

Research Article

Modification of Silica Rice Husk Ash to Solid Ammonium Sulphate for Second Generation Biofuels Productions

Kasim Mohammed Hello,¹ Majid Jari Mohammed,² Asstabraq Mohsen Yasser,² Farook Adam,³ and Zinab Farag³

¹Chemistry Department, College of Science, Al-Muthanna University, Iraq

²Chemistry Department, College of Science, Kufa University, Iraq

³School of Chemical Sciences, University Sains Malaysia, 11800 Penang, Malaysia

Correspondence should be addressed to Kasim Mohammed Hello; kasimhello@gmail.com

Received 25 August 2014; Revised 18 October 2014; Accepted 23 October 2014; Published 9 December 2014

Academic Editor: Mohammed M. Bettahar

Copyright © 2014 Kasim Mohammed Hello et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A new approach has been demonstrated for the synthesis of solid ammonium sulphate attached to silica rice husk ash. The 3-(aminopropyl)triethoxysilane was immobilized onto silica at room temperature to functionalize the silica with ammine end groups ($-\text{NH}_2$). The amine group was sulphated with sulphuric acid to produce a novel micro-rod-like shaped acidic catalyst (as seen with TEM) designated $\text{RHNH}_3\text{SO}_4\text{H}$ (RH = rice husk). The TGA analysis shows that the catalyst is stable at temperatures below 200°C . The acidity measurement of the catalyst indicates that it has Brønsted acid sites. Cellulose extracted from waste of rice husk and cellulose extracted from office paper were hydrolysed to glucose in 6 h, and the glucose was hydrolysed afterwards to other products within 13 h. The catalyst is reusable many times without a significant loss of catalytic activity.

1. Introduction

Until recently, most ionic catalysts were synthesised and used for different purposes in liquid solutions. These ionic liquids were showing very good catalytic activity compared with the commercial strong acids such as H_2SO_4 , HCl , and H_3PO_4 , which have limitations due to a tedious work-up procedure and the necessity of postneutralization of the strongly acidic media leading to production of undesired wastes. Therefore many challenges are facing the researcher regarding the characterization and the recycling of these ionic liquid catalysts. We have recently reported the synthesis of a new type of ionic catalysts in solid state form with less environmental concerns. Those catalysts are recyclable and can be used for the same purposes as where the ionic liquids catalysts are used [1].

Rice husk (RH) is a major by-product of the rice-milling industries and it is causing disposal problems. Moreover, after its burning approximately 20% ash content comprises over 95% of amorphous silica which has very fine particle

size, very high purity, high surface area, and high porosity. These properties would give rice husk utilization a very economically attractive perspective [2, 3]. One important application of silica is due to its ability to be modified with different silylating agents, which can introduce basic groups through an anchored pendant chain. The traditional procedure for immobilization of 3-(aminopropyl)triethoxysilane (APTES) onto different types of silica involves long reaction times, nonenvironmentally friendly organic solvents, harsh refluxing condition, and multiple steps [4–6]. Moreover, the vast majorities of these protocols call for expensive chemicals and techniques and cause environmental pollution. A more direct and simple method was introduced by us to immobilize APTES onto silica to give a $-\text{CH}_2-\text{NH}_2$ functionality on the silica surface [7, 8].

Recently, a new technique has been developed towards the production of second generation (2G) biofuels without the use of expensive enzymes [9]. Producing 2G bioethanol from dead plant tissue is environmentally friendly, but it is also currently expensive because the process that is used

today needs expensive enzymes. The goal is to produce bioethanol from cellulose containing waste plant parts. Cellulose is the major polymeric component of plant material and is the most abundant polysaccharide on Earth. In nature, a variety of microorganisms are known for producing a set of enzymes capable of degrading this normally insoluble polymer to soluble sugars, primarily cellobiose and glucose [10]. As cellulose is very difficult to break down, it cannot directly be used as a food source. Cellulose is found everywhere in nature in rich quantities, for example, in the stems of the corn plant, rice husk, and palm fronds. If we can produce bioethanol from the corn stems and keep the corn cobs for food, we have probably come a long way to make biofuel production more acceptable. In fact we can now report about an entirely new molecular compound, which can also replace enzymes in the work of breaking down cellulose to sugar for the production of 2G biofuels, following up on the procedures leading to the earlier reported sulfonic acid compound [9].

2. Materials and Methods

2.1. Raw Materials. The chemicals used in this study were sodium hydroxide (System, 99%), acetone (GCC, 99%), 3-(aminopropyl)triethoxysilane (Merck, 98%), nitric acid (Scharlau, 65%), 1-butanol (Fluka, 99%), cellulose (Riedle-De Haen, 99%), cyclohexanol (Riedle-De Haen, 99%), cyclohexanone (Riedle-De Haen, 99%), dimethylformamide (DMF) (System, 99%), dinitrosalicylic acid (DNS) (BDH, 99%), glucose (BDH, 99%), lithium chloride (Sigma, 99%), sodium chloride (Sigma, 99%), potassium chloride (Sigma, 99%), sulphuric acid (Poch, 95%), potassium chloride (Sigma, 99%), and sulphuric acid (Poch, 95%). The rice husks (RH) were collected from a rice mill in Samawah, Iraq. All other chemicals used were AR grade or of high purity and were used directly without further purification.

2.2. Sources of Silica. The rice husk ash (RHA) was chosen as the source of amorphous silica as it was available in abundance. The silica was extracted from rice husk using a previously reported method [11, 12].

2.3. Sources of Cellulose

2.3.1. Extraction of Cellulose from RH. RH was used as a source of cellulose as well as of silica. The cellulose was extracted from RH according to the method reported in [13]. In general the RH was washed twice with water and dried at room temperature for 24 h. A weight of 35 g of the cleaned RH was stirred with 700 mL of 1.0 M nitric acid at room temperature for 24 h and washed with distilled water. The wet material was subsequently dried in an oven at 100°C for 24 h. The rice husk treated with acid was weighed and then transferred into a 1.0 L plastic container. To purify the cellulose by removing silica and lignin from RH fibres, 500 mL of 1.0 M sodium hydroxide solution was added. Then the solution was stirred for 24 h at room temperature. It was then filtered using suction filtration. The dark brown filtrate (sodium silicate solution with lignin) was kept in a covered plastic container. The solid was filtered and washed

several times using distilled water. The solid was treated with 6.0 M NaOH for 6 h and then filtered to be used for cellulose extraction. The filtrate was titrated with acid at room temperature using 5.0 M sulphuric acid under continuous stirring until constant pH in the range of 5-6 was reached. The resulting suspension with hydrolysed material was then separated by vacuum filtration and washed roughly with distilled water. This method gives 6.0 g, 17.14% of cellulose.

2.3.2. Extraction of Cellulose from Waste Paper. Waste paper was also used as raw material for extraction of cellulose by a simple and economic method. Waste paper was collected from waste boxes of the offices in Al-Muthanna University. The cellulose was extracted from RH according to the method reported in [13]. In general, 5.0 g of waste paper was cut into small pieces and mixed with sodium hydroxide solution 7.5% in a plastic container equipped with stirrer. The mixture was stirred for 6 h and then filtered. The filtrate was titrated against 5.0 M sulphuric acid solution until the pH reached 5.0. After separating the mixture, the solid was washed with distilled water and dried at room temperature. This method gave about 1.0 g, 20% of cellulose.

2.4. Synthesis of $RHNH_3SO_4H$ Catalyst. The APTES was functionalization onto RHA to produce $RHAPrNH_2$ according to the method reported elsewhere [7]. The primary amine in $RHAPrNH_2$ was sulphated to the solid ammonium sulphate at room temperature. In general, 25 mL of 0.05 M sulphuric acid was added to the 2.0 g of dry $RHAPrNH_2$ in a 50 mL round bottom flask and it was stirred for 24 h. The solid ammonium sulphate formed was filtered and washed with copious amount of water and then dried in an oven at 100°C for 24 h. The resulting compound was labelled as $RHNH_3SO_4H$. About 1.9 g was collected using this method.

2.5. The Surface Acidity of $RHNH_3SO_4H$. The surface acidity measurement of $RHNH_3SO_4H$ was done as in the method reported in [2]. In general $RHNH_3SO_4H$ together with a beaker containing pyridine was placed in a desiccators equipped with a valve connected to a membrane vacuum pump (AMB Greiffenberger Antriebstechnik, MZ2C, CE 2002/06). The system was evacuated for 1 h at a rate of $1.7 \text{ m}^3 \text{ h}^{-1}$. The system was kept under sealed vacuum for 48 h. The atmosphere in the desiccators was then evacuated again for 1 h at the same pump rate. Then, the solid compound was removed and analyzed by FT-IR on a KBr disc.

2.6. Catalytic Hydrolysis Procedure

2.6.1. Hydrolysis of Cellulose. The cellulose hydrolysis was carried out in the liquid phase in a 50 mL round bottom flask equipped with magnetic stirrer and water condenser connected to the chillier to control the water temperature in between 10 and 15°C. 20 mL of DME, 0.2 g of LiCl, and 0.18 g cellulose were separately transferred to the round bottom flask containing 150 mg of the catalyst (predried at 110°C for 24 h and cooled in desiccators to minimize moisture content). The hydrolysis temperature was fixed at 120°C. The hydrolysis

mixture was refluxed for 13 h. A 0.5 mL portion of the clear hydrolyte solution from the reaction mixture was transferred into a vial and 2.0 mL of deionized water was added. To this solution were added 2.0 mL of DNS reagent and 2.0 mL of 2.0 N NaOH and the mixture was incubated in a water bath maintained at 90°C for 5 min [14, 15]. The DNS reagent was prepared according to IUPAC method [16]. The reagent blank sample was prepared with 2.0 mL of deionized water, 2.0 mL of DNS reagent, and 2.0 mL of 2.0 N NaOH and heated similarly to the other samples. Then the absorbance was measured at 540 nm, against the reagent blank, and glucose concentrations in the solutions were estimated by employing a standard curve prepared using glucose. The catalytic activity with different mass of catalyst (50, 100, 150, 200, and 500 mg), different temperatures (100, 110, and 120°C), different solvents, (i.e., 1-butanol, cyclohexanol, and cyclopentanone), and different solvent salt mixtures (LiCl, NaCl, and KCl) was studied by using the same procedure as described above.

2.6.2. The Reusability of the Catalyst. Reusability experiments were conducted by running the hydrolysis successively with the same catalyst under the same hydrolysis conditions. The hydrolysis was first run with the fresh catalyst to complete conversion and then the catalyst was filtered and washed with hot dioxane and then with a hot mixture of DMF and LiCl and dried at 130°C. After regeneration, the catalysts were reused under the optimised reaction conditions.

2.6.3. Hydrolysis Procedure for Homogenous Catalyst. The hydrolysis using the homogenous catalyst was studied with ammonium sulphate. Typically, a 50 mL capacity two-necked round-bottom flask, equipped with a magnetic stirrer (700 rpm) and water condenser, was used. 20 mL of DMF was transferred by pipette into the round bottom flask containing 4.6 mmol of ammonium sulphate. After the reaction temperature reached 120°C, 0.18 g of cellulose was added. The hydrolysis mixture was refluxed. Samples for analysis (~0.50 mL) were withdrawn at regular intervals from the hydrolysis mixture by means of a syringe equipped with filter (cotton wool). To this solution 2.0 mL of DNS reagent and 2.0 mL of 2.0 N NaOH were added and the mixture was incubated in a water bath maintained at 90°C for 5 min. The glucose concentrations in solutions were calculated by employing a standard curve prepared using glucose.

2.7. Sample Characterization. The prepared $\text{RHNH}_3\text{SO}_4\text{H}$ was characterized by elemental analysis (Perkin Elmer Series II, 2400), thermogravimetric analyses (TGA SDTA851^e), from 30 to 900°C at a heating rate of 20°C min⁻¹ under nitrogen flow. Powder X-ray diffraction (Siemens Diffractometer D5000, Kristalloflex), nitrogen adsorption porosimetry (Automatic Physisorption Autosorb-1 CLP, Quantachrome, USA), FT-IR spectroscopy (Perkin-Elmer System 2000), scanning electron microscopy (SEM) (Leica Cambridge S360), and energy dispersive spectrometry, EDX (Edax Falcon System), were all used as well. The TEM micrographs were obtained using Philips CM12 equipment.

TABLE 1: The chemical analysis of RHA, RHAPrNH₂, and RHNH₃SO₄H using a combination of elemental and EDX analysis.

Sample	Elemental analysis (%)				
	C	H	N	S	Si
RHA	0.42 (6.76)	1.76	—	—	(29.09)
RHAPrNH ₂ [7]	9.67 (19.52)	2.31	6.08 (6.1)	—	(23.48)
RHNH ₃ SO ₄ H	10.07 (20.79)	2.99	2.20 (3.43)	— (3.52)	(23.45)

3. Results and Discussion

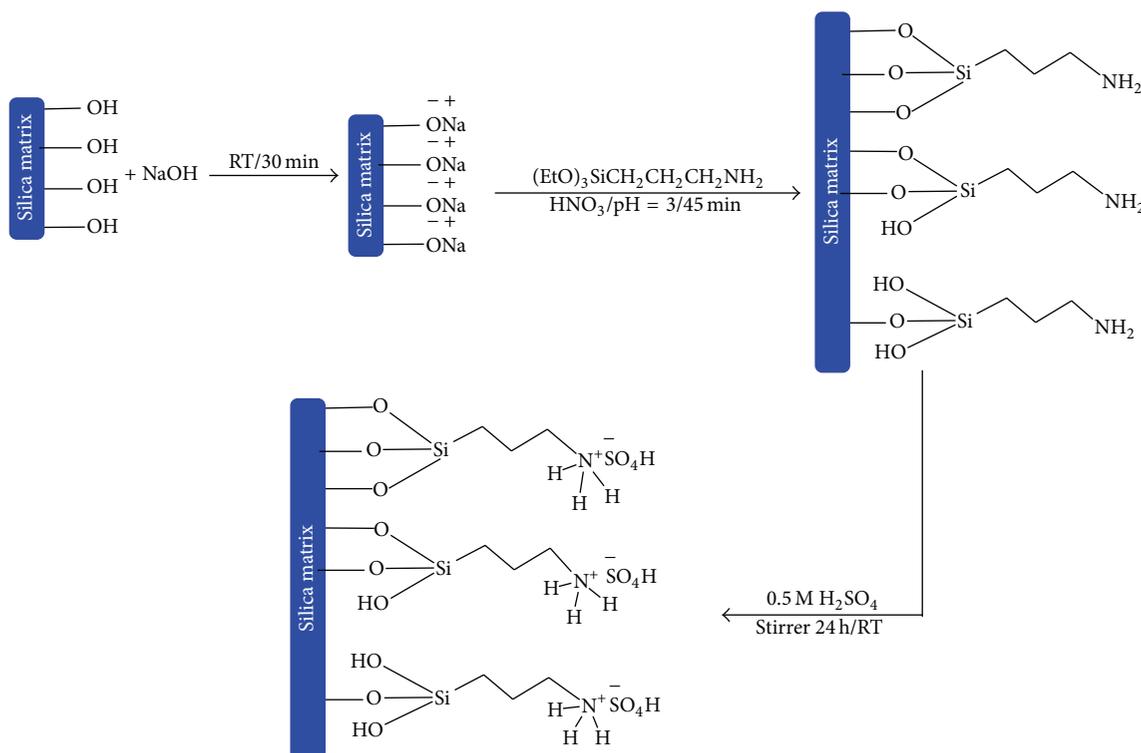
The amine group (-NH₂) in the RHAPrNH₂ was sulphated with sulphuric acid via a simple procedure at room temperature to produce a novel microstructure acidic catalyst RHNH₃SO₄H. The schematic representation for the synthesis of RHNH₃SO₄H is shown in Scheme 1.

3.1. CHN Analysis. Table 1 shows the chemical analysis of RHA, RHAPrNH₂ [7], and RHNH₃SO₄H. The analysis was carried out by a combination of elemental and EDX methods (presented between brackets). The combined analyses show that sulphur and nitrogen are exhibited in RHNH₃SO₄H, while only nitrogen is found in RHAPrNH₂. None of these elements were found in RHA, as was expected. The relative concentration values for silicon were much lower than in the starting RHA, which shows that a successful incorporation or attachment of new elements to the silica matrix has taken place.

3.2. Infrared Spectroscopy Analysis. Figure 1 shows the FT-IR spectra of RHAPrNH₂, RHNH₃SO₄H, and its difference spectrum. The strong and broad band in the range 3500–3400 cm⁻¹ region corresponds to the hydrogen bonded Si-OH groups. The RHAPrNH₂ and the difference spectra show bands at 3153 cm⁻¹ corresponding to the free NH₂ [17] and a weak band at 2939 cm⁻¹ corresponding to the aliphatic C-H stretching. The strong band at 1384 cm⁻¹ is related to the NO₃⁻ ions. The RHAPrNH₂ treated with H₂SO₄ showed some changes on the FT-IR spectrum. The band at 3153 cm⁻¹ (corresponding to the free NH₂) disappeared. This indicates the successful transformation of -NH₂ group to -NH₃ group. However, we also observe the disappearance of the strong band at 1384 cm⁻¹ (for nitrate ion), which may be due to a replacement by -SO₄H ions. This fact was confirmed by appearance of two bands at 1308 and 1162 cm⁻¹, assigned to the presence of the SO₂ group which is the main component of -SO₄H group [9].

The RHA spectrum (not shown) does not show these bands. In RHA the Si-O-Si vibration appears at 1082 cm⁻¹. This band was observed to shift to 1067, 1054 cm⁻¹ in RHAPrNH₂ and RHNH₃SO₄H, respectively.

3.3. Powder X-Ray Diffraction (XRD) and Nitrogen Adsorption Analysis. The XRD pattern (not shown) did not show sharp diffraction patterns. This is an indication that the sample is



SCHEME 1: The reaction sequence and the possible structures for RHAPrNH_2 and $\text{RHNH}_3\text{SO}_4\text{H}$. The approximate times taken for the completion of the experimental process are also shown. The whole process of dissolution and immobilization was done at room temperature (RT).

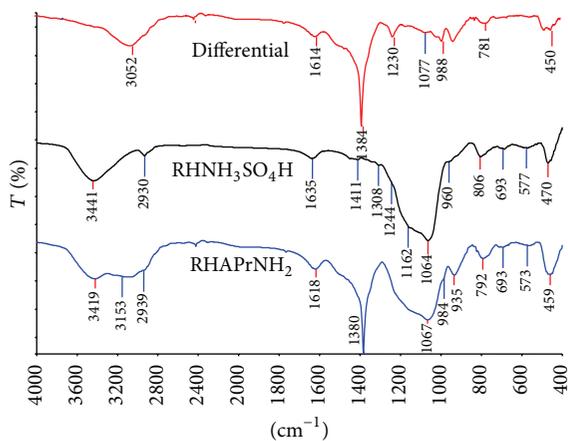


FIGURE 1: The FT-IR spectra of RHAPrNH_2 , $\text{RHNH}_3\text{SO}_4\text{H}$, and the difference spectrum.

amorphous. A broad diffraction band at 2θ angle of ca. 22° was observed which is typical for amorphous silica.

Figure 2 shows the nitrogen adsorption isotherm obtained for $\text{RHNH}_3\text{SO}_4\text{H}$ and inset is shown in the pore size distribution graph. The hysteresis loop observed in the range of $0.4 < P/P_0 < 1.0$ is associated with capillary condensation according to the IUPAC classification. The isotherm shown is type IV and exhibited an H3 hysteresis loop [19].

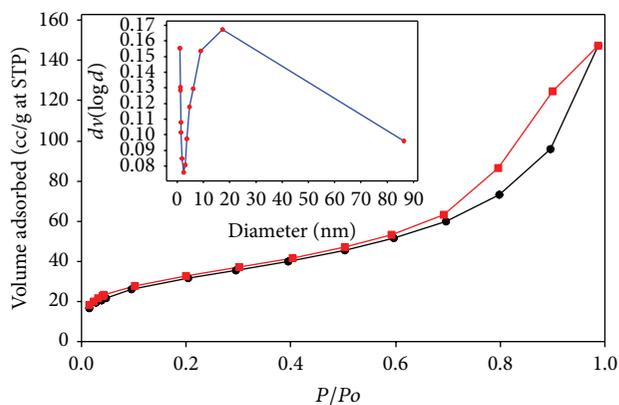


FIGURE 2: The N_2 adsorption/desorption isotherms of $\text{RHNH}_3\text{SO}_4\text{H}$ with the corresponding pore size distribution graph.

The BET analysis showed a specific surface area of $\text{RHNH}_3\text{SO}_4\text{H}$ was $113 \text{ m}^2 \text{ g}^{-1}$, while the specific surface area of RHAPrNH_2 was reported to be $1.32 \text{ m}^2 \text{ g}^{-1}$ [7]. The increase in the surface area of $\text{RHNH}_3\text{SO}_4\text{H}$ could be due to the use of H_2SO_4 , which may remove the entire nitrate ion (as it is shown in FT-IR) and reduce the crowding on the surface and thus lead to opening the pores. The $\text{RHNH}_3\text{SO}_4\text{H}$ (Figure 2) showed a broad pore size range from 5 to 90 nm with an average pore volume of 0.22 cc g^{-1} , which is in the mesoporous range.

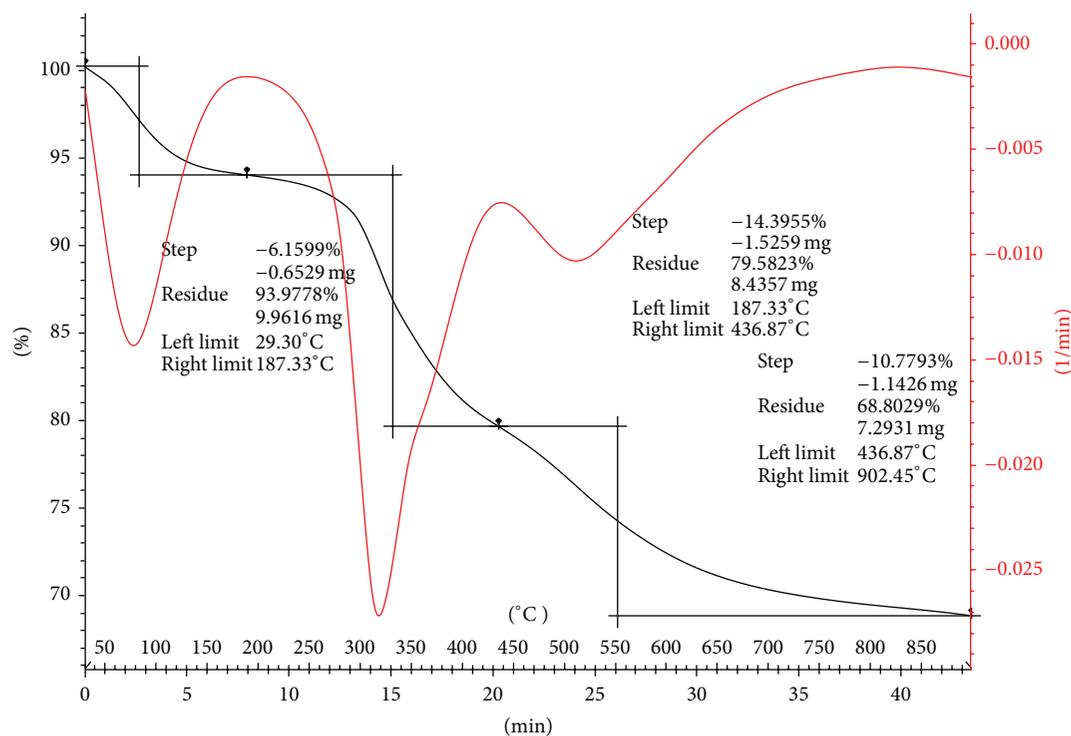


FIGURE 3: Thermogravimetric analysis (TGA)/differential thermal analysis (DTA) curves of RHNH₃SO₄H.

3.4. Thermogravimetric Analysis (TGA)/Differential Thermal Analysis (DTA). Figure 3 shows the TGA-DTA of RHNH₃SO₄H. The graph shows four characteristic decomposition stages. The first weight loss (ca. 6.2%) is due to the loss of adsorbed water, and the second mass loss (ca. 14.4%) is due to the decomposition of the aminopropyl sulphate groups anchored to the silica. According to this mass loss we found that 0.046 mmol/g of aminopropyl sulphate had been loaded onto RHNH₃SO₄H. This value was in agreement with our previous study with other ligands [20]. The slow, continuous weight loss (ca. 10.8%) was due to the condensation of silanol groups at higher temperatures.

In the DTA curve in Figure 3 three exothermic transformations were observed. The first peak occurs between 29 and 187°C, with a maximum at 75°C, the second occurs between 187 and 436°C, with a maximum at 330°C, and the third occurs between 436 and 902°C with a maximum at 520°C. The first exothermic change is due to the loss of adsorbed water, while the second and third are attributed to the arrangement of the structure of the polymer [21].

3.5. The SEM and TEM Analysis. The SEM micrographs at different magnifications are shown in Figure 4. These show the presence of a porous surface. The porosity is directly linked to the high specific surface area determined by the nitrogen adsorption studies. However, the SEM shows small particles with a bright, smooth surface. The smoothness of these particles is emphasized at the higher magnifications. These SEM micrographs are probably in good agreement with the BET analysis with regard to the specific surface area and specific pore volumes.

The TEM micrographs at different magnifications are shown in Figure 5. The RHNH₃SO₄H has rod-like morphology, and the diameters of the microrods are in the range of 0.1 μm to 0.26 μm and the length is about several millimetres.

3.6. Pyridine Adsorption Studies. The pyridine adsorption study of RHNH₃SO₄H obtained before and after pyridine adsorption in the region of 1700–1400 cm⁻¹ (as shown in Sup. 1 in the Supplementary Material available online at <http://dx.doi.org/10.1155/2014/128547>). By comparing the two FT-IR spectra, after and before the pyridine test, two new bands in the regions 1544 cm⁻¹ and 1489 cm⁻¹ have been observed. These two bands indicate the presence of Brønsted acid sites [22].

3.7. Hydrolysis of Cellulose over RHNH₃SO₄H Catalyst. The RHNH₃SO₄H was used to hydrolyze cellulose in a liquid-phase reaction. Various parameters were evaluated to optimize the hydrolysis conditions on the fully completed cellulose hydrolysis, such as the effect of hydrolysis time, mass of catalyst, temperature, solvent effects, and salt effects.

3.7.1. Influence of Hydrolysis Time. The effect of the hydrolysis time on the hydrolysis of cellulose to glucose over RHNH₃SO₄H and homogenous ammonium sulphate (NH₄)₂SO₄ [18] is shown in Figure 6. The hydrolysis was carried out with 150 mg catalyst using a DMF/LiCl as a solvent at 120°C. The initial hydrolysis of cellulose to glucose during the first hour was 65% and it reached the maximum hydrolysis of 98% in 6 h. The homogeneous ammonium

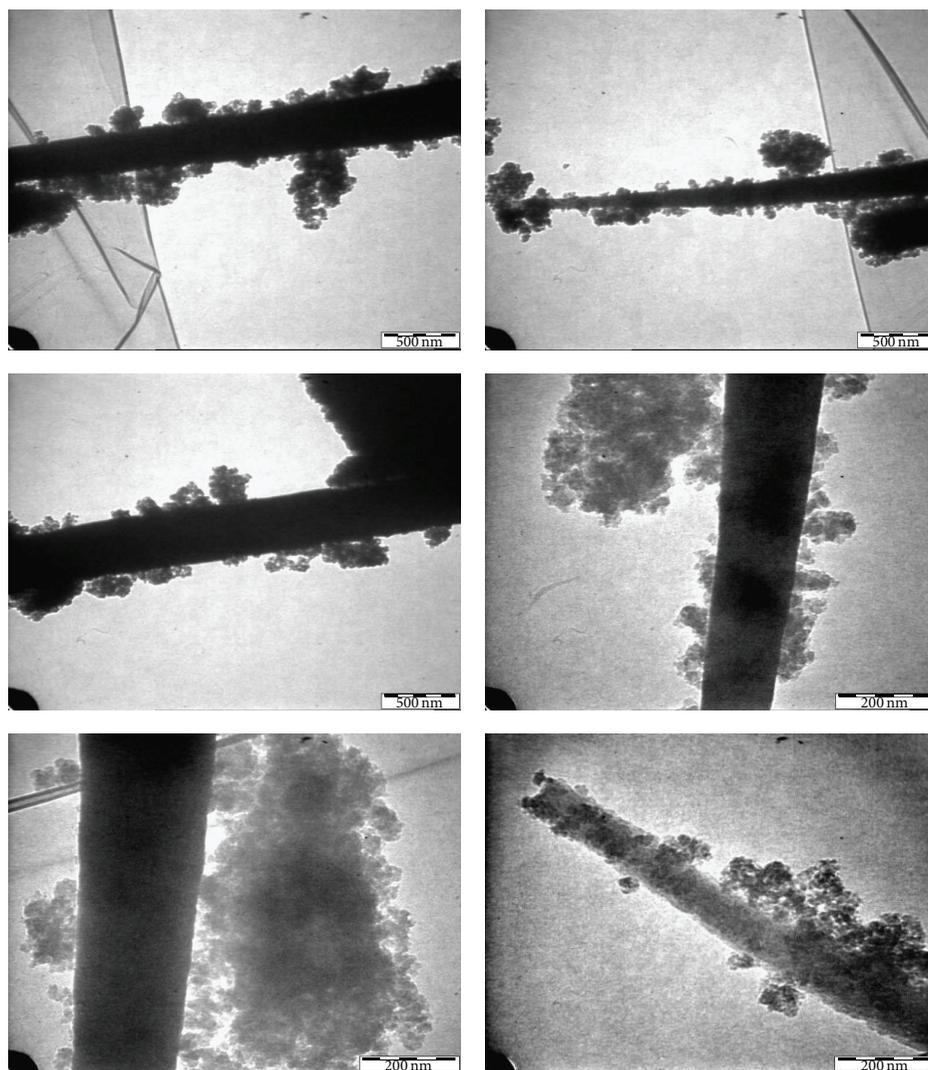


FIGURE 5: The TEM images of $\text{RHNH}_3\text{SO}_4\text{H}$, at different magnification.

TABLE 2: The effect of different parameters on the hydrolysis of cellulose with $\text{RHNH}_3\text{SO}_4\text{H}$.

Parameters	Variants	Glucose yield (mM %)	
		at 6 h	at 13 h
Variation of cellulose hydrolysis from different sources	Pure cellulose	98	10
	Cellulose from paper	94	11
	Cellulose from rice husk	93	18
Variation of metal chloride	LiCl	98	10
	NaCl	91	9
	KCl	90	13
Variation of solvent effects in LiCl	DMF	98	11
	Cyclohexanol	98	10
	Cyclopentanone	91	15
	1-Butanol	89	18
Reusability of catalyst with 150 mg	Fresh catalyst	98	10
	1st reuse	93	11
	2nd reuse	93	13

The reaction was run over 13 hours at 120°C of hydrolysis temperature and 150 mg of catalyst mass.

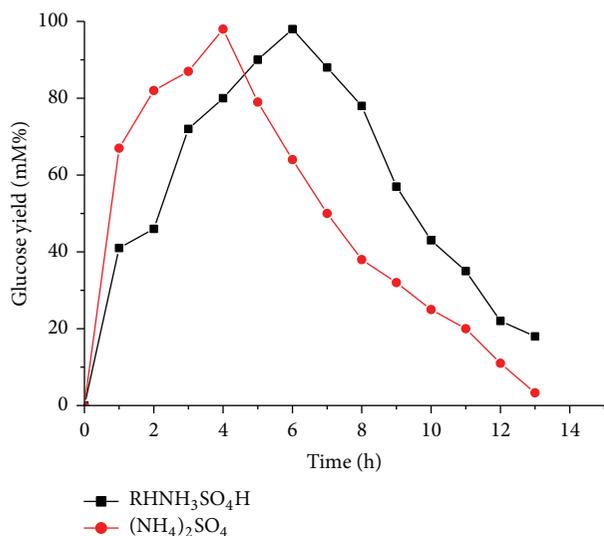


FIGURE 6: The hydrolysis of cellulose over RHNH₃SO₄H and (NH₄)₂SO₄ catalysts as a function of hydrolysis time. The hydrolysis conditions were the catalyst mass 150 mg of RHNH₃SO₄H, 4.6 mmol of (NH₄)₂SO₄ [18], at 120°C.

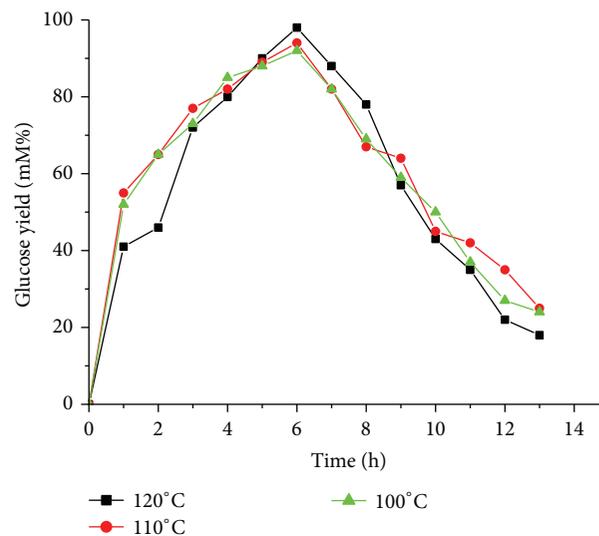


FIGURE 8: The hydrolysis of cellulose over RHNH₃SO₄H, at different temperatures. The hydrolysis conditions were catalyst 150 mg and 13 h as a hydrolysis time.

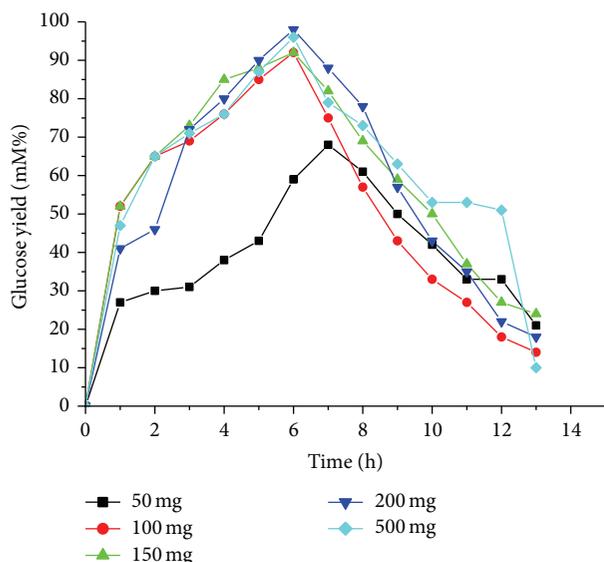


FIGURE 7: The hydrolysis of cellulose over RHNH₃SO₄H, as a catalyst mass function. The hydrolysis conditions were 13 h hydrolysis time at 120°C.

over these metal chlorides was increased according to the following order:



The chloride ion is playing a vital role in the solubility of cellulose. The metal ions are tightly linked with the carbonyl group of DMF while the chloride ions are left unencumbered. Thereby Cl⁻ is highly active as a nucleophilic base and plays a major role by breaking up the inter- and intrahydrogen bonds [23]. This could make the hydrolysis of cellulose much easier.

3.7.5. *Catalyst Experiments on Cellulose from Different Sources.* The effect of RHNH₃SO₄H on the cellulose extracted from different sources (waste of rice husk and waste office paper) is shown in Table 2. The run was done under the optimum conditions of the catalyst which were 150 mg catalyst mass, reaction temperature of 120°C, and 6 h reaction time. It was observed that the hydrolysis of the extracted cellulose from waste of RH was 93%, while the hydrolysis of cellulose extracted from waste paper was 94%. This clearly indicates that the catalyst was very active for the hydrolysis of cellulose from any sources.

3.7.6. *Catalyst Recycle Experiments.* Table 2 shows the RHNH₃SO₄H recycle experiments. After the first reaction was run using the catalyst at 120°C for 13 h, the mixture, including the solid catalyst and the cellulose residue, was then filtered and washed with hot cyclohexanol and then with hot mixture of DMF and LiCl (repeated three times), and finally the catalyst was heated at 130°C for 24 h. Next, fresh cellulose and DMF with LiCl were added to the catalyst obtained and a second run was conducted using the same procedure. As shown in Table 2, the product yield in the second run was similar to that in the first run, without any loss in the catalytic activity during the first 6 h of the hydrolysis. After the 6 h of the hydrolysis time a decrease in the cellulose hydrolysis was observed due to the hydrolysis of glucose to other products. These results indicated that catalytic performance was not lost in the course of the catalytic runs.

4. Conclusion

APTES was reacted with sodium silicate by following a purely homogenous route to form RHAPrNH₂ which converted to the solid ammonium sulphate-like structure. According to

the BET result the $\text{RHNH}_3\text{SO}_4\text{H}$ had a $113 \text{ m}^2 \text{ g}^{-1}$ specific surface area. The FT-IR clearly showed the presence of $-\text{SO}_2-$ absorption bands at the expected range. The TEM shows that the $\text{RHNH}_3\text{SO}_4\text{H}$ forms with a rod-like morphology. The diameters of the microrods are in the range of $0.1 \mu\text{m}$ to $0.26 \mu\text{m}$. The $\text{RHNH}_3\text{SO}_4\text{H}$ was used to fully hydrolyze cellulose to other products at 120°C for 13 h. The catalytic activity of the catalyst reaches the 98% of the glucose from cellulose and the selectivity was 100% at 6 h, after the hydrolysis continues to form other products for up to 13 h. The catalyst is simple to prepare and stable during the hydrolysis, and it can be used several times without significant loss of its catalytic activity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors would like to thank Department of Chemistry, College of Science, Al-Muthanna University for partly supporting this work.

References

- [1] F. Adam, H. E. Hassan, and K. M. Hello, "The synthesis of N-heterocyclic carbene-silica nano-particles and its catalytic activity in the cyclization of glycerol," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 43, no. 4, pp. 619–630, 2012.
- [2] F. Adam, K. M. Hello, and M. R. Ben Aisha, "The synthesis of heterogeneous 7-amino-1-naphthalene sulfonic acid immobilized silica nano particles and its catalytic activity," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 42, no. 5, pp. 843–851, 2011.
- [3] H. P. Wang, K. S. Lin, Y. J. Huang, M. C. Li, and L. K. Tsaor, "Synthesis of zeolite ZSM-48 from rice husk ash," *Journal of Hazardous Materials*, vol. 58, no. 1–3, pp. 147–152, 1998.
- [4] D. Hoegaerts, B. F. Sels, D. E. de Vos, F. Verpoort, and P. A. Jacobs, "Heterogeneous tungsten-based catalysts for the epoxidation of bulky olefins," *Catalysis Today*, vol. 60, no. 3, pp. 209–218, 2000.
- [5] D. J. Macquarrie, "Direct preparation of organically modified MCM-type materials. Preparation and characterisation of aminopropyl-MCM and 2-cyanoethyl-MCM," *Chemical Communications*, no. 16, pp. 1961–1962, 1996.
- [6] D. Brunel, "Functionalized micelle-templated silicas (MTS) and their use as catalysts for fine chemicals," *Microporous and Mesoporous Materials*, vol. 27, no. 2–3, pp. 329–344, 1999.
- [7] F. Adam, K. M. Hello, and H. Osman, "Synthesis of mesoporous silica immobilized with 3-[(Mercapto or amino)propyl] trialkoxysilane by a simple one-pot reaction," *Chinese Journal of Chemistry*, vol. 28, no. 12, pp. 2383–2388, 2010.
- [8] K. M. Hello, *The heterogenation os saccharin, melamine, and sulfonic acid onto rice husk ash silica and their catalytic activity in esterification reaction [Ph.D. thesis]*, University Sains Malaysia, 2010.
- [9] K. M. Hello, H. R. Hasan, M. H. Sauodi, and P. Morgen, "Cellulose hydrolysis over silica modified with chlorosulphonic acid in one pot synthesis," *Applied Catalysis A: General*, vol. 475, pp. 226–234, 2014.
- [10] N. Andersen, *Enzymatic hydrolysis of cellulose: experimental and modeling studies [PhD thesis]*, The Technical University of Denmark, Lyngby, Denmark, 2007.
- [11] F. Adam and J.-H. Chua, "The adsorption of palmytic acid on rice husk ash chemically modified with Al(III) ion using the sol-gel technique," *Journal of Colloid and Interface Science*, vol. 280, no. 1, pp. 55–61, 2004.
- [12] A. E. Ahmed and F. Adam, "Indium incorporated silica from rice husk and its catalytic activity," *Microporous and Mesoporous Materials*, vol. 103, no. 1–3, pp. 284–295, 2007.
- [13] H. R. Hasan and M. H. Sauodi, "Novel method for extraction of cellulose from agricultural and industrial wastes," *Indian Journal of Chemical Technology*, vol. 9, no. 1, 2014.
- [14] A. S. Amarasekara and B. Wiredu, "Aryl sulfonic acid catalyzed hydrolysis of cellulose in water," *Applied Catalysis A: General*, vol. 417–418, pp. 259–262, 2012.
- [15] C. Breuil and J. N. Saddler, "Comparison of the 3,5-dinitrosalicylic acid and Nelson-Somogyi methods of assaying for reducing sugars and determining cellulase activity," *Enzyme and Microbial Technology*, vol. 7, no. 7, pp. 327–332, 1985.
- [16] G. L. Miller, "Use of dinitrosalicylic acid reagent for determination of reducing sugar," *Analytical Chemistry*, vol. 31, no. 3, pp. 426–428, 1959.
- [17] M. Mureseanu, A. Reiss, I. Stefanescu et al., "Modified SBA-15 mesoporous silica for heavy metal ions remediation," *Chemosphere*, vol. 73, no. 9, pp. 1499–1504, 2008.
- [18] K. M. Hello, "Extraction of cellulose from waste palm fronds and its hydrolysis to glucose," *Indian Journal of Chemical Technology*. In press.
- [19] M. Thommes, "Physical adsorption characterization of nanoporous materials," *Chemie-Ingenieur-Technik*, vol. 82, no. 7, pp. 1059–1073, 2010.
- [20] F. Adam, K. M. Hello, and H. Osman, "The heterogenation of melamine and its catalytic activity," *Applied Catalysis A*, vol. 382, no. 1, pp. 115–121, 2010.
- [21] E. J. Nassar, C. R. Neri, P. S. Calefi, and O. A. Serra, "Functionalized silica synthesized by sol-gel process," *Journal of Non-Crystalline Solids*, vol. 247, pp. 124–128, 1999.
- [22] V. Luca, L. Kevan, C. N. Rhodes, and D. R. Brown, "A synthetic Zn-substituted smectite clay alkylation catalyst," *Clays and Clay Minerals*, vol. 27, pp. 515–519, 1992.
- [23] A.-L. Dupont, "Cellulose in lithium chloride/*N,N*-dimethylacetamide, optimisation of a dissolution method using paper substrates and stability of the solutions," *Polymer*, vol. 44, no. 15, pp. 4117–4126, 2003.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

