Preparation and Characterization of Thiourea-Silica Hybrid as Heterogeneous Catalyst

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Sodium silicate was prepared from rice husk ash (RHA), which then functionalized with 3-(chloropropyl)triethoxysilane via simple sol-gel technique to form RHACCI. The chloro group in RHACCI was replaced in iodo group to form RHACI. Thiourea was immobilized on RHACI to synthesize nanoheterogeneous catalyst labeled as RHA-TU-SO4H. The FT-IR analysis clearly indicated the presence of primary amine –NH2 and C-N absorption band. BET surface area measurement also showed that the surface area is 357 m2/g of catalyst with pore size distribution (2-20 nm) which falls within the mesoporous region. The elemental analysis has also proved the existence of nitrogen and sulfur in the structure of the catalyst. Upon application of RHATU-SO4H as a catalyst, the degradation of cellulose to glucose yields 81 % at 140 °C for 16 h. The synthesized catalyst is easy to synthesize, highly stable throughout hydrolysis of cellulose as well as reusability without loss of catalyst activity.

Keywords: Rice husk ash, Thiourea, Hydrolysis of cellulose, Glucose.

EXPERIMENTAL

Sodium hydroxide (BHD, England 99%), nitric acid (CDH, India 70 %), 3-chloropropyltriethoxysilane (Sigma, Garmins 99 %), thiourea (Sigma, Germany 99%), toluene (GCC, England 98 %), DMSO (GCC, England 97 %), triethylamine (CDH, India 98%), ethanol absolute (99 %), methanol (99 %), DMF (LOBA, Cheme 99.8%). All the chemicals used were of AR grade or a high purity and used directly without further purification.

Extraction and modification of silica from RHA

Source of silica: The RHA was chosen as an amorphous silica source, it is available in the profusion. The silica was extracted from rice husk ash as described in the literature [12,13].

Functionalization of RHA with CPTES: According to the procedure described in the reference [14], 3 g of RHA was placed in 200 mL of 2 M NaOH in a plastic container at 75 °C for 60 min. The produced sodium silicate was filtered to get rid of the undissolved particles. A 6.0 mL solution of CPTES was added to the prepared sodium silicate solution. This solution was added dropwise (1.0 mL/min) to 3.0 M of nitric acid with constant stirred. The difference in pH was observed by using pH meter. A white gel started to form when...
the pH decreased to less than 11. The titration was continued until the pH of the solution reached up to 3.0. The obtained gel was aged for 2 days in a covered plastic container. After 2 days, the aged gel was washed six times with distilled water and centrifuged at 4000 rpm for 8 min. The final washing was achieved with acetone and then dried at 100 °C. Finally, the obtained precipitate was ground to produce a final powder. This sample was labeled as RHACCl [14].

**Iodide-exchanged polymers:** 1 g of the polymer RHACCl was suspended in 50 mL dry acetone (50 mL containing 4 g sodium iodide) and the mixture was refluxed for 60 h. The formed solid precipitate was then filtered off, washed with water, methanol and ether and dried in vacuo at 100 °C [15], this sample was labeled as RHACI.

**Functionalization with thiourea:** 2 g (0.026 mmol) of thiourea (TU) was dissolved in dry toluene (30 mL) and mixed with 1.0 g of RHACI. Then, 3.79 mL (0.026 mmol) Et3N was added and the mixture refluxed at 110 °C for 60 min (Scheme-I). The solid phase was filtered and washed with DMSO, DMF and then ethanol. The precipitate was then dried at 100 °C for 24 h [16]. Finally, it was ground to form fine powder. A 0.85 g product was collected and then 2.0 g of the RHATU was stirred in the 40 mL of 0.5 M sulfuric acid at room temperature for 24 h to form thiourea sulfate catalyst RHATU-SO4H. The formed solid precipitate was filtrated, washed with distilled water and dried at 100°C for 24 h [17].

**Cation exchange capacity (CEC) of the catalyst:** 1 g (17 mmol) sodium chloride was dissolved in 25 mL distilled water in a conical flask with stirring. 1 g of RHATU-SO4H was added to mixture and left for 30 min. After that 2-3 drops of phenolthalein was added to the reaction mixture and titrated against standard sodium hydroxide solution. Three separated titration was performed and an average value for the CEC of RHATU-SO4H.

**Catalytic hydrolysis procedure:** The hydrolysis of cellulose was carried out in 250 mL round bottom flask equipped with magnetic stirrer and water condenser. 200 mg LiCl, 30 mL DMF and 180 mg cellulose were separately transferred to the round bottom flask containing the catalyst (which dried at 110 °C for 24 h and cooled in desiccator to minimize moisture content). The degradation temperature was adjusted to 140 °C. The hydrolysis suspension was refluxed for 14 h. A 0.5 mL of clear mixture of the hydrolysis suspension was transformed into vial and 2 mL of deionized water was added and the mixture was put in the water bath at 90 °C for 10 min. The blank sample was prepared with 0.5 mL of DNS and 2 mL deionized water and heated under the same conditions of the sample. The absorbance of the sample was measured at 450 nm against the blank and the glucose concentration were calculated by using a standard curve of glucose.

**Sample characterization:** The prepared RHATU-SO4H was characterized by elemental analysis (Eager 300 for EA1112), thermogravimetric analyses (TGA DTG, Q50 V6.3 Build 189), from 30 to 600 °C at a heating rate of 20 °C min⁻¹ under nitrogen flow. Powder X-ray diffraction (Siemens Diffractometer D5000, Kristalloglifex), nitrogen adsorption porosimetry (Belsorp Adsorption/Desorption Data Analysis Software BEL Japan, Inc.), FT-IR spectroscopy (FT-IR-8400 S shimadzu (Japan)), scanning electron microscopy (SEM) ([EDS]-Hitachi SU 750, Oxford instruments).

**RESULTS AND DISCUSSION**

**Infrared spectroscopy of analysis:** Figs. 1 and 2 show the FT-IR spectra of RHACI and RHATU-SO4H, respectively. The broad band about 3445 cm⁻¹ is generally attributed to O-H stretching vibration from SiO-H and HO-H of absorbed onto surface of silica. The band about 1631 cm⁻¹ represents the HO-H bending vibration. The band around 3188 and 3325 cm⁻¹ belongs to stretching primary –NH2 symmetric and asymmetric. The band around 2959 cm⁻¹ assigned to stretching vibration of CH2. While the bending vibration of the CH2 group appearance in 1448 cm⁻¹. The band of C-N can be seen at 1541 cm⁻¹. The Si-C

Scheme-I: Synthesis of catalyst RHATU-SO4H
vibration was observed at 1273 cm\(^{-1}\) [6]. The FT-IR spectrum of RHATU-SO\(_4\)H also appeared a broad stretching vibration of the Si-O-Si compared with narrower band of Si-O-Si in RHACI. The new bands and changes in some bands in FT-IR spectrum of RHATU-SO\(_4\)H portrays a good evidence for the successful functionalization of RHACI with thiourea [18].

Nitrogen adsorption-desorption analysis: The surface area analysis of RHATU-SO\(_4\)H was measured by the nitrogen adsorption-desorption. Fig. 3 shows the N\(_2\) adsorption-desorption isotherm and EJH distribution of pore size for RHATU-SO\(_4\)H. IUPAC classification of the isotherm for RHATU-SO\(_4\)H is in agreement with the type IV and H\(_2\) hysteresis loop [19]. It can be seen in Fig. 3 that the nitrogen adsorption isotherm of RHATU-SO\(_4\)H gave a hysteresis loop observed in the range of 0.4 < \(P/P_0\) < 1.0 which is associated with capillary condensation according to IUPAC classification. The BET analysis also showed that the specific surface area of the RHATU-SO\(_4\)H was 357 m\(^2\)/g whereas specific surface area of RHACI was 633 m\(^2\)/g. The decrease in the surface area of the RHATU-SO\(_4\)H could be due to the fact that the immobilization of thiourea on the silica surface was blocked some of the pores. RHATU-SO\(_4\)H has pore size distribution (2-20 nm) which falls within the mesoporous region.

Powder X-ray diffraction pattern: Bui et al. [20] reported that XRD patterns of RHA had a phase transfer of RHA to be amorphous silica in the temperature ranged from 300 to 700 °C. Fig. 4 has demonstrated XRD patterns for RHACI and RHATU-SO\(_4\)H which stated a broad diffraction band at 2\(\theta\) angle of about 22°. These results are typically corresponding with XRD patterns of amorphous silica of RHACI and RHATU-SO\(_4\)H [21].

Elemental analysis (CHNS): The CHNS analysis was estimated for RHACI and RHATU-SO\(_4\)H. This analysis have showed successful incorporation of thiourea on RHACI. Table-1 shows the elemental data analysis of RHA, RHACI and RHATU-SO\(_4\)H. The elemental analysis of RHACI explained that the C% and H% was 11.7 and 1.90 %, respectively [22], while elemental analysis of RHATU-SO\(_4\)H indicated the presence of N and S in addition to C and H. Thus, these results obviously indicated the successful immobilization of thiourea onto RHACI.

Scanning electron microscope (SEM): The scanning electron microscope (SEM) images of the RHATU-SO\(_4\)H are shown in Fig. 5. It seems that the surface of RHATU-SO\(_4\)H similar to some rocky particle with shaped shell that randomly distributed onto surface.
Thermogravimetric analysis (TGA/DTG): The thermogravimetric analysis TGA/DTG was performed in the range of 25 to 600 °C at the heating rate of 10 °C/min. Fig. 6 designates to TGA of the RHATU-SO₄H that showed two characteristic decomposition stages. The initial step appeared mass loss (about 2.015 %) at around 25-120 °C. This loss is attributed to the absorbed water onto surface of silica. The second mass loss (about 37.25 %) occurred between 250 to 460 °C and it seems to be degradation of propylthiourea moieties [23]. Additionally, The DTG analysis for the RHATU-SO₄H is shown in Fig. 7. The thermal decomposition of RHA TU-SO₄H has displayed two main weight loss steps. These two steps of DTG are in accordance with the results obtained from DTA in terms of the thermal decomposition of water absorbed onto surface of silica and alkyl thiourea group [24].

Hydrolysis of cellulose: The heterogeneous catalyst activity i.e. RHATU-SO₄H and homogeneous thiourea (TU) towards cellulose hydrolysis to glucose were studied. The parameters of hydrolysis such as temperature, mass of catalyst, effect of solvent and reusability of the RHATU-SO₄H catalyst were evaluated to optimize the condition of hydrolysis.

Effect of hydrolysis time: The time effect on hydrolysis of cellulose to glucose by RHATU-SO₄H and homogeneous thiourea (TU) are observed in Fig. 8. The hydrolysis were conducted by using 200 mg catalyst, DMF as a solvent and LiCl at 140 °C. The first degradation of cellulose hydrolysis to glucose was 16 % within the first 6 h and then increased to maximum of 81 % in 16 h. However upon increasing the hydrolysis time (more than 16 h), no change was observed in cellulose hydrolysis. Therefore the optimum time of cellulose hydrolysis over RHATU-SO₄H is 16 h. On the other hand, 200 mg homogeneous (thiourea) showed 27.4% of cellulose hydrolysis for the same period of time. Hence, this thiourea (TU) cannot be used as a catalyst in cellulose hydrolysis into glucose. While heterogeneous thiourea (thiourea functionalized RHATU-SO₄H) is currently much more valuable and should be taken into consideration since it gives reasonably greater hydrolysis.

Influence of catalyst mass: In order to find the best catalyst mass that required to hydrolysis of cellulose, the analysis was carried out by changing the amount of RHATU-SO₄H from (150-250 mg) at fixed hydrolysis temperature at 140°C, time of hydrolysis for 16 h and solvent DMF/LiCl. The results has shown in Fig. 9. It is clearly indicated that as the mass of catalyst increased from 150 to 200 mg, the hydrolysis of cellu-
lose into glucose raised from 68 to 81%. However, no significant influence on cellulose hydrolysis was noticed upon increasing the mass of catalyst. It was found that 200 mg chosen as the optimum value of the RHATU-SO4H catalyst.

**Influence of hydrolysis temperature:** Fig. 10 demonstrated the effect of hydrolysis temperature effects on role of RHATU-SO4H as a catalyst in the cellulose hydrolysis. It clearly observed that the cellulose hydrolysis increased when temperature rises from 120 to 140 °C whereby the hydrolysis increased to 81% at 140 °C.

![Fig. 10. Conversion of cellulose to glucose over RHATU-SO4H at different temperature](image)

**Influence of solvent:** It was also studied the effect of solvent on cellulose hydrolysis into glucose over RHATU-SO4H as given in Table-2. The condition of hydrolysis was fixed as follows: reaction time 16 h, hydrolysis temperature 140 °C and catalyst mass 200 mg. The solvents used i.e. toluene, 3-methylpropan-2-ol and DMF. It was noticed that there was a significant effect in the cellulose hydrolysis by using different solvents DMF > 2-methylpropan-2-ol > toluene. Therefore, the cellulose hydrolysis can be different according to the solubility of the cellulose into different solvents. In this study the cellulose was highly soluble in DMF and 2-methylpropan-2-ol consisting LiCl. Most of our suspension system could form hydrogen bonding between the solvent and layer of cellulose chain. DMF has appeared more solubility of cellulose because of it has more than one center able to form hydrogen bonding with chain of cellulose and this could make the hydrolysis higher and easier in contrast with other solvents that have less solubility of cellulose.

**Catalyst recycles:** The main advantage of utilization of heterogeneous catalyst is ability to be reused many times. The stability of the catalyst and the activity of its active site are the main parameters of its reuse. Since RHATU-SO4H is heterogeneous catalyst, hence it was successfully utilized for recycling. In the first hydrolysis it was run by using the catalyst with mixture, and then washed by hot DMF LiCl (this step was repeated three time) and the catalyst heated up to 100 °C for 24 h. Next, fresh cellulose and DMF with LiCl were added to the catalyst and washed. The consecutive runs were carried out similarly as in above method. As observed in Fig. 11, the results appears in the second and third runs. This product indicated that catalytic performance doesn’t lose its activity during the counts of the catalytic runs.

**Suggested mechanism for cellulose hydrolysis:** The RHATU-SO4H has acidic sulphate group. These group sites could interact rapidly with the glycosidic oxygen via a hydrogen bonding between layers of cellulose chains. Then the cleavage of the C−O bond in the cellulose chains takes place. After that the sulphate group attract the charged species via a hydrogen bonding. Finally the yield of monosaccharide after partial hydrolysis is occurred and the catalyst could hydrolyze new cellulose chains as in Scheme-II.

**Conclusion**

Thiourea was reacted with silica extracted from rice husk ash. The spectroscopic evidence showed the successful synthesis of RHATU-SO4H. The FT-IR spectrum indicated the presence of primary –NH2 and formation bond C-N in the catalyst. The N2 adsorption-desorption study also stated that RHATU-SO4H has higher specific surface area 357 m2/g. The TGA/DTG indicated the catalyst have two degradation temperature between 25-115 and 260-460 °C. The cellulose hydrolysis, by RHATU-SO4H to glucose yield 81 % of glucose at 140 °C for 14 h. The catalyst is easy to synthesize, stable, reusable and could be used many times without any activity loss.

**ACKNOWLEDGEMENTS**

The authors thank University of Kerbala, Ministry of Higher Education and Scientific Research, Republic of Iraq for the project supported.

**REFERENCES**

Scheme-II: Suggested mechanism of cellulose hydrolysis to glucose over catalyst RHATU-SO₄H