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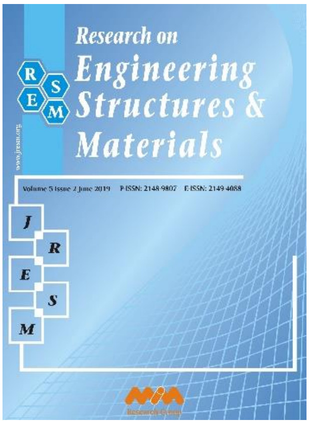

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Online Publication Date: 01 Apr 2019
URL: http://jresm.org/archive/resm2019.79ma1205.html
DOI: http://dx.doi.org/10.17515/resm2019.79ma1205

Journal Abbreviation: *Res. Eng. Struct. Mater.*

To cite this article

Tufaner G, Çalışkan A, Yener HB, Helvacı ŞŞ. Preparation of amorphous silica from a renewable agricultural waste of rice husk ash by calcination method combined with chemical activation *Res. Eng. Struct. Mater.*, 2019; 5(3): 299-310.

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Research Article

Preparation of amorphous silica from a renewable agricultural waste of rice husk ash by calcination method combined with chemical activation

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Article Info

Article history:
Received 12 Dec 2018
Revised 12 Mar 2019
Accepted 28 Mar 2019

Keywords:

SiO2;
Calcination;
Rice husk ash;
Alkali hydroxide;
Chemical Activation

Abstract

In the study, silica particles were synthesized from rice husk ash by calcination method in the presence of activating agents. The parameters which are effective in calcination method on structure and morphology of synthesized silica particles, activating agent type (NaOH and KOH), the calcination temperature (500-850°C), the calcination time (1-3 hours) and the weight ratio of activating agent to ash (4:1 and 5:1), were investigated. The crystal structures of the silica particles were determined by XRD, agent structures by FTIR, sizes and shapes by SEM, surface areas and porous structures by N2 adsorption-desorption analysis. Amorphous silica particles were synthesized in all experimental conditions. Optimum weight ratio, calcination temperature and time were determined as 4:1, 750°C and 2 hours, respectively. The activating agent NaOH was found to be more active than KOH in the preparation of silica.

1. Introduction

Silica particles are one of the most preferred and promising metal oxides due to their unique characteristics such as high thermal stability, porous structure, excellent adsorption properties, low cost, environmentally friendly nature, and good optical and electrical properties. Due to their remarkable properties, they have been used in several applications such as refractory material, high performance cement, paint, flame retardant, insecticide, bio-fertilizer, catalyst, adsorbents, drug carriers, food and cosmetics [1]. Silica particles can be synthesized using inorganic (sodium silicate) or organic (tetraethyl orthosilicate-TEOS) precursors. TEOS is commercial raw material whereas sodium silicate can be obtained from agricultural wastes (rice husk, rice straw, corn cobs, and bagasse). The use of agricultural wastes as a renewable resource has attracted interests due to their low cost, abundance and environmental friendliness. In addition, its usage as a raw material for the preparation of advanced materials reduces the environmental problems associated with agricultural wastes. The rice husk/ash is one of the natural silica sources due to its high silica content (83-90 wt%). Rice absorbs the silicic acid of the soil and accumulates around cellulosic parts. Silica particles are generally produced using NH_4F, CO_2, acidic solutions and by calcination of the shell or ash of rice husk treated with activating agents [2]. Depending on the calcination temperature, the silica produced from the rice husk ash (RHA) may be in the form of amorphous, partially crystalline or crystalline forms. Amorphous silica is more preferable because it is more reactive and the

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DOI: http://dx.doi.org/10.17515/resm2019.79ma1205

crystal silica is carcinogenic [1]. During the calcination of the RHA, the silica forming the majority of the inorganic content remains as the organic content, lignin and hemicellulose, are removed by thermal degradation. Hemicellulose is degraded around 200-260°C, and lignin around 280-360°C [3]. In the presence of activating agents, the calcination method allows the use of less chemicals and a shorter synthesis time.

Many experimental studies have been conducted on silica production by calcination method from rice husk/ash without using any activating agent. Sankar and coworkers [4] produced spherical and agglomerated silica nanoparticles from RHA by calcination method at 700°C for 2 hours. Wang et al. [5] conducted a study where spherical silica particles in amorphous form was obtained from rice husk at 800°C and 0.5 hour. There are also studies regarding to the synthesis of silica particles using alkali carbonates or hydroxides as activating agents. Liu et al [6] prepared activated carbon and silica particles from RHA simultaneously at 900°C using Na_2CO_3 as activating agent. Liu et al [7] used RHA for the preparation of activated carbon and silica at 1000°C using K_2CO_3 as activating agent. Liu et al. [8] synthesized amorphous silica particles from RHA by calcination method using KOH as the activating agent. They determined the optimum calcination conditions as 700°C and 1 hour. The experimental studies and literature surveys have shown that in order to obtain amorphous and spherical silica particles, it is appropriate to calcine rice husk/ash at temperatures below 900°C with alkali chemicals [3-5, 8-10]. Although, there are studies dealing with the synthesis of silica from RHA by calcination method, less literature is available interested in calcination method using activating agent for the control of the particle properties.

In this study, silica particles were synthesized from RHA using calcination method in the presence of two different alkali hydroxides, NaOH and KOH, as activating agents. The activation parameters investigated were the type of the activating agent (NaOH and KOH), the calcination temperature (500, 650, 750 and 850°C), the weight ratio of activating agent to ash (2:1, 3:1, 4:1 and 5:1), and the calcination time (0.5, 1, 2 and 3 hours). The rinsing water was reused in the synthesis of silica particles. Thus, the study covers the use of a renewable agricultural waste of RHA as the silica source, estimation of the optimum activation conditions to synthesize silica particles with the desired properties, and the reuse of rinsing water in the synthesis. In this respect, the study offers environmentally friendly and low-cost production technology.

2. Materials and Methods

2.1. Materials

Rice husk ash (RHA) kindly supplied by Erdoğanlar Food Industry and Business Company was used as a silica source. The company burnt the rice husk at 700°C for 6 hours under atmospheric conditions. The elemental content of RHA was analyzed with an atomic absorption spectrophotometer (AAS, VarianspectrAA-10Plus). It was found that the RHA contains SiO_2, K_2O and CaO in weight percentages of 91.6, 5.65 and 1.39, respectively, and the remaining are the trace amount of other oxides such as Na_2O, MnO, Al_2O_3 and Fe_2O_3. The ash also contains low amount of unburned carbon. KOH and NaOH (Merck, 99 %) were used as activating agents as received without further purification. The conductivity and pH of the double distilled water used during the experiments were 1.1 $\mu S\ cm^{-1}$ and 6, respectively.

2.2. Preparation of Silica Particles

For the synthesis of silica particles, a definite amount of RHA was mixed with aqueous KOH or NaOH solutions and stirred at 550 rpm for 30 minutes. The mixture was then dried at 110°C for 24 hours. Afterwards, the calcination process was performed in an electrical furnace (Protherm PLF130/9) at the predetermined calcination temperatures and time with a heating rate of 10°C/min. Since the calcination was performed at atmospheric conditions, the unburned carbon in the RHA structure was expected to be removed during the calcination. Thus, the products obtained after the calcination contains high amount of silica, potassium or sodium, and trace amounts of other elements (Fe, Ca, Mg, Al and Mn). The products were washed with distilled water nearly 10 times until they were free of these impurities. The purification process was followed by analyzing potassium and sodium ions in the washing waters using AAS. The products purified were dried at 110°C for 24 hours and then characterized. The rinsing water used for the purification of the particles was evaporated. The concentrated aqueous NaOH/KOH solutions obtained after evaporation was reused as activating agents by adjusting its concentration, and the water condensed as rinsing water. The schematic diagram of the synthesis is shown in Fig. 1.

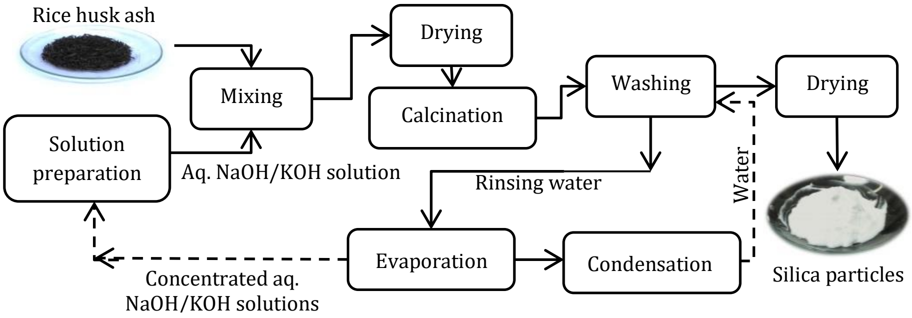


Fig. 1 Schematic representation of silica particle synthesis

2.3. Characterization

The chemical structures of the samples were determined by Fourier transform infrared spectroscopy attached with ATR (ATR-FTIR Perkin Elmer Spectrum 100, Diamond/ZnSe crystal). The crystal structure of the particles was determined by X-ray diffraction (XRD, Philips X'pert PRO–45 kV, 40 mA, 2θ=5-75°CuKα). The surface areas and porosity of the samples were determined by means of N_2 adsorption-desorption isotherms at 77.53 K using a volumetric adsorption system (Micromeritics Instruments Gemini V). The samples were degassed at 300°C for 24 hours prior to measurements to ensure that no gas molecules were adsorbed on the surface and in the pores of the particles. The shape and size of the particles were determined by a field emission gun scanning electron microscope (SEM, FEI QUANTA 250 FEG). Surface charges of the particles produced at optimum conditions were determined by means of the light scattering at different pH values (Malvern Zeta-sizer Nano ZS).

3. Results and Discussions

3.1. Characterization of RHA

The FTIR spectrum of RHA is given in Fig. 2a where the characteristics bands at 1050 and 789 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the Si-O-Si bonds, respectively. No peaks belonging to the other components in RHA were detected in the spectrum due to their low amounts in the structure. The calcination of rice husk at 700°C for 6 hours resulted in the partial removal of organic components and at the same time crystallization of silica [11]. Therefore, the XRD spectrum of RHA given in Fig. 2b indicated the characteristic peaks of crystalline silica, cristobalite and tridymite. The peaks at 2θ = 21.99, 28.46, 31.45, 42.68, 47.03 and 48.63° and at 2θ = 20.6 and 36.1 correspond to the cristobalite and tridymite, respectively. The SEM image of RHA (Fig. 2c) reveals low porosity and the heterogeneity in the shape and size of the RHA. The low carbon content in RHA resulted in low porosity and thereby the low surface area. The BET, external and micropore surface areas of RHA were estimated as 11.4, 8.1 and 3.3 m^2/g, respectively. Since the external surface area is greater than the micropore area, it can be said that mesopores are dominating in the RHA structure. The mesopore diameter estimated by BJH method was 10.7 nm.

3.2. Effects of activation parameters on silica particles

The effects of the activating agent (NaOH and KOH), the calcination temperature (500, 650, 750 and 850°C), the weight ratio of activating agent to ash (2:1, 3:1, 4:1 and 5:1), and the calcination time (0.5, 1, 2 and 3 hours) on the structure and morphology of the silica particles synthesized were investigated.

3.2.1 Calcination temperature

The calcination temperatures were selected as 650, 750 and 850°C for NaOH and 500, 750 and 850°C for KOH. For NaOH, a gray-black product was obtained at the end of the calcination time at 500°C, which was thought as an indication of the incomplete carbon removal and silica formation. For the complete removal of the organic compounds in the ash, the temperature should be higher than 500°C which was also determined by the literature research [12]. Thus, the minimum calcination temperature was selected as 650°C for NaOH.

The FTIR spectra of the particles produced using NaOH and KOH at different temperatures are given in Fig. 3. The FTIR spectra was quite similar to that of the RHA given in Fig. 2a. However, the characteristic bands at 1050 and 789 cm^{-1} belonging to the asymmetric and symmetric stretching vibrations of the Si-O-Si bonds shifted towards 974 and 679 cm^{-1}, respectively. The shifts towards the low wavenumbers were due to the inclusion of sodium or potassium ions into the silica structure. In addition, a band at 854 cm^{-1} was assigned to the bending vibrations of the Si-OH. All of these Si bonds showed the formation of the silica structure at all conditions studied. The bands at 1639 and 3372 cm^{-1} correspond to the bending vibrations of the adsorbed and coordinately bound water, respectively.

Although, the RHA consisted of a mixture of cristobalite and tridymite silica (Fig. 2b), the XRD spectra of the particles (Fig. 4) indicated the formation of amorphous silica with the characteristic broad peak between 25 and 30° [4-5, 8, 12]. No significant changes in the XRD spectra of the particles were observed with respect to the calcination temperature and activating agents.

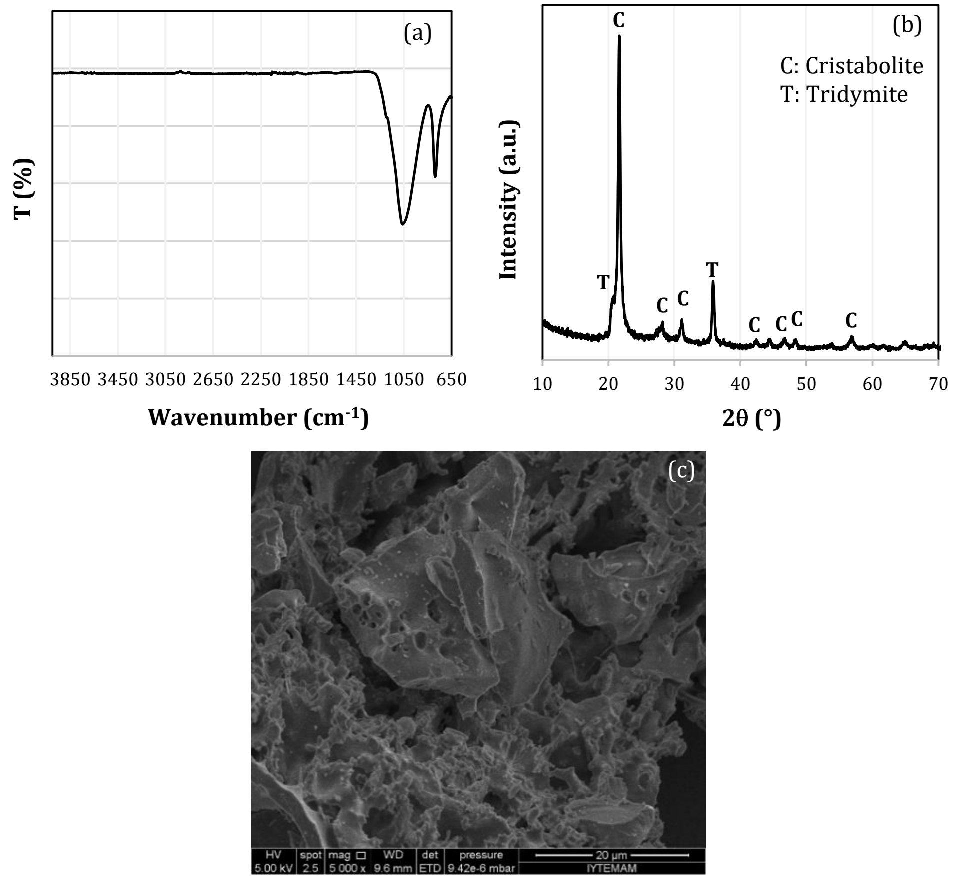


Fig. 2 (a) FTIR, (b) XRD, (c) SEM image of RHA

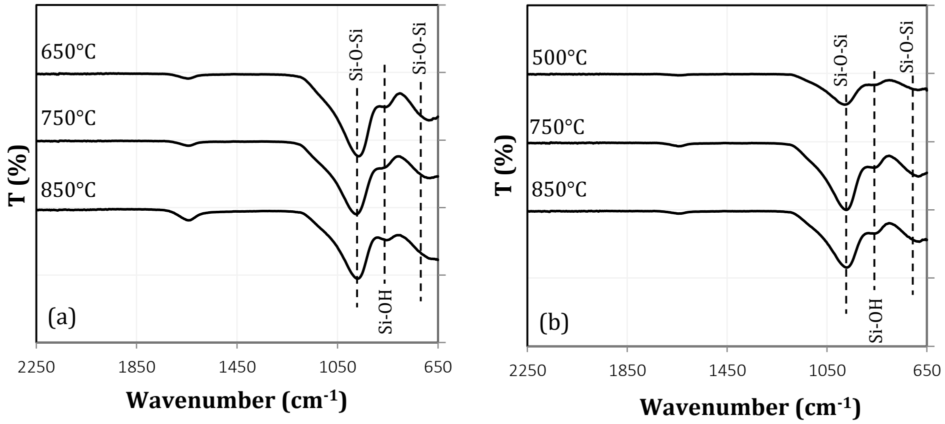


Fig. 3 FTIR spectra of the silica particles in the presence of (a) NaOH and (b) KOH

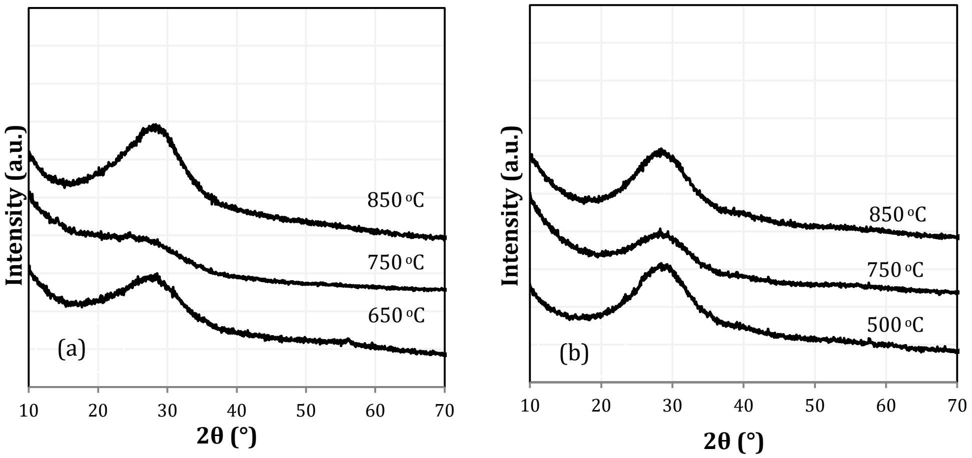
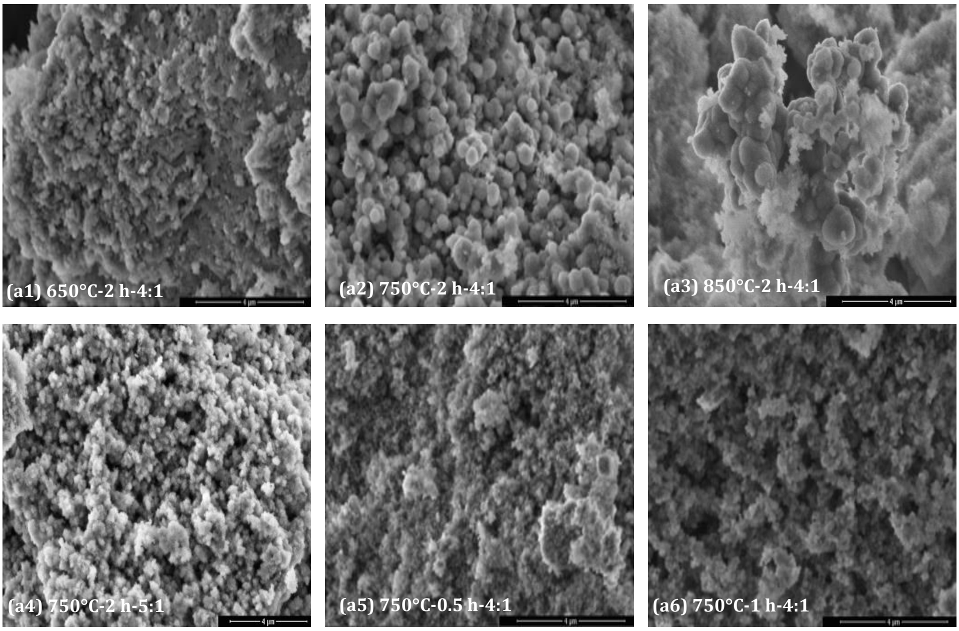


Fig. 4 XRD spectra of the silica particles in the presence of (a) NaOH and (b) KOH

The SEM images given in Fig. 5 (a1-a3 and b1-b3) show the effect of calcination temperature on the shape and size of the particles. For both activating agents, at the lowest temperatures studied, the particles have no clear shapes and have heterogeneous size distribution (Figs. 5-a1 and b1). As the calcination temperature increased from 650 to 750°C for the activating agent of NaOH and from 500 to 750°C for KOH, the shape of the particles became spherical and the size distribution more homogeneous. The size of the particles obtained at 750°C using NaOH (Fig. 5-a2) was found to be smaller than those of KOH (Fig. 5-b2). Further increase in the calcination temperature, from 750 to 850°C increased the agglomeration of the particles with deformation both in their shapes and sizes. The SEM images also show the high porosity of the particles which is different from the RHA's low porosity.



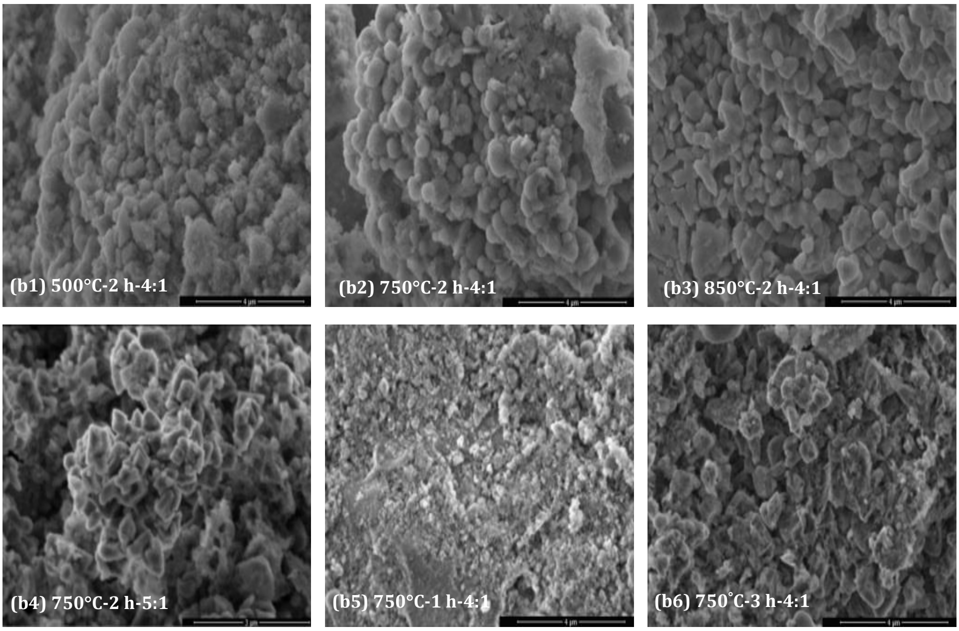


Fig. 5 SEM images of silica particles synthesized using (a) NaOH, (b) KOH

The textural properties of the particles are given in Table 1. Similar to the RHA, all silica particles have mesoporous structures. However, the surface areas of the silica particles (Table 1) were found to be higher than that of the RHA. The penetration of sodium or potassium into the RHA structure at high calcination temperature expanded the matrices in the structure, thereby increased the porosity. As shown in Table 1 for all conditions studied, the external surface areas are greater than the micropore areas indicating the mesoporous structure. It was also supported by the pore sizes changing between 2 and 50 nm. The increase in the calcination temperature speed up the activation reaction increased the consumption of the unburned carbon and so might open the fine and closed pores in the structure. Thus, increased the surface area and decreased the mesopore diameter.

For both activating agents, the most suitable calcination temperature was determined as 750°C. The result obtained was consistent with the studies in the literature [4-5, 8, 10, 12-18] where the optimum temperature was found to be changing between 600 and 800°C. Thus, further parametric studies were performed at the optimum calcination temperature of 750°C.

Table 1 The surface properties of silica particles produced

	Activating Agent					
	NaOH			**KOH**		
Temperature (°C)	**650**	**750**	**850**	**500**	**750**	**850**
BET surface area (m^2/g)	36.33	73.86	78.82	46.95	82.94	94.19
Langmuir surface area (m^2/g)	50.37	101.98	109.13	64.63	114.22	129.75
t-Plot micropore area (m^2/g)	0.64	3.63	2.11	3.70	6.02	6.37
t-Plot external area (m^2/g)	35.69	70.23	76.72	43.25	76.92	87.82
BJH Adsorption diameter (nm)	21.3	16.8	18.8	14.1	8.6	7.7

3.2.2 Weight ratio of activating agent to ash

The effect of the weight ratio of activating agent to ash, 2:1, 3:1, 4:1 and 5:1, were determined at the calcination temperature of 750°C and time of 2 hours. It was observed that the products obtained at the activating agent: ash ratio lower than the 4:1, were gray-black as given in Fig. 6. Since the products with the white color show the formation of silica and complete removal of other organic compounds during the calcination [4, 9, 12, 14, and 17], this gray-black color indicated the unburned organics. In that cases, the amounts of activating agents may be low for the activation reaction, and so silica formation was not completed. Therefore, the particles obtained at low activating agent: ash ratio were not considered as the targeted products, and not characterized. The characterization was performed for the particles obtained at the activating agent: ash ratios of 4:1 and 5:1.

The SEM images of the particles indicated that the increase in the NaOH amount caused the activation reaction to be very fast resulting small sized but highly agglomerated particles (Fig. 5-a4). A similar result was also obtained in case of the KOH, where the increase in the KOH amount caused formation of agglomerated particles with heterogeneous shapes (Fig. 5-b4). Thus, in order to obtain particles with homogeneous shape and size distribution, the activating agent: ash weight ratio of 4:1 is proper at the conditions studied.

Fig. 6 Photographs of the products obtained at different activating agent to ash ratios

3.2.3 Calcination time

The effect of different calcination time on the shape and size of the particles were investigated by keeping the calcination temperature at 750°C and the ratio of the activating agent to ash as 4:1.

The SEM images of the particles obtained using NaOH as the activating agent are given in Figs. 5-a5, a6 and a2 which belong to the calcination time of 0.5, 1 and 2 hours, respectively. It was observed that the calcination time of 0.5 and 1 hours were not long enough for the formation of particles in definite shape. They look like agglomerates of very small spherical particles. However, at the end of 2 hours calcination time, spherical particles with homogeneous size distribution were formed. A similar tendency between the time and particle shape and size was observed in the case of KOH. The calcination time of 1 hour was not enough for the particle formation (Fig. 5-b5), 2 hours resulted in spherical particles with homogeneous size distribution (Fig. 5-b2), and 3 hours heterogeneous particles in both shape and size (Fig. 5-b6). Thus, it can be easily concluded that, the short calcination time was not long enough for the formation of particle and longtime causes the particles to agglomerate. In addition, it is stated in the literature that the existing porosity of the particles has disappeared with increasing time [8]. For these reasons, the most suitable calcination time was determined as 2 hours for both activating agents.

Considering the relation between the activation parameters and the morphological and structural properties of the silica particles synthesized, the optimum activation conditions were found to be activation temperature of 750°C, activating agent to ash weight ratio of 4:1 and activation time of 2 hours for both activating agents. It was found that the activating agent NaOH was more effective in the formation of spherical silica particles and their homogeneous size distributions.

The zeta potentials of the silica particles synthesized at the optimum conditions were measured as a function of the solution pH and given in Fig. 7. The isoelectric points were found to be 2.3 and 2.7 for the particles obtained using NaOH and KOH, respectively. According to the literature, the isoelectric point of the pure silica is 2 [19]. So, the results were found to be consistent with the literature.

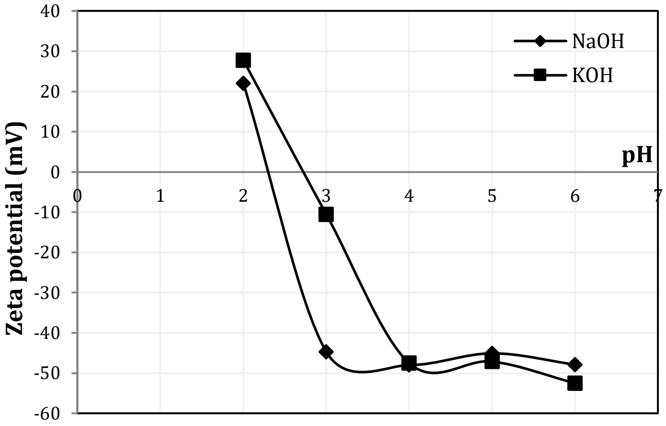


Fig. 7 The zeta potentials of the silica particles with respect to solution pH

4. Conclusion

The present study covers both the optimization of the activation conditions to produce silica particles with the desired properties and the preliminary work for the reduction of the synthesis cost by reusing the rinsing water.

Silica particles were synthesized from RHA by calcination method using alkali hydroxides, NaOH and KOH, as activating agents. The effects of the activation parameters (type of activating agents, calcination temperature, and activating agent to ash weight ratio and calcination time) on the morphological and structural properties of the silica particles were investigated. Although the silica source of RHA is a mixture of cristobalite and tridymite, the silica particles synthesized at all conditions studied were amorphous determined by XRD. For both activating agents, as the calcination temperature increases, the size of the particles increases due to the agglomeration. The increase in temperature speeds up the activation reaction, causing formation of the porous particles. The optimum calcination temperature was found to be 750°C where mesoporous particles with homogeneous size and shape distribution was obtained. A critical activating agent to ash weight ratio, 4:1, was found in the experimental studies. Below this ratio, no pure silica particles were obtained since the organics could not be completely removed at low ratios (2:1 and 3:1). In addition, above the critical ratio, 5:1, due to the fast activation reaction, small sized but highly agglomerated particles were synthesized. For both activating agents, at short calcination time the particles did not have clear shapes, whereas at long time the particles agglomerated causing nonuniform particles. The optimum calcination time was found to be 2 hours both for NaOH and KOH at the conditions studied. Thus, for the synthesis of amorphous, spherical, and homogeneous size distributed particles, the optimum activation conditions were determined as 750°C, 4:1 activating agent to ash weight ratio and 2 hours. Besides, the activating agent NaOH was found to be more effective in the formation of homogeneously distributed spherical particles.

Since the silica particles were amorphous and mesoporous, they have a potential usage as catalyst, adsorbent, or drug carrier in several industrial application fields.

Acknowledgment

The authors thank Prof. Dr. F. S. Ç. Ozkan and specialist Nesrin Tatlıdil (Department of Chemical Engineering, Izmir Institute of Technology) for surface area measurements and Erdoğanlar Food Industry and Business Company for the RHA.

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