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Research article

The effect of hydrothermal temperature on the properties of SBA-15 materials

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ABSTRACT

In present work, ordered mesoporous material SBA-15 was synthesized by using poly (alkylene oxide) block copolymer (Pluronic P123) as template and ethylsilicate as silica source in weak acid environment in a wide range of temperature. The focus of synthesis research was high hydrothermal temperature. The obtained products were characterized by various techniques, including XRD, N_2 sorption isotherms, FTIR spectroscopy and thermogravimetric. The effect of hydrothermal temperature on the specific surface area, pore volume and pore size of SBA-15 products was investigated systematically. As the hydrothermal temperature increases from the 100–120 °C, the specific surface area and the pore volume of the mesoporous molecular sieve increase greatly. When the hydrothermal temperature increase further, the pore volume of the mesoporous molecular sieve increase continually. But the specific surface area decrease significantly. When the hydrothermal temperature is too high (over 140 °C), the order degree begins to decrease, So the specific surface area and pore volume decrease significantly because the pores structure have significant destruction and collapse. Mechanism and structural characteristics of P123 block copolymer could explain in detail the effect of hydrothermal temperature on the property and structure of mesoporous molecular sieve SBA-15.

1. Introduction

Mesoporous materials have controlled morphology due to their large specific surface area and pore volume, uniform and continuously adjustable pore size in nanometer size, and orderly pore structure from one-dimensional to multi-dimensional. The SBA-15 material is one of the representative materials in ordered mesoporous silica-based molecular sieves. The SBA-15 mesoporous molecular sieve was synthesized by using P123 (polyvinyl ether-polypropylene ether-polyvinyl ether) as a template in a strong acidic environment by Zhao et al [1]. SBA-15 mesoporous molecular sieve has a high specific surface, an ordered pore structure, and a large volume. The most attractive feature is that the pore size can be modulated between 6-30nm. The synthesis conditions of SBA-15 are mild. So the surfactant is easy to remove and it is not easy to cause structural collapse; the rejection between neutral surfactant and neutral inorganic precursor is much less repulsive than the charged inorganic precursor and the charged inorganic precursor, so that a thicker pore wall can be formed, thereby improving the thermal and hydrothermal stability of the molecular sieve framework structure. Indeed, its 3–6nm solid pore wall ensures strong hydrothermal stability. The synthesis of SBA-15 overcomes the shortcomings of MCM-41 with poor hydrothermal stability and expensive templating agents, providing a wider space for modification and application. SBA-15 mesoporous material not only compensates for the lack of hydrothermal performance of MCM-41, but also has the characteristics of biodegradable degradation, non-toxicity and low price, which meets the needs of environmental protection and economic development. The characteristics of SBA-15 materials make them have good application prospects in the fields of macromolecular adsorption separation, chemical sensors, biomedicine, chemical catalysis, environmental protection and synthesis of nanomaterials. Organosilane compounds grafted SBA-15 was used to immobilize the lipase from Rhizomucor miehei [2], which gave a maximum improvement of enzymatic activity from 200.00 to 13211.11 U/g. Ni@ SBA-15 was used to catalyze the dry reforming of methane [3], which display excellent catalytic performance. Triethanolamine-modified SBA-15 were used as the catalyst for the cycloaddition of CO2 with epoxides [4]. It was highly

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active in the cycloaddition reaction, in which the maximum yield could achieve 93.47%. N-doped ordered mesoporous carbon material was synthesized by using the urea as nitrogen source, using the sucrose as carbon source and using SBA-15 as the hard template [5]. Mesoporous SiO_2 material was synthesized by partitioned cooperative self-assembly method using sodium silicate as silicon source and the material was applied for the drug release [6]. Al-SBA-15 with combined meso and microporosity was successfully hydrothermally synthesized from spent fluid catalytic cracking catalyst as a single silicon and aluminium source [7]. TiO2@SBA-15 material was synthesized by using chemical deposition [8]. This kind of material display excellent photocatalytic performance. Siliver NPs@CeO2 supported on the SBA-15 was synthesized by microwave-assisted alcohol reduction method [9]. This kind of material display excellent hydrogenation performance. The Zr-modified-SBA-15 material was synthesized by sol-gel method [10] and this kind of material is a good catalyst carrier. Au@SBA-15 material was synthesized by the solvent-free ball milling approach [11] and this kind of material display excellent catalytic performance.

The synthesis mechanism of SBA-15 conforms to the neutral template mechanism (S0I0): nonionic surfactant P123(S0), and the neutral inorganic silicon species (I0) are bonded by hydrogen bonding, and there is no strong electrostatic interaction, and the further hydrolysis and condensation of silanol leads to the accumulation of short-range hexagonal colloidal particles and the formation of a skeleton. The hydrothermal temperature will have a significant effect on the property of SBA-15 product. Commonly, the typically hydrothermal temperature for the SBA-15 is 100 °C. Few report on the synthesis SBA-15 was performed at high temperature>120 °C. In present work, ordered mesoporous material SBA-15 was synthesized by using poly (alkylene oxide) block copolymer (Pluronic P123) as template and ethylsilicate as silica source in weak acid environment in a wide range of temperature 100–180 °C. The focus of synthesis research was high hydrothermal temperature. The effect of hydrothermal temperature on the specific surface area, pore volume and pore size of SBA-15 products was investigated systematically. The obtained products were characterized by various techniques, including XRD, N_2 sorption isotherms, FTIR spectroscopy and thermogravimetric.

2. Materials

2.1. Preparation

This work mainly involves the following reagents: triblock copolymer P123, analytically pure PEO-PPO-PEO, Aldrich; ethanol, analytically pure; tetraethyl orthosilicate, analytically pure; concentrated hydrochloric acid, 0.20 mol/L; deionized water.

Sample preparation: 4.85 g of P123 was dissolved in 150 ml of 0.20 mol/L hydrochloric acid, stirred at room temperature for 1 h, P123 was dissolved to form a homogeneous solution, and TEOS was added to 11.0 ml. The initial ratio of each substance was n(P123):n (TEOS): n(HCl): n(H2O) = 0.017:1:3.049:169.307, the mixture was stirred at 25 °C for 12 h, and then used in a hydrothermal kettle of polytetrafluoroethylene at 100 °C, 120 °C, respectively. 140 °C, 160 °C, 180 °C temperature crystallization for 24h; the obtained crude product was suction filtered, washed with ethanol, filtered again, dried at 120 °C for 12h; in a muffle furnace at a temperature of 10 °C/min After being raised to 550 °C, calcined for 4 h, the template was removed to obtain SBA-15.

2.2. Characterization and testing

This work mainly involves the following characterization instruments: Fourier infrared spectrometer (FTIR, Antaris IGS, PerkinElmer, USA), N2 suction and desorption isotherm (ASAP2460, American McMurray (Shanghai) Instrument Co., Ltd.), X-ray crystal diffractometer (D2PHASER, BRUKER), integrated thermogravimetric analyzer (TG, Setsys Evalution, France Kay Technology), laser particle size analyzer (Malvern MS3000). The XRD measurement was carried out using a D2PHASER type X-ray crystal diffractometer manufactured by BRUKER, Germany. Cu target, Kα radiation source, tube voltage 30KV, tube current 10mA, scanning range 10–90°.

N_2 adsorption desorption was performed using ASAP2460 N_2 suction and desorption isotherm from McMurray (Shanghai) Instrument Co., Ltd., USA. The samples were vacuum treated at 150 °C for 12 h before testing, the specific surface area was calculated by Barrett-Emmett-Teller (BET) method, and the pore size distribution was calculated by Barrett-Joyner-Halenda (BJH) method.

Infrared spectroscopy was performed using FTIR, Antaris IGS type Fourier infrared spectrometer from PerkinElmer, USA. The scanning range is 4000–400cm-1. The sample and KBr were mixed and compressed, and the skeleton structure and some characteristic groups of the sample were tested by this method.

Thermogravimetric (TG) analysis was performed using the TG, Setsys Evalution integrated thermogravimetric analyzer from Cathy Technology of France. The temperature increase rate was 10 °C·min $^{-1}$ and the temperature was raised from room temperature to 900 °C.

3. Results and discussion

In present work, ordered mesoporous material SBA-15 was synthesized in a very weak acid environment and in a wide range of temperature. The focus of synthesis research was the effect of high hydrothermal temperature on the performance of the SBA-15 materials. In the existing literature reports, a strong acid medium was applied for the synthesis of SBA-15 materials. Typically, 2 mol/L hydrochloric acid solution was used for the dissolve of triblock copolymer P123. In present work, ten times lower (0.2 mol/L) hydrochloric acid solution was used for the dissolve of triblock copolymer P123. On the other hand, the typically hydrothermal temperature range for the SBA-15 synthesis is 90–120 °C. Few report on the synthesis SBA-15 was performed at high temperature (>120 °C) in the literature. In present work, a wide range of temperature 100–180 °C was investigated for the synthesis SBA-15 materials. Table 1 shows the physical and chemical properties of SBA-15 products synthesized at various hydrothermal temperatures. It can be seen from the table that the hydrothermal temperature has a significant effect on the specific surface area (S_{BET}), micropore surface area (S_{micro}), mesoporous surface area (S_{meso}), total pore volume (V_{total}), micropore pore volume (V_{micro}), mesoporous pore volume (V_{meso}) and pore diameter of SBA-15. As the hydrothermal temperature increases, the total specific surface area S_{BET} of SBA-15 initially increase from the 726.91 at 100 °C to 755.07 m^2/g at 120 °C, then decreases gradually, from the highest value of 755.07 m^2/g at 120 °C to 307.03 m^2/g at 180 °C, which is reduced by 60%. The micropore surface area S_{micro} of SBA-15 initially increase from the 65.55 at 100 °C to 70.95 m^2/g at 120 °C, then decreases gradually, from the highest value of 70.65 m^2/g at 120 °C to 22.08 m^2/g at 180 °C, which is reduced by 70%. The mesoporous surface area S_{meso} of SBA-15 initially increase from the 661.36 at 100 °C to 704.81 m^2/g at 120 °C, then decreases gradually, from the highest value of 704.81 m^2/g at 120 °C to 284.94 m^2/g at 180 °C, which is reduced by 60%. In contrast, hydrothermal temperature has a much less effect on the total pore volume (V_{total}), micropore pore volume (V_{micro}), mesoporous pore volume (V_{meso}) as compared with that on the surface area. The total pore volume V_{total} of SBA-15 initially increase from the 0.95 cm^3/g at 100 °C to 1.15 cm^3/g at 140 °C, then decreases gradually, from the highest value of 1.15 cm^3/g at 140 °C to 1.08 cm^3/g at 180 °C, which is reduced by 6%. With the hydrothermal temperature increasing, the significant variance of surface area could be observed as compared with the slight variance of pore volume. So it can be concluded that the pore size has significant variance. Indeed, the average pore size increases gradually from 5.26 nm to 14.09 nm with increasing temperature. This is consistent with the pore size results calculated by BJH. According to the literature's result, it will be difficult to keep the ordered mesoporous structure well for SBA-15 synthesis at higher hydrothermal temperature due to the strong acidic

Table 1. Physicochemical properties of SBA-15.

Samples °C	S_{BET} (m^2/g)	Smicro (m^2/g)	S_{meso} (m^2/g)	V_{total} (cm^3/g)	Vmicro (cm^3/g)	V_{meso} (cm^3/g)	average diameter D_p (nm)	BJH Pore diameter D_p (nm)
100	726.91	65.55	661.36	0.95	0.026	0.924	5.26	5.58
120	775.07	70.954	704.81	1.13	0.033	1.097	5.83	5.62
140	459.11	22.09	437.02	1.15	0.008	1.142	10.00	7.35
160	367.68	23.04	344.64	1.05	0.009	1.041	11.47	8.90
180	307.03	22.08	284.94	1.08	0.009	1.071	14.09	11.20

$S_{meso} = S_{BET}$-S_{micro}.
$V_{meso} = V_{total}$-V_{micro}.

medium following the classic SBA-15 synthesis steps. So at higher hydrothermal temperature, it is impossible to obtain SBA-15 materials product with high specific surface area and pore volume because the pore structure will collapse at the high temperature and strong acidic medium. In present work, the ordered mesoporous structure for SBA-15 materials still could keep well at higher hydrothermal temperature. The SBA-15 product obtained at high hydrothermal temperature would be expected to present promising performance.

Figure 1 is a N_2 adsorption-desorption curve of SBA-15 products synthesized at various hydrothermal temperatures in a weak acid environment. It can be seen from the figure that the adsorption-desorption curve of the sample is a type IV isotherm when the hydrothermal temperature is between 100 and 140 °C, indicating that it is a typical mesoporous material with a narrow pore size distribution. As the hydrothermal temperature increases, the adsorption-desorption loop moves gradually to the right and the corresponding pore size increases. When the P/P_0 is 0.6–0.8, the amount of adsorption suddenly increases. After P/P0>0.8, the saturation is basically reached, and the adsorption amount is basically no longer increased. It seem that the adsorption-desorption curves of the samples of 160 and 180 °C changed from IV to type III adsorption-desorption isotherms. So it can be concluded that the pore size gradually change from mesopores to macropores. Indeed, the BJH pore size distribution results as shown in below confirm that with the hydrothermal temperature increasing, the pore size of the material increases from 5.58 nm at 100 °C to 11.2 nm at 180 °C. This is consistent with the phenomenon that the adsorption-desorption loop is shifted to the right from 0.6 at 100 °C to 0.8 at 180 °C. It is well known that higher hydrothermal temperature would lead to the better stability for the synthesized materials, based on the practical consideration. Commonly, the SBA-15 material was synthesized at relatively low hydrothermal temperature (90–120 °C), according to the literature's report. It is very challenging to obtain SBA-15 product via high hydrothermal temperature because both high hydrothermal temperature and strong acidic medium will lead the collapse of porous channel. Comparing to the methods available in the literature, the SBA-15 product was synthesized under a weak acidic medium and high hydrothermal temperature in present work.

Figure 2 is a plot of BJH pore size distribution of SBA-15 products synthesized at various hydrothermal temperatures in a weak acid environment. As can be seen from the figure, the hydrothermal temperature has a significant effect on the pore size distribution of SBA-15. As the crystallization temperature is increased, the pore size of SBA-15 is significantly increased. It increases from 5.58 nm at 100 °C to 11.2 nm at 180 °C, and the distribution of pores is also gradually widened. This indicates that the lower crystallization temperature of SBA-15 is favorable for the uniform distribution of the pore size, and the increase of the crystallization temperature will lead to an increase in the pore size of SBA-15 and a broadening of the pore distribution. The main reason for the influence of crystallization temperature on the pore size of SBA-15 may be that the temperature affects the structure and properties of surfactant P123 during crystallization. P123 is an EO20PO70EO20 triblock copolymer polymer which is mainly composed of a hydrophobic PO segment and is embedded with a hydrophilic EO segment. Under acidic conditions, the non-ionic surfactant will lead to a (S0H+) (X–I+) mechanism for mesoporous molecular sieves synthesis, and the silicon source TEOS is hydrolyzed by H_3O + to form protonated silica. The protonated silica is then partially polycondensed and the hydrophilic long-chain EO block is subjected to an acidic reaction with anion and hydration H+, then combining with protonated silicon oxide by electrostatic attraction, hydrogen bonding or coordination bonding. In summary, the surfactant P123 interacts with silicon species in solution. Hydrolysis and polycondensation of silicon species via surfactant-silicon lead to the formation of SBA-15. The mutual combination of species eventually formed a stable two-dimensional hexagonal mesoporous structure of SBA-15 finally. The exterior of the surfactant consists of a hydrophilic EO segment. The increase in hydrothermal temperature reduces its hydrophilicity and reduces the interaction with the silicon wall. As a result, the pore size increases and the specific surface area decrease.

Figure 3 is a high angle XRD pattern of SBA-15 products synthesized at various hydrothermal temperatures in a weak acid environment, with a broad diffraction peaks appearing around 22.2° due to amorphous silica. Amorphous SiO2 mesoporous materials, usually with an ordered array of

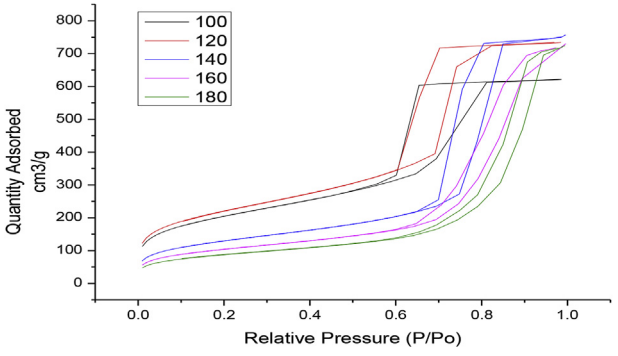

Figure 1. N_2 adsorption-desorption curve of SBA-15 synthesized at different crystallization temperatures.

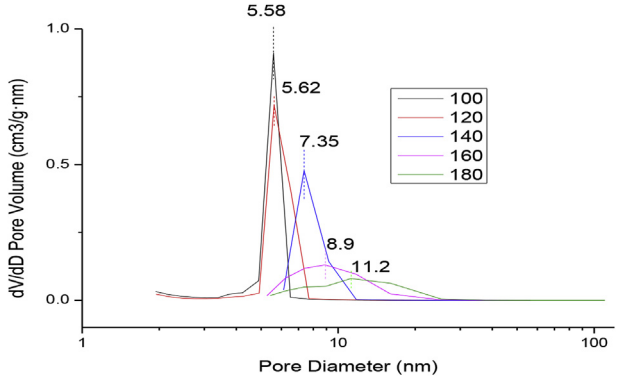

Figure 2. BJH pore size distribution result of SBA-15 synthesized at different crystallization temperatures.

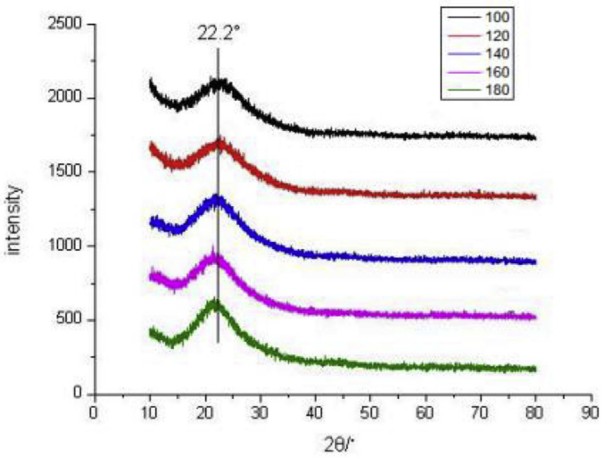

Figure 3. XRD pattern of SBA-15 synthesized at different crystallization temperatures.

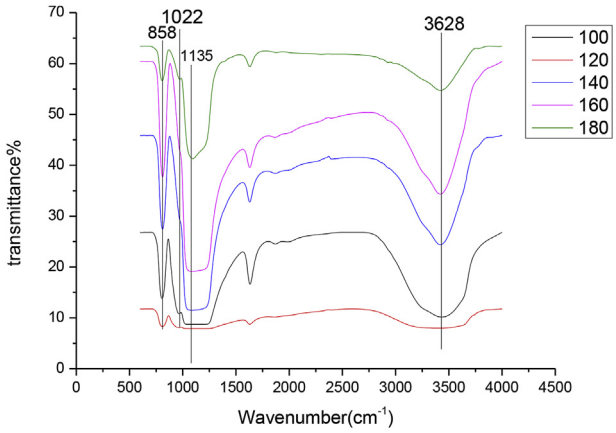

Figure 4. SBA-15 infrared spectra of SBA-15 synthesized at different crystallization temperatures.

pores, have this diffraction peak. Figure 4 is an infrared spectrum of SBA-15 products synthesized at various hydrothermal temperatures in a weak acid environment. There are several characteristic peaks in SBA-15 samples: the absorption peak at 498 cm^{-1} belongs to the absorption peak generated by the bending vibration of Si–O; the absorption peak at 858 cm^{-1} belongs to the absorption generated by Si–O–Si symmetric stretching vibration. Peak; the absorption peak at 1022 cm^{-1} belongs to the absorption peak generated by the bending vibration of Si–OH; the absorption peak at 1135 cm^{-1} belongs to the absorption peak generated by the anti-symmetric stretching vibration of Si–O–Si; at 3628 cm^{-1} the absorption peak belongs to the characteristic peak of stretching and vibration of OH in the adsorbed water. The above characteristic peaks indicate the presence of the molecular sieve SBA-15 skeleton. Figure 5 is hydrothermal temperatures dependency of the mass loss ratio of SBA-15 before and after calcination synthesized at different hydrothermal temperatures. It can be seen that the hydrothermal temperature has a significant effect on the mass loss ratio of SBA-15 products. As the hydrothermal temperature increases, the mass loss ratio gradually decreases and reaches a minimum at 160 °C. However, when the temperature is 180 °C, the mass loss ratio rises. The excessive temperature may cause the templating agent P123 to decompose, leading to the increasing of the mass loss ratio. Figure 6 compare the yield of SBA-15 at different crystallization temperatures. Commonly, the synthesis was carried on in the strong acid environment, typically in 2M HCl solution. Actually, the weaker acid environment will be unfavor to the synthesis of SBA-15. Because it will lead to the incomplete hydrolysis of TEOS, resulting in the lower product yield. As can be seen from the figure, the hydrothermal temperature has a significant effect on the yield of SBA-15. As the hydrothermal temperature increases, the yield of SBA-15 increases significantly from 71.86% at 100 °C to 93.73% at 180 °C. The higher hydrothermal temperature will favor the complete hydrolysis of TEOS. So higher product yield could be obtained. Figure 7 is a particle size distribution diagram of SBA-15 products synthesized at various hydrothermal temperatures in a weak acid environment. Under weak acidic conditions, inorganic species react weakly with nonionic block copolymer surfactants through hydrogen bonding, electrostatic attraction or coordination bonds. And with the polycondensation of the silicon species, the silicon species will accumulate and grow under the action of surfactant micelles to form big aggregation. As the hydrothermal temperature increases, the hydrolysis and polycondensation of silicon species strengthen, meanwhile the surface charge density of inorganic silicon species will increase. The interaction between the silicon species and the surfactant increases and the bending energy of the interface decreases, thereby the aggregation could be depressed, which is conducive to the formation of SBA-15 product with small particle size, At higher hydrothermal temperature 180 °C, The SBA-15 with small particle size will be

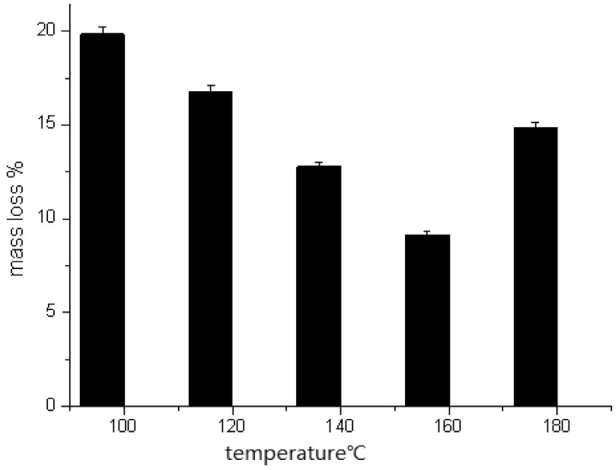

Figure 5. Mass loss ratio before and after SBA-15 roasting.

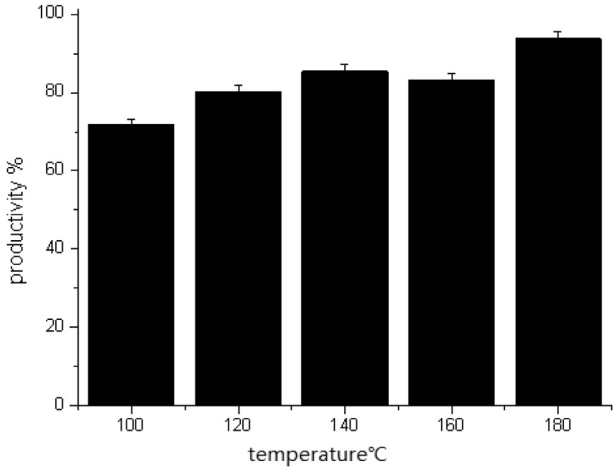

Figure 6. Yield of SBA-15 synthesized at different crystallization temperatures.

obtained. Figure 8 is a thermogravimetric analysis curve prior to calcination of SBA-15 products synthesized at various hydrothermal temperatures in a weak acid environment. During the synthesis of SBA-15, P123 acts as a structure directing agent. In the TG curve of SBA-15, there are two mass loss zones. The first mass loss zone occurs before 180 °C, which is caused by the decomposition of P123 acting as a structure directing agent within

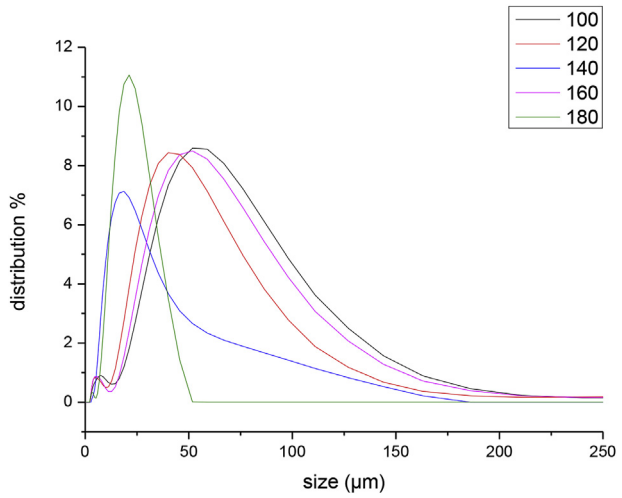

Figure 7. Particle size distribution of SBA-15 synthesized at different crystallization temperatures.

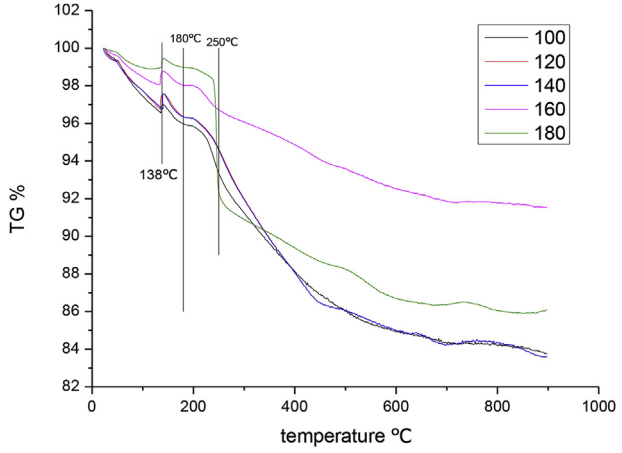

Figure 8. TG curve of SBA-15 synthesized at different crystallization temperatures.

the SBA-15 structural framework. At 138 °C, a slight increase in mass may be an incomplete oxidation of P123. There is another mass loss zone at 250 °C, which is caused by the oxidative decomposition of the unreacted bulk phase P123 in the system. As can be seen from the figure, SBA-15 still has good thermal stability at 900 °C.

In summary, P123 surfactant stick micelles interact with silicon species in solution. With the hydrolysis and polycondensation of silicon species, a stable SBA-15 two-dimensional hexagonal matrix is formed by the combination of surfactant-silicon species. Since the core of the surfactant consists of a hydrophobic PO block, the outer wall is made of hydrophilic. The EO block is connected to the silicon species. As the temperature increases, the hydrophobicity of the EO block increases and the hydrophilicity decreases, so the length of the EO block interacting with the silicon wall decreases, resulting in surfactant aggregates. The hydrophobic volume increases, and eventually the pore size of SBA-15 increases with increasing temperature. As the pore size increases, the specific surface area decreases.

4. Conclusions

Mesoporous SBA-15 materials were synthesized by using P123 triblock copolymer surfactant as structure-directing agent and ethylsilicate as silicon source in a weak acidic environment. The effect of hydrothermal temperature on the specific surface area, pore volume and pore size of SBA-15 products was investigated systematically. As the hydrothermal temperature increases from the 100–120 °C, the specific surface area and the pore volume of the mesoporous molecular sieve increase greatly. When the hydrothermal temperature enhances further, the pore volume of the mesoporous molecular sieve increase continually. But the specific surface area decrease significantly. When the hydrothermal temperature is too high (over 140 °C), the order degree begins to decrease. The specific surface area and pore volume decrease significantly because the pores structure has significant destruction and collapse. Mechanism and structural characteristics of P123 block copolymer could explain in detail the effect of hydrothermal temperature on the property and structure of mesoporous molecular sieve SBA-15.

Declarations

Author contribution statement

Kaiyu Bai: Conceived and designed the experiments.
Junsheng Hao: Performed the experiments.
Aniu Qian: Analyzed and interpreted the data; Wrote the paper.
Yongxing Yang: Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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