

Final Report

Pressure-Assisted Synthesis of Mesoporous Silica

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ABSTRACT

While a variety of strategies have been invented for surfactant-templated synthesis of mesoporous silica, researchers considered only temperature as a thermodynamic variable of synthesis, completely neglecting pressure. Hereby I report the synthesis of mesoporous silica under pressure ranging from 0.1 MPa (atmospheric pressure) to 22 MPa (critical point of water). Results from three different surfactants, CTAB, C₁₆₋₃₋₁, and C₁₈GluA, confirmed that pressure itself is not a critical parameter in determining their structure or morphology. However, using the fact that the boiling point of water rises as the given pressure increases, the temperature limit for aging steps is dramatically elevated under high pressure, enabling us to react over 100 °C. Under condition of 15 MPa, where boiling point of water is 342 °C, synthesis of mesoporous silica from C₁₆₋₃₋₁ and C₁₈GluA was carried out at 100–300 °C and their powder XRD patterns were observed. While C₁₆₋₃₋₁ had not been highly influenced by the temperature in this range, C₁₈GluA over 150 °C showed substantial difference from the existing results made under atmospheric boiling point.

KEY WORDS: Mesoporous silica, High pressure, Anionic Surfactant Templated Mesoporous Silica (AMS), Co-structure directing agent (CSDA)

1. Introduction

In the early 1990s, Kresge *et al.* first utilized a nano-structural self-assembly technique to synthesize mesoporous silica with uniform channels, namely, M41S. Overcoming all the shortcomings of the nonordered (amorphous) mesoporous materials, these materials become a hot topic in the field of material science all over the world.^{1,2}

The characteristics of ordered mesoporous silica including pore diameter, shape, composition, and morphology could be easily manipulated by a various experimental conditions such as pH, temperature, and choice of surfactants.¹ This fact inspired scientists to create large diversity in this material family. However, none of them considered pressure as a thermodynamic variable for the synthesis. The only known approach using high pressure to create mesostructures focuses on so-called “nanocasting”³ method which can be applied for carbides or nitrides, but not for oxides like silica, which are mainly synthesized by “soft-templating”

method that we are discussing here. In this paper, we will try to introduce high pressure into the reaction system during the soft-templating syntheses of mesoporous silica to seek a new structure that cannot be obtained other way.

Three different routes to synthesize mesoporous silica were tried out, both in normal condition and high pressure condition, to seek the possible effects of high pressure during the synthesis of mesoporous silica. (1) The cationic surfactant CTAB was first tried, which is the most classic and the simplest template for mesoporous silica. Based on electrostatic interaction S^+T^- and S^+XT^- pathways, they form well-ordered mesoporous silica and their characteristics are easily controllable.^{1,2} (2) The Gemini surfactant C₁₆₋₃₋₁ was tried in existence of CES as co-structure directing agent (CSDA) to form carboxylic group functionalized mesoporous silica (CFMS).⁴ The interaction between the surfactant and the CSDA produces a uniform distribution of the organic groups, and a regular array of the groups will be formed following the arrangement of the surfactant.⁴ (3) The

anionic surfactant $C_{18}GluA$ was also tried in existence of APS as CSDA.^{5,6} The alkoxy silane sites of APS are co-condensed with TEOS, to be assembled subsequently to form the silica network, consequently producing well-ordered structures with uniform pore diameters.

Meanwhile, according to the phase diagram of water (Figure 1), the freezing point of water falls and the boiling point rises as the given pressure increases. This implies that available temperature range for the synthesis widens if we deploy high pressure to the reaction system. For instance, under pressure of 218 atm, solution can be cooled down to $-1.98\text{ }^{\circ}C$ or heated up to $373.99\text{ }^{\circ}C$. In other words, by introducing high pressure to the reaction system, we will be able to increase the temperature higher than $100\text{ }^{\circ}C$ with the reaction system remain as a homogeneous liquid state. I hereby name this strategy “pressure-assisted synthesis” of mesoporous materials. Since it is widely known that temperature is a key factor in determining structure and morphology of mesoporous materials⁷, this will give opportunity to create materials that cannot be made under atmospheric condition.

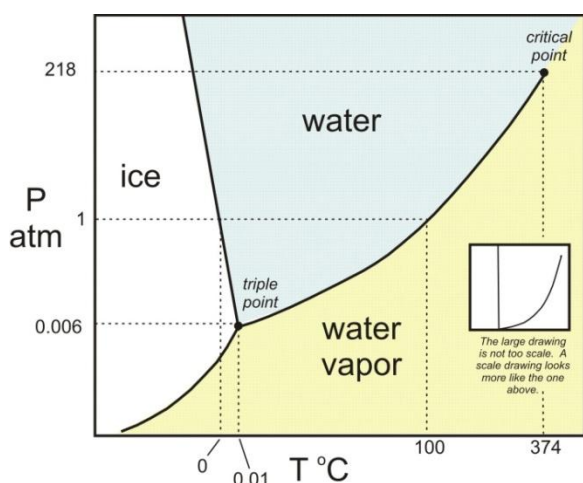


Figure 1. Phase diagram of water.

Conventional Teflon bottles used for synthesis are not suitable for pressure-assisted synthesis for they are easy to explode and unable to prevent vapor from leaking out. There are two methods to give high pressure to the reaction system. One method involves a metal bottle in which the reacting solutions fill the entire volume up without any air letting in. The bottles should be tightly sealed with screws to create closed system for reactions. If the bottles are heated over $100\text{ }^{\circ}C$ (atmospheric boiling point of water), the pressure inside the bottle will increase along the liquid-gas phase transition curve. (Figure 1) This method will be referred as ‘closed systems’ from now on.

The other method is to use a high pressure reactor to control the air pressure of the reaction system. The

solutions were put into the reactor and compressed nitrogen gas was injected to achieve a designed pressure. This method will be referred as ‘high pressure reactor.’

2. Experimental Procedures

2. 1. Materials preparation

All materials were used as purchased without further purification. Tetraethyl orthosilicate (TEOS, from Aldrich, USA), cetyltrimethylammonium bromide (CTAB; from SCRC, China) *N,N*-dimethyl-*n*-octadecylamine (from TCI, Japan), (3-bromopropyl)trimethylammonium bromide (from Aldrich, USA), carboxyethylsilanetriol sodium salt (CES; from Fluorochem, UK), 3-aminopropyltrimethoxy silane (APS; from Aldrich, USA)

CTAB was used as purchased. The Gemini surfactant $[C_{16}H_{33}N(CH_3)_2(CH_2)_3N(CH_3)_3]Br_2$ (C_{16-3-1}) and the anionic surfactant *N*-stearoyl-L-glutamic acid ($C_{18}GluA$) were synthesized as in the previous literature⁵.

2. 2. Synthesis of mesoporous silica

Three kinds of surfactants are discussed in this paper: CTAB, C_{16-3-1} , and $C_{18}GluA$. (1) Cationic surfactants such as CTAB and C_{16-3-1} , were mixed with distilled water, sodium hydroxide, and CES as a co-structure directing agent if needed. The mixture was stirred at room temperature to give a homogenous solution. A designed amount of TEOS were added at room temperature and stirred for 1 h and then allowed to react in a Teflon bottle at $100\text{ }^{\circ}C$ under static conditions for 1 d. (2) The anionic surfactant $C_{18}GluA$ was mixed with distilled water and APS as a co-structure directing agent. The mixture was stirred at $80\text{ }^{\circ}C$ to give a homogenous solution. A designed amount of TEOS were added at $80\text{ }^{\circ}C$ and stirred for 1 h. and then allowed to react in a Teflon bottle at $80\text{ }^{\circ}C$ under static conditions for 2 d.

The resultant white precipitates were filtered and dried overnight at $100\text{ }^{\circ}C$. The surfactants and the organic portion of the CSDA used were removed by calcination at $550\text{ }^{\circ}C$ for 6 h. All experiments were performed in duplicate.

2. 3. Pressure-assisted synthesis of mesoporous silica

(1) ‘Closed system’ method: The mixture of reactants was poured into a metal bottle to fill the entire volume up and the bottle was tightly screwed so that no air can leak out. Then they were heated to a designed temperature over $100\text{ }^{\circ}C$ (atmospheric boiling point of water), making the pressure inside the bottle increases along the liquid-gas phase transition curve. (2) ‘High pressure reactor’ method: The mixture of reactants was poured into a metal bottle that is connected to a reactor. After tightly sealing the

bottle, compressed nitrogen gas was injected to achieve a designed pressure. The solutions then were heated to a designed temperature. After this aging step, the resulting precipitates were processed as are in 2. 2.

2. 4. Characterization of materials

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC equipped with Cu K α radiation (40 kV, 20 mA) at the rate of 0.1 deg. min⁻¹ over the range of 0.6-6° (2θ). The microscopic features of the sample were observed with SEM (JEOL, JSM-7401F).

3. Results and Discussion

3. 1. Effects of high pressure on the synthesis of mesoporous silica

The effects of high pressure on the synthesis of mesoporous silica were studied by comparing the powder XRD patterns of the products synthesized in normal conditions and in high pressure condition, using same composition of reaction mixtures. Figure 2 shows the XRD patterns of mesoporous silica from CTAB with composition 1 CTAB : 10 TEOS : 5 NaOH : 1250 H₂O, one aged at atmospheric condition in a Teflon bottle and one at 15 MPa in the high pressure reactor. Two patterns are almost identical, showing strong evidence for typical 2D-hexagonal $p6mm$ mesophase, which is consistent with the literature⁴.

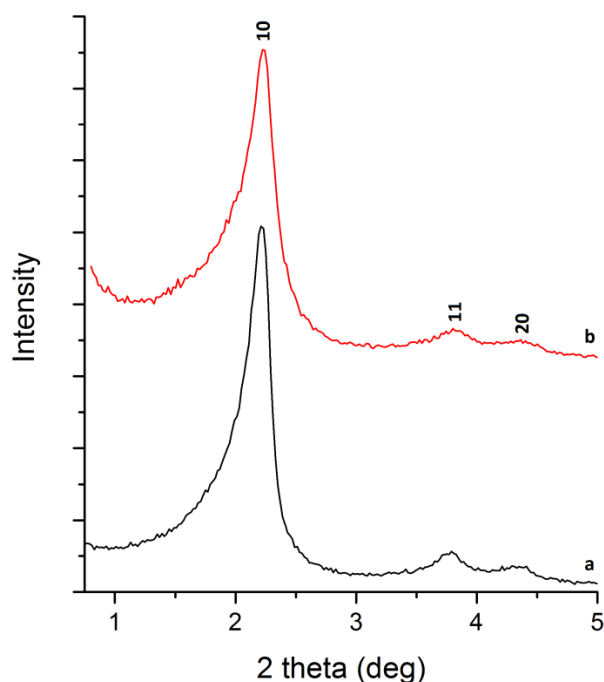


Figure 2. XRD patterns of calcinated samples made from the mixture of 1 CTAB : 10 TEOS : 5 NaOH : 1250 H₂O (a) at atmospheric pressure (b) 15 MPa.

The three strong and well-resolved peaks at $2\theta = 2.21^\circ, 3.82^\circ, 4.42^\circ$ imply a $1 : \sqrt{3} : 2$ d -spacing ratio, and can be indexed to the 10, 11, and 20 reflections of a hexagonal structure with unit cell parameter $a = 3.99$ nm, and this applies for both data. Thus, it can be concluded that 15 MPa of pressure does not affect the synthesis of mesoporous silica from CTAB.

For C₁₆₋₃₋₁, four different conditions were performed: atmospheric pressure in a Teflon bottle, closed system in a metal bottle, 15 MPa, and 22MPa in the high pressure reactor. Figure 3 shows the XRD patterns of mesoporous silica synthesized in each condition with composition 1 C₁₆₋₃₋₁ : 1 CES : 15 TEOS : 2000 H₂O. In accordance with the literature⁴, the three well-resolved peaks were indexed as 111, 220, and 311 reflections on the basis of a cubic $Fm\bar{3}m$ structure with a unit cell parameter of $a = 9.00, 8.91, 8.51,$ and 8.23 nm, respectively. This means pressure decreases the pore size of C₁₆₋₃₋₁ templated mesoporous silica; however, the amount of change by pressure is relatively small compared to the change by pH or temperature. Meanwhile, observing from the shape of the first and highest peak, the structure possible has intergrowth with hexagonal $P6_3/mmc$ symmetry structure, which was previously reported⁴.

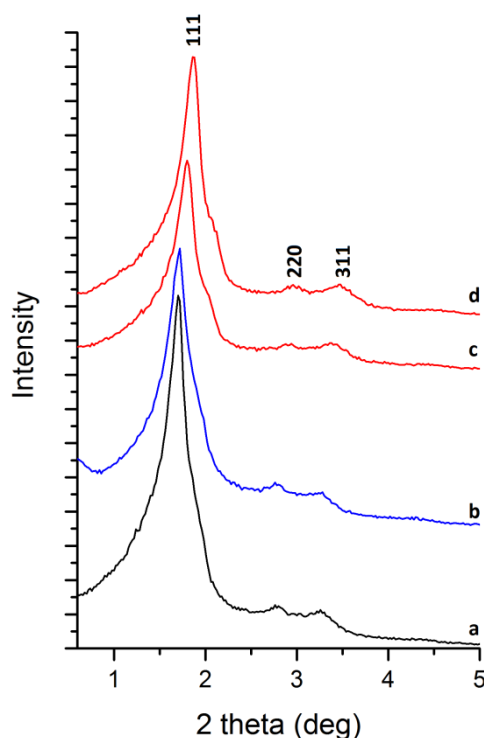


Figure 3. XRD patterns of calcinated samples made from the mixture of 1 C₁₆₋₃₋₁ : 1 CES : 15 TEOS : 2000 H₂O (a) at atmospheric pressure (b) in closed system (c) 15 MPa (d) 22 MPa. Red line means that the reaction took place in the high pressure reactor, blue line a metal bottle, and the black line a Teflon bottle.

Same experiments were carried out by using $C_{18}GluA$ with composition 1 $C_{18}GluA$: 12 APS : 15 TEOS : 2500 H_2O and their XRD patterns are shown in Figure 4. Since the data are from as-made samples instead of the calcinated ones, it is hard to judge the symmetry or space group of these products. It is still observable that the structure itself has not been affected by high pressure, except that the peaks are slightly shifted to the right, implying lower d -spacing and smaller pore diameter.

It is inferable from the results above that high pressure in the synthesis of surfactant templated mesoporous silica, when all the other conditions remain unchanged, does not have any significant influence other than slightly enlarging the d -spacing of the structure. It is assumed that pressure in 10^1 MPa scale has negligible effects on the molecular behavior within the liquid where reaction takes place in.

The effects of high pressure on morphology of mesoporous silica were also studied by observing the microscopic features of the sample using SEM. SEM images taken from the samples of Figure 3 are shown in Figure 5. However, none of them seem to be having any kind of morphology. Concluding from the SEM images including those that are not shown in this paper, high pressure itself cannot change the morphology of the mesoporous silica when all the other conditions remain unchanged.

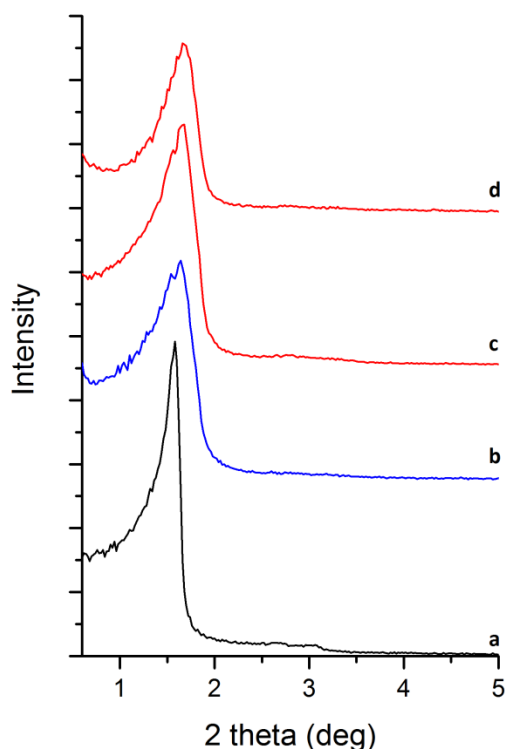


Figure 4. XRD patterns of as-made samples made from the mixture of 1 $C_{18}GluA$: 12 APS : 15 TEOS : 2500 H_2O (a) at atmospheric pressure (b) in closed system (c) 15 MPa (d) 22 MPa.

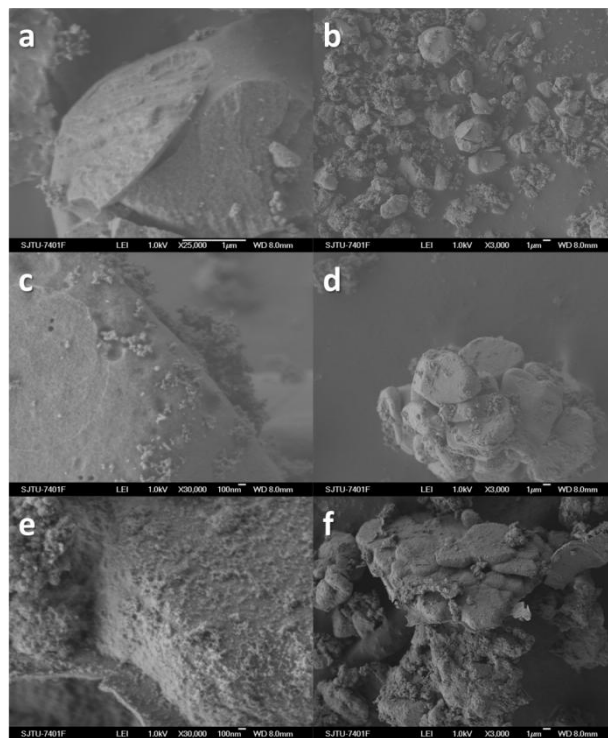


Figure 5. SEM images of the samples from Figure 3. (a, b) atmospheric condition (c, d) closed system (e, f) 15 MPa.

3. 2. Pressure-assisted synthesis of anionic surfactant templated mesoporous silica (AMS)

As explained above, high pressure condition enables solutions to react at the temperature that is much higher than $100\text{ }^\circ\text{C}$ and still be in a homogeneous liquid state. Insofar as the pressure per se is not a critical parameter in controlling mesostructures, pressure-assisted synthesis will be worth performing only in the aspect of broadening the choice of the aging temperature. Synthesis of anionic surfactant templated mesoporous silica was carried out at the temperature ranging from $80\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ by two pressure-assisted synthesis methods.

Figure 6 shows the powder XRD patterns of the calcinated samples synthesized by using $C_{18}GluA$ with composition 1 $C_{18}GluA$: 12 APS : 15 TEOS : 2500 H_2O in different temperature and pressure. Below $150\text{ }^\circ\text{C}$, the pattern with 3 peaks that can be indexed to the 111, 200, 311 reflections of cubic $Fm\bar{3}m$ structure are in good accordance with previously reported materials, with a unit cell parameter around $a = 7.97\text{ nm}$. However, the pattern changes dramatically above $150\text{ }^\circ\text{C}$; the peaks become much broader and shift to the left. 2θ of the first peak become even lower than 1.00° at the temperature $250\text{ }^\circ\text{C}$, with corresponding d -spacing over 8.9 nm , which is the greatest value ever made by anionic surfactant template routes. Further information on the symmetry group of these materials is unavailable due to lack of additional data such as HRTEM pattern.

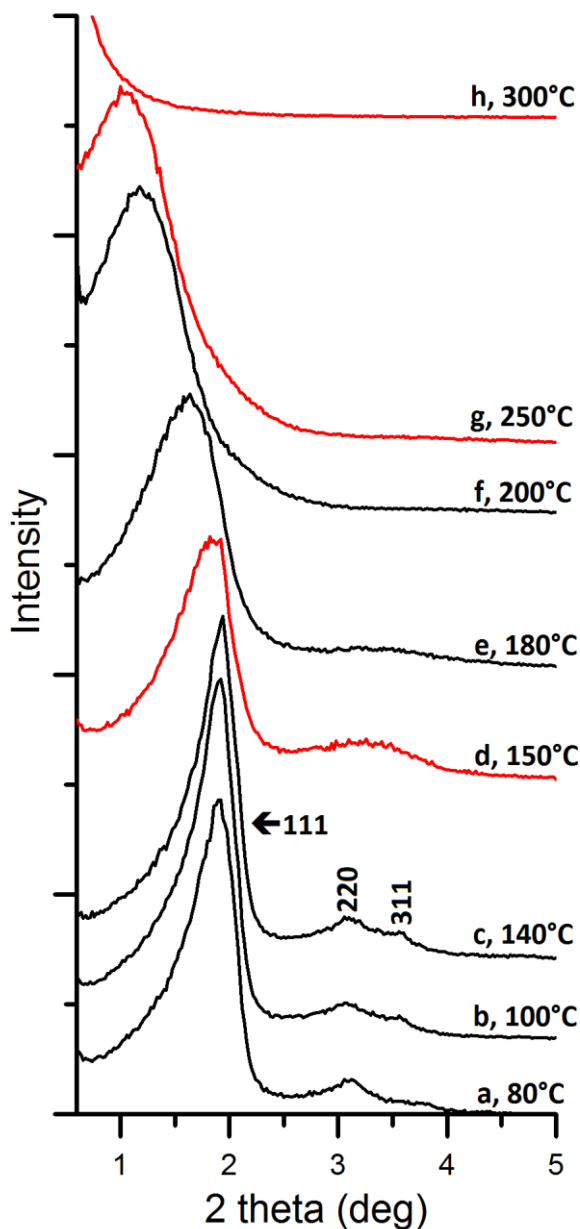


Figure 6. XRD patterns of calcinated samples made from the mixture of 1 $C_{18}GluA$: 12 APS : 15 TEOS : 2500 H_2O (a) at 80 °C (b) 100 °C (c) 140 °C (d) 150 °C, 15 MPa (e) 180 °C (f) 200 °C (g) 250 °C, 15 MPa (h) 300 °C, 15 MPa. Black line means closed system and red line means the high pressure reactor.

The molecular basis of this phenomenon is not known yet, either. Presumably there is a mesoscopic phase transition from micellar cubic to columnar or bicontinuous phase. It should be further discussed theoretically, considering the g value of the surfactant.

Meanwhile, it is confirmed that the organic molecules used are easily decomposed above 300 °C, so that the mesostructures cannot be formed. This point of decomposition also varies by the surfactants although they are not discussed in this paper.

3. 3. Pressure-assisted synthesis of Gemini surfactant templated mesoporous silica

Same experiments were carried out with C_{16-3-1} to study the temperature dependency in the range from 100 °C to 300 °C. Figure 7 shows the powder XRD patterns of the calcinated samples synthesized by using C_{16-3-1} with composition 1 C_{16-3-1} : 1 CES : 15 TEOS : 2000 H_2O in different temperature and pressure. C_{16-3-1} turned out to be decomposing at much lower temperature so that the deformation of mesostructures happens below 200 °C. Presumably CES is an easily degradable substance.

Comparing the sample **a** and **b**, it is inferable that the peak shifts to the left as the temperature increases, which is in accordance with the result from $C_{18}GluA$. However, a dramatic change like what happened in the case of $C_{18}GluA$ did not happen this time.

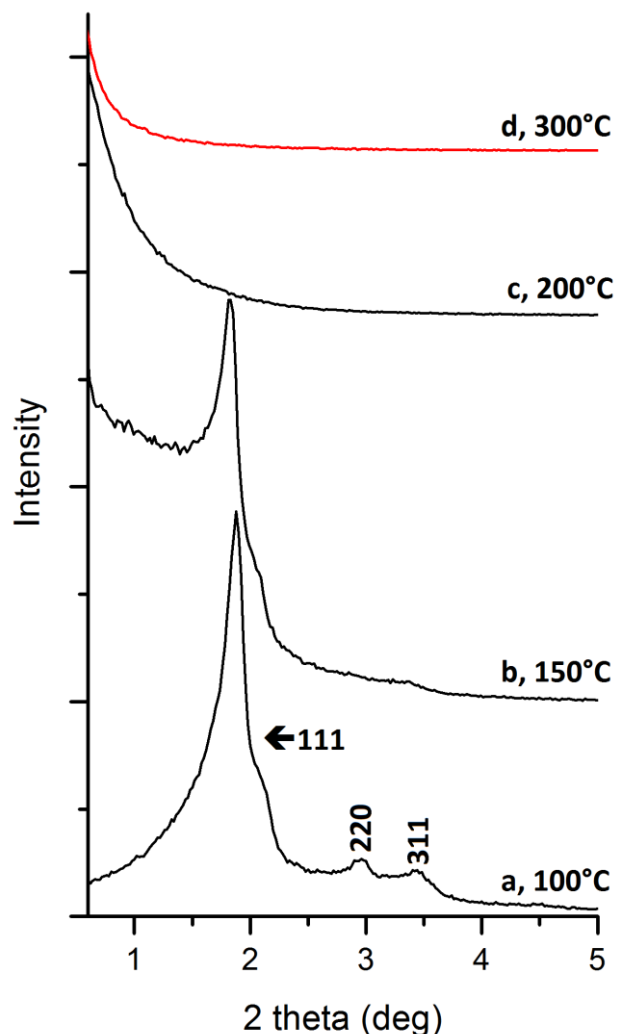


Figure 7. XRD patterns of calcinated samples made from the mixture of 1 C_{16-3-1} : 1 CES : 15 TEOS : 2000 H_2O (a) at 100 °C (b) 150 °C (c) 200 °C (d) 300 °C, 15 MPa. Black line means closed system and red line means the high pressure reactor.

4. Conclusion

High pressure turned out to be having insignificant effects on determining structure and morphology of mesoporous silica, according to the experiments carried out by using CTAB, C₁₆₋₃₋₁, and C₁₈GluA. However we have confirmed that high pressure enables us to increase the temperature of reaction system higher than 100 °C, giving us opportunity to seek new materials that are possibly unable to create under atmospheric condition. Utilizing this 'pressure-assisted synthesis' method, AMS with new XRD patterns were made at the temperature over 150 °C. Its *d*-spacing is over 8.9 nm, which is the largest ever made using anionic surfactant route. Meanwhile, C₁₆₋₃₋₁ did not show such big difference at the temperature over 100 °C.

Further research will focus on the mechanism and molecular basis of the structural change during pressure-assisted synthesis. For this, it is highly desired to acquire additional characterization data from the products, such as HRTEM images, SEM images, and nitrogen adsorption.

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