Malays. J. Bioeng. Technol. Vol. 2, No. 1, (2025): 36-41
https://doi.org/10.70464/mjbet.v2i1.1546

MALAYSIAN JOURNAL OF
BIOENGINEERING AND TECHNOLOGY

Characterisation of Silica Extracted from Rice Husk Functionalised by Guanine (RHACGua)

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ARTICLE INFO

Received:14 February 2025
Accepted:3 March 2025
Online:29 March 2025
eISSN: 3036-017X

ABSTRACT

This study seeks to answer how the incorporation of guanine affects the structural properties and catalytic behaviour of the silica support. This study presents the characterisation of an organic-inorganic hybrid catalyst, named as RHACGua, derived from silica extracted from rice husk (RH). The catalyst was developed by incorporating guanine onto rice husk ash (RHA)-supported silica, utilising (3-chloropropyl) triethoxysilane (CPTES) as an anchoring agent to facilitate the binding of guanine to the silica. Characterisation of RHACGua was performed using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), powder x-ray diffraction (XRD), nitrogen sorption analysis, and solid-state nuclear magnetic resonance (NMR) spectroscopy for 29Si and 13C. SEM, XRD, and nitrogen sorption analyses revealed that RHACGua possesses a porous agglomerate structure with a specific surface area of 77.67 m^2/g and a pore diameter of 15.81 nm. FTIR spectra demonstrated a shift in the Si-OSi band from 1038 cm^{-1} in the precursor RHACCl to 1042 cm^{-1} in RHACGua, confirming the successful incorporation of guanine and the presence of all expected functional groups. MAS NMR spectroscopy identified distinct silicon environments (Q4, Q3, T3, T2) in RHACGua, indicating effective modification of the Cl functional group with guanine. These findings confirm that the RHACGua catalyst was successfully synthesised via the modification of RHACCl with guanine, showcasing its potential for use in heterogeneous catalysis.

Keywords: Rice Husk; Heterogeneous Catalyst; Organic-inorganic Hybrid Catalyst; Guanine

1. Introduction

Rice husk (RH) is a valuable agricultural biomass with significant potential, particularly in Asian countries where it is abundant and easy to obtain. RH offers several environmental benefits as a renewable energy source, including reducing greenhouse gas emissions and providing an eco-friendly alternative to traditional fuels [1]. It is essential to explore and optimise the use of RH, not only as an energy source but also for its potential to address disposal and pollution issues, as RH is typically burned to produce ash. One of the key advantages of RH is its high silica content, approximately 20%, which distinguishes it from other biomasses [2]. This high silica content, combined with its porous structure and large surface area, enhances its value, particularly as a catalyst support material [3]. Silica extracted from RH is more cost-effective and efficient compared to silica derived from quartz using conventional methods [4]. This study explores the potential of RH-derived silica in the development of organic-inorganic catalysts, particularly those formed by combining guanine, an organic compound, with silica, an inorganic compound. Both compounds offer unique benefits, making the resulting catalyst particularly valuable. By utilising renewable resources, this research contributes to a sustainable ecosystem and promotes better health outcomes by mitigating the environmental impact of biomass waste.

2. Materials and Methods

2.1 Removal of Contaminants from the RH

Initially, the rice husks were thoroughly washed with water to eliminate surface impurities, followed by rinsing with distilled water to ensure the complete removal of residual dirt and debris. After washing, the clean rice husk samples were dried to remove any moisture content. Subsequently, the dried samples underwent an acid treatment to purify the rice husks further and prepare them for the silica extraction process. This acid treatment was essential for breaking down any remaining organic materials and enhancing the accessibility of silica for extraction.

2.2 Silica Extraction from RH and Functionalisation with Organic Compound Guanine

30g of RH were mixed with 1.0M of nitric acid and allowed to react for 24 hours. The mixture was then rinsed with distilled water until the pH of the rinse stabilised between 5.00 and 7.00. The clean RH were then dried and subjected to combustion in a muffle furnace for 6 hours at 800ºC to obtain the rice husk ash (RHA). Subsequently, 3.0g of RHA was mixed with 1M sodium hydroxide (NaOH) for an hour. Afterwards, the mixture was filtered through Whatman filter paper no. 1 and yielded a clear solution of sodium silicate, which was used to prepare RHACCl for the catalyst synthesis. Next, 0.015 mmol of (3-chloropropyl) triethoxysilane (CPTES) was added to the sodium silicate solution, and it was titrated with 3M nitric acid until the formation of the white gel was obtained. The white gel produced then was allowed to age for 48 hours at room temperature. The gel was then centrifuged, resulting in a precipitate of RHACCl. 0.0015 mmol of guanine was dissolved in 30 ml of dry toluene and mixed with RHACCl. Then, 0.0015 mmol of triethylamine (Et3N) was added. All the added chemical was refluxed for 24 hours at ~110°C. A solid particle was formed after the reflux process, then underwent filtration and was rinsed with toluene and dichloromethane (DCM). The particles were then washed with distilled water and dried in an oven at 100°C for 24 hours. Finally, the dried solid material was ground into a fine powder designated as RHACGua.

2.3 Characterisation of RHACGua Catalyst

The RHACGua catalyst was characterised using a range of analytical techniques to determine its elemental composition, physical structure, and chemical properties. X-ray diffraction (XRD) was conducted using a Bruker D2 Phaser Power system to determine the phase and crystallinity of the catalyst. Surface morphology and microstructure were analysed using a JSM-IT100 Scanning Electron Microscope (SEM). Nitrogen sorption analysis, performed with a Quantachrome ASIQC060111-6 analyser, provided data on surface area, pore volume, and pore size distribution. Chemical bonding and functional groups were identified using a Perkin Elmer Spectrum 100 Fourier Transform Infrared (FTIR) system. Additionally, the molecular structure and atomic environment of the catalyst were investigated using a Bruker 400 MHz Avance III HD Nuclear Magnetic Resonance (NMR) spectrometer. These techniques collectively provided a detailed understanding of the catalyst's properties, essential for evaluating its catalytic performance.

3. Results and Discussion

3.1 Physical Properties of RHACGua Catalyst

The physical properties of the RHACGua catalyst were examined through powder X-ray diffraction (XRD) in Fig. 1, which revealed both amorphous and crystalline characteristics, classifying the material as semi-crystalline. A broad diffraction pattern observed at specific two-theta values indicates the presence of the amorphous phase, consistent with findings in previous studies [5]. In contrast, sharp peaks in the diffractogram correspond to the crystalline regions of the sample [6]. Notably, sharp peaks observed at 14.102°, 26.402°, and 27.920° are attributed to the crystalline structure of guanine, as reported by Ng et al. [7]. These distinctive features highlight the unique structure of the RHACGua catalyst.

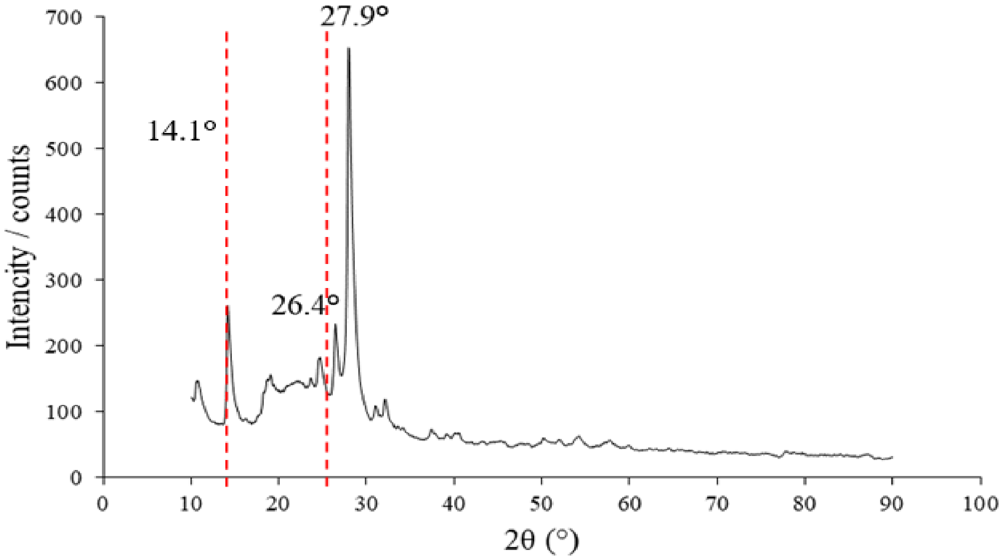

Fig. 1: XRD diffractogram of RHACGua

The RHACGua catalyst exhibits an average pore size of 15.807 nm, which is smaller than the 17.829 nm observed for RHACCl and the 6.839 nm for RHA. This reduction in pore size is attributed to the incorporation of the organic compound into the silica support of RHA. Among the samples, RHACCl displays the largest surface area, with values of 132.467 m²/g for RHA, 154.853 m²/g for RHACCl, and 77.667 m²/g for RHACGua. Scanning electron microscopy (SEM) images in Fig. 2 revealed that the surface structures of RHACCl and RHACGua are agglomerated and spherical, similar to the findings reported by Yuan et al. [8]. In contrast, RHACGua presents a surface with uneven, rock-like particles that are randomly distributed, contributing to a unique and rough topography. When correlating these SEM observations with X-ray diffraction (XRD) results, regions exhibiting smooth surfaces or uneven, rock-like particles were identified as crystalline, a finding consistent with the work of Doğruyol [9].

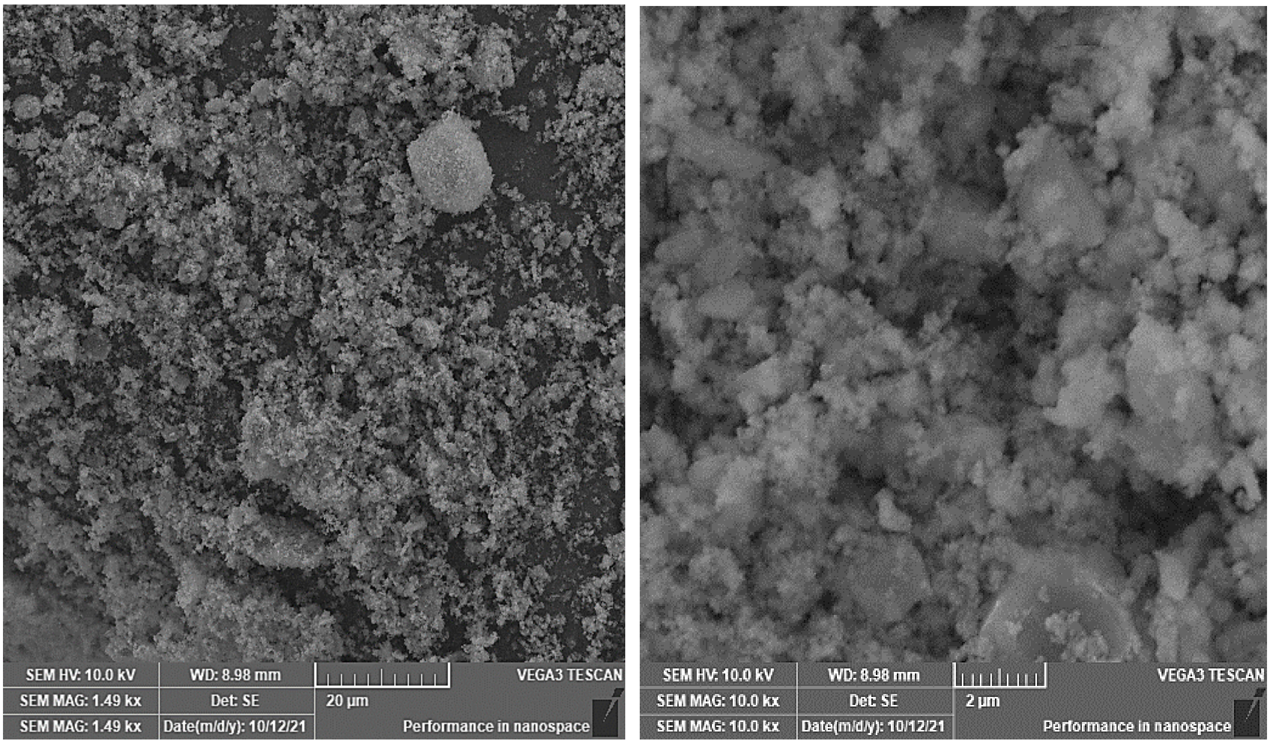

Fig. 2: The SEM image of RHACGua 1.49kx and 10kx

3.2 Chemical Bonding for the Incorporation of Silica and Guanine

The NMR results for the siloxane group align with the FT-IR analysis in Fig. 3, confirming the presence of Si-O-Si, Si-OH, and Si-OH bonds in the material. Notably, the Si-OH groups in the silica structure are substituted by Si-O-Gua bonds through a reaction with the guanine-derived organic compound, leading to the formation of the RHACGua catalyst. This substitution marks a chemical modification of the siloxane structure, where hydroxyl groups are replaced by bonds with the guanine derivative, influencing the material's properties and causing chemical shifts in the NMR spectra.

Magic angle spinning (MAS) NMR spectroscopy revealed distinct shifts in the retention times at the silicon centres in RHACGua compared to RHACCl. These shifts were observed at Q4 (-111.54 ppm), Q3 (-103.54 ppm), T3 (-66.51 ppm), and T2 (-58.32 ppm) in the 29Si NMR spectrum of RHACGua. Additionally, the FT-IR spectra confirmed the functionalisation of CPTES onto RHA silica, with a peak at 2957 cm^{-1} corresponding to aliphatic groups and a peak at 695 cm^{-1} associated with the chlorine functional group (C-Cl). The formation of the RHACGua catalyst was further confirmed by the presence of peaks corresponding to amine groups (2989 cm^{-1}), aromatic amines (1259 cm^{-1}, 1313 cm^{-1}), aliphatic amines (3315 cm^{-1}), and double bonds (1671 cm^{-1}, 1474 cm^{-1}). These peaks collectively indicate the successful incorporation of the guanine structure into the RHACCl framework, confirming the successful functionalisation of the silica surface.

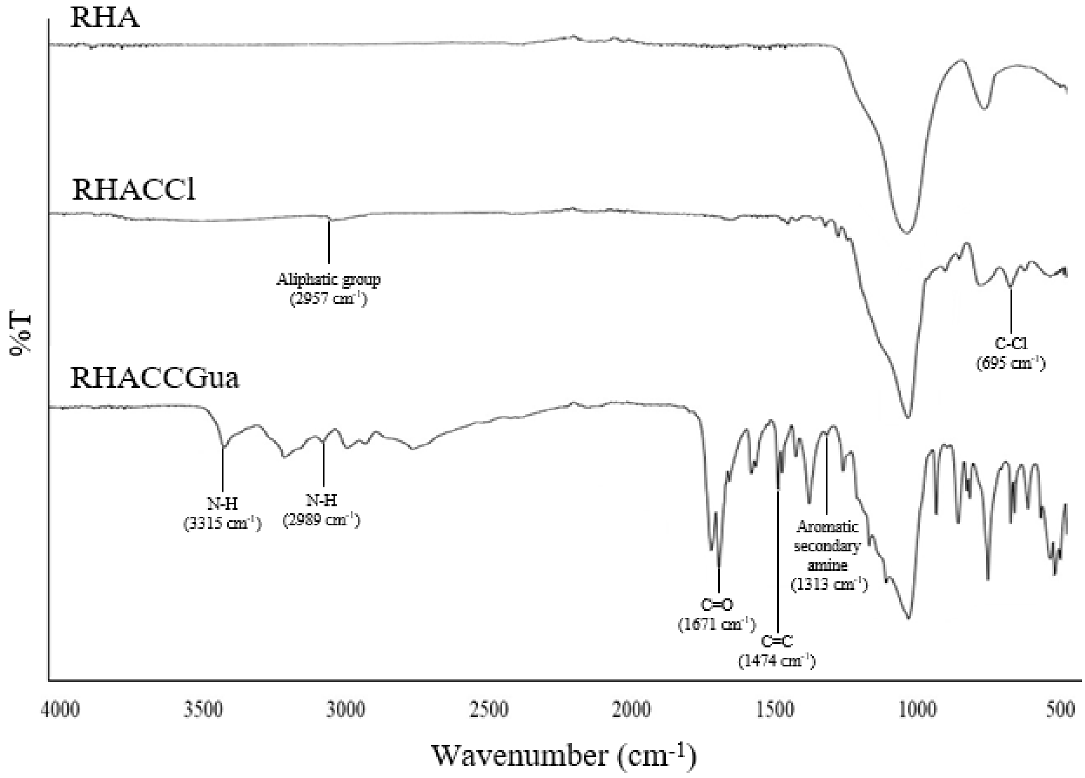

Fig. 3: FTIR spectra

4. Conclusion

Heterogeneous catalysts offer significant advantages, particularly in their ability to be regenerated for repeated use. In this study, a green and sustainable catalyst, RHACGua, was successfully developed by utilising rice husk, an agricultural waste, as a silica source, combined with the organic compound guanine. The extraction of silica from rice husk was accomplished effectively, and the resulting catalyst demonstrated the successful incorporation of rice husk silica and guanine through detailed characterisation. Various analytical techniques, including XRD, SEM, BET, FTIR, and NMR, were employed to assess the structural and functional properties of the RHACGua catalyst. Unlike most rice husk-based catalysts, which often rely on non-renewable metal elements to enhance catalytic activity, RHACGua represents a more sustainable alternative. The findings from this study contribute to the growing body of knowledge on the use of renewable agricultural waste for catalyst development, offering promising insights for eco-friendly catalytic applications in various chemical processes.

Acknowledgement

I want to thank Universiti Malaysia Kelantan for providing the resources and environment that made this work possible. This work was supported by the Malaysian Government for funding this research through FRGS-RACER [RACER/1/2019/STG01/UMK/2]

References

[1] Akhter F, Soomro SA, Jamali AR, Chandio ZA, Siddique M, Ahmed M. Rice husk ash as green and sustainable biomass waste for construction and renewable energy applications: a review. Biomass Convers Biores, 2021;1-11.

[2] Temeche E, Yu M, Laine RM. Silica depleted rice hull ash (SDRHA), an agricultural waste, as a high-performance hybrid lithium-ion capacitor. Green Chem, 2020;22(14):4656-4668.

[3] Pan Y, Li N, Ran S, Wen D, Luo Q, Li K, Zhou Q. Efficient catalysis for low-temperature CO selective catalytic reduction over an Fe-Cu bimetal oxide catalyst supported on amorphous SiO_2. Ind Eng Chem Res, 2022;61(28):9991-10003.

[4] September LA, Kheswa N, Seroka NS, Khotseng L. Green synthesis of silica and silicon from agricultural residue sugarcane bagasse ash–a mini review. RSC Adv, 2023;13(2):1370-1380.

[5] Agusnar H, Sugita P, Nainggolan I. Preparation sodium silicate from rice husk to synthesize silica nanoparticles by sol-gel method for adsorption water in analysis of methamphetamine. S Afr J Chem Eng, 2022;40(1):80-86.

[6] Ali A, Chiang YW, Santos RM. X-ray diffraction techniques for mineral characterization: A review for engineers of the fundamentals, applications, and research directions. Minerals, 2022;12(2):205.

[7] Ng JC, Tan CY, Ong BH, Matsuda A, Basirun WJ, Tan WK, Singh R, Yap BK. Novel palladium-guanine-reduced graphene oxide nanocomposite as efficient electrocatalyst for methanol oxidation reaction. Mater Res Bull, 2019;112:213-220.

[8] Yuan S, Hou Y, Liu S, Ma Y. A Comparative Study on Rice Husk, as Agricultural Waste, in the Production of Silica Nanoparticles via Different Methods. Materials, 2024;17(6):1271.

[9] Doğruyol M. Characterization of historic mortars and the effect of rice husk ash (RHA) on quicklime. Case Stud Constr Mater, 2024;21:e03542.