Colloidal Structure-directing-agent-free Hydroxy-sodalite Nanocrystals

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ABSTRACT

Our previous work showed that colloidal structure-directing-agent-free hydroxy-sodalite nanocrystals could be synthesized by the direct transformation of silicalite nanocrystals. The structure directing agent TPAOH molecules trapped in the dried silicalite nanocrystals proved to play an important role in confining the structure transformation. In the presence of TPAOH, silicalite nanocrystals reacted with alkaline $NaO-Al_2O_3$ aqueous solution and formed hydroxy-sodalite nanocrystals without substantial change in the sizes and morphologies. In this presentation, different colloidal silica sources were used to examine the effect of the crystalline structure of starting nanoparticles. The results indicated that sodalite crystals and a mixture of zeolite A and sodalite crystals were produced, and their sizes ranged from less than 100 nm to a couple of microns when amorphous colloidal silica nanoparticles were used. This again suggests that a combination of silicalite nanocrystals and TPAOH is advantageous for formation of hydroxy-sodalite nanocrystals.

Keywords: silicalite, sodalite, nanocrystals, transformation, structure directing agent

1 INTRODUCTION

There has been continuously growing interest in the synthesis and application of zeolite nanocrystals since colloidal zeolite suspension was first reported in the early 1970s. [1] Owing to the success of the synthesis of zeolite nanocrystals, it has become more convenient for studying the mechanisms of zeolite crystallization; the improved performance of zeolites has been seen in their traditional uses such as in catalysis, ion exchange and adsorption , and more importantly zeolite nanocrystals have brought about some new applications including low-k dielectrics in microelectronics, optoelectronics, chemical sensing and nanostructured membranes in fuel cells and separation processes.

To produce colloidal zeolite nanocrystals, a large amount of organic structure directing agent (SDA) is required in most syntheses, and the use of SDA makes zeolite crystallization controllable. Recently, SDA-free syntheses of zeolite nanocrystals have been developed through the use of the space-confinement additives such as carbon black, starch, gelling polymer and even carbon nanotubes. However, a novel method for rational synthesis of the zeolite nanocrystals with narrow size distribution is still highly demanding. [1]

Amongst various types of zeolites, sodalite is very attractive as functional material for a wide range of applications such as optical materials, waste management, hydrogen storage and hydrogen separation. Colloidal hydroxy-sodalite nanocrystal sols were synthesized by homogeneous nucleation in the presence of tetramethylammonium hydroxide (TPAOH). [2] By solid–solid transformation of pillared clay SDA-free, sodalite particles (500 nm) composed of small crystallites were synthesized. [3-5] Very recently, we have reported our findings that colloidal SDA-free hydroxy-sodalite nanocrsystals can be obtained by the transformation of silicalite-1 nanocrystals. [6] Silicalite nanocrystals were employed as the silica source for hydroxy-sodalite synthesis since synthesis of silicalite had been well established. After the incorporation of the alkaline solution and the transformation of crystal structure, the resulting hydroxy-sodalite nanocrystals possessed the similar sizes and morphologies as the original silicalite nanocrystals. In this presentation, we will further the use of different silica sources in the synthesis of sodalite and discuss the effect of silica source on sodalite growth.

2 EXPERIMENTAL

2.1 Sample preparation

Two SiO_2 sols, i.e., Ludox HS-30 (Sigma Aldrich), and Snowtex 20L (20wt%, 40-50 nm, Nissan Chemicals) were used as received. TEOS (tetraethyl orthosilicate, Sigma-Aldrich) derived sol was prepared by mixing 10 g of TEOS, 7.1 g of deionized water and 1 g of 4 M HCl, followed by stirring at room temperature for 3h. TPAOH (tetrapropylammonium hydroxide) solution (1 M, Sigma Aldrich) was added under stirring into Ludox HS-30 sol, TEOS derived sol and Snowtex 20L sol, respectively. The silica sources with TPAOH were obtained by directly drying the three mixtures with a molar composition of 1 TPAOH: 4.8 SiO_2: 44 H_2O at 80-90 °C. As a comparison, another batches of three silica sols were prepared and the dried under the same conditions without adding TPAOH.

A colloidal silicalite nanocrystal solution was synthesized as follows. [7] A clear synthesis solution was prepared by dropwise addition of 1 M TPAOH into TEOS under stirring, and stirring continued at room temperature for 3 h. The final solution composition was 1 TPAOH: 4.8 SiO_2: 44 H_2O. After crystallization at 80 °C for 3-4 days, colloidal silicalite suspension was dried at 80-90 °C as silica source for synthesis of sodalite nanocrystals.

The alkaline solution with a molar composition of 6.07 Na_2O: 1 Al_2O_3: 66.0 H_2O was prepared by mixing 20 g of sodium hydroxide (Merck), 9.2 g of sodium aluminum (Sigma-Aldrich) and 60 g of deionized water at room temperature for 1-2 h. Different silica sources, with an equivalent weight of 0.72 g silica, was added in 11 g of the alkaline solution, and aged at room temperature for 4 h. The crystallization was conducted at 80 °C for 3 h. The samples obtained were cooled to room temperature, and the zeolite crystals were collected by repeating three cycles of washing with deionized water and centrifugation, followed by drying at 90-100 °C overnight.

2.2 Characterization

Scanning electron microscopy (SEM) images were taken with a JSM-6300F microscope (JEOL), and transmission electron microscopy (TEM) images were taken with a Philips CM120 microscope. X-ray diffraction (XRD) patterns were collected with a Philips PW1140/90 diffractometer using Cu Kα radiation. Thermogravimetric analysis (TGA) (Perkin Elmer, Pyris 1 TGA) was conducted in air at a heating rate of 5 °C/min up to 700 °C.

3   RESULTS AND DISCUSSION

3.1 Dried silica sols as silica sources

Fig. 1 shows SEM images of the samples from three dried silica samples without adding TPAOH. Microsized crystals were formed from Ludox HS-30 and TEOS derived silicas, (Fig. 1a,b) whereas zeolite nanocrystals (50-60 nm) were produced from Snowtex 20L silica (Fig. 1c). XRD patterns shown in Fig.2 revealed that all of three samples are zeolite A mixed with a small amount of sodalite. This clearly indicates that the silica particle size has a significant influence on the zeolite crystal size. During aging and hydrothermal treatment, Ludox HS-30 and TEOS derived silicas can be easily dissolved to form amorphous NaO-SiO_2-Al_2O_3-H_2O gels, in which solution-mediated nucleation and crystallization facilitates zeolite growth. Therefore, large crystals tend to grow from dried Ludox HS-30 and TEOS derived sols with small silica particles. By contrast, it took a much longer time to dissolve Snowtex 20L silica nanoparticles (40-50 nm in size) in the alkaline solution. Highly likely, silica dissolution is not complete before zeolite crystallization is carried out at hydrothermal conditions. A large number of nuclei are produced from

localized NaO-SiO_2-Al_2O_3-H_2O gels leading to small crystal sizes.

Effect of hydrothermal time was also examined in this study. A mixture of zeolite A and sodalite was obtained from all amorphous silica sources after 2 h of hydrothermal reaction whereas pure sodalite was produced when was extended to 3 h. [6] When hydrothermal time was extended to 16 h for dried Snowtex 20L silica sol, pure sodalite crystals were synthesized as shown in Fig. 3. However, the crystal sizes grew up to around 200 nm. This result suggests that the crystal structure evolves from *zeolite A* to *sodalite* under present synthesis conditions.
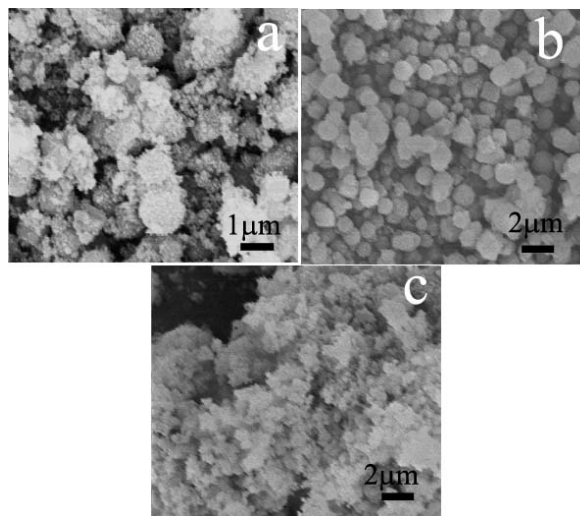

Figure 1 SEM images of zeolites prepared from dried silica sols without TPAOH. (a) Ludox HS-30 sol, (b) TEOS derived sol, and (c) Snowtex 20L sol.
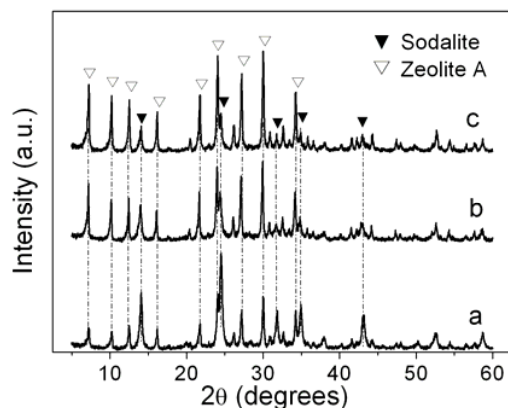

Figure 2 XRD patterns of zeolites prepared from dried silica sols without TPAOH. (a) Ludox HS-30 sol, (b) TEOS derived sol, and (c) Snowtex 20L sol.

3.2 Dried silica sols with TPAOH as silica sources

In the presence of TPAOH molecules in dried silica sols, zeolite nanocrystals were produced from all three silica sources (Fig.4). It is obvious that zeolite crystal sizes grown with TPAOH molecules around are much smaller than those prepared from silica sol without TPAOH involved (Fig. 1). Crystal structure of zeolite nanocrystals was identified by XRD (Fig.5) to be a mixture of zeolite A and sodalite. However, as compared with those zeolites produced without using TPAOH (Fig.2), the proportion of sodalite phase in all samples is substantially larger. As a result, TPAOH molecules can not only act as a barrier preventing big crystal formation, but also promote the silica transformation into sodalite.
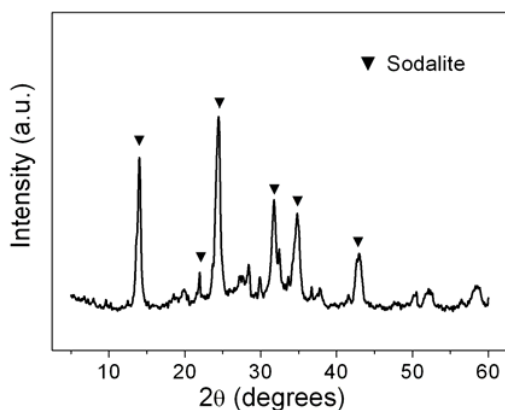

Figure 4 SEM images of zeolites prepared from dried Ludox HS-30 sol-TPAOH (a), dried TEOS derived sol-TPAOH (b) and dried Snowtex 20L sol-TPAOH (c).

Figure 3 XRD pattern of sodalite prepared from directly dried Snowtex 20L silica sol (40-50 nm in size) and hydrothermal for 16 h.

Figure 5 XRD patterns of zeolites prepared from dried Ludox HS-30 sol-TPAOH (a), dried TEOS derived sol-TPAOH (b), and dried Snowtex 20L silica sol-TPAOH (c).

3.3 Silicalite nanocrystals as silica source

When silicalite nanocrstals dried from colloidal suspension were used as silica source, pure sodalite nanocrystals were produced. Interestingly, sodalite nanocrystals exhibit similar morphologies. The average crystal size somewhat decreases from about 80 nm for silicalite to 60 nm after phase transformation of silicalite into sodalite (Fig. 6). The crystalline nature of silicalite seems to facilitate sodalite formation, and offer high resistance to dissolution in alkaline solution. Therefore a combination of silicalite nanocrystals and TPAOH molecules forms a unique way to synthesizing sodalite nanocrystals.
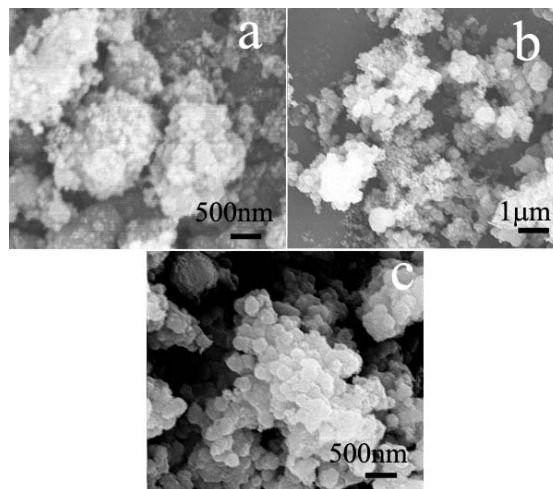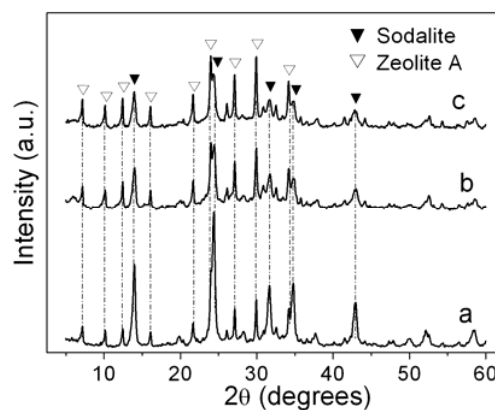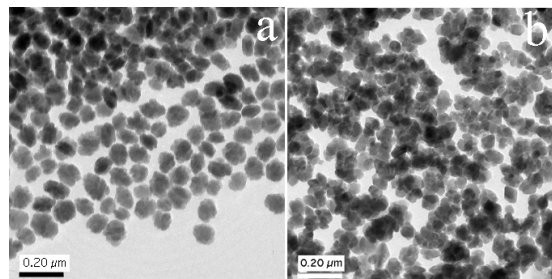

Figure 6 TEM images of silicalite (a) and hydroxy-sodalite (SOD-D) (b) from directly dried silicalite

4 CONCLUSIONS

Colloidal SDA-free hydroxy-sodalite nanocrystals were prepared by the transformation of silicalite nanocrystals. A mixture of zeolite A and sodalite was grown from amorphous silica sources. The presence of TPAOH molecules significantly reduced crystal sizes of zeolites synthesized from amorphous silicas. It can be concluded that silicalite is preferred for the formation of sodalite nanocrystals, and TPAOH molecules serve as a temporary barrier and effectively confine the zeolite transformation. Work is in progress to synthesize sodalite nanocrysals from amorphous silicas. It is likely other types of zeolite nanocrystals such as A, X and Y would be synthesized from both silicalite and amorphous silica by optimizing synthetic conditions.

5 ACKNOWLEDGEMENTS

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