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The utilization of bagasse fly ash for mesoporous silica synthesis

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Abstract. Natural silica sources such as from biomass ashes provide an alternative cheap silica precursor for synthesizing advanced materials. Mostly, the silica content in the biomass is in the form of amorphous structure which is suitable to be used directly into the material formation. Bagasse fly ash (BFA) contains carbon and silica in a significant amount. The silica content can be recovered by a simple NaOH fusion method followed by water dilution to produce sodium silicate solution. Then, the obtained solution can be used for various material preparations such as zeolites and mesoporous silica materials. It was observed that the alkaline dissolution method is not only extracting silica but also other content such as Alumina and trace metals. Two different type of mesoporous silica, MCM-41 and SBA-15, have been synthesized by incorporating suitable template and sol-gel hydrothermal method using extracted silica source. The synthesized materials were characterized using TEM and XRD to confirm the morphology and crystal structure. Gas adsorption experiment of n-hexane has been done to examine the adsorption behaviour of the two prepared mesoporous silica. The results suggest that low cost natural silica sources can be an alternative for advanced material preparation.

1. Introduction

Recent trend in material science is utilizing abundant solid waste materials such as biomass [1], manure [2], coal ash [3] and bagasse fly ash [4] to create novel products. In terms of fly ash, there are two major source of this waste which are coal and biomass combustion system. Bagasse fly ash (BFA) is a solid residue from bagasse burning system in sugar industries. The main content inside the ash are silica and carbon which open many possibilities in utilization. The carbon rich particles can be easily separated from silica rich ash fraction by mechanical sieving or floatation method [5]. The carbon fraction then can be used for activated carbon preparation using chemical activation [5] and chemo-physical activation [6] while the silica rich particles can be used for preparing synthetic zeolites [7]. Moreover, a specific zeolite type can be grown on the carbon particles for creating a unique carbon-zeolite composite from BFA [8]. To increase the flexibility and reliability in preparing silica based material, the silica content inside the ash should be extracted to get liquid (supernatant) or powder precursor.

Ordered mesoporous silica is one of novel materials that commonly synthesized from expensive pure silica precursors such as TEOS, fumed silica and water glass. Recently the greener precursors obtained



from natural or solid waste resources for mesoporous silica preparation are intensively studied. In the early attempt of using other source of silica than the commercial ones, coal fly ash was the potential option due to its abundant availability [9], high silica content [10] and can be processed by green approach [10]. Up to now, many different silica sources have been used that can be categorized into three large groups. The first group is from agricultural residues such as rice husks [11], wheat straws [12], cane leaves [13], stems [14], bagasse [15] and weeds [16]. The second group is from mineral processing related activities such as mine tailing [17], iron ore tailing [18], clays [19], slag [20], and geothermal sludge [21]. And the third group is from urban waste such as LCD-TFT electronic waste [22] and municipal solid waste residue [23]. The type of prepared mesoporous silica were diverse from highly ordered such as MCM-41, SBA-16, and SBA-15 to less ordered solid structure such as silica gels and amorphous aluminosilicate.

From the three silica source groups, the precursor from agricultural waste is considered lower in the content of impurities (heavy metals), easier extraction process of amorphous natural silica and renewable resources. However in general, the problem of this resource is the collection since the agricultural sites is usually widespread. Unless the agricultural products are brought to a large post harvesting industry such as cane which is collected and transported to cane sugar industries. By this consideration, bagasse fly ash (BFA) side product of bagasse (pressed cane) burning in sugar industry can be a potential candidate for silica based advanced materials preparation in a mass production.

In here, silica extraction using NaOH fusion method has been performed to obtain sodium silicate solution from BFA. This method can ensure a better extraction efficiency of silica content than NaOH dissolution method under room condition [5]. The obtained solution contains high silica content that sufficient as a chemical precursor for preparing highly ordered mesoporous silica i.e. MCM 41 and SBA 15. The usage of this resources for preparing highly ordered materials is still rare to be found.

2. Methods

The Bagasse fly ash was collected from Indonesian sugarcane industry which its properties has been reported before [5]. To extract the silica content, BFA was mixed with sodium hydroxide (1 : 1.2, BFA : NaOH by weight) and heated at 673 K for 1 h to obtain a fused mass using closed container (hydrothermal reactor), which was cooled to room temperature and milled for several minutes. The obtained fused powder was mixed with water in a weight ratio of 1:4 and aged for 1 day at room temperature with agitation. The resultant suspension was then filtered to obtain the supernatant. The concentrations of Si, Al and Na in the supernatant measured by ICP method (Perkin Elmer Optima 8300) are 27,000, 1,700 and 7,000 ppm, respectively.

In a typical MCM-41 synthesis, 0.433 g of $C_{16}H_{33}(CH_3)_3NBr$, 7.5 ml water and 0.35 g aq. NH_4OH were combined with 19 ml of the supernatant and the mixture hydrothermally treated at 97 °C for 3 days. The synthesis pH was adjusted at about 10.25 by using 1 M acetic acid solution before hydrothermal treatment. Further details about such hydrothermal apparatus can be found elsewhere [24].

For synthesizing of SBA-15, the surfactant used in the synthesis was triblock polymer $(EO)_{20}(PO)_{70}(EO)_{20}$. SBA-15 was prepared by using 1.8 g of triblock polymer dissolved in 75.0 ml aq. HCl (2 M), and then 20.0 ml of the supernatant was added at room temperature under vigorous stirring. To this reaction mixture, 5.0 ml of 35% HCl and 25.0 ml of distilled water was quickly added. The resulting gel was aged at room temperature for 1 day and subsequently heated at 90 °C for 2 days. All samples were calcined at 550 °C for up to 6 h. Then, MCM-41 and SBA-15 samples were characterized using XRD (Rigaku, Multiplex) for determining the ordered pore structure of the solid, and TEM (JEOL) to observe the pore structure and morphology of the materials, and also Surface Area Analyzer (Quantachrome, Autosorb 1) to understand the porosity of the materials. Beside common characterization methods, the samples adsorption capacity was studied using vapour (n-hexane) adsorption method at room temperature by a self-assembled gravimetric adsorption apparatus.

3. Result and discussion

The MCM-41 and SBA-15 prepared from silicate solution have been characterized by nitrogen adsorption, SEM and XRD. The results displayed in Figure 1 are nitrogen adsorption isotherm profile and PSD (pore size distribution) of the materials. The capillary condensation of MCM-41 appears at about $P/P_0 = 0.35$ while for SBA at about $P/P_0 = 0.7$ which are typical for those materials [25]. This steep increase and decrease (hysteresis loop type H1) of the adsorbed nitrogen volume indicates the narrow pore size in a mesoporous range. Higher P/P_0 of the hysteresis loop belongs to the higher pore size materials (SBA 15) as shown also in the PSD (Figure 1.d). The detailed porosity of SBA-15 and MCM-41 is listed in Table 1.

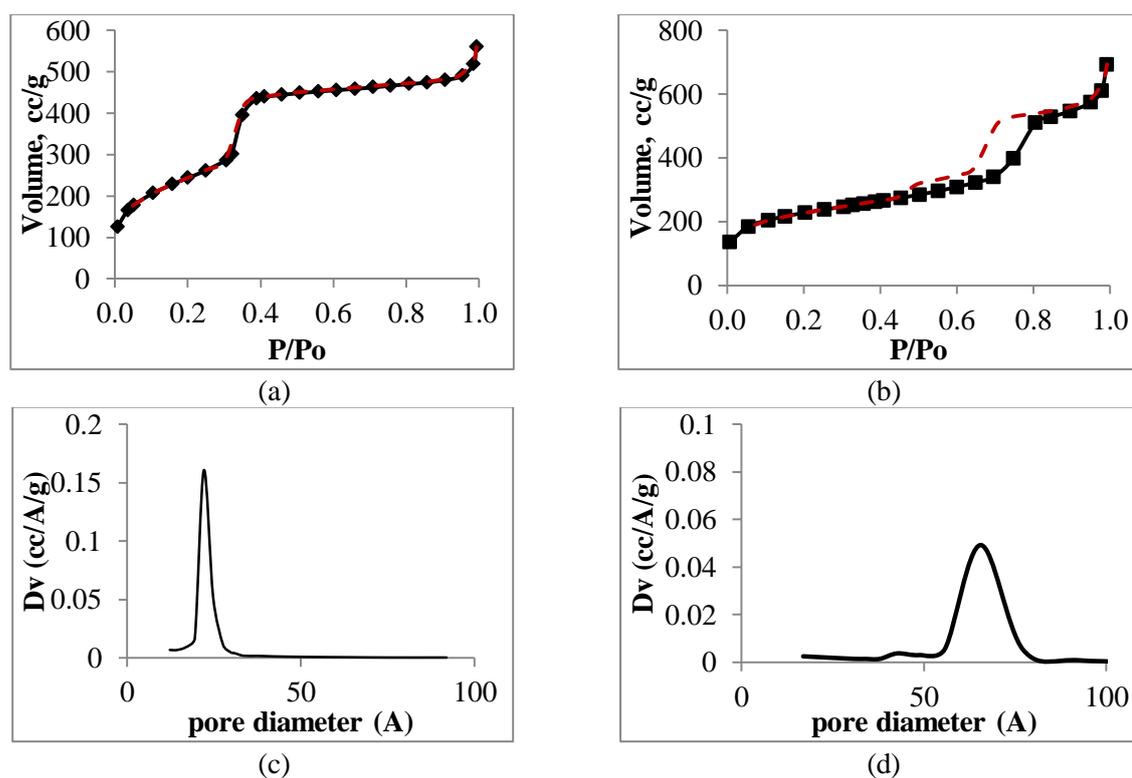


Figure 1. N₂ adsorption (black line) and desorption (red dashed line) isotherms of MCM-41 (a) and SBA-15 (b) and pore size distribution of MCM-41 (c) and SBA-15 (d).

From the TEM image in Figure 2, well ordered pore structure can be observed which confirm the suitability of the preparation method. From the images, it is shown that the pore inside SBA-15 is larger than in MCM-41 which is similar to PSD from the nitrogen adsorption results above. Thicker pore wall of SBA-15 than MCM-41 is also can be observed which suggest the suitability of this material for aqueous application. In brief, all these characterization results are supported each other such as BET pore size distribution and SEM image which shows ordered pore structure with similar pore size.

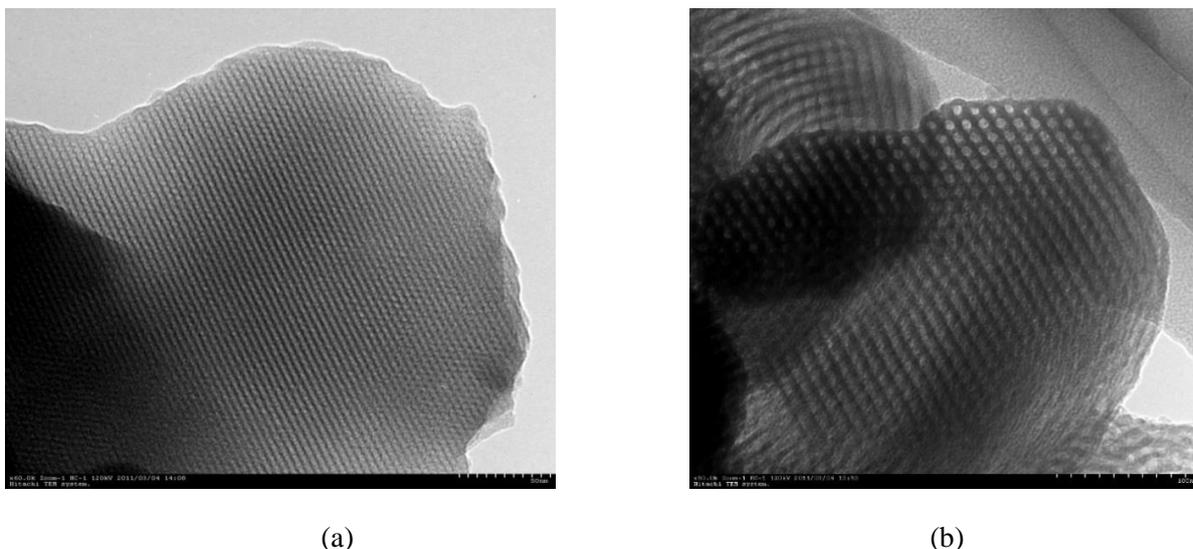


Figure 2. TEM image of MCM-41 (a) and SBA-15 (b).

The ordered pore structure of mesoporous silica has also been confirmed by XRD analysis as shown by Figure 3. The XRD profile has a good agreement with early report [26]. The pattern basically consists of a single intensive peak at very low angle and followed by weak peaks at higher 2θ degree. These peaks can be indexed on a hexagonal unit cell.

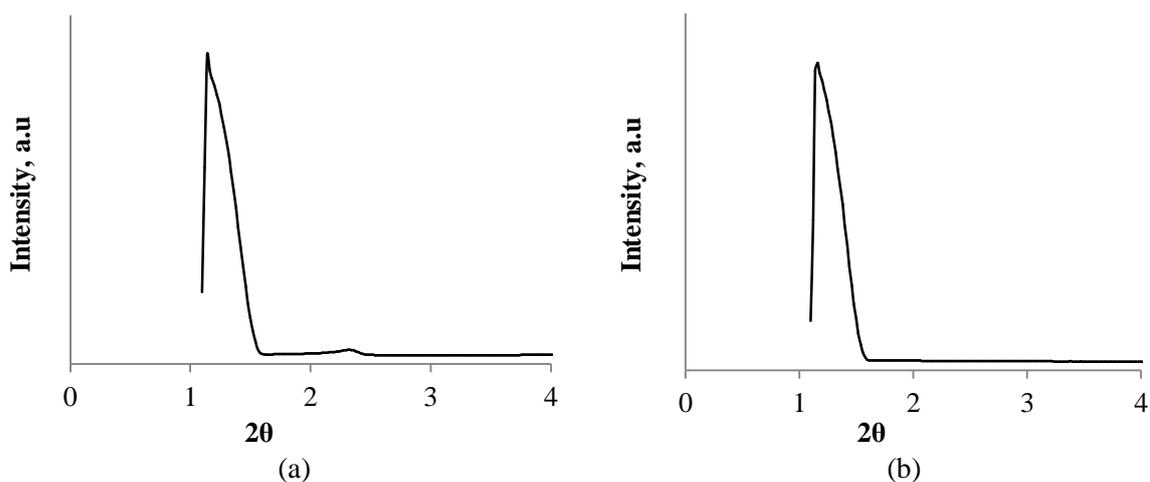


Figure 3. XRD pattern of MCM 41(a) and SBA 15 (b).

The porosity data of mesoporous silica is provided in Table 1. From the data, high surface area materials have been successfully obtained with most of the pore volume is in the mesopore range. It is indicated that the sodium silicate extract from BFA has reasonable purity and contain no inhibitory substance for mesoporous silica formation.

Table 1. Porosity of synthesized mesoporous silica material.

Sample	Vol.microporous (cc/g)	Porosity Vol. Mesoporous (cc/g)	Surface area BET (m ² /g)
MCM-41	0.30	0.56	885
SBA-15	0.37	0.50	775

In the literature, some synthesis schemes variation have been implemented using several agricultural waste as the silica precursor. A summary of the experiments is provided in Table 2. From the sample's porosity point of view, it is indicated the most residue are suitable to be used for silica precursor. The results in this study is also comparable with the high porosity samples in the table.

Table 2. Previous synthesis of mesoporous silica results from agricultural residues.

Raw materials	Silica type	Extraction route	Template	Optimum properties	Ref.
Rice husk	na	Boiled in NaOH solution	lignin	surface area: 471.7 m ² /g	[11]
Wheat straw ash	MCM 41	Boiled in NaOH solution	CTAB	Surface area: 1311.6 m ² /g total pore vol.: 1.053 cc/g	[12]
Sugarcane leaf ash	SBA-15	Sonication in heated NaOH solution	P123	surface area: 632 m ² /g. total pore vol.: 1.232 cc/g	[13]
Stem cane ash (SCA)	SBA 16	Boiling in NaOH solution and crystallization	F127	surface area: 316.5 m ² /g total pore vol.: 0.3 cc/g	[14]
Bagasse ash	na	Boiling in NaOH solution	PEG	surface area: 656 m ² /g total pore vol.: 0.8 cc/g	[15]
Sedge (<i>Carex riparia</i>) ash	MCM 41	Acid refluxing and leaching	CTAB	Surface area: 1174 m ² /g total pore vol.: 0.98 cc/g	[16]

Vapour isotherm curves of the two mesoporous silica are provided in Figure 4 which are typical of type IV adsorption–desorption isotherms. The vapour uptake process can be described as several steps which are monolayer formation at low relative pressure, then multilayer formation followed by capillary condensation of mesopore filling indicated by high increase of adsorbed vapour uptake and then external surface adsorption represented by very low uptake to the highest achievable partial pressure. In terms of hysteresis loop, the phenomenon is observable only for SBA-15 while for MCM-41 the adsorption and desorption is almost reversible. This can be a clue of larger pore size existence in SBA-15. At low partial pressure (less than 0.5) the uptake capacity of MCM-41 is superior to SBA-15, this could be due to small pore size of this material which attract hexane molecule stronger than larger pore size. However at higher pressure, the larger pore size in SBA 15 can be filled with more hexane molecule thus the adsorption capacity surpassing the capacity of MCM-41.

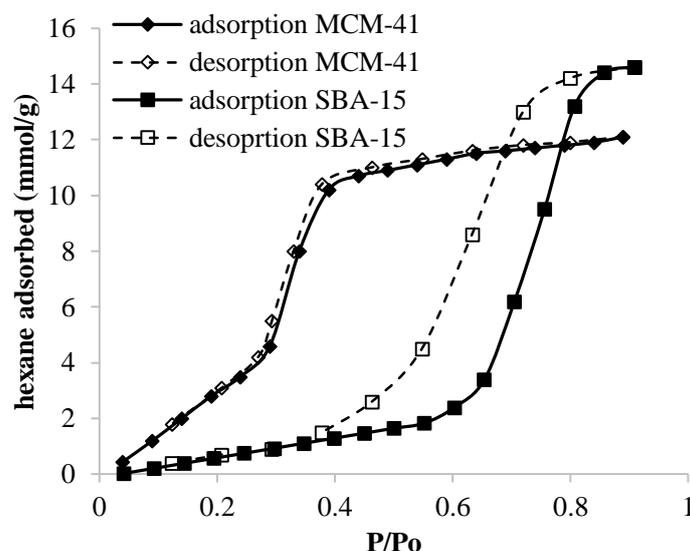


Figure 4. N-hexane adsorption-desorption isotherm of MCM-41 and SBA-15.

4. Conclusions

High ordered mesoporous silica materials have been successfully prepared from alkali fusion supernatant of BFA. The prepared samples exhibited highly ordered hexagonal structure, high surface area and narrow pore size distributions. The successful attempt indicated that the silicate extract is suitable to be used as the precursor. The other impurities such as aluminate and trace metal elements inside the supernatant are not hindering the material synthesis. This finding opens a wide possibility in utilizing waste to produce advanced material such as catalysts and adsorbents.

5. References

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