Biogenic Silica from Rice Husk Ash - Sustainable Sources for the Synthesis of Value Added Silica

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Ordered mesoporous silica with two dimensional MCM-41 or three dimensional MCM-48 pore structure are prepared via pseudomorphic transformation. Rice husk ash (RHA) with high purity was used as silica source for the first time. Additionally, the kinetics of pseudomorphic transformation of rice husk ash into MCM-41 was studied. MCM-48 was synthesized by pseudomorphic transformation of preformed MCM-41. The obtained MCM-41 and MCM-48 materials possess high specific surface areas of 1,210 and 815 m^2 g^{-1}, respectively. Both materials are characterized by uniform mesopores and high pore volumes (pore width of 4.1 nm and pore volume of 1.0 cm^3 g^{-1} for MCM-41, whereas MCM-48 exhibits a mean pore width of 3.3 nm and pore volume of 0.75 cm^3 g^{-1}). In addition, the preservation of the macroscopic morphology of rice husk ash after pseudomorphic transformation is shown.

1. Introduction

Biogenic silica, e.g. rice husk ash, can be considered as alternative source to synthesize value-added porous silica rather than the common water glass (Sanhueza et al., 2006). There are many studies on the transformation of commercial amorphous porous silica species to ordered mesoporous MCM-41 or MCM-48 type silica via the so-called pseudmorphic transformation (Galarneau et al., 2002; Petitto et al., 2005). It is worth to note in this context that the macroscopic morphology of the original silica is maintained during transformation. An advantage of this method consists in the possibility to generate materials with a high specific surface area and a highly ordered pore system that can later be used as stationary phases for liquid chromatography (Galarneau et al., 2006). In the current study, the pseudomorphic transformation was applied to prepare ordered mesoporous silica of MCM-41 and MCM-48 types from rice husk ash. The kinetics of pseudomorphic transformation of biogenic silica to MCM-41 materials was studied in the first step. The applied synthesis procedure was similar to that recently applied by Einicke et al. (2013). It was only slightly modified in this work by an additional stirring step. The kinetics of pseudomorphic transformation of rice husk ash into MCM-48 does not follow the common behaviour of MCM-41/MCM-48 phase transition as a function of the reaction time (Petitto et al., 2005), even by the utilization of a higher concentration of the surfactant (Cetyltrimethylammonium Hydroxide). The phase transition MCM-41/MCM-48 was obtained only by pseudomorphic transformation of the calcined MCM-41.

2. Materials and Techniques

2.1 Preparation of biogenic silica precursor

The precursor rice husk ash (RHA) was obtained by a thermo chemical treatment of Egyptian rice husk (Alyosef et al., 2013), except for the milling step. Pre-shaped RHA is completely amorphous and characterized by a silica content of about 97.7 wt.-% with other constituents of about 2.7 wt.-% represented by Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Cl, P_2O_5, SO_3, an average particle diameter $d_P > 100$ μm (dp 10 [μm] = 106.8 ± 0.7; dp 50 [μm] = 220.5 ± 0.4; dp 90 [μm] = 361.6 ± 0.5, where dp 10, dp 50, dp 90 are the average particle diameters at 10 %, 50 % and 90 % of the cumulative size distribution of the

analyzed powder), a specific surface area according to BET of 313 m^2 g^{-1}, a specific pore volume of 0.38 cm^3 g^{-1} and the average pore diameter of 4.9 nm from adsorption branch of the nitrogen adsorption isotherm according to BJH.

2.2 Preparation of the surfactant

0.08 M and 0.12 M Hexadecyltrimethylammonium Hydroxide (CTAOH) solutions were prepared by double ion exchange of Hexadecyltrimethylammonium Bromide (CTABr) (Purum, ≥96.0 %, Fluka, Germany), using an AMBERSEP® 900 OH ion exchange resin (total exchange capacity 0.8 meq ml^{-1} minimum (OH$^-$) form, Alfa Aesar, Karlsruhe, Germany).

2.3 Preparation of mesoporous silica systems

Mesoporous materials MCM-41 and MCM-48 were prepared by utilization of two systems.

System 1 was used to prepare MCM-41 with the molar composition of 1 SiO$_2$: 0.20 C$_{16}$H$_{33}$(CH$_3$)$_3$N: 0.20 OH: 140 H$_2$O and pH = 12.2 of 0.08 M CTAOH. 1 g of rice husk ash was poured into 42 mL of the surfactant solution. The reaction mixture was stirred (~ 500 rpm, RCTB, IKA, Germany) for 1 h at room temperature. The hydrothermal synthesis was performed in a stainless steel autoclave lined with Polytetrafluoroethylene (PTFE) bottle (60 mL, type 4744, Parr Instrument GmbH, Germany). After filling the autoclave with the reaction mixture, the system was degassed at 0.8 M bar for 15 min. Thereafter the autoclave was sealed and heated at 393 K for a desired time to form of the surfactant - silica mesophase. After each time interval, the autoclave was removed from the oven and quenched in cold water. The obtained product was filtered and washed with deionized water 3 times and dried at 383 K overnight. To remove the surfactant, the dried sample was calcined in air employing a muffle furnace (type N 11/H, Nabertherm, Germany) at 823 K for 5 h with a linear temperature ramp of 10 K min^{-1} and two plateaus of 120 min at 473 K and 673 K.

System 2 was used to prepare MCM-48. The molar composition was 1 SiO$_2$: 0.29 C$_{16}$H$_{33}$(CH$_3$)$_3$N: 0.29 OH: 140 H$_2$O, and pH = 12.7 of 0.12 M CTAOH. MCM-48 was obtained by pseudomorphic transformation of preformed MCM-41 (as silica source) after 3 days under the molar composition used in system 2.

2.4 Characterization

X-ray powder diffraction (XRD) patterns were recorded by using a D8 Advance (Bruker AXS) operated at 40 mA and 40 kV and equipped with a Ni – filter and Cu Kα radiation λ = 1.54 Å. The small angle X-ray diffraction patterns of the mesoporous samples range from 2θ = 1° to 10°. A step width (Δ) of 0.005° with a step time (t) of 2 second was used. Elemental analysis of the samples was made by X-ray fluorescence analysis (S4 Explorer, WDXRF, Bruker AXS, Karlsruhe, Germany). Particle size analysis of the samples was performed by using particle size analyzer (CILAS 1064, Quantachrome Instruments, Boynton Beach, FL, USA). The textural properties of the samples were determined by Nitrogen physisorption (ASAP 2010, micromeritics, DR- Norcross, GA, USA). Before analysis, all samples were pre-treated at 363 K under vacuum for 6 - 8 h to obtain a constant weight. The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) method. The specific mesopore volume (Vmeso) was measured by the t-plot method assuming a layer thickness between 0.8 to 1.4 nm, the mean diameter of mesopores (pd(DFT)) was calculated according to non-linear density functional theory (NLDFT) applied to the adsorption branch of the isotherms, in addition nitrogen adsorption at 77 K is considered and a cylindrical pore shape is assumed. Although it is known (Lefevre et al., 2005) that the BJH method can underestimate the pore size by up to 20 %, the BJH method (pd(BJH)) (Barrett et al., 1951) is still used in this work for the purpose of determination of the pore wall thickness. The surface morphology of the materials was studied by scanning electron microscopy (SEM, ZEISS, SPECTRO Analytical Instruments GmbH, Kleve, Germany) using an Ultra 55 operated at 5 keV. The yield of Cetyltrimethylammonium (CTA$^+$) -species in the as-synthesized samples was determined from thermogravimetric weight loss in the temperature range between 473 and 823 K. For that purpose the thermal analyses were performed using Thermo Gravimetry/Differential Thermal Analysis (TG/DTA) equipment (STA 409 – QMG 421 apparatus, Netzsch Instruments), with ambient air supplement of 150 mL min^{-1}. The investigated temperature range was between 293 and 873 K with a heating rate of 10 K min^{-1}.

3. Results and discussion

3.1 System 1

The kinetics of pseudomorphic transformation of rice husk ash into MCM-41 was studied in a time interval between six hours and six days. The Nitrogen sorption isotherm of rice husk ash exhibits the common characteristics of a type II isotherm with a very broad pore size distribution (meso- and macropores) (Alyosef et al., 2013). After a treatment for 6 hours, the isotherm type II changes into an isotherm of type IV (IUPAC, 1994) (Figure 2a). The amount of adsorbed Nitrogen increases by increasing the reaction time

and the slope of the Nitrogen sorption isotherm at relative pressures in the range between p/p0 = 0.30 - 0.45 changes to a sharp step at about p/p0 = 0.37 after 6 days. The amount of conjugated surfactant remained constant between 95 and 96 mole % after three days of reaction (Table 1). Additionally, the amount of incorporated surfactant and the specific pore volume (Vmeso) of 1 cm^3 g^{-1} suggests that the whole amount of silica in rice husk ash was transformed into MCM-41 after 6 days. Enke et al. (2013) produced a standard MCM-41 sample by pseudomorphic transformation of LiChrosphere® 60. The resulting MCM-41 with mesopore volume of 1.05 cm³ g^{-1} is considered as MCM-41 reference system. The XRD patterns in Figure 2b show the typical hkl reflections of hexagonal p6mm symmetry with a poor long range order. This can be explained by the small dimensions of the hexagonally ordered domains resulting from a highly disordered mesostructure (Zhan et al., 2008). It is worth to note that the constant consumption of surfactant after three days in the reaction solution might be an indication of equilibrium between the silica in rice husk ash and synthesis medium, leading to a further rearrangement of mesostructure. As the result, a shrinkage of the lattice parameter (a0, W) was observed by increasing the reaction time to six days. In contrast, the increase in the specific surface area (AB.E.T), specific pore volume (Vmeso) and pore width (pd(DFT)) was recorded (Table 1). The morphology of the RHA (backbone structure) was preserved during the pseudomorphic transformation into MCM-41 (Figures 1a). The initial particle size was slightly increased after 6 days of reaction which might be due to a particle aggregation (dp 10 [µm] = 107.5 ± 1.3; dp 50 [µm] = 223.9 ± 0.3; dp 90 = 364.5 ± 0.8 [µm]). Galarneau et al. (2006) suggested that a complete preservation of the macroscopic structure of the initial silica material is occurred if the rate of the silica dissolution is equal to the rate of precipitation of the ordered mesoporous material. This suggestion could be the reason of conservation of the morphology of the initial RHA. Figure 1b shows the pore structure of a cross-section of RHA-6days. The precipitation of the silica-micelle template species occurred inside the preserved macropores of rice husk ash which had a diameter between 1 - 1.5 µm. This can be explained with the presence of higher ratio of silica/surfactant inside the rice husk ash particles than overall composition of the system, as it was suggested by Galarneau et al. (2002) during the studying of pseudomorphic transformation on some commercial silica materials. Thus, the silica was dissolved by the alkaline solution and the resulting silicate species reassembled with the surfactant. Afterwards the species condensed into MCM-41 mesostructure. Furthermore, a hierarchical pore system was achieved composed of macropores of rice husk ash and mesopores formed via pseudomorphic transformation.

Table 1: Pseudomorphic transformation of rice husk ash into MCM-41; [1] unit cell parameter, a0 = d$_{100}$.2/√3 (Russo et al., 2007); [2] wall thickness, W = a0-pd(BJH) (Russo et al., 2007)

Reaction time	Meso-structure type	Yield CTMA mole [%]	SBET [m^2 g^{-1}]	Vmeso [cm^3 g^{-1}]	pd(DFT) [nm]	pd(BJH) [nm]	a0[1] [nm]	W[2] [nm]
6h	hexagonal	71	545	0.36	---	3.1	---	---
1day	hexagonal	86	718	0.51	---	2.8	---	---
2days	hexagonal	92	918	0.64	3.5	2.8	---	---
3days	hexagonal	92	1120	0.80	3.6	2.8	4.3	1.5
4days	hexagonal	95	1180	0.84	3.6	2.8	---	---
5days	hexagonal	96	1188	0.86	3.8	2.8	---	---
6days	hexagonal	96	1210	1.00	4.1	2.8	4.1	1.3

MCM-41 material was also found on the outer surface of the RHA-3days sample in form of spherical particles (between 300 - 700 nm in sizes) (Figure 1c). This can be explained in terms of an equilibration between the surfactant-rich phase and the silica species dissolved in the outer alkaline solution (Galarneau et al., 2006).
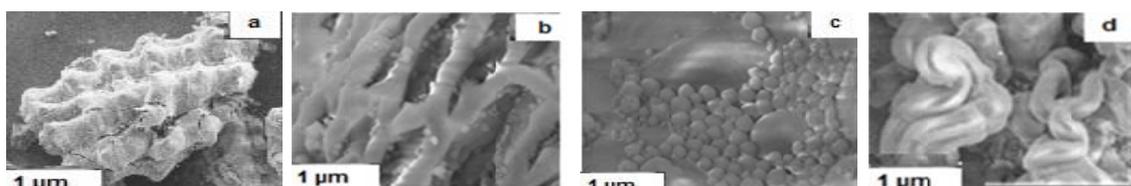

Figure 1: (a) Scanning electron micrographs of (a) skeleton of RHA-6days (MCM-41), (b) cross-section of the inner surface of RHA-6days, (c) outer surface of RHA-3days, (d) outer surface of RHA-6days

After six days of reaction, the mesostructured silica forms large crystals like with size between 3 to 5 µm on the outer surface of the rice husk ash particles by Ostwald ripening (Figure 1d). This is probably due to the presence of larger ordered domains of MCM-41 at the outer surface of the RHA-6days particles rather than smaller domains in their centers (Finsy, 2004). About 2 wt.- % of inorganic impurities was found in the RHA-6days sample resulting from the level of purity in the starting material. This means the impurities in the starting material (RHA) were dispersed in the MCM-41 framework during the pseudomorphic transformation.
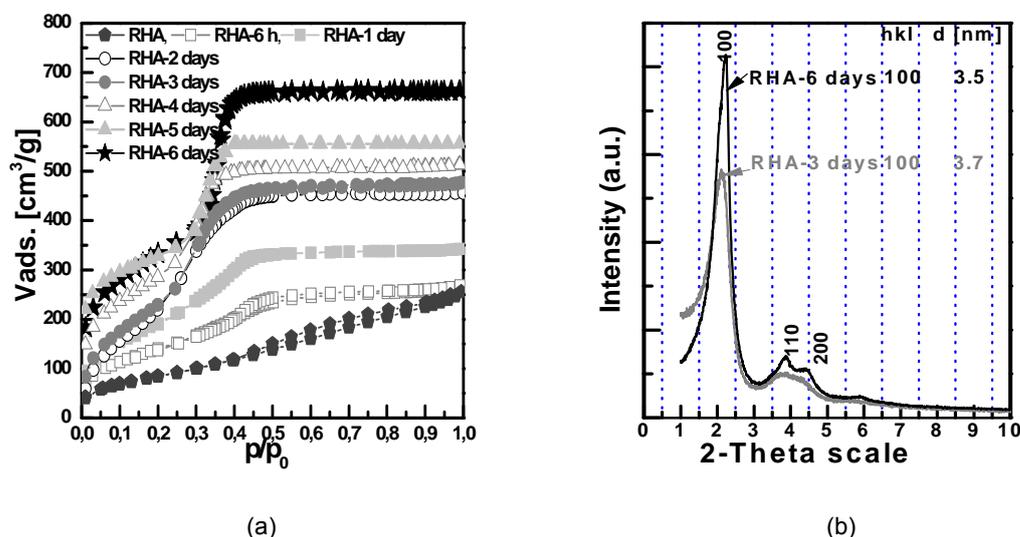

(a) (b)

Figure 2: (a) Nitrogen sorption isotherms and (b) XRD patterns after pseudomorphic transformation of rice husk ash RHA into MCM-41at different transformation times

3.2 System 2

Between 6 h and 6 days of the synthesis time, the Nitrogen sorption isotherms (Figure 3a) show a typical isotherm of type IV which corresponds on the transformation of rice husk ash into MCM-41. By increasing the reaction time to 3 days, the consumption of CTMA increases from 76 % to 96 % and the specific mesopore volume reached 1 cm^3 g^{-1} (Table 2). This serves as an indication that 100 % MCM-41 was formed. In addition the pore size (pd (DFT)) increased to 3.6 nm. However, the obtained MCM-41 samples possess a poor long range order (Figure 3b), which may indicate a transition to MCM-48. By prolongation the reaction time from 1 to 3 days, MCM-41 mesostructures with reduced dimensions of the unit cell parameter (a0), pore wall thickness (W), and pore size pd(DFT) are obtained. In addition the specific surface area (SBET) and the specific mesopore volume (Vmeso) increased to 1,387 m^2 g^{-1} and 1 cm^3 g^{-1} respectively as it is shown in Table 2. When increasing the reaction time from 4 to 6 days, a remarkable constancy of the unit cell parameter (a0) and the pore wall thickness (W) was observed. This was not the case with the pore textural parameters (SBET) and (Vmeso).

Table 2: Pseudomorphic transformation of rice husk ash into MCM-41 / MCM-48; [1] unit cell parameter, a0 = d$_{100}$.2/√3 (Russo et al., 2007), a0 = d$_{211}$√6 for MCM-48 (Zhan et al., 2008); [2] wall thickness, W = a0-pd(BJH) (Russo et al., 2007), and W = a0/3.0919-pd(BJH)/2 for MCM-48 sample (Zhan et al., 2008)

Sample	Meso-structure type	Yield CTMA mole [%]	SBET [m^2 g^{-1}]	Vmeso [cm^3 g^{-1}]	pd(DFT) [nm]	pd(BJH) [nm]	a0[1] [nm]	W[2] [nm]
RHA-6h	hexagonal	76	672	0.46	3.1	2.8	4.2	1.4
RHA-1day	hexagonal	86	915	0.70	3.2	2.7	3.8	1.1
RHA-2days	hexagonal	96	1,139	0.73	3.4	2.7	3.9	1.2
RHA-3days	hexagonal	96	1,387	1.00	3.6	2.6	3.6	1.0
RHA-4days	hexagonal	88	945	0.65	3.3	2.6	3.6	0.9
RHA-5days	hexagonal	90	1,055	0.80	3.5	2.6	3.6	0.9
RHA-6days	hexagonal	92	1,175	0.80	3.6	2.6	3.6	0.9
2RHA-3days	cubic*	65	815	0.75	3.3	2.5	7.6	1.2

*MCM-48 = 2RHA-3days

For instance, at 6 days of the synthesis, the MCM-41 materials had a specific pore volume of 0.80 cm^3 g^{-1}, and a specific BET surface area of 1,175 m^2 g^{-1}. A closed hysteresis loop at relative pressure p/p0 = 0.45 (Figure 3a) appeared at some MCM-41 materials at prolonged reaction time of 6 days, possibly due to the progressive breaking and collapse of the morphology of the initial rice husk ash. Hence, the lack of stability can be interpreted by the growth of large particles (needle shape) of MCM-41 which cover the outer shell of the rice husk ash (Figure 4a) after a long synthesis time, e.g. 6 days.
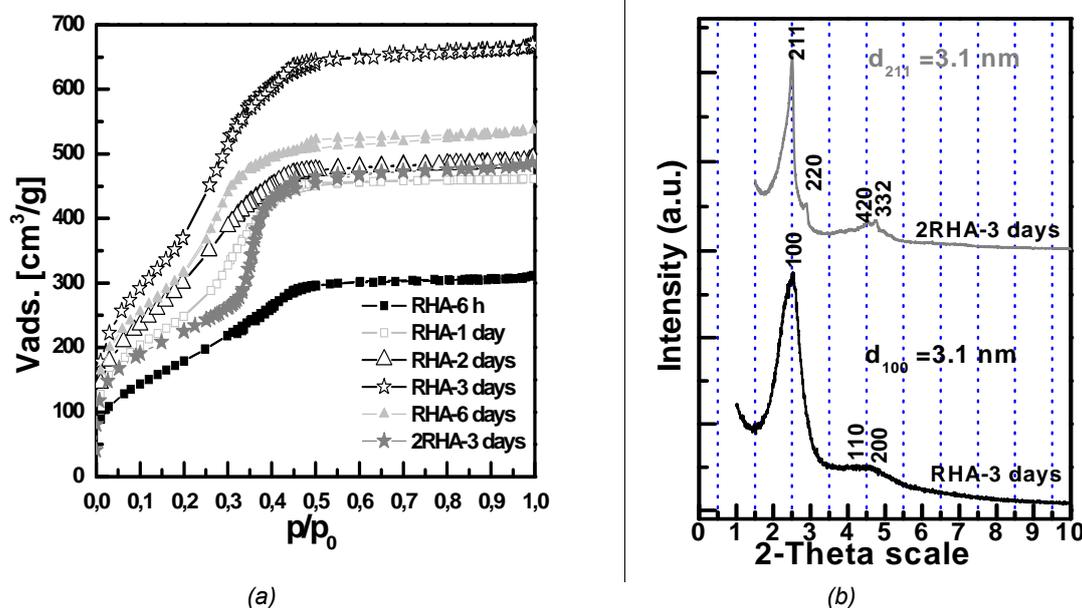

(a) *(b)*

Figure3: (a) Nitrogen sorption isotherms and (b) XRD patterns after pseudomorphic transformation of rice husk ash RHA into MCM-41 / MCM-48 at different transformation times

The decrease in surfactant yields being observed after increasing the reaction time to 4 days might be due to the separation of a small fraction of MCM-41 resulting from cracks of the particles. These fine particles might be lost by filtration (Galarneau et al., 2005). Accordingly, the changes in textural characteristics of MCM-41 obtained by pseudomorphic transformation were noted by increasing the reaction time between (4 - 6 days) and no MCM-41/MCM-48 phase transition is observed. MCM-48 species could be obtained using RHA-3days from system 2 as starting material for a second pseudomorphic transformation step. This was not described yet. A reaction mixture with a molar composition: MCM-41: 0.29 C$_{16}$H$_{33}$(CH$_3$)$_3$N: 0.29 OH: 140 H$_2$O was used. The mixture was heated at 393 K for 1 day. The cubic MCM-48 sample was denoted as 2RHA-3days. The XRD pattern (Figure 3b) shows four characteristic peaks corresponding to (211), (220), (420) and (332) Bragg diffractions. These peaks indicate that a strong restructuration to Ia3d symmetry occurred. The MCM-48 phase with a typical unit cell parameter (a0) of 7.6 nm was formed. The specific surface area (SBET), the specific pore volume (Vmeso.) and the pore width (pd(DFT)) of the resulting MCM-48 material (2RHA-3days) decreased to 815 m^2 g^{-1}, 0.75 cm^{3}g^{-1}, and 3.3 nm respectively, compared to the starting material, i.e. MCM-41 (RHA-3days) (Table 2). These results are additional indications for the successful phase transformation of MCM-41 in MCM-48 via a dissolution / re-precipitation of the silica material. The precipitation of some smooth spherical MCM-41 particles on the outer surface of the rice husk ash with a size between 600 nm and 1 μm was observed in the case of the starting material RHA-3 days (Figure 4c). This can be explained with the progressive dissolution of the silica species from the rice husk ash and their re-precipitation with the surfactant existing in the initial porosity. The growth of the MCM-48 particles on the outer surface of rice husk ash up to approximately 2.5 μm (Figure 4d) indicates that the MCM-41/MCM-48 phase transition occurred inside MCM-41 domains through a short-range transport mechanism (Galarneau et al., 2005). Furthermore, a slight increase in the mean particle size was observed after the double transformation step ((dp 10 [μm] = 110.4 ± 0.3; dp 50 [μm] = 228.2 ± 0.8; dp 90 = 370.8 ± 0.4 [μm]). The complete preservation of the original morphology of RHA (Figure 4b) could be achieved for this sample. Additionally, the MCM-48 containing material is characterized by a high purity with a SiO$_2$ -content at about 99 wt.- %.
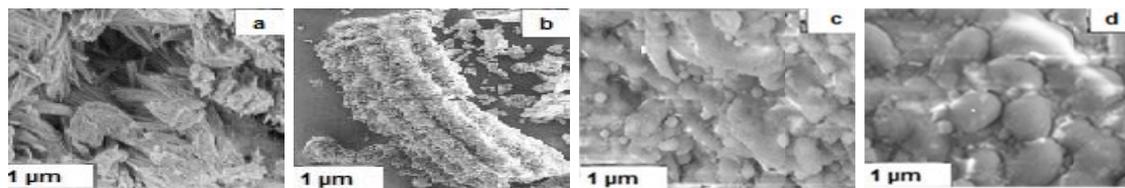
Figure4: Scanning electron micrographs of (a) outer surface of RHA-6days, (b) skeleton of 2RHA-3days, (c) outer surface of RHA-3days (MCM-41), (d) outer surface of 2RHA-3days (MCM-48)

4. Conclusions

In the present study, rice husk ash was utilized for the first time as cost-efficient meso / macroporous silica source for the synthesis of ordered mesoporous materials of the type MCM-41 or MCM-48 via pseudomorphic transformation. The results of Nitrogen physisorption and SEM indicate the presence of a hierarchically structured pore system comprised of (i) ordered mesopores generated via pseudomorphic transformation of RHA into MCM-41 or MCM-48 materials and (ii) the original macropores provided by the initial RHA. The kinetics of the transformation of the biogenic silica into ordered mesoporous materials was also investigated. In the case of MCM-41, a clear time-dependency was observed. A direct pseudomorphic transformation of RHA into MCM-48 material was not possible. However, preformed MCM-41 from a first transformation could be successfully converted into MCM-48 via a second transformation step. In both cases, the macroscopic morphology of the RHA particles could be completely retained. The new route offers the interesting possibility of direct conversion of renewable agricultural residues into advanced silica-based functional materials.

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