Characteristics of Aluminosilicates Prepared From Rice Husk Silica and Aluminum Metal

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ABSTRACT

This study investigated the use of electrochemical method to prepare aluminosilicates from rice husk silica and aluminum metal.   The aluminosilicate precursors were characterized using Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy. The precursors were subsequently sintered at 700 – 1400 °C and their microstructures and phase compositions were characterized.   Results showed that the proposed method could be used to prepare aluminosilicates with high uniformity in terms of surface morphology and the particle size with mullite and quartz as the major phases formed.

Key words: Rice husk, silica, al**uminosilicates, electrochemical method**

INTRODUCTION

Aluminosilicate minerals with the basic formula of Al_2SiO_5 are composed of aluminum, silicon, and oxygen, in which some of the Si^{4+} ions are replaced by Al^{3+} ions in silicate to produce frameworks with Al-O-Si linkages. Many types of natural aluminosilicates are known, with different chemical compositions and crystal structures. These differences lead to varied physical characteristics, which make these minerals suitable for many industrial applications such as fabrication of glasses[1], ceramics[2], adsorbents[3], fuel cells[4], catalysts[5], building materials[6], and synthetic zeolites[7]. In recognition of the important roles of aluminosilicates mentioned above, the production of synthetic aluminosilicates from pure chemicals has been widely explored by many researchers all around the world. Synthetic aluminosilicates offer several advantages over natural aluminosilicates, which thus support a growing interest in this field. The use of pure chemicals as raw materials facilitates the production of purer and more uniform products, with a desirable

composition and structure, which are not exhibited by natural aluminosilicates. This possibility offers an opportunity to produce aluminosilicates with the desired properties to suit specified applications. As an example, it was reported that aluminosilicates are promising acid catalysts[8]. Aluminosilicates have been applied as catalysts for alkylation of phenol with tert butanol[9] and for the production of dimethylether from methanol[10], as adsorbents for organic dyes from aqueous solution[11], production of alumonosilicate-zeolite[12], and preparation of siliceous-zeolite membranes[13].

In the context of aluminosilicate synthesis, the choice of raw materials and optimization of experimental conditions have been the main focus of many studies. Currently, the sol-gel route is most commonly applied using various chemicals as the source of aluminum and silicon. Liu et al (2000)[14] reported the synthesis of a typical hexagonal aluminosilicate mesostructure with the Si:Al ratio 9:1 by mixing $NaAlO_2$ solution and sodium silicate solution, followed by acidification of the mixture using sulfuric acid to transform the mixture into a gel and aging of the gel produced for 20 hours. In another study[15,16], the synthesis of submicron-sized mesoporous aluminosilicate spheres was carried out using $Al_2(SO_4)_3$ solution and tetraethylorthosilicate (TEOS) as raw materials. The aluminosilicate gel was produced by dropwise addition of TEOS into $Al_2(SO_4)_3$ solution under stirring. The gel was aged at room temperature for 16 hours and dried at ambient temperature before subjected to calcination treatment at 200 °C for 4 hours. Several other studies have reported the synthesis of aluminosilicates from a variety of raw materials, such as sodium silicate and aluminum nitrate[5], potassium metoxy silicate ($K_2O.SiO_2$) and $Al(NO_3)_3$[17], $Al(NO_3)_3$ and TEOS[18], sodium silicate and sodium aluminate[19].

The present study was carried out with the aim of exploring the feasibility of using the electrochemical method to produce aluminosilicate precursors from rice husk silica and aluminum metal as alternative to commonly used aluminum salts. The precursor produced was then subjected to thermal treatment to investigate the phase development of aluminosilicate from the precursor. Rice husk silica was chosen because of the high availability of rice husk as agriculture residue, which makes it a cost effective alternative as silica source. In addition, the potential of rice husk was investigated in recognition of its high silica content[20,21] and the solubility of the silica in alkaline solution, thus enabling the production of rice husk silica in the form of sols.

In this study, an electrochemical method was applied to produce aluminum ions since aluminum metal is known as a reactive electrode, with the standard oxidation potential of 1.66 V, and therefore could be electrochemically oxidized to produce Al^{3+} ions with relatively low potentials. In aqueous solution, the Al^{3+} ions produced by electrochemical oxidation of aluminum metal will react with water to produce various Al(lII) species depending on the pH, which in

alkaline condition the prominent species is Al(OH)$_4^-$ [22,23]. In this study, the pH of the silica sol was 10.2, and therefore it is assumed that the Al(lII) species present in the sample are Al(OH)$_4^-$ ions. Transformation of the mixture from sol to gel will promote the reaction between Al(OH)$_4^-$ and silica to produce the aluminosilicate precursor according to the following reaction[22].

$$(HO)_{4-x}SiO_x^{x-} + Al(OH)_4^- \longrightarrow (HO)_3AlOSiO_x(OH)_{3-x}^{(x+1)} + H_2O$$
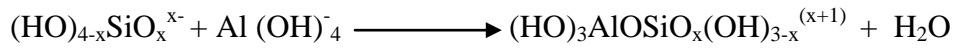
The above chemical equation clearly indicates that the quantity of hydroyaluminosilicate {$(HO)_3AlOSiO_x(OH)_{3-x}^{(x+1)}$}formed is determined by the quantity of Al(OH)$_4^-$ available, which in turn depends on the quantity of Al^{3+} formed during the electrochemical process. In this respect, the amount Al^{3+} ions produced by electrochemical process is governed by the potential applied. Taking the role of this electrochemical variable into account, this study was carried out with particular purpose to study the effect of oxidation potentials on the characteristics of the aluminosilicates precursors produced. Variation of potentials was considered as a base to choose the suitable potential for production of the most homogeneous precursor to be subjected to sintering treatment at different temperatures to study phase development of the aluminosilicate. In this regard, the experiments were conducted at different potentials of 4, 6, and 8 V for a fixed time of 30 minutes. The selected samples were then subjected to sintering treatment at different temperatures of 700, 850, and 1400 °C, and then characterized using x-ray diifraction and scanning electron microscopy.

EXPERIMENTAL

A.   Materials and Instruments

Potassium hydroxide and hydrochloric acid used are reagent grade chemicals obtained from Merck. Two aluminum rods and two graphite rods were used as cathodes and anodes. Rice husks were obtained from local rice milling industry. Before use, the husks were soaked in distilled water overnight for cleaning to remove the dirt, followed by oven dried at 110 ^{o}C overnight. Characteristics of the aluminosilicate were studied using SEM (Philips-XL), FTIR (Perkin Elmer spectrometer), and XRD (Shimadzu XD-610 diffractometer). A Nabertherm electrical furnace was used for heat-treating the samples.

B.   Procedure

Rice husk silica was obtained using an alkali extraction method reported in literature[20,24]. Typically, a sample of 50 g dried husk was mixed with 500 ml of 5% KOH solution in a beaker glass. The mixture was boiled for 30 minutes, and then allowed to cool to room temperature and

left for 24 hours. The mixture was filtered through a Millipore filter to separate the filtrate which contains silica (silica sol). To obtain solid silica, the sol was acidified by dropwise addition of 10% HCl solution until the sol was converted into gel. The gel was aged for three days, and then rinsed repeatedly with deionised water to remove the excess of acid. The gel was oven dried at 110 ^{o}C for eight hours and ground into powder. A specified amount of silica powder was redissolved in 5% KOH solution to obtain silica sol as a sample for electrochemical process.

Preparation of aluminosilicate was carried out using an electrochemical apparatus which consists of a home-made glass container with cover having four drilled holes for assembling the electrodes. Four electrodes were used, two graphite rods as cathode and two aluminum rods as anode, respectively. The electrodes were fixed on the cover and inserted vertically into the cell at a distance of 2 cm from each other, with a 3 cm distance between the bottom of the electrodes and the bottom of the cell to allow easy stirring of the sample during the experiment. The cell was then connected to a variable voltage supply to allow the conduct of experiments at different potentials. To commence the experiment, an aliquot of 200 mL of silica sol was poured into the cell, and the potential was adjusted to specified value. Electrolysis was carried out for 30 minutes, during which the sample was constantly stirred to promote distribution of Al^{+3} ions produced into the silica matrix. The experiments were carried out at potentials of 4, 6, and 8 volts.

After the completion of the experiment, the sample was transferred into beaker glass. The sample was acidified dropwise addition of HCl solution (10%) to trasnform the sample into gel, followed by overnight aging of the gel. The gel was the oven dried at 110 ^{o}C for 8 hours to produce dry solid aluminosilicate precursor, followed by grinding, and the ground powder was subjected to sinterring at 700, 850 and 1400 ^{o}C, at a heating rate of 5 ^{o}C /min and holding time of 6 hours at peak temperatures.

C.   Characterisation

Microstructural analysis was conducted using SEM Philips-XL, on polished and thermally-etched samples. The functionality of the sample was investigated using a Perkin Elmer FTIR spectrometer. The sample was ground with KBr of spectroscopy grade, and scanned over the wave number range of 4000-400 cm^{-1}. Powder XRD patterns were recorded to analyze phase development of aluminosilicate in order to gain information regarding the effect of sintering temperatures. The samples were examined using an automated Shimadzu XD-610 X-ray diffractometer. The operating conditions used were CuK$_\alpha$ radiation (λ = 0.15418), produced at 40 kV and 30 mA, with a 0.15^o receiving slit. Patterns were recorded over goniometry (2θ) ranges from 5-100° with a step size of 0.02, and using post-diffraction graphite monochromator with a NaI

detector. The diffraction data were analyzed using the JADE software after subtracting background and stripping the $CuK_{\alpha2}$ pattern[25].

RESULTS AND DISSCUSION

A. Characteristics of aluminosilicate precursors

As previously stated, the preparation of aluminosilicate precursor was carried out using three different potentials. To evaluate the effect of potentials on the surface morphology, the three samples were characterized using SEM, and the micrographs produced with the magnification of 20.000 are shown in Figure 1. By visual inspection of the micrographs it can be seen that the effect of potential on the particle size and the homogeneity of the surface is quite evident. The sample prepared using the potential of 4 volts is characterized by the existence of particles with different sizes, indicating the presence of silica and Al(III) species, as discussed later in the FTIR results.

In this sample, the prominent particles are most likely the silica present as larger particles with grey color, suggesting that the sample is dominated by the silica. The presence of aluminum species distributed in the silica matrix is indicated by the existence of smaller particles with bright color. This feature of heterogeneous morphology suggests that the Al^{+3} ions produced from the anodic oxidation of the Al metal anodes were insufficient to mix homogeneously with the silica, considering the standard oxidation potential of aluminum is 1.66 volts, whereas the process was carried out in non-standard condition.

Fig.1. Micrographs of the samples prepared using the potentials of (a) 4, (b) 6, and (c) 8 V.

Increasing the potential to 6 V was found to result in significantly different features when compared to that observed for the sample prepared using the potential of 4 V. As can be seen in Fig. 1b, the surface of this sample is characterized by smaller particle size and more homogeneous distribution of aluminum species within the silica matrix as a result of increased number of Al^{+3} ions produced with higher applied electrochemical potential. This feature also indicates that the aluminum species incorporated homogeneously within the silica, since the Al^{+3} ions are able to form chemical bonds with the silanol groups of silica molecules.

When the potential was increased further to 8 V, the sample was marked by the formation of clusters of different sizes. Formation of clusters in this sample is most likely due to agglomeration of aluminum species as a results of further increases in the amount of Al^{+3} ions during the electrochemical process. The results of SEM analyses clearly indicate that the most homogeneous sample was produced using the potential of 6 V, and based on this feature, this sample was further

characterized using FTIR and XRD. This sample was also subjected to sintering at 700, 850, and 1400 °C, followed by characterization using SEM and XRD.

Figure 2 shows the infrared spectrum of the sample prepared with potential of 6 V which indicates the existence of several absorption bands with varied relative intensities. The most obvious peak is located at 3454 cm^{-1}, which is commonly assigned to stretching vibration of O-H bond in silanol group and water molecule. The contribution of water is confirmed by the presence of absorption band at 1647 cm^{-1} [21,26], as a result of bending vibration of the H-OH. The presence of **peaks associated with O-H bond is most likely due to the presence of aluminum hydroxide species,** $Si(OH)_4$, and trapped water. Two peaks located at 1383 and 468 cm^{-1} are commonly assigned to stretching vibration of Si-O-Si, 803 and 1068 cm^{-1} to vibration of Al-O-Al, suggesting that some of the $Si(OH)_4$ and aluminum hydroxide was converted into their corresponding oxides

Fig. 2. FTIR Spectrum of the sample prepared using the potential of 6 V

The sample prepared with the potential of 6 V was further characterized using XRD. This characterization was carried out to evaluate the crystallographic structure of the sample in order to get more insight on the formation of aluminosilicate moiety and to ascertain whether the sample was amorphous or crystalline phase. The XRD pattern of the sample is shown in Figure 3.

Fig. 3.   The x-ray diffraction pattern of the sample prepared using the potential of 6 V

As can be seen, the diffraction pattern presented in Figure 1 indicates that the sample is essentially amorphous, marked by the existence of a broad peak at 2θ in the range of 20-35º, which is attributable to amorphous aluminosilicate[27]. This suggests that silica and Al(III) species existed as hydrogel, which is supported by the presence of hydroxyl groups in the FTIR spectrum. This finding is in good agreement with the existence of $Al(OH)^{4-}$ gel and amorphous silica at lower temperature as suggested by others [16].   These results confirmed that the sample is composed of $Al(OH)^{4-}$ species and silica, therefore has the potential as aluminosilicate precursor. For this reason, this sample was subjected to sintering at different temperatures in order to evaluate the phase transformation of precursor as a function of sintering temperature.

B.   Phase development studies

To examine the phase development, the sintered sample   at   700, 850, and 1450 °C were characterized using XRD and SEM. The XRD patterns obtained are shown in Figure 4a-c, in which the phases were identified with the aid of PDF diffraction lines using the search-match method [28].

Fig. 4. The x-ray diffraction patterns of the samples prepared using the potential of 6 V sintered at different temperatures, (a) 700, (b) 850, and (c)1400°C. Legend: m = Mullite, q = Quartz.

The diffraction patterns in Figure 4a indicate that the sample sintered at 700 °C was still amorphous, marked by the existence of a broad peak, most likely resulted from accumulation of small amount of silicon oxide, aluminosilicate, and aluminum oxide. These phases were proposed based on the findings of others[29], who described the formation of γ-alumina and crystoballite in the aluminosilicate sample prepared from $AlCl_3$ and TEOS using sol-gel technique.   Formation of crystalline phases was observed for samples sintered at higher temperatures. In the sample sintered at 850 °C (Fig. 4b), three phases were identified. The first phase is quartz, which is indicated by the most intense peak at 2θ = 25.2 (PDF-46-1045), the second phase is mullite with the most intense peak at 2θ = 28.2 (PDF-15-0776), and the last peak is alumina with the most intense peak at 2θ = 34.9 (PDF-46-1212).   Detections of quartz and alumina demonstrate that at 850 °C, significant transformation of amorphous rice husk silica and aluminum hydroxide has taken place, and some of quartz and alumina reacted to produce metastable mullite phase, as has also been reported by others[30]. When the sintering temperature was further increased to 1400 °C (Figure 4c) a substantial change in crystallinity of the sample was observed, as characterized by sharp increase of mullite phase and diminish of quartz as well as alumina phase, suggesting that both quart and alumina have completely transformed into mullite.   In previous studies[30,31,32], it has been reported that at temperature around 1400 °C, quartz was converted into liquid silica which penetrated alumina grain aggregates, and the two reacted to produce mullite. This is in good agreement with this study where mullite was the major phase present at 1400 °C.

Fig. 5. SEM images showing the microstructures of samples sintered at different temperatures,
(a) 700, (b) 850, and (c) 1400 °C.

Figure 5 shows microstructures of samples after they were subjected to sintering at different temperatures, revealing quite the   effect of sintering temperature on the surface morphology. Comparison of the sample sintered at 700 °C with the unsintered sample (Figure 1b) shows that sintering led to agglomeration of aluminum oxide particles. This process resulted in separation of aluminum oxide agglomerates from silica agglomerates, producing clusters of different shapes and sizes (Figure 5a) in amorphous state as evidently displayed by the XRD pattern of the sample (Figure 4a). The microstructure of sample sintered at 850 °C was characterized by the existence of larger grains with different shape, indicating that increased temperature intensified the

agglomeration of the particles separated by grain boundaries. As seen by the XRD, this sample is characterized by the existence of quartz and small amount of mullite. This suggests that at this temperature, the siliceous phase has started to melt and reacted with alumina aggregates to form mullite. The microstructure of sample sintered at 1400 °C displays very uniform grains with smooth surface and without clear grain boundaries. The existence of granular microstructure with smooth surface suggest that at this temperature the quartz had converted into liquefied silica which penetrated the alumina aggregates, thus intensifying the formation of mullite as supported by XRD results (Figure 5 c), in which the only phase detected is mullite.

Conclusions

The present work demonstrates that it is possible to prepare aluminosilicate precursors by using the electrochemical method from rice husk silica and aluminum metal to replace the commonly used raw materials. Overall, the results demonstrate that the aluminosilicate precursor with high uniformity in terms of surface morphology and the particle size could be obtained using the proposed method. Characterization of samples using XRD and SEM show that the precursor synthesized could be transformed into mullite at 1400 °C, thus suggesting that the electrochemical method is a promising technique for producing aluminosilicate materials.

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