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^{29}Si Solid-State NMR Spectroscopy of Guanine-Modified Rice Husk Silica (RHACGua)

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ABSTRACT

This study details the characterisation of an organic-inorganic hybrid catalyst named RHACGua, using Solid-state NMR Spectroscopy. The catalyst was developed by incorporating guanine onto silica derived from rice husk ash (RHA), with (3-chloropropyl) triethoxysilane (CPTES) used as an anchoring agent to facilitate the binding of guanine to the silica. Characterisation of RHACGua was conducted through nitrogen sorption analysis and solid-state nuclear magnetic resonance (NMR) spectroscopy for ^{29}Si. The ^{29}Si solid-state NMR spectra revealed distinct silicon environments (Q^4, Q^3, T^3, T^2) in RHACGua, indicating successful modification of the Cl functional group with guanine. These results confirm the successful synthesis of the RHACGua catalyst through the modification of RHACCl with guanine, demonstrating its potential for applications in heterogeneous catalysis.

Keywords: NMR solid state, characterisation, silica from rice husk ash

1. Introduction

This study investigates the synthesis and characterisation of guanine-modified silica derived from rice husk ash (RHA) using ^{29}Si solid-state nuclear magnetic resonance (NMR) spectroscopy. Rice husk ash, a byproduct of rice milling, contains a high concentration of silica (SiO_2) [1], making it a valuable resource for silica nanoparticles with various potential applications. The modification of silica with organic compounds, such as guanine, a purine base found in DNA, aims to enhance the properties of silica nanoparticles for use in nanotechnology and biomedical applications. Guanine's modification of silica is of particular interest due to its biological compatibility and potential to form stable interactions with other biomolecules. By utilising ^{29}Si solid-state NMR spectroscopy, this study provides a comprehensive analysis of the chemical environment and structure of the silica surface after guanine modification [2]. This technique provides valuable insights into the interaction mechanisms and structural transformations that occur during the functionalization process. The findings from this research add to the growing body of knowledge on utilising agricultural waste, such as rice husk, to produce valuable nanomaterials. Additionally, it highlights the potential for functionalizing these materials with biological molecules, such as guanine, for applications in drug delivery, biosensors, and nanomedicine.

2. Materials and Methods

2.1 Removal of Impurities from Rice Husk

The rice husks were first washed thoroughly with water to remove surface impurities, followed by rinsing with distilled water to ensure the complete removal of any residual dirt and debris. After washing, the cleaned rice husk samples were dried to eliminate moisture. The dried samples were then subjected to an acid treatment to purify the rice husks further and prepare them for the silica extraction process [3]. This acid treatment was crucial for breaking down any remaining organic material and improving the accessibility of silica for extraction.

2.2 Silica Extraction from Rice Husk and Modification using the Organic Compound Guanine

Thirty grams of rice husks (RH) were mixed with 1.0M 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. After cleaning, the rice husks were dried and subjected to combustion in a muffle furnace at 800ºC for 6 hours to obtain rice husk ash (RHA). Next, 3.0 g of RHA was mixed with 1 M sodium hydroxide (NaOH) and stirred for 1 hour. The mixture was then filtered through Whatman filter paper no. 1, yielding a clear sodium silicate solution, which was subsequently used to prepare RHACCl for catalyst synthesis. Following this, 0.015 mmol of (3-chloropropyl) triethoxysilane (CPTES) was added to the sodium silicate solution, and the mixture was titrated with 3M nitric acid until a white gel formed. The gel was allowed to age for 48 hours at room temperature. After ageing, the gel was centrifuged, resulting in a precipitate of RHACCl. Subsequently, 0.0015 mmol of guanine was dissolved in 30 ml of dry toluene and mixed with RHACCl, followed by the addition of 0.0015 mmol of triethylamine (Et3N). The mixture was then refluxed for 24 hours at approximately 110°C. After the reflux process, a solid particle was formed, which was then filtered and rinsed with toluene and dichloromethane (DCM). The particles were 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, which was designated as RHACGua.

2.3 Solid-state MAS NMR Spectroscopic Analysis

The RHACGua material was characterised using a Bruker 400 MHz Avance III HD Nuclear Magnetic Resonance (NMR) spectrometer to examine its molecular structure and atomic environment. These techniques offered a comprehensive insight into the catalyst's properties, which is crucial for assessing its catalytic performance. During the analysis, the rotor spinners with an external diameter of 4.0 mm were utilised, operating at spinning frequencies of 83 kHz for ^{29}Si. The solvent used for ^{29}Si NMR spectroscopy analysis is acetone. The spectra of ^{29}Si were recorded at 79.51MHz. The analysis was conducted at the Faculty of Science, University of Technology Malaysia. The magnetic field with magic angle spinning (MAS) is used to analyse organic and inorganic chemistry. Moreover, this analysis can also demonstrate the effectiveness of integrating the organic molecules onto the solid substrate. NMR is an effective method for identifying the peak attributes of ^{29}Si in the samples.

3. Results and Discussion

The success of CPTES in combination with RHA and RHACCl in conjunction with guanine has been identified. Earlier research has demonstrated that RHA silica isolated from RH typically contains Q^4 and Q^3 silicon connections [4]. Additionally, Q^0 to Q^2 sites are predominantly present in the structure of unreacted RHA and fly ash that was detected at a peak of 67.5 to 74.5 ppm [5]. The NMR spectrum shows no appearance of Q^0 to Q^2 in RHACCl or RHACGua, as the RHA had been treated with acid before being converted into ash. The silicon connection structures of Q^4, Q^3, and Q^2 are illustrated in Fig. 1. According to a study conducted by Azman et al. [6], a formula was determined to calculate the quantity of siloxane groups present. The formula, $Q_n = Si(OSi)_n(OH)_4$-n, allows for the calculation of the number of siloxane groups based on the value of "n," which ranges from 0 to 4.

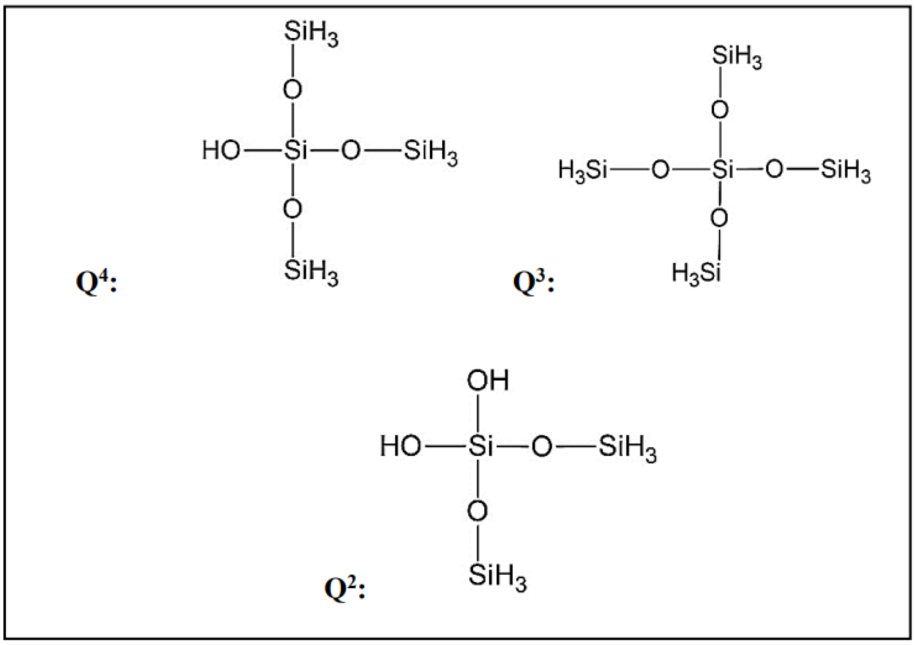

Fig. 1: The structure of silicon connections

In this study, solid-state ^{29}Si NMR spectroscopy was used to analyse the structure of RHACGua by comparing it with the spectrum of RHACCl. Solid-state NMR is a powerful technique for revealing the structure and surface characteristics of catalysts, providing detailed insights into their properties. Fig. 2 presents the results of ^{29}Si CP/MAS NMR analyses for both RHACGua and RHACCl. The analysis identified the presence of siloxane groups (Si-O-Si), categorised as Qn, where "n" represents the number of bridging bonds (-O-Si) attached to the central silicon atom [1]. By comparing the RHACGua spectrum with that of RHACCl, two distinct peaks were observed. In the RHACCl spectrum, the Q^4 peak appeared at -109.59 ppm, while the Q^3 peak was at -101.57 ppm.

In contrast, the RHACGua spectrum showed noticeable shifts: the Q4 peak (indicating siloxane bridges) appeared at -111.54 ppm, and the Q^3 peak (representing single silanol groups) was observed at -103.35 ppm. These chemical shift differences are illustrated in Fig. 2, highlighting the distinct Q^4 and Q^3 peaks for both RHACGua and RHACCl. The NMR results for the siloxane group align with FT-IR analysis, showing the presence of Si-O-Si, Si-OH, and Si-OH bonds. Notably, the Si-OH groups are substituted by Si-O-Gua bonds through a reaction with a guanine-derived organic compound to form the RHACGua catalyst. This substitution reflects a chemical modification of the siloxane structure, where bonds replace hydroxyl groups with the guanine derivative. This modification not only alters the material's properties but also leads to chemical shifts in the NMR spectra. A similar phenomenon is described by [1], where a peak shift in their measurements indicated the integration of a chemical compound into the silicate backbone during the alkali activation process. This shift suggests a structural change in the silicate network resulting from its interaction with the chemical compound.

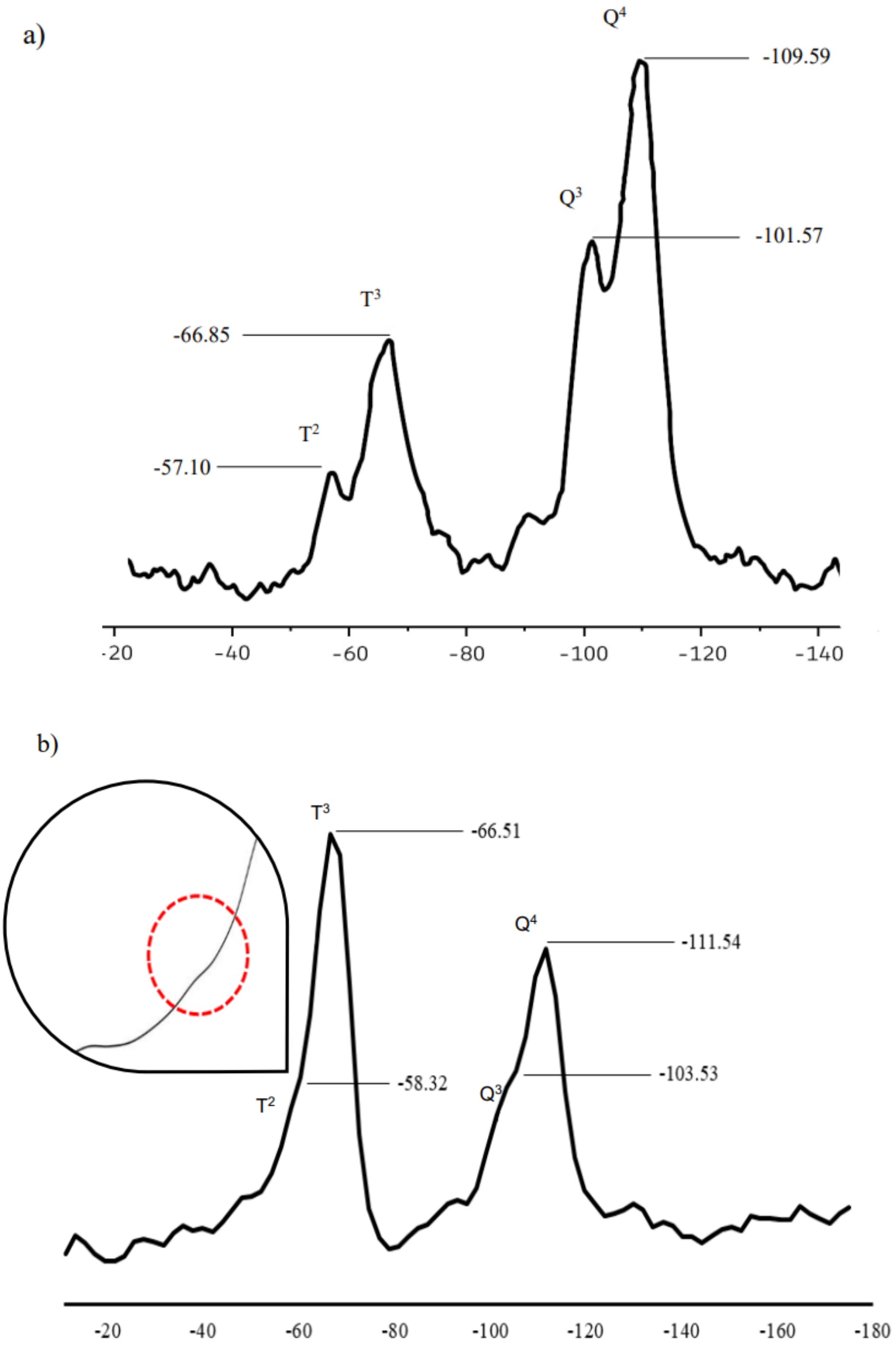

Fig. 2: The ^{29}Si CP/MAS NMR spectrum of a) RHACCl and b) RHACGua

The bond formed between the silica surface and the silicon atoms of alkyl silanes is known as the siloxane bond, which corresponds to three distinct environments for the siloxane group, referred to as "m". This siloxane bond exhibits various T_m species, representing the trifunctional derivative of silica, with "m" ranging from 1 to 3, as described by the formula $T_m = RSi(OSi)_m(OH)^{3}{}_{-m}$ [1]. The peaks for T_m appear in the range of -45 to -80 ppm, indicating the covalent incorporation of the functional groups. The formation of linkages between CPTES and the silicon atoms of silica through 3, 2, and 1 siloxane bonds is illustrated in Fig. 3. The results show that RHACGua exhibits T^3 and T^2 species, which are indicative of organosilicon atoms known as organic moieties [1]. A slight shoulder corresponding to the T^2 species appears at -58.32 ppm, while the T^3 species is observed at -66.51 ppm. Notably, a shift is observed from the RHACCl spectrum to the RHACGua spectrum, with RHACCl showing T^2 at -57.10 ppm and T^3 at -66.85 ppm. Additionally, the substitution of the C-Cl bond with a C-N bond from the –NH group of guanines is evidenced by a slight chemical shift in the NMR spectra of both RHACCl and RHACGua.

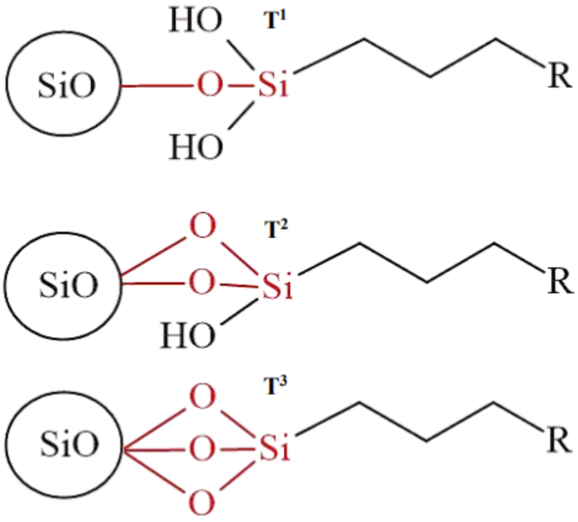

Fig. 3: The linkage formation between (3-chloropropyl) triethoxysilane (CPTES) and silica atom

4. Conclusion

This study presents the characterisation of an innovative organic-inorganic hybrid catalyst, RHACGua, using solid-state NMR spectroscopy. The catalyst was developed by incorporating guanine onto silica derived from rice husk ash (RHA), with (3-chloropropyl) triethoxysilane (CPTES) acting as an anchoring agent to facilitate the binding of guanine to the silica surface. The characterisation of RHACGua was carried out using nitrogen sorption analysis and ^{29}Si solid-state NMR spectroscopy. The ^{29}Si NMR spectra revealed distinct silicon environments (Q^4, Q^3, T^3, T^2), confirming the successful modification of the Cl functional group with guanine. These findings validate the effective synthesis of the RHACGua catalyst through the modification of RHACCl with guanine, highlighting its potential for use in heterogeneous catalysis. Unlike many rice husk-based catalysts, which typically rely on non-renewable metal elements to enhance catalytic activity, RHACGua represents a more sustainable and eco-friendlier alternative. The successful incorporation of rice husk silica and guanine, along with the detailed characterisation of the catalyst, underscores the viability of utilising renewable agricultural waste for catalyst development. This study contributes to expanding the knowledge base on the use of sustainable materials in catalytic processes, offering promising prospects for environmentally friendly applications in various chemical industries.

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