pyrolysis operation was carried out at different temperatures in a furnace to get maximum rice husk ash. Ash thus produced was then leached by alkalis. Alkali-leached solution was then titrated with HCl. The silica catalysts thus prepared were characterized by different characterization techniques i.e. BET, SEM, EDX and XRD analysis by which amorphous nature of silica was confirmed. The average surface area and total pore volume were obtained by using N₂ adsorption-desorption calculations by BET analysis. Oxidation of styrene was carried out for the prepared metal modified catalyst at different pH levels. The products formed were analysed by GC-MS. A better conversion was found at lower pH. Obtained high surface areas further confirmed the amorphous nature of the prepared sample. Studies on the characteristics-properties of the prepared samples confirmed the catalytic nature implying the development of good biogenic catalyst.

1. Introduction
Rice husk, an agricultural waste material is 23% (by mass) of rice paddy [1]. Due to its high production, it has also been used as fuel to generate steam for heating. Low-density ash causes disposal problems. Ash of rice husk contains chemically reactive (amorphous) silica (>90%). The conditions of burning (temperature and duration of incineration) significantly change the final quality of the ash. The chemical composition of rice husk is similar to that of many common organic fibers and it contains cellulose 40-50%, lignin 25-30%, ash 15-20% and moisture 8-15%. Rice husk ash contains 85%-95% silica in amorphous form for which this agro waste material is used for the production of metal silica [1]. Researchers have found the use of rice husk for production of a variety of inorganic material such as silica, sodium and potassium silicate, zeolite, solar grade silicon metal, silicon tetrachloride, thermal insulating materials, building materials, polymer composite, glasses, drilling fluids, and organic fertilizer and as a nonconventional energy source [2]. MG - Si and solar - grade silicon were produced from rice husk [3], [4]. A 95% silica powder was produced after heat-treating at 700°C for 6h and the specific surface area of particles was increased after wet milling [1]. The researchers also observed that controlled thermal decomposition of rice husk is a convenient method for the liberation of silica [5]. A number of silicon compounds [2], especially silica [5], [6], silicon carbide [7], [8] and silicon nitride [8] have been produced from rice husk due to its high silicon content. This amorphous silica has many uses in microelectronic devices especially in semiconductors, chips, optical fibers, telescope glasses, silica aero-gels in space craft, adsorbent etc. [9]. Many
researchers have reported the importance of the leaching process before rice husk pyrolysis to produce good quality biogenic silica [10].

2. Materials and methods
Metal modified Silica catalyst was prepared from rice husk in three steps: (i) Pre-treatment and pyrolysis of rice husk to get rice husk ash, (ii)Extraction of Amorphous Silica from rice husk ash and (iii) Preparation of Metal modified silica from amorphous silica.

2.1. Pre-treatment and pyrolysis of rice husk
The clean rice husk was treated with HNO$_3$ or oxalic acid and heated in a magnetic stirrer hot plate for one hour at 90-100°C. The solution was cooled and washed with water thoroughly until the washout reaches pH of 7. The husk was vacuum filtered and dried it in an oven at 80-90°C for 10 hours. After pretreatment, the obtained rice husk was pyrolysed under controlled conditions of temperature range, 650 to 850°C to produce ash.

2.2. Extraction of amorphous silica
2.5N NaOH solution was added to the prepared rice husk ash and was heated on a magnetic stirrer cum heating plate with constant stirring at 85-95°C for 90 minutes. The obtained solution was filtered and titrated with concentrated HCL. This suspension was then vacuum filtered to obtain gelatinous residue of silica. The residue was washed with 50 ml of boiling water to remove any salt (NaCl) formed during titration. Finally, the obtained silica was dried in a hot air oven at 90°C.

2.3. Extraction of metal modified silica
Acid washed rice husk ash was taken with 2.5N NaOH and 0.01M CTAB solution in a beaker. The solution was titrated with HNO$_3$ acid containing 10%(W/W) chromium and 10%(W/W) copper in the form of chromium nitrate and copper nitrate respectively. The titration process was continued till the pH was attained at the required level. The gel formed is the metal incorporated silica. The same procedure was also repeated to obtain bi-metal incorporated silica with 5%(w/w) copper loading and 10%(w/w) chromium loading. The gel initially kept for 24 hours and then centrifuged and dried. The resulting silica sample modified with Cr-Cu was ground to powder and stored for further analysis.

2.4. Oxidation of styrene in liquid phase
Oxidation test of styrene was carried out for the prepared catalyst. Then the prepared sample was analysed by GC-MS analysis.

3. Results and discussion

3.1. XRD analysis of pyrolysed char

![Figure 1. XRD plot of RHA treated with Oxalic acid](image-url)
The pyrolysed rice husk ash (RHA) treated with oxalic acid and HNO$_3$ at three different temperatures (650, 750 and 850°C) were analysed by XRD. The sample plots for XRD analysis reports of acid treated RHA are shown in Figure 1 and Figure 2. From these figures, it is seen that the broad peaks occur in the range of 2θ=18-30° which indicates the characteristics of the amorphous structure. However, the presence of amorphous silica is confirmed by the broad range of peaks [5]. From the above figures it is observed that pyrolysed rice husk treated with oxalic acid and HNO$_3$ exhibit amorphous nature of silica. However peaks observed with HNO$_3$ acid wash are not very much sharp for which HNO$_3$ acid wash is considered to be more effective for leaching treatment.

3.2. XRD analysis of silica obtained from RHA

Silica obtained from above treatments are characterised through XRD-analysis and the XRD pattern of silica obtained at temperatures of 650°C and 750°C are shown in Figure 3 and Figure 4 respectively. From the XRD pattern it is observed that no peak is formed at 2θ=26° which indicates the absence of crystoballite thereby confirming the presence of amorphous structure of silica. Comparatively more sharp peaks are observed with HNO$_3$ treated rice husk ash pyrolysed at 750°C. Therefore RHA obtained with HNO$_3$ treatment and pyrolysis temperature of 750°C was processed further to get silica.
Rice husk ash produced at temperature of 750°C with HNO₃ acid treatment was used to obtain the silica. Metal modified silica catalysts with different percentages of copper i.e. 10%Cr-10%Cu and 10%Cr-5%Cu were synthesized by sol-gel technique from acid treated rice husk ash at different pH
levels. The sample plots for XRD analysis of 10%Cr-10%Cu and 10%Cr – 5%Cu synthesized silica catalyst from acid treated rice husk ash at different pH values are shown in Figure 5 and Figure 6. Presence of Chromium and Copper were confirmed by ordered crystalline structure in all these XRD reports. Oxalic acid treated RHA was further analysed to study the effect of acid treatment on metal modified silica catalyst by maintaining other conditions constant i.e. pH of 10, pyrolysis temperature of 750°C and metal loading of 10%Cr – 5%Cu.

3.4. SEM and EDX of pyrolysed RHA
The FESEM images of the ash obtained from the rice husk inner and outer surfaces through pyrolysis are shown in Figure 7 and Figure 8. The EDX analysis of rice husk ash pyrolysed at 650°C with and without oxalic acid treatments are shown in Figure 9. The presence of silica and oxygen are confirmed in the ash for both the cases. The structure of rice husk ash and silica obtained from it with oxalic acid leaching and pyrolysed at 650°C are analysed through FESEM images (Figure 10 and Figure 11).
Figure 9. Comparison of EDX analysis reports for RHA at 650°C

(a): oxalic acid leached rice husk ash

(b): RHA without acid treatment

Figure 10. FESEM image of oxalic acid treated RHA at 650 °C
3.5 FESEM and EDX analysis of silica

The sample picture of SEM image of silica, pyrolysed at different temperature and acid wash is shown in Figure 11. EDX confirms the presence of silicon and oxygen. EDX analysis for oxalic acid treated RHA pyrolysed at 750°C is shown in Figure 12 in which the presence of 96.99% silicon in form of SiO₂, 1.56% of Cl and 0.75 % Na are seen. FESEM image of metal modified silica catalysts obtained at pH of 10 at 750°C is shown in Figure 13. The presence of silica in SiO₂ form is found to be very less i.e. 29.2% at 750°C as seen from EDX analysis (Figure 14). This may be due to the presence of chromium and copper resulting from metal loadings.

3.6 Nitrogen sorption analysis
Nitrogen sorption analysis reports for Oxalic acid treated rice husk is shown in Figure 15. The surface area, total pore volume and pore diameter were calculated using BET model and the results for the silica obtained from RHA pyrolysed at different temperatures are tabulated in Table 1 and Table 2. These parameters for metal modified silica catalyst obtained from RHA treated with oxalic acid for different pH levels and pyrolysis temperatures are shown in Table 3 and Table 4 respectively. It is observed that the surface area decreases with the increase of the pyrolysis temperature.

![Figure 14. EDX of metal modified silica catalyst from Oxalic acid treated RHA](image)

![Figure 15. The N₂ Adsorption-Desorption analysis of Silica synthesized from RHA](image)

**Table 1.** The N₂ Adsorption-Desorption Analysis Parameters with HNO₃ acid treated RHA

| Type of Silica    | BET surface area (m²/g) | Pore volume (cc/g)                      |
|------------------|-------------------------|----------------------------------------|
| Silica (RhSi650°C) | 343.36                  | 0.4796 for pores smaller than 225.9 nm |
| Silica (RhSi750°C) | 243.25                  | 0.2943 for pores smaller than 256.4 nm |
| Silica (RhSi850°C) | 119.56                  | 0.1748 for pores smaller than 229.36 nm |

**Table 2.** The N₂ Adsorption-Desorption Analysis Parameters with oxalic acid treated RHA

| Type of Silica (°C) | BET surface area (m²/g) | Pore volume (cc/g)                      |
|---------------------|-------------------------|----------------------------------------|
| Silica (650°C)      | 362                     | 1.158 for pores smaller than 241.9 nm  |
| Silica (750°C)      | 359                     | 0.54 for pores smaller than 256.4 nm   |
| Silica (850°C)      | 234                     | 0.175 for pores smaller than 237.36 nm |

**Table 3.** The N₂ Adsorption-Desorption Analysis Parameters of Metal modified Silica Catalyst

| Type of Silica Catalyst | BET surface area (m²/g) | Pore volume (cc/g)                      |
|-------------------------|-------------------------|----------------------------------------|
| RhSi-Cr/Cu-10           | 182.7                   | 0.2798 for pores smaller than 197.35 nm |
| RhSi-Cr/Cu-7            | 111.1                   | 0.2402 for pores smaller than 217.15 nm |
| RhSi-Cr/C               | 79.94                   | 0.1943 for pores smaller than 235.23 nm |
Table 4. The \( N_2 \) Adsorption-Desorption Analysis Parameters for oxalic acid treated RH

| Type of Silica Catalyst | BET surface area (m\(^2\)/g) | Pore volume (cc/g) |
|-------------------------|-----------------------------|-------------------|
| RhSi-Cr/Cu-10 (650°C)   | 161                         | 0.902 for pores smaller than 225.6 nm |
| RhSi-Cr/Cu-10 (750°C)   | 104                         | 0.869 for pores smaller than 224.1 nm |
| RhSi-Cr/Cu-10 (850°C)   | 72                          | 0.524 for pores smaller than 228.4 nm |

3.7 \( N_2 \) Adsorption-desorption analysis of metal modified silica catalyst

\( N_2 \)-Adsorption-desorption analysis of metal modified silica catalyst was carried out through BET isotherms. The BET isotherms of metal modified silica catalyst extracted at different pH-values and temperatures are shown in Figure 16 (a) and (b) respectively. From Figure 16 (a) it is found that all the three catalysts exhibit type-III adsorption isotherm curves. The volume of \( N_2 \) adsorbed on the catalyst extracted at lower pH is found to be lower than that extracted at higher pH.

3.8 GC-MS analysis/styrene oxidation

A maximum conversion of 76.65% of styrene was observed for RhSi-Cr/Cu-3 while only 12.56% conversion of styrene was observed for RhSi-Cr/Cu-10(Table 5). RhSi-Cr/Cu-7 is found to have a medium conversion of 43.41%. RhSi-Cr/Cu-10 and RhSi-Cr/Cu-7 have higher surface area. The effect of pH on prepared catalyst during oxidation of Styrene test is shown in Table-5. Keeping all other parameters like \( H_2O_2 \) to styrene ratio, temperature of reaction and mass of catalyst same, effect of metal loading on catalyst is depicted in Table 6. Conversion percentage is seen to increase further with increase on copper loading content. The incorporation of bimetal into the silica matrix has also helped to further increase selectivity to benzaldehyde with considerable reduction in byproduct formation.
### Table 5. The effect of pH on catalyst during oxidation of Styrene

| Catalyst          | Conversion (%) | Bhd (%) | PhAhd (%) | AcPh (%) | BzA (%) |
|-------------------|----------------|---------|-----------|----------|---------|
| RhSi-Cr/Cu-10     | 12.56          | 99.84   | 0         | 0.16     | 0       |
| RhSi-Cr/Cu-7      | 43.41          | 82.14   | 5.6       | 6.3      | 5.96    |
| RhSi-Cr/Cu-3      | 76.65          | 79.42   | 4.4       | 4.09     | 12.09   |

### Table 6. The effect of copper loading on the catalyst

| Catalyst          | Conversion (%) | Bhd (%) | PhAhd (%) | AcPh (%) | BzA (%) |
|-------------------|----------------|---------|-----------|----------|---------|
| RhSi-Cr/Cu-3, 5%  | 76.65          | 79.42   | 4.4       | 4.09     | 12.09   |
| RhSi-Cr/Cu-3, 10% | 89.41          | 82.13   | 3.6       | 3.26     | 11.01   |

### 4. Conclusions

The removal of mineral contaminants from the rice husk is found to increase the yield of silica. The contaminants were also removed by acid washing by using organic (Oxalic acid) as well as mineral (HNO₃) acid. Pyrolysis was carried out in the temperature range of 650˚C to 850˚C. On comparison of acid washings between mineral acid and organic acid, it is found that the mineral acid is not environment friendly and it needs high amounts of water for the removal of acid. But it removes mineral contaminants efficiently than the organic acid. During extraction of catalyst by sol-gel technique, acid precipitation was found to occur. It is also observed that metal modified silica is obtained at three different pH levels of final solution (i.e. at pH of 3, 7 and 10).

This study proved that the obtained silica contains high surface area in microporous range which can be used as catalyst framework and adsorbents. EDX analysis further confirmed the presence of silica in white ash and presence of metals and silica in metal modified silica were also confirmed. This study revealed that the conversion of styrene is more for pH of 3 and for catalyst prepared with 10% copper loading. It is further observed that although the conversion is high for catalyst prepared at pH of 3, its surface area is less compared to the catalysts prepared at pH of 7 and 10. This study further proves that the catalytic activity not only depends on surface area but also on other factors like metal loading. This catalyst is found to be useful in many catalytic activities in industries.

### Nomenclature

- RH: Rice Husk
- RHA: Rice Husk Ash
- CTAB: CetylTetramethyl Ammonium Bromide
- SDA: Structural Directing Agent
- RhSi: Rice Husk Silica
- RhSi-Cr/Cu: Rice Husk Silica Impregnated with Copper and Chromium
- GC-MS: Gas Chromatography Mass Spectroscopy
- XRD: X-Ray Diffraction
- SEM: Scanning Electron Microscope
- EDX: Energy Dispersive X-ray
- BET: Brunauer–Emmett–Teller Surface Area Measurement

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