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SYNTHESIS OF SULFONATE MODIFIED SILICA FROM RICE HULL ASH

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Abstract: Synthesis of sulfonate modified silica from rice hull ash has been done. Other silica sources such as sodium silicate, tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) were used as comparison. Synthesis was carried out by employing sol gel process via mercapto modified silica pathway followed by oxidation using hydrogen peroxide. New synthesis approach of introducing the functional group at the same time hydrolysis and condensation processed for the preparation of mercapto modified silica was applied. The results show that the final products of sulfonate modified silica synthesized from rice hull ash has similar characteristics as the ones that were synthesized from other silica resources (sodium silicate, TEOS and TMOS). Higher ordered silica framework was indicated for sulfonate modified silica compared with that in unmodified silica gel.

Introduction

Silica gel surface can be modified by two distinct processes, organofunctionalization, where the modifying agent is an organic group, and inorganofunctionalization, in which the group is anchored on the surface, is an organometallic composite or a metallic oxide [1]. In organofunctionalization, the reactivity of the trialkoxy silyl groups as the silylating agents towards the free silanol groups of silica surface leads to the successful incorporation of different functional groups. One of the common silylating agents used for silica gel modification is 3–(trimethoxy silyl)-1-propanethiol or mercaptopropyl trimethoxy silane (MPTS) [2-5].

There are several methods of modification processes e.g. modification through impregnation, immobilization of silane reagent, and modification through sol gel process or sol gel route. Serano et al. [2] modified silica surface with MPTS through impregnation, while Surdem [3], Tertyth and Yanishpolskii [4] and Shylesh et al. [5] modified silica surface with MPTS by immobilization of the silane reagent with dry toluene under nitrogen atmosphere. Cestari et al. [6] and Airoldi and Arakaki [7] modified silica surface by sol – gel process as well as Narsito et al. [8] and Mujianti et al. [9].

Mercapto modified silica is also called as thiol functionalized silica. According to Yang et al. [1], thiol functionalized materials have attracted much attention since they are good heavy metal adsorbers and they can act as solid ion exchangers after oxidation of thiol into sulfonic acid groups. In the conversion of thiol to sulfonic acid groups, hydrogen peroxide can be used as oxidation agent.

On the other hand, there are various resources of silica from nature, such as diatomite or diatomaceous earth as biological deposits of sea algae diatomae, the inside space of the bamboo stems, the rice straw, and quartz silica sand [10], as well as rice hull ash [11]. As an agricultural country, Indonesia produces a lot of rice, so there are a lot of rice hulls that can be used as a fuel source in some home industries, for example tofu, brick, roof etc. These home industries generate rice hull ash as the waste.

In this study, the rice hull ash was used as silica source to synthesize mercapto modified silica via the formation of sodium silicate. The resulted sodium silicate was then reacted with MPTS and an acid through sol gel process to obtain mercapto modified silica. Finally, the mercapto moieties were oxidized by peroxide to get sulfonate modified silica. We have also synthesized mercapto modified silica from technical grade and pro-analysis sodium silicate, TEOS and TMOS for comparison. The conversion into sulfonate was performed by oxidation using peroxide as well. The resultant solids were characterized with FTIR spectroscopy, X-Ray Diffraction (XRD) and scanning electron microscopy (SEM).

Materials and Methods

Sodium silicate technical grade, sodium silicate pro analysis (Aldrich), TEOS (Aldrich) and TMOS (Aldrich), NaOH (Merck), HCl (Aldrich), H₂O₂ (Merck), and MPTS (Merck) were used as received. The rice hull ash used for the sodium silicate precursor was mixed with demineralized water, treated by HCl to pH 1, stirred at room temperature for 2h, filtered and washed until reaching neutrality. The resultant solids were denoted as acid-washed rice hull ash. The unwashed rice hull ash was also used as comparison. Prior the treatment, the rice hull ash was sieved to have 200 mesh grains.

Silicate precursor preparation. Thirty gram of rice hull ash and 1L of 1M NaOH were boiled for 1 h in Teflon container with stirring according to Savita [13]. The solids were then filtered and the carbon
residue was washed with 500 mL of boiling water. The filtrate was sodium silicates.

**Synthesis of mercapto modified silica.** Twenty ml of dilute sodium silicate solution was mixed with 2 mL of MPTS in a teflon container, then 1M HCl was added dropwisely under vigorous stirring until the solution reached neutrality. A soft gel was then formed and aged for about 18 h. After aging, the gel was gently broken and stirred for 10 minutes. This gel was washed with demineralized water until reaching neutrality, filtered and dried in an oven. Silica gel was also prepared by using the same procedure omitting the addition of MPTS. For TEOS or TMOS as silica resources the procedures were as the following:

Ten mL of TEOS was mixed with 2 mL of MPTS and 20 mL of demineralized water in the glass container and stirred for 30 minutes. A soft gel was then formed and aged for about 18h. After aging, the gel was gently broken, stirred, washed, filtered and dried in an oven.

Silica gel from TEOS or TMOS was also prepared by mixing 10 mL of TEOS or TMOS with 3 mL of 0.1M acetic acid and 0.1 ammonium chloride dropwisely until reaching pH 5. After aging over night, a soft gel was formed, washed with demineralized water until reaching neutrality, filtered, and dried in an oven.

**Synthesis of sulfonate modified silica.** One gram of mercaptomodified silica was mixed with 16 ml of 33% hydrogen peroxide into the Teflon container. The solid suspension was kept under stirring for 1h at room temperature, then filtered off and washed three times with demineralized water. In order to ensure that all the sulfonic groups were protonated, the solid was suspended in a 10% sulfuric acid (16 mL) for 1h. The solid was then filtered off, washed with demineralized water, and dried in an oven.

The functional groups of the resultant solids at each synthesis procedure were characterized by FTIR spectrometry, while the crystallinity was accessed by XRD and the grain morphology was characterized by scanning electron microscopy (SEM).

**Results and Discussion**

The infra red spectra of silica gel and modified silica from acid-washed rice hull ash are shown in Figure 1. The spectra of silica gel shows peaks in the range of 3600 – 3200 cm⁻¹ attributed to the hydroxyl stretching of the hydrogen bonded internal silanol groups. The band at 1200, 1100 and 800 cm⁻¹ are the characteristic band of SiO₂ assigned to the Si-O stretching vibrations while the band at 950 and 470 cm⁻¹ are assigned to the bending vibrations of the surface silanols and Si-O respectively. The spectra of silica gel from other silica sources (not shown) have shown similar peaks.
The infra red spectra of mercapto modified silica from acid-washed rice hull ash displays the same peaks as silica gel structure, instead of the presence of prolyl groups attached to the silicon framework as identified by the methylene stretching bands in the range of 2950–2850 cm\(^{-1}\). The peak corroborates the attachment of organic moiety into the silica surface. The weak band at 1430 cm\(^{-1}\) would be related to the methylene group adjacent to the thiol group, while the band at 1450 cm\(^{-1}\) can be assigned to the methylene symmetric bending mode vibration as seen in alkane. The bands for thiol stretching vibrations are clearly seen at 2575 cm\(^{-1}\). The spectra of mercapto modified silica from other silica sources (not shown) have shown similar peaks, except IR spectra of the mercapto modified silica from TEOS, which has weaker band at 2575 cm\(^{-1}\).

The infra red spectrum of sulfonate modified silica from acid-washed rice hull ash is shown in Figure 1c. The spectrum indicates similar peaks to the spectra of mercapto modified silica. In sulfonate modified silica, the thiol groups were oxidized by H\(_2\)O\(_2\) to sulfonic acid. The relative increase of the intensity of hydroxyl band frequency in the range of 3200 and 3400 cm\(^{-1}\) and the disappearance of the weak –SH peak at about 2580 cm\(^{-1}\) indicate that the sulfonation reaction had indeed occurred, with the subsequent oxidation of –SH groups into –SO\(_3\)H groups. These infrared spectra have shown the successful preparation of sulfonate modified silica from rice hull ash employing sol gel technique via mercapto modified silica pathway at room temperature and aqueous system. The resultant solids have shown characteristics similar as modified silicas previously synthesized under nitrogen atmosphere and dry toluene [5].

Figure 2 shows diffraction patterns of sulfonate modified silica from acid-washed rice hull ash. The diffraction patterns display broad hump around diffraction angle of 15\(^{\circ}\)-35\(^{\circ}\) which is characteristic of an amorphous structure as has been observed for unmodified silica [12]. The diffraction patterns of mercapto modified silica and sulfonate modified silica from other silica resources (not shown) were also similar. However, it is noted that the peak of sulfonate modified silica is slightly narrow indicating the presence of higher ordered silica framework than that of unmodified silica gel (not shown).
Figure 3 to 5 depicts the electron micrographs of silica gel, mercapto and sulfonate modified silica resulted from synthesis using different silica sources. It can be seen that there were differences on molecular profile of silica gel, mercapto and sulfonate modified silica, respectively based on the raw materials used.

Figure 3. Scanning electron micrographs of silica gels made of different silica resources: a. acid-washed rice hull ash, b. sodium silicate technical grade, and c. TEOS

Figure 4. Scanning electron micrographs of mercapto modified silica made of different silica resources: a. acid-washed rice hull ash, b. sodium silicate technical grade, and c. TEOS

Figure 5. Scanning electron micrographs of sulfonate modified silica made of different silica resources: a. acid-washed rice hull ash, b. sodium silicate technical grade, and c. TEOS

by sol gel process via mercapto modified silica pathway,. Conversion into sulfonate modified silica was performed via oxidation of mercapto ones with H2O2. The successful synthesis of modified silica from rice hull ash was confirmed by their corresponding infrared spectra. It is observed that rice hull ash derived modified silica has comparable chemical characteristics as modified silica from other silica sources (sodium silicate, TEOS and TMOS). Studies of the material porosity are still underway as well as their prospective application as adsorbent toward metal ions.

Conclusions

Sulfonate modified silica has been made from rice hull ash as silica resources. Synthesis was carried out

References