COMPARATIVE ANALYSIS OF TEXTURAL PROPERTIES OF SBA-15 PREPARED FROM RICE HUSK AND TETRAETHYLORTHOSILICATE

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Abstract

SBA-15 materials were synthesized using rice husk. In addition, SBA-15 was synthesized by using tetraethylorthosilicate as a reference material. The obtained materials were characterized by XRD, TEM and adsorption/desorption nitrogen method. Though less ordered hexagonal mesoporous SBA-15 materials could be obtained from rice husk they exhibit high surface area and large pore size in comparison with one from tetraethylorthosilicate. Morphology of SBA-15 prepared from rice husk consists of curve-rod like silicas while that of SBA-15 from tetraethylorthosilicate consists of rod-like silicas. The difference in mesoporous tubular structure and textural properties of synthesized SBA-15 could be assigned to inherent impurities of metal ions in rice husk.

1. INTRODUCTION

Rice husk is a by-product from rice mill that was used as an energy source in many industries such as biomass power plant and rice mill. Rice husk is rich in silica and can be an economically valuable raw material for production of natural silica [1, 2]. In Vietnam, a large amount of rice husk is produced and practically used later in agriculture as low-value material.

Highly ordered large-pore mesoporous silica SBA-15, which has considerably thicker pore walls than MCM-41 was recently synthesized in acid media using amphiphilic triblock copolymer as the structure-directing agent and various silica sources: sodium silicate, tetraethylorthosilicate (TEOS) [3]. Thus silica source from rice husk would be alternative for synthesis of SBA-15. This benefit is to enhance the rice husk value.

In this paper, SBA-15 was prepared by using silica source from rice husk. The textural properties were then compared with those of SBA-15 synthesized from tetraethylorthosilicate (TEOS).

2. EXPERIMENTAL

Raw materials used in this paper were rice husk collected from Thua Thien Hue province. Silica solution was extracted from rice husk under refluxing in NaOH solution. Obtained filtrate was used as silica source. The SBA-15 sample was synthesized by using triblock copolymer (P123) as surfactant and rice husk as silica source [4]. The molar ratios of reactant were $1SiO_2$: 0.0167P123: 5.16 HCl: 162 H_2O. P123 was dissolved in distilled water until a clear solution was obtained before an addition of HCl and silica solution to form precipitation. Finally, the resulting solid product was filtered, washed with distilled water, dried at 373 K for 24 hours and then calcined at 773 K for 10 hours. The obtained SBA-15 materials were denoted as RH-SBA-15. In addition, SBA-15 was synthesized by using TEOS as a reference material by procedures described by Stucky et al [3] and denoted as TEOS-SBA-15.

The silica content of dried rice husk was analyzed by gravimetric method.

Nitrogen adsorption/desorption isotherms of calcined samples were obtained using Omnisorp-100 sorptometer at 77K, after degassing at 200^{o}C and 10^{-5} mmHg for at least 4 hours. The specific surface areas (S_{BET}) were calculated by the standard BET method for adsorption data in a relative pressure range from 0.05 to 0.3 [5] The pore-size distribution (PSD) was determined by the Barrett-Joyner-Halenda (BJH) method from desorption isotherm data. Primary mesopore diameter, d_p, was determined from the maximum of a PSD curve. *t*-plot method has been applied to quantitatively determine the mesopore surface area (denoted as S_{BJH}). The t is a function of relative pressure expressed as Eq. 1 [6].

$$t = \left[\frac{13.99}{0.034 - \log \frac{P}{P_o}} \right]^{\frac{1}{2}} \quad (1)$$

Usually, when micropores are present the *t*-plot will exhibit a positive intercept from which the micropore volume is calculated. Using the slop(s) of linear part of the *t*-plot in the range 0.45 < t < 1.0 nm, the mesopore surface area S_{BJH} can be calculated by Eq. 2, considering mesoporous surface as external one of material.

$$S_{BJH} = s \times 15.47 \quad (2)$$

The constant 15.47 represents the conversation of the gas volume to liquid volume. The micropore surface area can be therefore calculated as the difference between the total surface area S_{BET} and the mesopore surface area S_{BJH}.

The total pore volume V_t was determined from the amount of nitrogen absorbed at 77 K at the relative pressure of 0.99. At such a pressure the main channels of the sample are assumed to be completed filled with nitrogen. The total mesopore volume was obtained by integrating the PDS curves from pore size of about 2.0 nm to the upper limit of 50 nm. The micropore volumes were calculated from the difference between total pore volume V_t and total mesopore volume

The mesoporous phases of Si-SBA-15 were monitored by powder low-angle X-ray diffraction (XRD), recorded on 8D Advance (Bruker, Germany) with CuK_α radiation in the range of 2θ from 0.5 to 10° with a scan step size of 0.01° and a scan step time of 0.04s. The length of the hexagonal "unit cell" a_o was calculated using the formula $a_o = \frac{2d_{100}}{\sqrt{3}}$ [6]. Pore wall thickness, t_w, was assessed by subtracting d_p from a_o. The morphology was studied by TEM (JEM microscopy-1010).

3. RESULTS AND DISCUSSION

The silica content of rice husk was analyzed by gravity method. This amount of SiO_2 was obtained up to considerable values. The amount of impurities was also found such as CaO, MgO, MnO_2 etc. The results of element analysis were listed on table 1.

SiO_2	CaO	MgO	MnO_2	Na_2O	K_2O
8.96%	0.0024%	0.0026%	0.0043%	0.0200%	0.0300%

It is noted that the silica source from rice husk contains remarkable amount of transition metals including magnesium, calcium, magnesium etc. while one from TEOS does not. Thus the textural properties of synthesized SBA-15 materials should depend on silica sources.

Fig. 1 shows XRD patterns of RH-SBA-15 and TEOS-SBA-15. Three reflections of mesoporous phases were found at low angle reflection which were indexed as (100), (110), and (200) [7]. These sharp signals indicated the long-range orders of the uniform hexagonal mesoporous structure. It is noted that in the case of RH-SBA-15, the peak (100) is broader than that of TEOS-SBA-15. The $d_{spacing}$ of (100) peak increases from 10.4 nm for TEOS-SBA-15 to 11.7 nm for RH-SBA-15. This implies the enlargement of the distance between two centers of adjacent pores ("unit cell" a_o) in hexagonal arrangement. This effect may be due to the introduction of metals as impurities in rice husk in which the Me-O bond are longer than the Si-O bond.

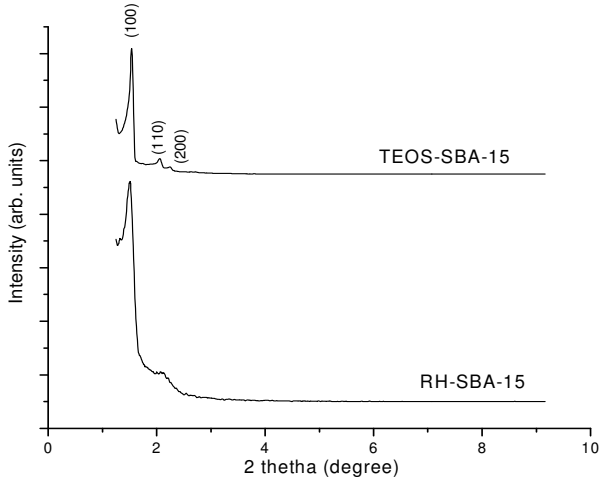

Fig. 1: The XRD patterns of RH-SBA-15 and TEOS-SBA-15 materials

Figs. 2 and 3 show TEM observations of TEOS-SBA-15 and RH-SBA-15, respectively. Both top and side views obtained from TEM indicate the well-ordered hexagonal mesoporous structure for all samples. The cross sectional patterns showed hexagonal structure which is the distinctive feature of SBA-15. The pore diameters estimated from the top view were approximately 4-5 nm for both SBA-15. The highly ordered TEOS-SBA-15 consists of the gathering of rod-like silica while RH-SBA-15 consists of curve-rod like silica.

The nitrogen adsorption-desorption isotherms of RH-SBA-15 and TEOS-SBA-15 were shown in Fig. 3. Very similar type IV isothermers and large desorption hysteresis were observed for both samples, which is characteristic of mesoporous materials with cylindrical pores.

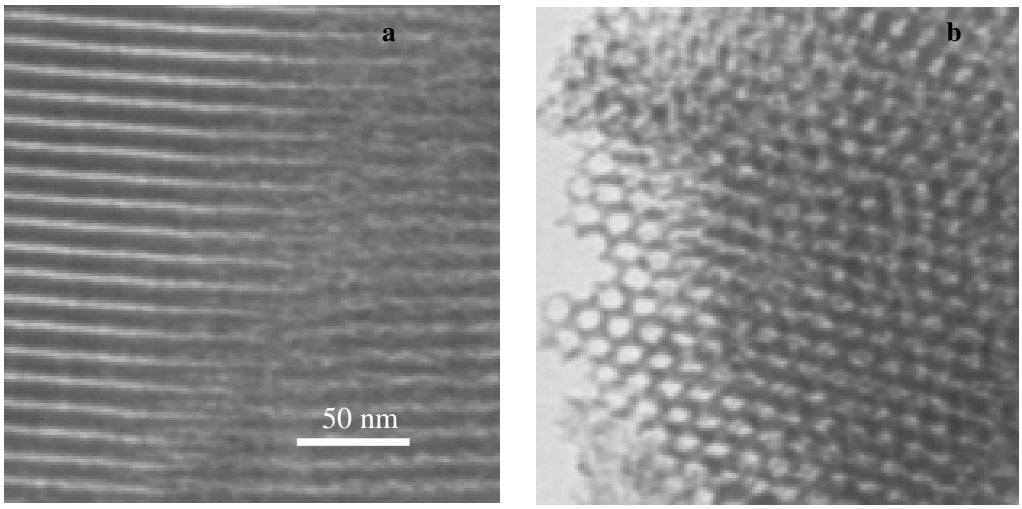

Fig. 2: TEM images of TEOS-SBA-15: side view (a) and top view (b)

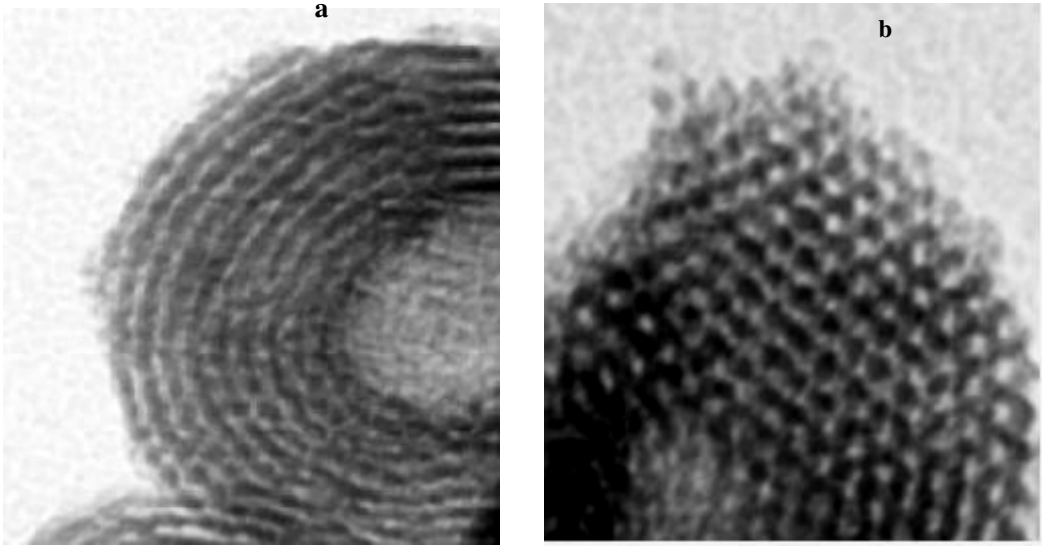

Fig. 3: The TEM images of RH-SBA-15: side view (a) and top view (b)

The textural parameters of mesoporous silicas calculated from adsorption/desorption nigtrogen data are summarized in table 2. As can be seen, S_{BET} of RH-SBA-15 is rather higher than that of TEOS-SBA-15. Even d_p of RH-SBA-15 is larger than that TEOS-one its S_{mes} is lower than that of TEOS-SBA-15. The increasing total surface area for RH-SBA-15 should be related to the formation of microporosity.

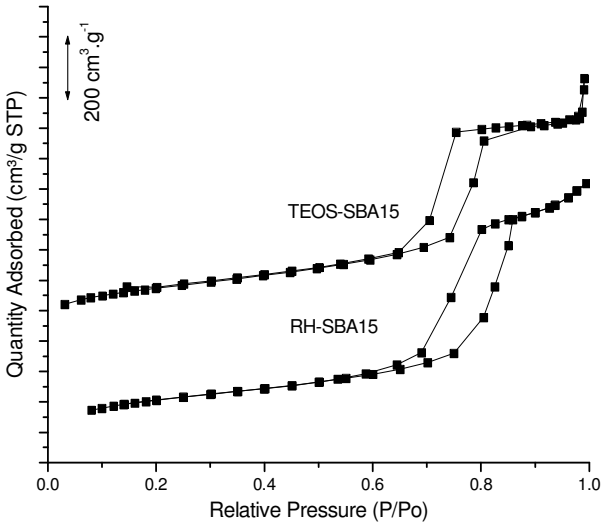

Fig. 4: Adsorption/desorption nitrogen isotherms of SBA-15 synthesized from TEOS and rice husk

Table 2: Textural properties of synthesized SBA-15 samples

Sample	S_{BET} ($m^2.g^{-1}$)	S_{mes} ($m^2.g^{-1}$)	S_{mic} ($m^2.g^{-1}$)	d_p (Å)	V_{mes} ($cm^3.g^{-1}$)	t_w (Å)
TEOS-SBA-15	626.0	511.9	114.1	77.2	1.17	43.4
RH-SBA-15	733.7	466.4	267.3	91.3	1.43	37.7

It is clear that the polymer-ion interaction plays an important role in the morphology. In fact, it is well-known that metal ions form crown-ether-type complexes with polymeric PEO and PPO units [8], the multivalent metal species (M^{n+}) can associate preferentially with the hydrophilic PEO moieties, because of their different binding affinities for PEO and PPO. It is known that, the SBA-15 materials are prepared by the use of nonionic surfactants as organic structure directing agents in acid media *via* $(S^0H^+)(X^-I^+)$ synthesis route where S^0 is nonionic surfactant, H^+ proton, X^- acid anion, and I^+ protonated silanol group.

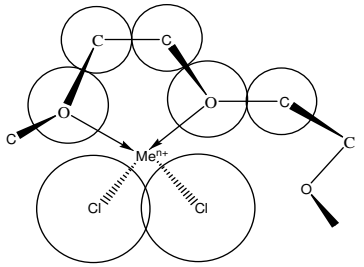

Fig. 5: Molecular model of the transition metal-PEO interaction

In the case of synthesis mixture containing metal ions, the modified pathway can be now denoted as $N^0[(M^{n+}H^+)X^-]I^+$, where M^{n+} is metal ions such as Mn^{2+}, Mg^{2+}, K^+, etc. Thus, the proposed assembly mechanism for these diverse mesoporous metal oxides includes PEO-metal chelating interactions in conjunction with electrostactics, van der Waals forces, ect., to direct mesostructure formation.

Futhermore, since the structure directing effect is irrespective of the anions used in the synthesis, and only the Cl^- anion resulted in a branched, network-like structure, presumably the complex symmetry as illustrated in Fig. 5 may also play an important role in the synthesis by modification of the electrostatic interaction or the local curvature energy at the interface of the inorganic silica and the surfactant

4. CONCLUSIONS

Synthesis of SBA-15 material from rice husk was investigated. The obtained SBA-15 material possesses high specific surface area, large pore diameter. The silica from rice husk can be utilized for synthesis of SBA-15 material instead of commercial silica.

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