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Research Article

Hydrothermal Synthesis of SBA-15 Using Sodium Silicate Derived from Coal Gangue

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Well-ordered SBA-15 was prepared with a hydrothermal route by sodium silicate derived from coal gangue. The as-prepared sample was analyzed by SAXRD, BET, TEM, and SEM, respectively. The results indicate that at a low hydrothermal temperature of 100°C the well-ordered mesoporous SBA-15 could be synthesized. The surface area, pore volume, and pore size of the sample are 552 m^2/g, 0.54 cm^3/g, and 7.0 nm, respectively. It is suggested that coal gangue could be used in obtaining an Si source to prepare mesoporous materials, such as SBA-15.

1. Introduction

The coal production of China now ranks top in the world, and so there is the biggest coal gangue yield. Despite being used as alternative material in road, pavement, embankment, foundation, or building construction, and so forth [1, 2], most of the coal gangue is still open-air stack-stored near by the coal mines and occupies vast pieces of land leading to a series of environmental problems, such as pollutions of air, water, and soil induced by the spontaneous combustion and eluviations. This became one of the highly important factors in restricting the economic sustainable development and the ecological civilization construction of the coal production area. Nevertheless, the coal-based energy structure could not change in the short term and thus the comprehensive utilization of coal gangue with high added value and minimal environmental impact turns into a big challenge.

Mesoporous silica has attracted much attention over the past decades due to not only their uniform mesostructures and excellent properties but also their amazing potential applications [3–6]. SBA-15 is one of the most extensively studied and applied example which could be prepared with highly reproducible pathways using commercial availability surfactants (such as P123), silica precursors, and facile [7, 8]. In addition, small particle size and rod-like morphology of SBA-15 received increasing interest for their fast adsorption and mass transfer [9]. Previously, most of the SBA-15 was obtained using expensive TEOS as silica precursors; thus efforts have been made to use inexpensive sodium silicate as a silica source [10–12]. In some earlier reports, the sodium silicate from fly ash has been used in the synthesis of SBA-15 [13–16], giving a good example for making good use of waste and reducing material costs.

It is well known that coal gangue mainly consists of about 20 wt.% carbon, 25 wt.% alumina, and 48 wt.% silica, and so sodium silicate could be made from the waste [17–20]. However, in the literatures, the SBA-15 synthesized using sodium silicate from coal gangue as a silica source was not reported.

Here we synthesized well-ordered SBA-15 successfully using sodium silicate derived from coal gangue under low-temperature hydrothermal condition to gain insight into the possibility of high-quality application of coal gangue.

2. Experimental

2.1. Materials. Coal gangue was donated by Lu'an Group (Shanxi, China) and used after being grinded to particles

about 200 μm in size. Hydrochloric acid (HCl, 36%), sodium carbonate (Na_2CO_3, 98%), sodium silicate ($Na_2Si_3O_7$, with 25 wt.% SiO_2 and 14 wt.% NaOH), and acetic acid (HAc) were purchased from SCR. The triblock copolymer $EO_{20}PO_{70}EO_{20}$ (P123) was from Aldrich.

2.2. The Preparation of Sodium Silicate from Coal Gangue. Raw coal gangue was ground to powder with a mesh size of less than 1000 μm using a mechanism grinder. The powder was calcined at 750°C for 2 h and then leached with 36% HCl at 40°C until no weight loss being observed. By this way, most aluminum oxide, ferric oxide, and other impurities were removed, which could be used to produce polyaluminum chloride employed as waste water purifier. The remained mixture was collected as silica slag. After that, soluble sodium silicate was prepared with the silica slag by a new developed low-temperature comelting method. Silica slag was mixed with Na_2CO_3 at a 3 : 2 weight ratio and grinded for 1 h using a ball mill (about 5–10 μm). The mixture was calcined at a heating rate of 5°C/min up to 850°C for 3 h in a muffle furnace. Afterwards, the liquid melt was quenched in boiled water to get small fragments and transferred into a high-pressure reactor filled with water and heated up to 150°C for 5 h. The obtained liquid mixture was filtered and then the as-prepared sodium silicate solution was obtained. The contents of the coal gangue, the silica slag, and the as-prepared sodium silicate are listed in Table 1. It can be seen that there is over 95% SiO_2 in the as-prepared sodium silicate.

2.3. Preparation of SBA-15. The mesoporous silica was prepared using a slightly modified hydrothermal route [10]. P123 2 g was dissolved in 48 mL of 2 M HCl, in which 3.1 g HAc was added and stirred for 4 h to obtain solution A. 25 mL of the as-prepared sodium silicate solution was stirred for 10 min at room temperature as solution B. At 40°C, solution B was added into solution A dropwise under vigorous stirring. The mixture was stirred for 10 min at 40°C and then was kept motionless at room temperature for 12 h. The sediment was filtrated and washed with deionized water several times until Na^+ could not be detected in the washing liquor. Then, 20 g of deionized water was added in the washed sediment. The pH of the obtained mixture was adjusted to 1.7 with 2 M HCl before being transferred into a hydrothermal reaction kettle. After the hydrothermal reaction at 100°C or 200°C for 24 h, the collected samples were filtered, washed, dried in air, and then sintered at 650°C for 5 h to get as-prepared SBA-15 (S-slag). For comparison, pure SBA-15 samples were prepared using commercially available (pure) sodium silicate as a silica source at 100°C and 200°C, which were denoted as S-100 and S-200.

2.4. Characterization. Small-angle X-ray diffraction (SAXRD) analysis of the as-prepared SBA-15 samples was carried out at room temperature using a Rigaku D/MAX-RB diffractometer with Cu Kα radiation with graphite crystal monochromized. Nitrogen adsorption/desorption was performed at 77 K using in a Micromeritics ASAP2010 Sorptometer. The surface area and the pore sizes were obtained from nitrogen adsorption isotherms by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Transmission electron microscopy (TEM) measurements were taken on a JEOL JEM-2100F field emission electron microscope with an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 electron microscope.

Table 1: The components of coal gangue, silica slag, and prepared sodium silicate.

Components (wt.%)	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2
Coal gangue	32.35	57.79	3.37	2.77	1.15
Silica slag	80.49	8.37	0.53	1.14	2.31
Soluble sodium silicate	95.21	0.07	—	4.61	—

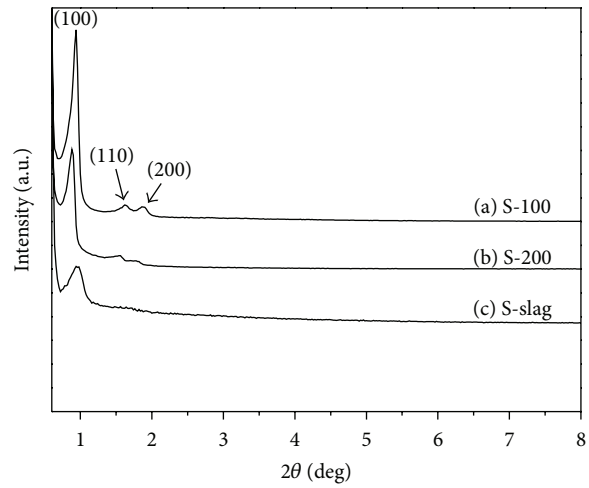

Figure 1: XRD patterns of the SBA-15 samples ((a) S-100, (b) S-200, and (c) S-slag (100°C)).

3. Results and Discussion

3.1. Small-Angle X-ray Diffraction. Figure 1 shows the XRD patterns of the SBA-15 samples, S-100, S-200, and S-slag, after calcinations at 650°C for 5 h. The peaks of curve (a) of S-100 in Figure 1 show a characteristic intense (100) and two higher-order (110) and (200) reflections at 2θ values of 0.94°, 1.60°, and 1.87°, respectively, which are characteristics of SBA-15 *p6mm* hexagonal symmetry. In comparison with the XRD patterns of SBA-15 prepared at 200°C showed as curve (b) in Figure 1, the diffractions of S-100 shift to higher 2θ degrees indicating small pore volume formed at lower hydrothermal temperature. However, significant enhancement in peak intensity can be observed when hydrothermal temperature decreased from 200°C to 100°C, indicating that the sample is highly long-range ordered with hexagonal symmetry [10]. The peak of curve (c) in Figure 1 at 0.96° gives the confirmation of typical SBA-15 structure in S-slag. The other two peaks assigned to the (110) and (200) planes do not appear in curve (c), showing a weak long-range order in the sample. This may be explained by weak long-range ordered

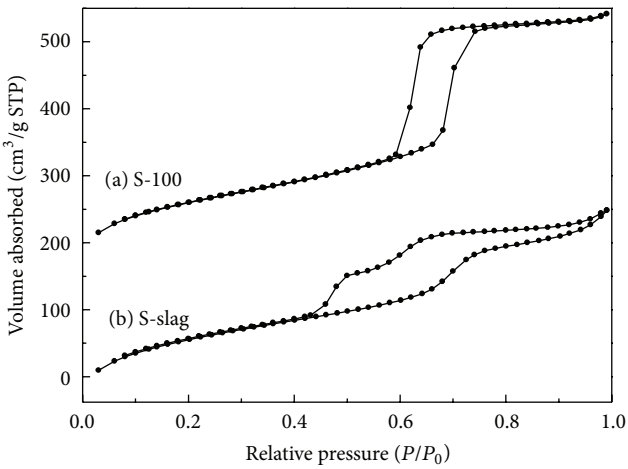

Figure 2: N_2 adsorption isotherms of (a) S-100 and (b) S-slag.

Table 2: Textural parameters of the samples.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)
S-100	567	0.68	7.2
S-slag	552	0.54	7.0

S_{BET}: specific surface area; V_p: total pore volume, and d_p: pore diameter.

crystalline formation of mesoporous silica due to lower silica content in reactant solution [13, 14]. In addition, the trace impurities introduced from S-lag, Cl^- anions, and SO_3^{2-} anions, for example, may also influence the formation of long-range ordered SBA-15. Since the existence of Cl^- and SO_3^{2-} anions may affect the micelle structures during the sol-gel process, the influence mechanism will be further investigated in detail.

3.2. Nitrogen Adsorption/Desorption. The N_2 adsorption/desorption isotherms and corresponding pore size distribution of the samples are shown in Figures 2 and 3, respectively. Curve (a) in Figure 2 (S-100) exhibits a typical-type IV isotherm [13] and a steep capillary condensation step occurred at a relative pressure (P/P_0) ranging from 0.59 to 0.76. Hysteresis appearing in the multilayer range of physisorption isotherms indicates capillary condensation in mesoporous structures. The curve exhibits H1 hysteresis loops; two branches are almost vertical and nearly parallel. According to the classification of IUPAC [21], this type is associated with porous materials consisting of agglomerates or compacts of approximately uniform rods-like particles in fairly regular array, therefore showing narrow pore size distribution (curve (a) in Figure 3). The surface area, pore volume, and pore size are 567 m^2/g, 0.68 cm^3/g, and 7.2 nm, respectively (seen in Table 2).

According to curve (b) in Figure 2, it can be seen that the isotherm of S-slag is analogous to that of S-100, but it shows a less steep capillary condensation step in a wider P/P_0 range from 0.43 to 1, indicating low pressure needed for the capillary condensation due to small pores formation and wide distribution of pore sizes (curve (b) in Figure 3). In addition, the hysteretic loop belongs to type H4, exhibiting that the stacking pores are slit-shaped tunnels which are generally induced by the irregular morphology of mesoporous silica. Clearly, the result of N_2 adsorption/desorption isotherms is consistent with the result of XRD analysis. This was also in agreement with the conclusion drawn by Wang et al., who claimed that impurities from fly ash may affect mesoporous construction [22]. By Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, the surface area, pore volume, and pore size of the SBA-15 samples were calculated and listed in Table 2. The surface area, pore volume, and pore size of the S-slag are 552 m^2/g, 0.54 cm^3/g, and 7.0 nm, respectively.

3.3. TEM and SEM. TEM images of S-100 and S-slag are shown in Figure 4. It can be found that both S-100 and S-slag are analogous to each other exhibiting well-ordered mesoporous materials arrayed along (100) and (110) directions as 2-dimensional hexagonal structures, in agreement with the XRD results.

The pore sizes of the particles of S-100 and S-slag were measured directly along the (110) directions in the TEM images. The results are 6.62 μm and 7.01 μm (shown in Figures 4(b) and 4(d)), respectively. The measured size of S-100 is smaller than the average pore size obtained from BET analysis, which could be explained by the difference between the methodologies.

SEM images of S-100 and S-slag are illustrated in Figure 5. It is clearly observed from Figure 5(a) that the particles of S-100 show both worm-like and rod-like morphology and aggregate together with a particle size less than 1 μm, which is very similar to an earlier report [9]. On the contrary, Figure 5(b) shows that several spherical particles with diameters less than 2-3 μm together with some small irregular-shape particles are observed in the S-slag sample, indicating poor long-range ordered structures.

4. Conclusion

Sodium silicates derived from coal gangue was used as a silica source for SBA-15 synthesis via a low-temperature hydrothermal route. The characteristic of an SBA-15 *p6mm* hexagonal symmetry structure in the as-prepared sample, S-slag, was confirmed by SAXRD, N_2 adsorption/desorption, and TEM. A weak long-range ordered crystalline formation of the mesoporous silica has been found in the sample due to lower silica content in reactant solution and the trace impurities introduced from S-slag. The results suggest that sodium silicate derived from coal gangue is a promising candidate for preparing mesoporous silica, such as SBA-15.

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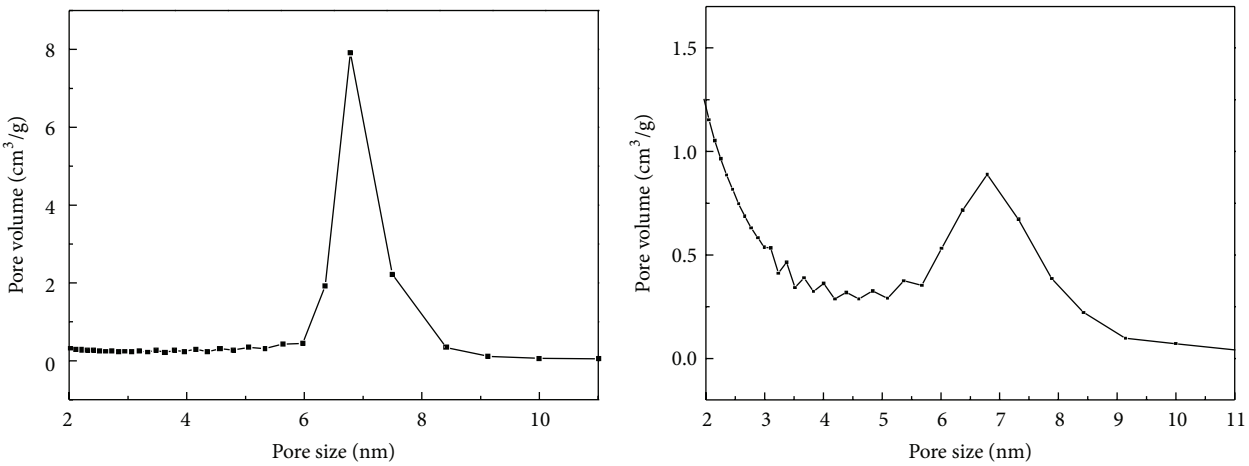


Figure 3: Pore size distribution of (a) S-100 and (b) S-slag.

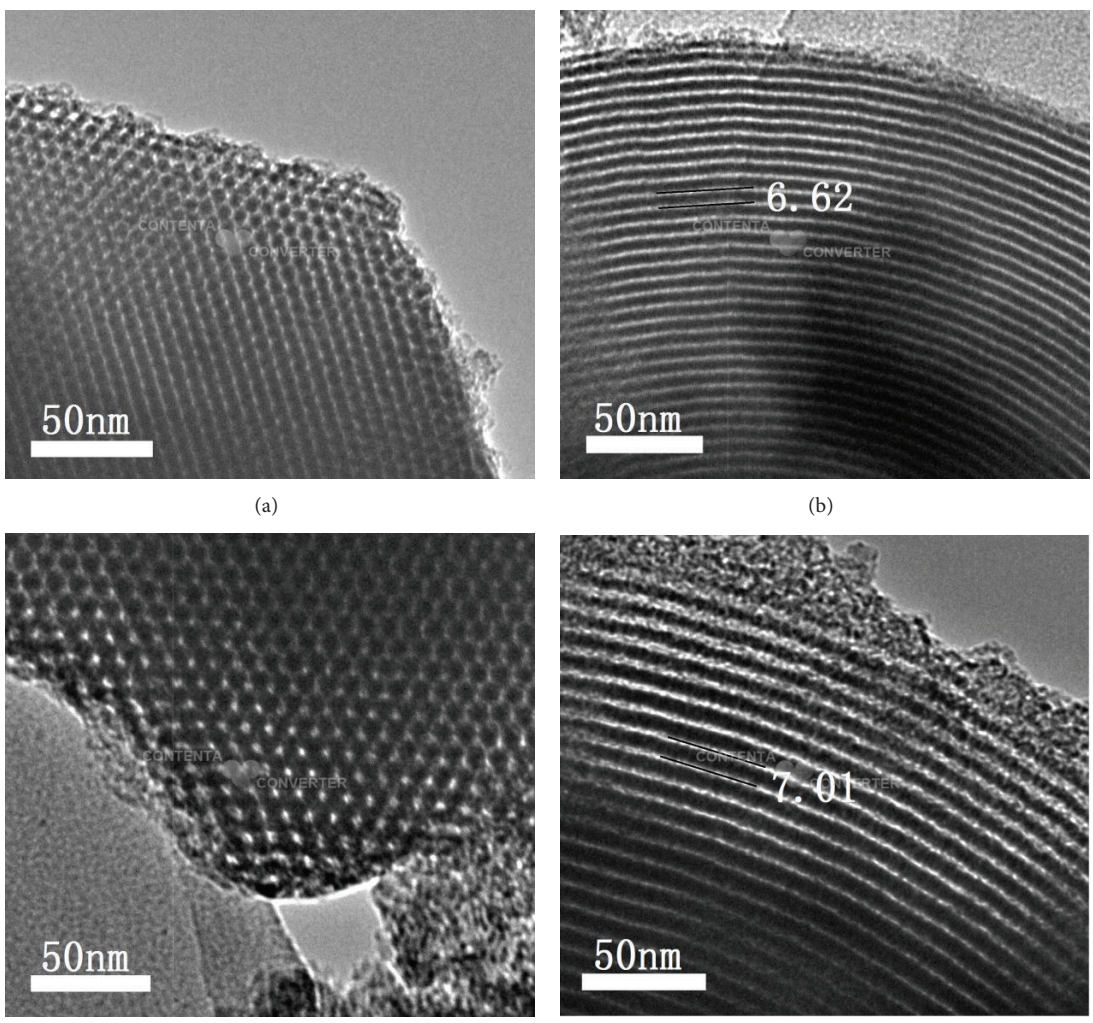
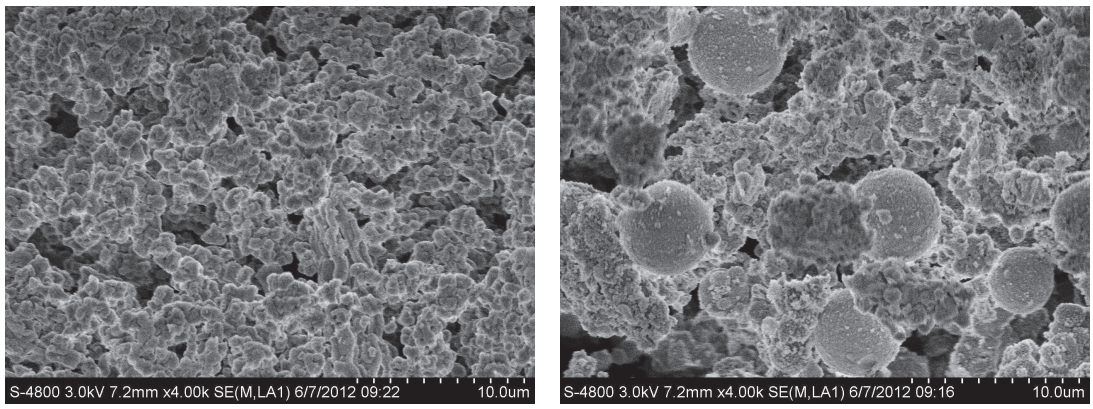


Figure 4: TEM images of S-100 viewed along (100) (a) and (110) (b) directions, and S-slag viewed along (100) (c) and (110) (d) directions.



(a) (b)

Figure 5: SEM images of (a) S-100 and (b) S-slag.

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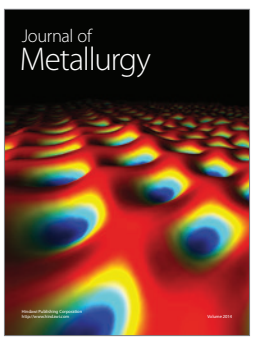

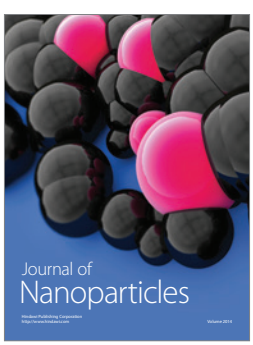

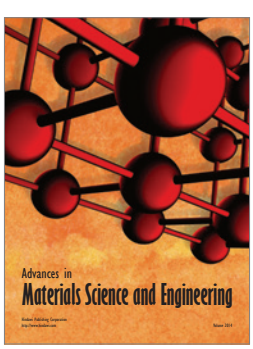

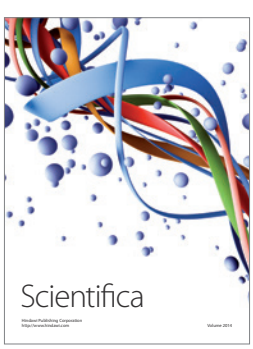

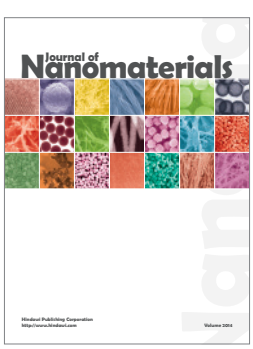

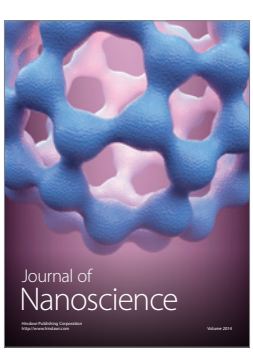

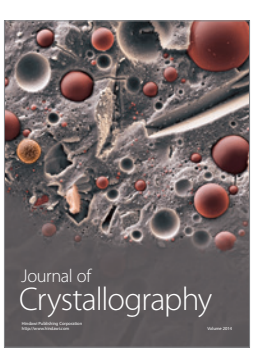

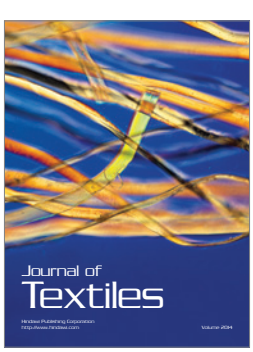

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