

Bio-template Synthesis of Silica-Ruthenium Catalyst for Benzylation of Toluene

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Abstract: *Silica-ruthenium-tryptophan catalyst was synthesised from rice husk via a simple solvent extraction and sol-gel technique at room temperature. The catalyst was labelled as RH-Ru-T and characterised by various physico-chemical methods. RH-Ru-T had a high specific surface area at $399 \text{ m}^2 \text{ g}^{-1}$ and a bimodal pore size distribution between 30–50 Å. The catalyst was found to be amorphous. Transmission electron microscopy image revealed the formation of wormlike structure. The use of RH-Ru-T as catalyst in the benzylation of toluene resulted in a conversion of 99.9% and 86% selectivity for the mono-substituted (ortho- & para-) products within a short reaction time.*

Keywords: Sol-gel preparation, rice husk silica, bio-template, silica-ruthenium

1. INTRODUCTION

Rice husk (RH) is an agricultural waste produced from the milling of rice. RH is the outer cover of the rice that constitutes about 20% by weight of the paddy. A typical RH composition contains 18.8–23.3% of silica, 28–38% of cellulose, 9–20% of lignin and other metallic impurities.¹ RH is a source of environmental problem if improperly disposed. The uncontrolled burning of RH can generate undesirable atmospheric pollutions.² In addition, rice husk ash generated can cause breathing problem due to its fine particle size which is easily transported by air.³ Due to this, many scientists have used the abundant rice husk waste to transform it into more valuable products such as silica.

Silica is stable both thermally and chemically.⁴ It has high surface area and pore size ranging from microporous to mesoporous (5–500 Å) and is one of the major reasons for its effectiveness as a catalyst support material. Silica is an attractive support for metals because it is only mildly acidic and is relatively inert. Amorphous silica is well known and commonly used as support material for metals due to its high surface area. The silica obtained from rice husk can be used as raw material for production of construction material, fillers, adsorbents, chromatographic agents, catalyst and as catalytic supports.^{5,6}

Today, one of the most challenging issues in the synthesis of porous silica is the ability to control the pore size and pore structure. In order to tailor the pore structure of these mesoporous supports, suitable templates are required. Many templates have been used for the synthesis of mesoporous silica. Some examples of the templates include bio-templates such as amino acid, yeast, enzyme and chitosan.⁷⁻¹⁰ These templates are useful to develop structured material for a wide range of applications. Among the amino acids, tryptophan has not been used as a template before. Since most of the templates used as structure directing agents contain nitrogen atoms, it was thought that the use of tryptophan might result in the generation of new structures which might have important properties that can be explored.

In this study, silica-ruthenium-tryptophan complex was successfully synthesised by solvent extraction and sol-gel technique at room temperature. To promote green chemistry, the biomass RH and bio template (tryptophan) were used to prepare the catalyst. The synthesised catalyst was characterised by powder X-ray Diffractometry (XRD), nitrogen sorption analysis, transmission electron microscope (TEM) and scanning electron microscope – energy dispersion X-ray (SEM-EDX). The prepared catalyst was evaluated in the benzylation of toluene under mild reaction condition to yield substituted diphenylmethanes. Diphenylmethanes are industrially important compounds and are used as pharmaceutical and in fine chemical synthesis.

2. EXPERIMENTAL

2.1 Raw Materials

Rice husk (RH) was obtained from a local rice mill in Penang, Malaysia. The following chemicals were used in this work: Nitric acid (QreC, 65%), sodium hydroxide (QReC, 99%), acetone (QRec) and ruthenium(II) chloride (R&M Chemical). All chemicals are of AR grade and used as received without further purification.

2.2 Preparation of RH-Ru-T Catalyst

Preparation of sodium silicate was carried out as reported in a previous study.¹¹ 0.2670 g of tryptophan (5% w/w) was weighed and added into the prepared sodium silicate solution and stirred until a homogeneous solution was formed. The solution was titrated with 3 M HNO₃ containing 10.0% (w/w) Ru³⁺ (1.0959 g of RuCl₃.xH₂O) until it reached pH 3. The resulting suspension was kept in a covered container and aged for 10 days. The aged gel was recovered by centrifuge and washed with distilled water and finally acetone. The gel was then

left to dry in an oven at 110°C for 24 h. The catalyst was ground to fine powders and labelled as RH-Ru-T. The mass of RH-Ru-T obtained was 3.8439 g.

2.3 Catalytic Reaction

The benzylation of toluene over the prepared catalyst was carried out in a magnetically stirred two-neck flask with a reflux condenser. 15 mL of toluene was pipetted into the 50 mL round bottom flask that contained 1 mL of benzyl chloride as the reactant and 1 mL of decane as the internal standard. 0.2 g of the catalyst (activated at 110°C for 24 h) was weighed and transferred directly into the flask. The reaction was carried out under refluxing for 6 h. The reaction mixture was analysed by gas chromatography – mass spectroscopy.

3. RESULTS AND DISCUSSION

The N₂ adsorption-desorption isotherm and the pore size distribution of RH-Ru-T are shown in Figure 1. The sample exhibited a type IV isotherm and H2 hysteresis loop according to IUPAC classification.¹² The hysteresis loop was observed in the range of $0.4 < P/P_0 < 1.0$, which was a result of capillary condensation taking place in the mesopores. The specific surface area of RH-Ru-T was found to be 399 m² g⁻¹ and the pore volume was 0.006 cc g⁻¹. The catalyst showed a bimodal pore size distribution with 2 different pore ranges, i.e., at 30 to 35 Å and 35 to 50 Å.

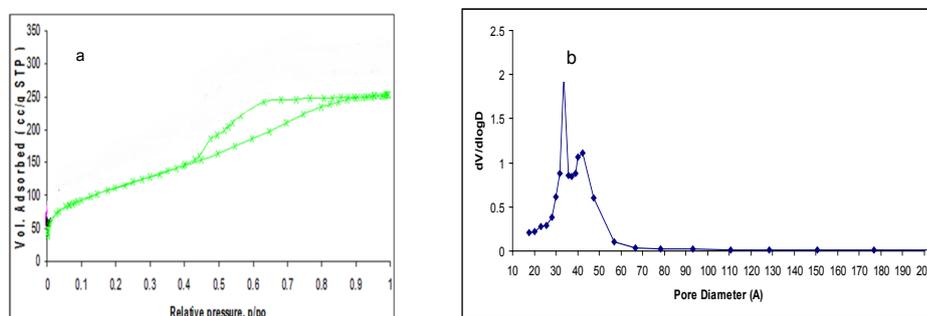


Figure 1: The nitrogen adsorption analysis of RH-Ru-T: (a) The isotherm showing the hysteresis loop; and (b) The bimodal pore size distribution found in the catalyst.

XRD analysis of RH-Ru-T is shown in Figure 2. No crystalline phase was detected in the X-ray diffractogram of the prepared catalyst. The catalyst showed a broad spectrum which indicated the amorphous nature¹³ of the material at $2\theta = 23^\circ$.

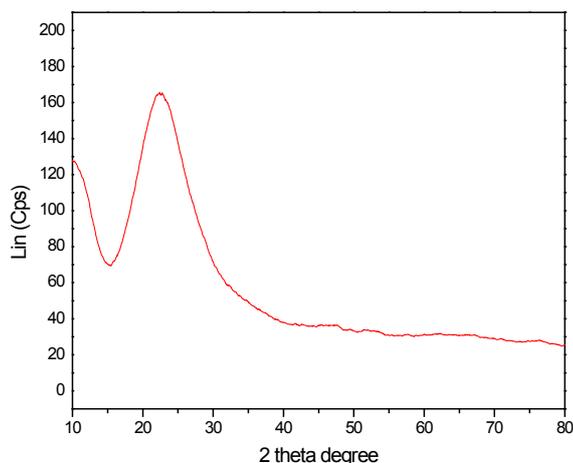


Figure 2: The X-ray diffractogram of RH-Ru-T showing the broad diffraction at $2\theta = 23^\circ$.

The morphology and the pore structure of RH-Ru-T was examined by transmission electron microscope and shown in Figure 3. RH-Ru-T consisted of disordered channels forming wormlike networks. Some aggregation of particles was observed in the micrograph. The surface morphology of RH-Ru-T was examined by scanning electron microscope (SEM). As shown in Figure 4, RH-Ru-T at low magnification (5 k) showed a layered arrangement.

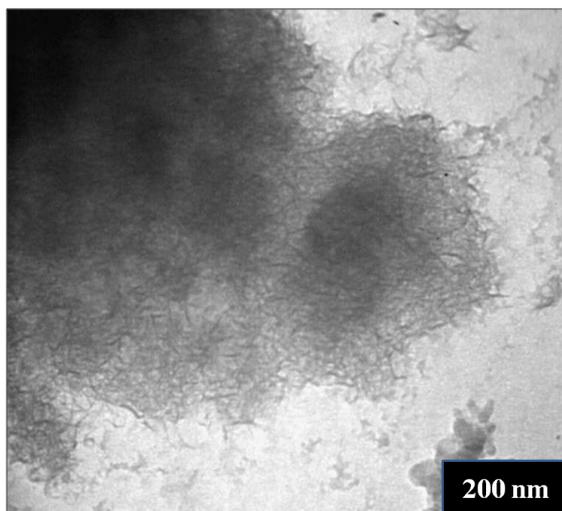


Figure 3: The TE micrographs of RH-Ru-T (at magnification 150,000 times).

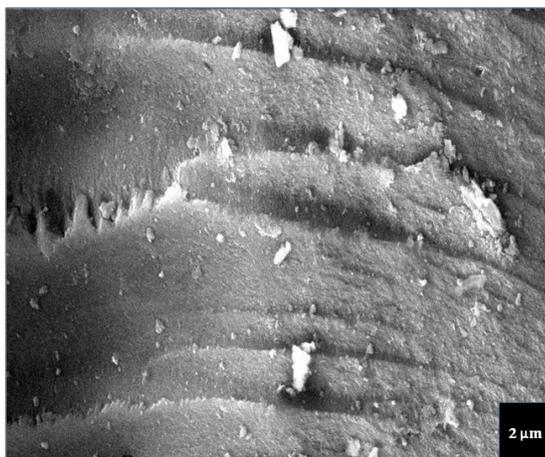


Figure 4: The SE micrograph of RH-Ru-T showing layered structure (at magnification 5,000 times).

The chemical composition of RH-Ru-T was determined by energy dispersive X-ray (EDX) analysis. EDX analysis (Table 1) detected the presence of carbon, oxygen, silicon and ruthenium. The presence of the 7.15% of ruthenium in the silica matrix is quite close to the amount of ruthenium loading in the preparation procedure. Hence, the ruthenium had been successfully incorporated in the silica matrix. The presence of carbon is consistent with the incorporation of tryptophan. No attempt was made to remove the organic template in this study. This is because removal of the template will involve calcination at high temperatures, which will increase the cost of preparation of the catalyst.

Table 1: The elemental composition of RH-Ru-T.

Element	Average Weight %
C	5.38
O	56.21
Si	31.26
Ru	7.15
Total	100.00

The prepared RH-Ru-T was evaluated in the benzylation of toluene under refluxing condition (Figure 5). As the reaction time increased to 6 h, the conversion of benzyl chloride was 99.9% with high selectivity to mono-substituted products of ~86%. The mono-substituted products were further identified as the *ortho*- and *para*- isomers. As the reaction time increased, the

mono-substituted products decreased. This was due to further benzylation of mono-substituted product to form di-substituted product as a result of the prolonged contact time.

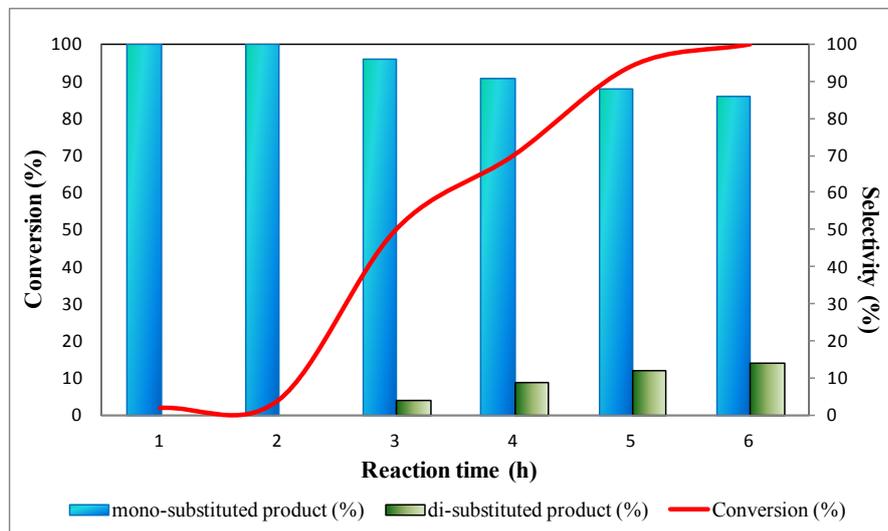


Figure 5: The catalytic profile of RH-Ru-T in the benzylation of toluene. The conversion and the product distribution are shown.

4. CONCLUSION

In this study, an attempt has been made to use silica from rice husk to produce RH-Ru-T. No attempt was made to remove the bio-template in this study. This is a cost effective and energy efficient method to produce the catalyst for the benzylation of toluene. In the reaction, the mono-substituted (*ortho*- and *para*-) products were obtained as the major constituent. The catalyst showed excellent catalytic performance with almost complete conversion (99.9%) towards benzylation of toluene and high selectivity (86%) to the mono-substituted products.

5. ACKNOWLEDGEMENT

The authors wish to thank the Government of Malaysia for the Research University (RU) grant (1001/PKIMIA/811092) which partly supported this work.

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