Solid Sulfamic acid Catalyst for Glucose Production

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Abstract Silica from rice husk ash was immobilized with sulfamic acid to form strong solid acid catalyst labeled as RHANS (RH = Rice Husk). The spectroscopic evidence confirms that the sulfamic acid was heterogenized onto silica. The XPS with the elemental analysis shows the presence of C, N, S, O, and Si onto RHANS. The FT-IR spectra supported both XPS and elemental analysis via showing the presence of NH₂, SO₂, CH₂, and Si-O-Si functional groups which include the elements showing by XPS and elemental analysis. The RHANS had 139 m² g⁻¹ as a specific surface area with thermal stability reached to 252°C according to the TGA. The AFM, TEM and SEM showed that the RHANS had nano shape. The RHANS was efficient catalyst for cellulose hydrolysis to glucose. Approximately 96% of glucose was formed within 2 h at 140 °C over RHANS. The repeatable catalyst was stable during the cellulose hydrolysis without a significant loss of its catalytic activity.

Key words: Sulfamic acid, Cellulose, Rice husk.

1. Introduction

Rice husk (RH) is an agriculture waste and able to recycling [1]. Rice is grown in over 75 countries [2]. The amounts of rice production globally were found to be 400– 545 million metric tons, and the husk is less than 11% [3, 4, 5]. The husk had high continent about 20% of silica [6], which make this free raw material economically valuable for recycling in different areas of chemistry as similar to commercial silica [7]. Burning the RH causes environmental pollution. Therefore, efforts have been made to burn the husks under moderated temperature and pressure. When RH burnt, a white ash which is porous silica with high specific surface area can be obtained [8]. This ash (RHA) contains more than 95 % of silica.

Cellulose is the most abundant and renewable carbon source. Cellulose hydrolysis was constitutes a large fraction of the lignocellulosic materials i.e. glucose and ethanol [9]. Cellulose hydrolysis was studied through various processes catalyzed by enzymes or chemical processes in order to obtain valuable compounds like soluble sugars [10,11,12], lactic acid [13] or 5-hydroxymethylfurfural (5-HMF) [14] among others. The type of the catalyst, reaction medium, and the reactions conditions were the most important factor which controls the conversion of cellulose into other products [15]. In our previous study cellulose was hydrolysis to glucose in 13 h at 140 °C with 82 % yelled when silica immobilized with Salicylaldehyde Phenylhydrazone and used as a catalyst [16]. The hydrolysis was reached to 99 % in 8h at 120 °C when the hydrolysis catalyzed by Si-SO₃H [12]. Later the time was reduced to be 6 h over Si-(CH₂)₃NH₂SO₄H with high yelled of glucose [11].
In this study the hydrolysis time was reduced to be only 2 h with high yield of glucose. The silica from rice husk ash was fabricated with sulfamic acid in sol-gel technique.

2. Materials and Methods

2.1 Raw materials and chemicals

All chemicals were directly used without further purification. The rice husk was collected from a rice mill in Samawah governorate, Iraq. The chemicals used in this study were sodium hydroxide (Systerm, 99%), 3-(chloropropyl)triethoxysilane (CPTES) (Sigma, 98%), nitric acid (Scharlau, 65%), toluene (Fluka, 99%), cellulose (Riedle-De Haen, 99%), glucose (BDH, 99%), cyclohexanol (Riedle-De Haen, 99%), dimethylformamide (DMF) (Systerm, 99%), dinitrosalicylic acid (DNS) (BDH, 99%), lithium chloride (Sigma, 99%), sulfamic acid (Fluka, 99%).

2.2 Preparation of silica – sulfamic acid catalyst

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 [17]. The silica was immobilized with CPTES according to the method published elsewhere [17] and the product was labelled as RHACCl. The sulfamic acid (2.45 g, 25.3 mmol) was adding to the mixture of RHACCl (2.0 g) in 30.0 mL of dry toluene and tri ethylamine (Et₃N) (2.56 mL, 25.3 mmol). The reaction mixture was refluxed in an oil bath at 110 °C for 24 h. The solid was filtered and then was washed first with distilled water, after that with DMF, and then dried at 100 °C for 24 h. Finally, the dried product was ground to produce a fine powder and was labelled as RHANS. About 1.75 g of was collected by using this method.

2.3 Hydrolysis of cellulose over RHANS

The cellulose hydrolysis was carried out in liquid phase reaction using in a 100 mL three necked round bottom flask equipped with magnetic stirrer and a water condenser. About 30 mL of DMF, 0.18 g cellulose, and 0.2 g LiCl were separately transferred to the round bottom flask containing 0.20 g of RHANS catalyst (pre dried at 110 °C for 24 h and cooled in a desiccator to minimize moisture content). The hydrolysis temperature was fixed at 140 °C and the hydrolysis mixture was refluxed for 24 h. In order to estimate the concentration of the produced glucose from cellulose hydrolysis, 3,5-dinitrosalicylic acid (DNS) method was used [18]. The amount of 3-amino-5-nitrosalicylic acid formed is proportional to the amount of glucose yielded at visible wave length 540 nm. The DNS reagent was prepared according to IUPAC method [18]. The reagent blank sample wa[]s prepared with 2.0 mL of deionized water and 2.0 mL of DNS reagent and heated similarly to reaction samples. 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 and 200 mg), different temperatures (120, 130, and 140 °C), and different solvents, (toluene, 1,4-dioxane, cyclohexanol, and distill water) was studied by using the same procedure as described above.

2.4 The reusability of the catalysts

Reusability experiment was conducted by running the reaction successively with the catalyst under the same hydrolysis condition. The hydrolysis was first run with the fresh catalyst to complete hydrolysis and the catalyst was filtered and washed with a hot mixture of DMF and LiCl and dried at 110 °C. After regeneration, the catalysts were reused under the optimized hydrolysis conditions.

2.5 Hydrolysis procedure for Homogeneous Catalysts

Hydrolysis cellulose using homogeneous sulfamic acid catalyst was studied. 20 mL of DMF was transferred by pipette into the round bottom flask containing, 22.7 mg sulfamic acid. The
amount of sulfamic acid which was equivalently to that loaded onto silica was calculated by using TGA results. After the hydrolysis temperature reached 140 °C, 0.18 g of cellulose was added. The hydrolysis mixture was refluxed for 7 h. 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) and the produced glucose concentrations in the solutions were determined by using a standard curve as method described in above.

2.6 Sample characterization

The RHANS was characterized by elemental analysis (Perkin Elmer Series II, 2400). Thermogravimetric analysis (TGA/DSC) was performed using a ASAP 20 automatic chemisorptions analyzer. Powder X-ray diffraction pattern was performed using Siemens Diffract meter D5000 and also XRD-6000, Shimadzu. The FT-IR spectroscopy was recorded by Schimadzo-8400S. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDX) was performed using (Em 3200, company kyky). The Atomic force microscopy (AFM) was obtained using (CSPM-AA30000). The TEM micrographs were obtained using Philips CM12 instrument (Germany).

XPS was performed in a SPECS system, including a Phoibos 100 analyzer. The samples were in the form of a white small size grained powder. This powder was deposited on the top surface of a double sided sticky carbon tape attached to a stainless steel sample holder. The deposited powder was uniformly covering the carbon tape and inserted in the vacuum system and pumped down to 3 × 10−10 Torr overnight. XPS spectra were recorded with Mg Kalpha and Al Kalpha radiation, and the spectra were compared to discriminate between Auger and photoemission peaks. A wide scan spectrum covering a wide range of binding (and kinetic) energies, recorded with Al Kalpha radiation, and a resolution of around 2.5 eV, for monitoring the concentration of the elements in the sample, and a detailed scan with a resolution of 1.4 eV, which serves to detect chemical shifts and to separate overlapping peaks. The resolution for the survey scans was 2.5 eV. Element peaks were identified with the Casa XPS software.

3. Results and Discussion

3.1 The synthesis and characterization of catalyst RHANS

RHANS (RH = rice husk) nano catalyst has been prepared via heterogeneous, reaction between RHACCl in a solid phase and sulfamic acid. A nucleophilic substitution has been occurred between the amine groups onto sulfamic acid with the chlorine end group of RHACCl. The Et3N was used as a deprotonating agent and to remove the HCl liberated as a salt, in order to increase the efficiency of the reaction, yielding the products as shown in Scheme 1.

Scheme 1: The reaction sequence and the possible structure for RHANS. The reaction time and condition were shown
3.1.1 CHNS and Nitrogen adsorption analysis

The percentage of elements content determined by elemental analysis and EDX analysis were shown in table 1. The elemental analysis of RHACCl showed that the percentages of C and H were 11.70 and 1.90%, respectively [17]. RHANS showed 2.07 % of nitrogen composition and 3.11% of sulfur. The C content of RHANS 21.17% was slightly higher than RHACCl, which was expected. The EDX analysis also showed 3.4 % of nitrogen and 4.6 % of sulfur in RHANS, from which it can further conclude that the sulfamic acid was incorporated onto silica. It was calculated the percentage loading of sulfamic acid onto the silica beside the amount of chloride before and after the immobilization of sulfamic acid onto silica and found to be 42.34%.

The specific surface area of RHANS was found to be 139.6 m² g⁻¹, while the specific surface area of RHACCl was 633 m² g⁻¹. The decrease in the specific surface area could be due to the successful immobilization of the sulfamic acid onto silica surface.

Table 1: The percentage of elements content determined by elemental analysis and EDX analysis. The result of BET analysis was also shown in brackets.

| sample  | C (%)  | Si (%) | Cl (%) | S (%) | N (%) | Specific Surface area (m² g⁻¹) |
|---------|--------|--------|--------|-------|-------|-----------------------------|
| RHA [17]| 0.84   | _      | _      | _     | _     | 347                         |
|         | (6.76) | (29.09)| _      | _     | _     |                             |
| RHACCl [17]| 11.70 |        | _      | _     | _     | 633                         |
|         | (23.93)| _      | (3.07) | _     | _     |                             |
| RHANS   | 21.17  | (23.42)| _      | 3.11  | 2.07  | 139.63                      |
|         | (27)   | (1.3)  | (4.6)  | (3.4) |       |                             |

3. 1. 2 Powder X-ray diffraction pattern (XRD)

The XRD diffraction pattern of RHASN (not shown), showed the presence of a broad band in 2θ angle of ca. 22° which indicated that the catalyst has amorphous beaver.

3. 1. 3 Fourier transformed infrared spectroscopy

The FT-IR spectra of RHACCl and RHANS were shown in Fig.1. The FT-IR spectrum of RHA had been described previously by Ahmed and Adam [19]. From the FT-IR spectrum of RHASN (Fig.1b) the absorption band of Si-O-Si group was shown at 1195cm⁻¹. This absorption band was shifted compared with the absorption band of RHACCl (Fig. 1a) which shown at 1087 cm⁻¹. The broad bond around 3604 cm⁻¹ and 3554cm⁻¹ are assigned to the O–H vibration from Si–O–H and HO–H of adsorbed water [16]. In RHANS spectrum the band at 3385 cm⁻¹ was due to the presence of N–H group. The methylene C–H stretching band was observed at 2952 cm⁻¹ and 2495 cm⁻¹ [20]. The band around 1635 cm⁻¹ which is appearing at the 1635 cm⁻¹ was assigned to the H–O–H bending. The weak band at 1429-1442 cm⁻¹ could attribute to the stretching methylene group adjacent to the NH group [20]. The band observed at 1228 cm⁻¹ was assigned to the stretching or Si–C bond. The symmetrical and asymmetrical vibrations of O=S=O were observed at frequency 1195 cm⁻¹ and 1348 cm⁻¹ respectively. The appearance of vibrations due to N-H and SO₂ groups indicate the successful incorporation of the sulfamic acid with the RHACCl, forming the new catalyst, RHANS.
3.1.4 Atomic force microscopy (AFM)

The AFM images technique was used to characterize the topographical and morphological on the RHANS surfaces. Fig. 2(a and b) shows the AFM of RHANS where a relative layer surface with a mean value of occasional peaks of 77.45 nm average diameter were observed. From these images RHANS has an average particle size in the range of 60-100 nm was shown in the chart granularity normal distribution (Fig. 2 (b)). The observed relative layer surface with a value of surface roughness (Rq) was 1.01 nm and occasional peaks of 46.95 nm average diameter (not shown). The granularity accumulation distribution chart (Fig.2(c)) the chart shows the distribution of the particles size. It was observed from the chart that the particles were distributed in the range of 30-60 nm. This indicates that most of the particles were in the nano size.
Fig. 3: (a) Three-dimensional AFM images for RHANS. (b) Granularity normal distribution chart of RHANS. (c) Granularity normal distribution chart of RHACCl3.

3.1.5 Electron micrographs (SEM and TEM)

The SEM results are shown in Fig. 3. The analyses showed a small degree of pore arrangement and in general supported the amorphous nature of the catalysts. Morphology of the catalyst was studied by TEM and a dark particle was observed. No significant shapes were observed in Fig. 4.

Fig. 4: The SEM images of RHANS at different magnification.
3.1.6 Thermo gravimetric analysis (TGA)/ Differential Scanning Calorimetry (DSC)

The thermo gravimetric analyses of RHANS shows in Fig. 5. The graph TGA/DSC of RHANS shows three characteristic decomposition stages. The first mass loss (ca. 2%) is due to the loss of adsorbed water. The second mass loss (ca. 47.%) is due to the decomposition of the N-propylsulfamic group anchored to the silica. According to this collective loss and found that 0.0047 mmol/g of propyl sulfamic may have been loaded on RHANS. Both these mass losses were not observed on the RHA (not shown). In the DSC curve in (Fig. 5), it was observed four exothermic transformations the first peak which occurs between 33 °C and 182 °C, with a maximum at 120°C. The first exothermic change is due to the loss of water adsorbed. The second mass loss occurs between 182 and 335 °C, with a maximum at 252°C. The third occurs between 335 and 425°C with a maximum at 342°C. The fourth occurs between 425 and up to 600 °C. The second and third are attributed to the arrangement of the structure of the polymer [32].

3.1.7. X-ray photoelectron spectra (XPS)

The photoelectron peaks of O 1s, Si 2p, S 2p, and N 1S of the catalyst are presented in Fig. 6. The Si 2p was presented at binding energy 104 and 106 eV (Fig.6 (a)). The binding energy at 103.7 eV was due to the presence of SiO2 (Si 2p) which was in agreement with the literature [21]. The peak at the 532.9 eV could be due to the Si–O–Si bond. The weak signal at binding energy of 532.1 and 533.7 eV might be related to the physical adsorbed water as seen in the TGA. While the C1s spectrum recorded from this sample as in Fig.6 (d). The binding energy of 285.4 eV was due to the C1s that represented of C–C or C–H. The spectrum consisted of the signal at the 289.7–292 eV that represented of C–N and this give evidence that the reaction between C-Cl and primary amine of sulfamic acid was took place. The peak at 400-403 eV related to the N 1s. From Fig.6 (a), it was found that the RHASN has S 2s with binding energy of 229 and 231 eV while S 2p has a binding energy in region of 165 –169 eV [22]. The XPS results imply that the sulfamic acid was immobilized onto RHACCl successfully.
Fig. 6: The thermo gravimetric analysis for RHANS.

Fig. 7: The XPS spectrum of RHANS. The Si, S, C, N and O content are shown. (a) A wide scan spectrum. (b) Narrow scan for Si 2p. (c) Narrow scan for O 1s. (d) Narrow scan for C 1s.
3.1.8 Cation exchange capacity (CEC)

The calculation of acids concentrations immobilized onto support was mostly done by base titration technique. In this work, NaOH as a basic probe compound was used. The concentrations of acid sites on the RHANS was determined in water, by exchanging with excess Na+ (from NaCl) followed by titration with a standard NaOH solution. The CEC was found to be 4.5 mmol/100g.

3.2 Hydrolysis of cellulose over RHANS Catalyst

The cellulose was hydrolyzed to glucose and then the glucose was hydrolysis to other products over RHANS. The glucose was deducted by using UV-Visible spectroscopy. The following subtitles were discussed the optimized conditions of the catalyst.

3.2.1 Influence of hydrolysis time

The effect of the time on the hydrolysis of cellulose to glucose over RHASN and homogenous sulfamic acid is shown in Fig. 8. The hydrolysis was carried out with 50 mg catalyst using a DMF as a solvent contain LiCl at 140 °C. The initial hydrolysis of cellulose during the first hour was 41 % then increased to a maximum of 96 % in 2 h. The homogeneous sulfamic acid (22.7 mg) also showed 58 % at 2 h and then the hydrolysis was decreased due to the hydrolysis of glucose itself to other products.

3.2.2. Effect of catalyst mass

In order to find the best mass required for high percentage of cellulose hydrolysis, the hydrolysis of cellulose was carried out by varying the amount of RHASN (ranged 50 and 200 mg) while keeping the other parameters constant as (2 h hydrolysis time at 140 °C and 0.18 g of cellulose). The results are shown in Table 2. It is clear from the table 2 when the catalyst mass was decreased from 200 to 50 mg, the cellulose hydrolysis increased from 63 % to 96%. The decrease in the hydrolysis with the increased amount of the catalyst probably is due of the closure of the active sites by increasing of mass catalyst and also, could be due to the increases on the hydrogen bonding between active sites itself which leads to lack of catalyst surface.

Fig.8: The conversion of cellulose to glucose using either RHANS (heterogeneous), Homogeneous sulfamic acid (22.7 mg) as a function of hydrolysis time.

3.2.3 Influence of hydrolysis temperature

The effect of the temperature on the cellulose hydrolysis over RHANS shows in Table2. The cellulose hydrolysis increased when the temperature increased from room temperature to 140 °C. The results from this study were compared with other results to show the activity of the catalyst. The maximum glucose yields at 100°C were found to be 80% after 8 h, when SO₃H-functionalized silica
used as a catalyst [22]. Other study [12] was showed that the cellulose hydrolysis could reached to 92% at 100°C and 98% at 120°C in 6 h when catalyst prepared from rice husk was used. In this work the glucose yield reaches ≈ 75 at 120 °C and 96% at 140 °C in 2 h over RHANS catalyst. This clearly indicates that the use of RHANS is more effective to promote the hydrolysis of cellulose as it was used only 50 mg to hydrolysis cellulose 96% in very short time approximately 2 h.

3.2.4 Influence of the solvent’s effect.

In our previous study it was found that the cellulose was highly soluble in DMF and cyclohexanol containing LiCl [12, 23]. Table 2 show, the cellulose hydrolysis over different solvents such as DMF, cyclohexanol, dioxane, H₂O and toluene. It was observed that the cellulose hydrolysis over RHANS in these solvents was increased according the following order: DMF > cyclohexanol > toluene > 1,4- dioxane ≈ H₂O

We believe that the high percentage of cellulose hydrolysis was depending on the solubility of cellulose in the solvent. Most of the used dissolution systems could form hydrogen bonding between layers of cellulose chains and the solvents. The DMF contain more than one center able to form a hydrogen bonding with the cellulose and this could lead to increase the solubility of cellulose. As this catalyst continent high percentage of silica which may have the ability to form a hydrogen bonding. This reason could explain the low cellulose hydrolysis over water.

3.2.5 Catalyst Recycle Experiments.

The RHANS recycles experiments shows in Table 2. After the first hydrolysis was run using the catalyst at 140 °C for 2 h, the mixture including the solid catalyst and the cellulose residue, was then filtered and washed with hot DMF then with hot mixture of DMF and LiCl (repeated three times) then with distill water and the catalyst was heated at 110 °C for 24 h. The fresh cellulose and DMF with LiCl were added to the catalyst obtained and a second run was conducted, as well as a third run, using the same procedure. As shown in Table 2 the product yields in the second and third runs were similar to that in the first run, without any loss in the catalytic activity. These results indicated that catalytic performance was not lost in the course of the catalytic runs.

Table 2: The effect of different parameters on the cellulose hydrolysis

| Entry | Parameters | Variants | Glucose Yield (%) |
|-------|------------|----------|-------------------|
| 1     | Variation of catalyst mass | 0.5 | 61 |
|       |            | 1.0 | 65 |
|       |            | 2.0 | 88 |
|       |            | 200 | 63 |
|       |            | DMF | 47 |
| 2     | Variation of solvent effects | Cyclohexanol | 70 |
|       |            | 1.4_Dioxane | 38 |
|       |            | Toluene | 40 |
|       |            | H₂O | 37 |
|       |            | RT | 15 |
| 3     | Variation of reaction temperature °C | 100 | 30 |
|       |            | 120 | 70 |
|       |            | 140 | 95 |
|       |            | Fres | 96 |
| 4     | Catalytic cycle h | Run | 95 |
|       |            | 1 Run | 95 |
|       |            | 2 Run | 95 |
3.2.6 The kinetic of cellulose hydrolysis

The data obtained in this study was used to determine the reaction kinetic parameters of the RHANS catalyst. These data found to be in agreement with pseudo zero order rate law.

The apparent rate constant for the cellulose hydrolysis over RHANS increased from 0.0041 to 0.031 (mol. L \(^{-1}\) h\(^{-1}\)), when the temperature was increased from 100 to 140 °C and also the cellulose hydrolysis was increased, due to the proportional relation between the temperature and rate of the reaction. The data obtained from this equation at different temperatures show in Fig. 9. The activation energy (Ea) for RHANS was found to be 65.7 k J mol\(^{-1}\) (Fig. 10). The low activation energy shows that the RHANS is an efficient catalyst for the cellulose hydrolysis. The results are tabled in Table 3.

![Fig.9: The pseudo zero rate plots for the hydrolysis of cellulose over the surface of RHANS. The reaction condition at different temperature.](image)

![Fig.10: Arrhenius plot for the cellulose hydrolysis over the surface of RHANS at different temperatures.](image)
Table 3: The kinetic parameters of the cellulose hydrolysis over the RHANS catalyst. ka factor is the apparent rate constant, Ea activation energy and A frequency.

| Temperature (K) | 373 | 393 | 413 |
|----------------|-----|-----|-----|
| ka (L mol⁻¹ h⁻¹) | 0.0041 | 0.0265 | 0.031 |
| A (L. mol⁻¹ h⁻¹) | 6.5 *10⁷ |
| Ea (kJ mol⁻¹) | 65.7753 |

4. Conclusions

The RHANS was successfully synthesized via a sol-gel technique under mild reaction conditions. According to the BET result the RHANS had 139 m² g⁻¹ as a specific surface area. The XPS shows the presence of O, Si, S, and N peaks. The presence of S 2p on the XPS spectra indicated that the sulfur has (+6) oxidation state which corresponded to the sulfamic acid groups (−SO₂−), while S 2p was presence at binding energy in the region of 165 −169 eV. The FT-IR clearly showed the presence of −SO₂− absorption band at the expected range. The RHANS was used successfully to hydrolysis cellulose to glucose at 140 °C for 2 h. The catalytic activity of the catalyst reach to 96 % of glucose and the selectivity was 100 %. It was found that the hydrolysis of cellulose became much more easily when cyclohexanol or DMF containing LiCl were used as a solvent. The catalyst was stable during the hydrolysis and could use several times without loss of its catalytic activity.

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