Modification of silica with sulfuric acid and phosphoric acid for cellulose hydrolysis

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Abstract. Different percentages (5, 10, 15, and 20 %) of sulfuric and phosphoric acids were successfully loaded with Silica. Both phosphate and sulfate groups were observed onto silica in different spectroscopic techniques. Oxigene, silicon, and sulfur were shown during the analysis of silica-sulfuric catalyst by photoelectron peaks (XPS). The main functional groups of Brønsted acid sites at the expected range in the FT-IR were confirmed by Pyridine test. Cellulose was hydrolyzed to glucose in 9 h over a silica-sulfuric catalyst, and 10 h over the silica-phosphoric catalyst. The recycle experiment shows both catalysts were stable during the hydrolysis and many times at the same catalytic activity.

Keywords: Pyridine test; Silica; Cellulose hydrolysis; Sulphuric acid; Phosphoric acid

1. Introduction

Rice husk (RH) is a by-product of the rice-milling productions and is creating disposal problems. Moreover, after burning of rice husk approximately 20 % of ash was produced. This ash is mainly amorphous silica which has a 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 [1, 2].

Cellulose, the most abundant renewable and biodegradable polymer, is the promising feedstock for the production of chemicals for their applications in various industries. The main components of cellulosics are cellulose, hemicellulose, pectins, lignin and tannins with the distribution varying by structure and function of the cellulosics [3]. Cellulosics exhibit a wide range of dimensional stability. They are stable at room temperature, undergoing pyrolysis on heating and combustion on burning. These physical properties vary by chemical composition of the cellulosics. A deep understanding of cellulosics is important to allow prediction of such properties. The base molecule of cellulose is made up of β-1,4-glycosidic linked glucose units [4]. The development of methods for hydrolyzing cellulose either to glucose or directly to biofuels, is highly desirable. These difficult transformations are not readily feasible using the current best technology, which employs cellulytic enzymes, as they require water solvents and mild conditions under which cellulose is not readily soluble. An extensive number of works have been devoted to the degradation of cellulose using enzymes, mineral acids and supercritical water [5, 6]. These methods have drawbacks such as slow reaction rate, difficult separation of products and catalysts, corrosion hazards, harsh conditions and generation structures of cellulose and amylase [7]. Heterogeneous catalysis has advantages to overcome these drawbacks. In
our previous work, we had reported the catalytic degradation of cellulose to glucose by supported acid-base catalysts [8,9,10]. The glucose is useful precursors for the production of alcohols and pharmaceuticals.

As cellulose is very difficult to break down, it cannot directly be used as a food source. In this work simple catalyst has probably come a long way to make biofuel production more acceptable and it can break down cellulose to glucose easily.

2 Materials and methods

2.1 Raw materials

The chemicals used in this study were Sodium hydroxide (Systerm, 99%), Nitric acid (Scharlau, 65%), Cyclohexanol (Riedle-De Haen, 99%), Dimethylformamide (DMF) (Systerm, 99.5%), Dinitrosalycilic acid (DNS) (BDH, 99%), Glucose (BDH, 99%), Lithium chloride (Sigma, 99%), Sulphuric acid (Poch, 95%), Phosphoric acid (Poch, 95%). All chemicals used were AR grade or of high purity and were used directly without further purification.

2.2 Silica modification with phosphoric or sulfuric acid

The reported method [11,12] was followed during the silica extraction from rice husk. A 1.5 gm of RHA was stirred with (5%) phosphoric acid or sulfuric acid in the round bottom over 24 h, after this process, the mixture was filtered and dried at 110 °C. The other loading of 10, 15, and 20% of the catalysts were synthesized by following a similar procedure. The catalysts were labeled as SiO2-PO4 in case of using phosphoric acid in the modification and SiO2-SO4 in case of using sulfuric acid after the modification.

2.3 Pyridine acidity test

The sample concurrently with a beaker including pyridine was stored in a desiccator provided with a valve attached to a membrane vacuum pump. The system was saved under a tight vacuum to 48 h. the atmosphere in the desiccator was emptied again for 1 h at the similar pump rate. The specimen was then removed and examined by FT-IR in KBr plate.

2.4 Hydrolysis of cellulose

In 100 mL a cellulose hydrolysis was done over the catalysts. Mixture of cellulose (0.18 gm) and lithium chloride (0.02 gm) of were transferred to three-necked round bottom flask contains 30 mL of DMF. After the reaction temperatures reached to 140 °C about 0.20 gm of the catalyst SiO2-PO4 or SiO2-SO4 (pre-dried at 110 °C for 24 h and cooled in desiccators to minimize moisture content) was added. The reaction mixture was refluxed for 24 h. The method reported by [18] was followed to estimated hydrolysis products. The optimized of SiO2-PO4 or SiO2-SO4 catalytic activity (mass of catalyst, solvents effect, and temperatures) were followed the procedure above.

3. Results and Discussion

3.1 Silica modified with acids

The silica which extracted from rice husk was successfully modified with different loading of phosphoric or sulfuric acid. The reaction was done at room temperature in one pot-synthesis. Scheme 1 shows the reaction process of this modification.
Scheme 1: The modification of silica with acids. (a) The modification with phosphoric acid SiO$_2$-PO$_4$.
(b) The modification with sulphuric acid SiO$_2$-SO$_4$.

### 3.1.1 IR spectroscopy analysis

Fig.1 (a) shows the FT-IR of 5% SiO$_2$-PO$_4$. It shows a vibration band at 3454 cm$^{-1}$ due to the presence of silanol groups. The band at 1633 cm$^{-1}$ as a result of the physical absorb of water. The PO$_2$ band was observed in 1433 – 1199 cm$^{-1}$. The band at 1101 cm$^{-1}$ was due to the siloxane bands. Fig.1 (b) shows the FT-IR of 10% SiO$_2$-PO$_4$. No change on the absorption bands of silanol and siloxane bands after the acid loading increases. While the PO$_2$ band was shifted and became very strong as the acid loading increase as shown in Fig. 1 (c).

Fig.2 shows the FT-IR of 15% SiO$_2$-SO$_4$. It shows an absorption band at 3465 cm$^{-1}$ due to the unmodified silanol group onto silica. The band at 1647 cm$^{-1}$ as a result of the physical absorb of water. The SO$_2$ band was observed in 1382 – 1127 cm$^{-1}$. The band at 1095 was due to the siloxane band. No change on the absorption bands of the silanol, SO$_2$ and siloxane bonds were observed after the acid loading increases.
Fig.2: The FT-IR spectrum of silica modified with 15% of SiO$_2$-SO$_4$.

3.1.2 Thermogravimetric analyses

The thermogravimetric analyses of SiO$_2$-SO$_4$ and SiO$_2$-PO$_4$ shows in Fig.3 (a, and b). The TGA graphs show about 5% of mass loss of 5% SiO$_2$-SO$_4$ or SiO$_2$-PO$_4$ was occurred at the temperature below 300 °C. The mass losses of other catalysts with different loading were found almost similar to the loading percentage (10, 15, and 20%) which was loaded onto silica.

Fig.3: The thermo gravimetric analysis for (a) SiO$_2$-SO$_4$ and (b) SiO$_2$-PO$_4$.

3.1.3 Pyridine acidity test

Pyridine test method was followed to deducted catalyst Brønsted and Lewis acid site. The catalysts were in charged with Pyridine under room temperature. The test was done in the range of 1700-1400 cm$^{-1}$ in the absorbance mode using KBr disc. Fig. 4(a) shows the 15% SiO$_2$-PO$_4$ before and after Pyridine test. The bands at 1633, 1556 and 1544 cm$^{-1}$ were due to the interaction of Pyridine with phosphate groups onto the silica surface. These bands were not shown in the spectra before the
Pyridine test as in Fig. 4 (b). This result is clearly shown that the phosphoric acid was bonded into silica surface and presence as a Brønsted acid side. No change on the FT-IR was observed when the loading of acid was change.

Fig. 5(a, b) shows the 20% SiO$_2$-SO$_4$ before and after Pyridine test. Fig. 5 (b) show bands at 1537, 1544 and 1512 cm$^{-1}$ were due to the interaction of Pyridine with sulfuric acid on the silica surface and forming Brønsted acid site. These bands were not shown in the spectra before the Pyridine test as in Fig. 5 (a). This result is clearly shown that the sulfuric acid was bonded into silica surface.

3.1.4 X-ray photoelectron spectra (XPS)

The 15 % and 20 % of SiO$_2$-SO$_4$ were characterized by using X-ray photoelectron spectra Fig.6 (a, b). The spectra of 15 %, and 20 % of SiO$_2$-SO$_4$ were compared with our previous study [9] (Fig.6 (c)) which shows the silica immobilized with ClSO$_4$H by using different strategy. The photoelectron peaks of O 1s, Si 2p, S 2p for the catalyst are presented in Fig. 6(a, b). The formation of sulphur-oxygen species, which typically have binding energy in region 167-169 eV, is already seen. Spectral peak of S 2p XPS of SiO$_2$-SO$_4$ has been occurred at ca. 168–169 eV associated with sulphate (S 6+) species due to sulfuric acid groups. This result was consistent with another study [13]. The O 1s binding energy was found at 532.3 eV for SiO$_2$-SO$_4$ while the Si 2p binding energy at 102.7 eV that was obtained from an overlap of Si 2p3/2 and Si 2p1/2 binding energy [14]. This indicates that all Si
and S present in the sample are oxidized. Comparing with our previous study [9], the Fig. 6(c) shows peak at 400 eV which was related to the \(-\text{O}^+\text{Na}\). This peak was not present in the both spectra of 15% and 20 % of SiO\(_2\)-SO\(_4\). The intensities of all peaks in Fig. 6(a, b) were less than those in Fig. 6(c). The all spectra are almost similar which indicated that the components of the catalysts are similar. The XPS results imply that the sulfuric acid was immobilized onto silica.

Fig. 6: A wide scan spectrum XPS of SiO\(_2\)-SO\(_4\). (a) A wide scan spectrum XPS of 20 % SiO\(_2\)-SO\(_4\). (b) A wide scan spectrum XPS of 15 % SiO\(_2\)-SO\(_4\). (c) A wide scan spectrum XPS of RHSO\(_3\)H catalyst from our previous study [10].

3.2 The hydrolysis of cellulose over SiO\(_2\)-PO\(_4\) and SiO\(_2\)-SO\(_4\)

The catalytic activity of the silica modified with acids SiO\(_2\)-PO\(_4\) and SiO\(_2\)-SO\(_4\) were studied onto hydrolysis of cellulose to glucose. The subsection below shows the different parameters used in this study.

3.2.1 The effect of hydrolysis time

Fig. 7 shows the hydrolysis of cellulose over silica modified with phosphoric acid SiO\(_2\)-PO\(_4\). It was found that the hydrolysis of cellulose was 65 % at 6 h then increased to 94% at 10 h. The hydrolysis was decreased after the 10 h due to the hydrolysis of the glucose to other products. From our previous studies, the maximum hydrolysis of cellulose to glucose without catalyst was found to be in less than 19 % [14-16]. The low hydrolysis of cellulose over RHA comparing with high hydrolysis
of cellulose over SiO$_2$-PO$_4$ indicates that the activity of SiO$_2$-PO$_4$ was due to the presence of Brønsted acid sites as a result of loaded the silica with phosphoric acid.

The effect of the hydrolysis time on the hydrolysis of cellulose to glucose over 20% SiO$_2$-SO$_4$, is shown in Fig. 7. The hydrolysis was carried out with 150 mg catalyst using a DMF/LiCl as a solvent at 140°C. The initial hydrolysis of cellulose during the fourth hour was 23% and it reached the maximum hydrolysis 92% in 9 h. The hydrolysis of cellulose over SiO$_2$-SO$_4$ was reached to the optimum at the 9 h of the hydrolysis time. After the optimum time of the cellulose hydrolysis to glucose over SiO$_2$-SO$_4$, the glucose was started to hydrolyze to other products. It was observed that the hydrolysis of cellulose over SiO$_2$-SO$_4$ is higher than that with SiO$_2$-PO$_4$.

![Graph](image.png)

Fig. 7: The hydrolysis of cellulose over silica loaded with 20% SiO$_2$-PO$_4$ and 20% SiO$_2$-SO$_4$ as a function of the hydrolysis time. The hydrolysis condition was 150 mg of catalysts at 140°C, 180 mg cellulose with 30 mg LiCl in DMF.

### 3.2.2 The effect of catalysts mass on the hydrolysis of cellulose

The catalytic activity with different mass of 20% SiO$_2$-PO$_4$ or 20% SiO$_2$-SO$_4$ (100, 150, and 200 mg) were studied and the results were shown in Table 1(entry 1). The hydrolysis was carried out at 140°C. It was observed that the maximum hydrolysis of cellulose was reached 63% when 100 mg of catalyst mass was used, while the hydrolysis was found to be 93% when 150 mg of the catalyst 20% SiO$_2$-PO$_4$. Therefore 150 mg was chosen as the optimum mass of 20% SiO$_2$-PO$_4$ catalyst. The hydrolysis of cellulose was found to be 96% over 200 mg of 20% SiO$_2$-SO$_4$ for 9 h. These results indicate that the using of higher mass of SiO$_2$-SO$_4$ could lead to increase the hydrolysis of cellulose.

### 3.2.3 The optimization of the hydrolysis temperature and the solvents effect

The catalytic activities of 20% SiO$_2$-PO$_4$ and 20% SiO$_2$-SO$_4$ at different temperatures 120, 130 and 140°C were studied and the results were shown in Fig.8(a, b). In general when the temperature increased the cellulose hydrolysis was increased too. The optimum temperature was 140°C for both catalysts.
The hydrolysis of cellulose with different solvents i.e. (Ethanol, Cyclohexanol, and DMF) over 20% SiO₂-PO₄ and 20% SiO₂-SO₄ were studied and the results were shown in Table 1(entry 2). The hydrolysis was carried out at 140 °C for 10 h as hydrolysis time. It was observed that the hydrolysis of cellulose increased when DMF used as a solvent and decreased when alcohol used as a solvent. The hydrolysis of cellulose was depending on the solubility of cellulose in the solvent. It was observed that the cellulose was completely soluble in the N,N-diethylacetamide containing LiCl [15]. In our previous study [8-10] it was found that the cellulose was highly soluble in DMF. The solubility was depending on the forming of a hydrogen bonding between layers of cellulose chains and the solvents. The DMF contains more than one centre able to form a hydrogen bonding with the cellulose and this could lead to increasing the solubility of cellulose. This could make the hydrolysis much more easily comparing with the low solubility of cellulose in the other solvents.

![Fig. 8: The hydrolysis of cellulose over (a) 20% SiO₂-PO₄ and (b) 20% SiO₂-SO₄ as a function of the hydrolysis temperature.](image)

3.2.4 The effect of different loading of acid and recycles experiments

The hydrolysis of cellulose with different loading of acids for both catalysts (20, 15, 10, 5 %) was studied as shown in Table 1(entry 3). It was observed that the hydrolysis of cellulose increased when the loading of the acid was increased too. This could be due to the availability of the active centers which increase the hydrolysis.

The catalyst was also used in recycling experiments Table 1(entry 4). After the first reaction was run using the catalyst at 140 °C, the mixture including the solid catalyst and the cellulose residue was then washed with hot DMF and LiCl (repeated three times) and the catalyst was heated at 140 °C for 24h. 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 1(entry 4), the product yields in the second had minimum decreases of that in the first run. While the 20% SiO₂-SO₄ was lost 30% of his activity after the second run and then the catalyst show stability in his activity.
Table 1: The effect of different parameters on the hydrolysis of cellulose to reducing sugar over 20 % SiO$_2$-PO$_4$ and 20% SiO$_2$-SO$_4$.

| Entry | Parameters                              | Variants      | Cellulose hydrolysis Yield (mM %) over SiO$_2$-PO$_4$ in 10 h | Cellulose hydrolysis Yield (mM %) over SiO$_2$-SO$_4$ in 9 h |
|-------|-----------------------------------------|---------------|---------------------------------------------------------------|-------------------------------------------------------------|
| 1     | Variation of catalyst mass effects mg   | 100           | 63                                                           | 52                                                          |
|       |                                         | 150           | 93                                                           | 94                                                          |
|       |                                         | 200           | 94                                                           | 96                                                          |
| 2     | Variation of solvent effects            | DMF           | 93                                                           | 94                                                          |
|       |                                         | Cyclohexanol  | 69                                                           | 91                                                          |
|       |                                         | Dioxane       | 66                                                           | 94                                                          |
|       |                                         | Ethanol       | 28                                                           | 22                                                          |
| 3     | Variation of silica modified with acid % | 5             | 33                                                           | 4.0                                                         |
|       |                                         | 10            | 77                                                           | 53                                                          |
|       |                                         | 15            | 86                                                           | 75                                                          |
|       |                                         | 20            | 93                                                           | 94                                                          |
| 4     | Variation of reusing the catalyst       | Fresh         | 93                                                           | 94                                                          |
|       |                                         | Run 1         | 86                                                           | 69                                                          |
|       |                                         | Run 2         | 84                                                           | 66                                                          |

4. Conclusions

Cellulose was hydrolyzed successfully by using acid loaded into silica as simple solid acid catalysts. Silica was modified with different phosphoric and sulfuric acids 5, 10, 15, and 20%. The FT-IR of the SiO$_2$-PO$_4$ shows the presence of PO$_2$ and O-Si-O bands at the expected range. The Pyridine acidity test was shown that the SiO$_2$-PO$_4$ had Bronsted acid sites. The XPS analysis was supported the successfully loaded the acids onto silica. The both catalysts SiO$_2$-PO$_4$ and SiO$_2$-SO$_4$ were used to hydrolyse cellulose to glucose at 140 °C for the time less than 10 h. The catalytic activities of the catalysts were found to be up to 90 % of the glucose over both catalysts. The catalysts are simple and stable during the hydrolysis.

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