Synthesis of Size Distribution Controllable Zeolite Nanocrystals *via* a Novel Confined Space Strategy

Yi Huang, Monash University, Melbourne, VIC, Australia
Dr. Anita J. Hill, Commonwealth Scientific and Industrial Research Organization Materials Science & Engineering, Melbourne, VIC, Australia
Dr. Huanting Wang (corresponding author), Monash University, Melbourne, VIC, Australia

Abstract

A novel confined-space synthesis method has been developed to synthesize zeolite nanocrystals. Colloidal silica nanoparticles serving as the silica source as well as the hard template were embedded in the mesoporous carbon *via* in situ polymerization of furfuryl alcohol (FA) in the presence of tri-block copolymer (Pluronic P123), and then reacted with an alkaline aqueous solution (Na_2O-Al_2O_3-H_2O) infiltrated through the mesoporous channels of the carbon matrix. The synthetic zeolite nanocrystals possess similar size distribution corresponding to that of colloidal silica nanoparticles. The synthesis of zeolite NaA nanocrystals is demonstrated. The amount of FA, aging time and hydrothermal time showed significant effects on the morphology and crystal size of zeolite NaA. N_2 sorption, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to characterize the mesoporous carbon-silica composite and zeolite NaA nanocrystals. Dynamic Light Scattering (DSL) was used to measure the particle size and size distribution of zeolite nanocrystals as well as colloidal silica nanoparticles. Zeolite nanocrystals synthesized in this study are useful to fabricate zeolite-polymer nanocomposite membranes and the as-synthesized carbon-zeolite nanocomposite has high potential to serve as hierarchical nano-structured zeolite adsorbent for wastewater treatment.
Keywords: confined space synthesis; carbon-silica composite; NaA zeolite; nanocrystals

Introduction

Zeolite nanocrystals with high crystallinity have been attracted great interests because it is very important for various studies and applications, such as the fundamental understanding of the crystal growth process at the zeolite external surface, especially nucleation and growth processes zeolite [1-9] and the emerging nontraditional applications [10-11]. Moreover, small zeolite crystals are favorable in many catalytic reactions because of the reduced transport path and a substantial increase of the specific external area [12]. Therefore, to synthesize high-quality zeolite nanocrystals is of great interest. Different types of zeolite nanocrystals such as NaA [1], MFI [3] and FAU [8] have been already reported. For instance, Zeolite NaA nanocrystal, a highly versatile member of the LTA family, is one of the most important zeolites which have been extensively used in ion exchange, adsorption, catalysis and other aspects [12-15].

Many efforts have been made to synthesize zeolite with nanometer size and narrow size distribution. In most syntheses, organic templates, structure directing agent, seeding crystals and many other additives were often added to synthesize zeolite crystals with reduced sizes. Recently, confined-space synthesis has been developed for preparation of zeolite nanocrystals within an inert matrix. Many types of zeolite have been prepared using this procedure within carbon black matrixes, such as ZSM-5, Zeolite Beta, X and Zeolite A [16-17]. In this method, the hard media such as carbon

black, and carbon nano-tubes were often used as space-confining porous media. The carbon black matrix provides not only limited space which is effective in confining zeolite growth but also preventing intergrowth of zeolite crystal during crystallization and aggregation of zeolite nanocrystals during calcination. However, careful investigation should be always drawn to identify the suitable porous system of inert support materials for the purpose of yielding zeolite nanocrystals with desirable particle size and size distribution.

In this work, a novel confined-space synthesis method that takes advantages of both space confined synthesis and a templating approach was developed to prepare zeolite NaA nanocrystals with tunable crystals size and controllable crystal size distribution. The synthesis of zeolite NaA nanocrystals is demonstrated by using colloidal silica particles (SNOWTEX ST-ZL: 70-100 nm) as the starting silica source as well as templates. Firstly, silica-carbon composite was prepared by carbonization of a gel prepared by mixing colloidal silica particle, FA and Pluronic P123. Secondly, colloidal silica particles wrapped silica-carbon composite were completely converted into zeolite NaA nanocrystals in a template-free alkaline alumina solution under hydrothermal treatment. The major advantages of this method are: (i) the absent of structure directing agent, seeding crystals and many other additives in model system and (ii) tunable crystals size and controllable crystal size distribution characteristics of as-synthesized zeolite.

Experimental Details

1. Confined space synthesis of NaA zeolite

The detailed procedures of our novel confined space synthesis can be found in the paper we have reported [18]. Typically, 2g of P123 [$(EO)_{20}(PO)_{70}(EO)_{20}$] ($M$n ca. 5 800, Aldrich) was mixed with 5g Furfuryl alcohol (FA, 98%, Aldrich) until a uniform and homogeneous solution was obtained. Then 2.5 g of aqueous colloidal silica (SNOWTEX ST-ZL: 70-100 nm) was added. 1g of moderate concentrated acid solution (2 M, HCl) was added to complete the starting gel for the purpose of achieving an acidic circumstance and controlling the polymerization rate of FA [19]. The solvent evaporation and acid-catalyzed polymerization of FA were carried out in an uncapped polypropylene bottle at room temperature for 2 days and then at 70 °C in an oven for 2-3 days, leading to a black SiO_2-P123-PFA monolith with a mass ratio of 1 SiO_2: 2 P123: 5 PFA. After polymerization, a black solid was obtained. To prevent silica from dissolving out of mesoporous silica-carbon composite particles during the penetration of the alkaline solution, the SiO_2-P123-PFA monoliths were crushed into particles with a size range of 3-6 mm for surface coating. A silica free P123-PFA solution with the same mass ratio of the monolith was employed to produce the mesoporous carbon coating. After re-polymerization, the coated SiO_2-P123-PFA monoliths were calcined under flowing nitrogen gas in the furnace up to 500 °C at the heating rate of 1 °C /min and then kept for 5 h to develop the mesoporous silica-carbon composite. After calcination, 31.17 g of alkaline solution was ultimately mixed with the given amount of mesoporous silica-carbon composite to form the molar ratio of 5.85 Na_2O: 1.00 Al_2O_3: 182 H_2O: 2 SiO_2. The final mixture was sealed and then left it in the fume cupboard aging for 2-7 days after which the mixture was transferred into an 80 °C electrical oven for zeolite transformation. After hydrothermal treatment, carbon-zeolite composite was rinsed thoroughly with doubly deionized (DDI) water and dried at room temperature for around 2 days. Zeolite nanocrystals were retrieved by burning off mesoporous carbon in air at 550 °C for 6 h, a temperature that was reached at a heating rate of 1 °C /min.

2. Characterization

Powder X-ray diffraction (XRD, Philips PW1140/90 diffractometer using Cu Kα radiation) was used to determine sample phase and crystallinity. Data was collected at a scan rate of 1º /min from 5º to 45º with a step size of 0.02º. Nitrogen adsorption-desorption experiments were carried out at 77 K on a Micrometrics ASAP 2020 to determine the Brunauer-Emmett-Teller (BET) surface area. The micropore volume and pore size distribution were determined by t-pot method and BJH (Barrett-Joyner-Halenda) method, respectively. The total pore volume, V_{total}, was evaluated from the desorption branch of the isotherm at P/P_o =0.98, assuming complete pore saturation. SEM images were taken with a JEOL JSM-6300F scanning electron microscope operating at a voltage of 15 kV. Elemental analysis of the samples was conducted by an energy dispersive X-ray spectrometer (EDXS) attached to the JEOL JSM-6300F scanning electron microscope. Suspended particle size distributions of colloidal silica and synthesized Zeolite NaA nanocrystals were determined using a Malvern Instruments (Malvern, UK) Zetasizer Nano ZS series (ZEN 3600) at pH around 9 [18].

Results and discussion

To successfully synthesize zeolite nanocrystals with designed particle size and particle size distribution, it is very important to prepare SiO_2-P123-PFA monoliths with preferable mass ratio which would subsequently supply sufficient carbon confinement and expected mesoporous system in silica-carbon matrix. Therefore, four mass ratios including 1 SiO_2: 2 P123: 3 FA, 2 SiO_2: 2 P123: 3 FA, 1 SiO_2: 2 P123: 5 PFA, and 2 SiO_2: 2 P123: 5 FA were examined. However, uniform silica-P123-PFA composite was only prepared by adopting the mass ratio of 1 SiO_2: 2 P123: 5 FA [18]. The SiO_2-P123-PFA monolith and its calcined sample were denoted as SiO_2-5F and SiO_2-5C, respectively. SEM images show that SiO_2-5F and SiO_2-5C monoliths are quite uniform (Figure 1a, b). Silica particles are well separated in both samples by respective P123-PFA copolymers and mesoporous carbon walls.
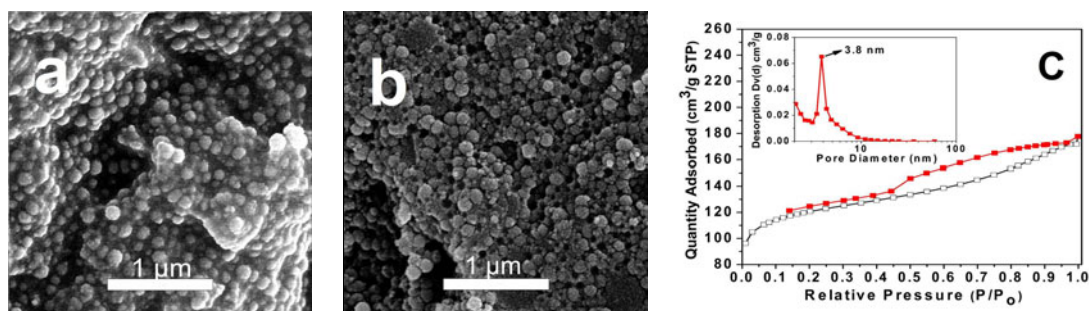

Figure 1. SEM images for (a) SiO_2-5F, (b) SiO_2-5C and (c) Nitrogen adsorption and desorption isotherm and pore size distribution (inset) of SiO_2-5C.

Figure 1 (c) shows the Nitrogen analysis for SiO_2-5C sample. The nitrogen sorption isotherm shows a hysteresis at relative pressures starting from approximately 0.45, indicating a mesopore structure. Despite a wide pore size distribution, the SiO_2-5C composite possessed relatively more uniform mesopores and a smaller mean mesopore size (3.8 nm) than other compositions [18]. SiO_2-5C exhibits a BET surface area of 225 m^2/g, and a pore volume of 0.30 cm^3/g.

SiO_2-5C monoliths were subsequently soaked in a designed amount of alkaline solution under decreased pressure for certain period. The lost weight was compensated by the addition of DDI water, after which the mixture was sealed for 2-7 days before subjection of hydrothermal treatment at 80 °C

for a designed period. It is well known that longer aging time would lead to more pre-nuclei, and then favor formation of small particles. However, in our mesoporous carbon confined synthesis, crystal sizes become less sensitive to the aging and crystallization conditions, making nanocrystal growth more controllable. According to experimental investigation, when the aging time and crystallization time was fixed in the range of 4-7 days and 6-8 h respectively, highly crystallized zeolite nanocrystals with expected particle size and size distribution were finally synthesized [18].
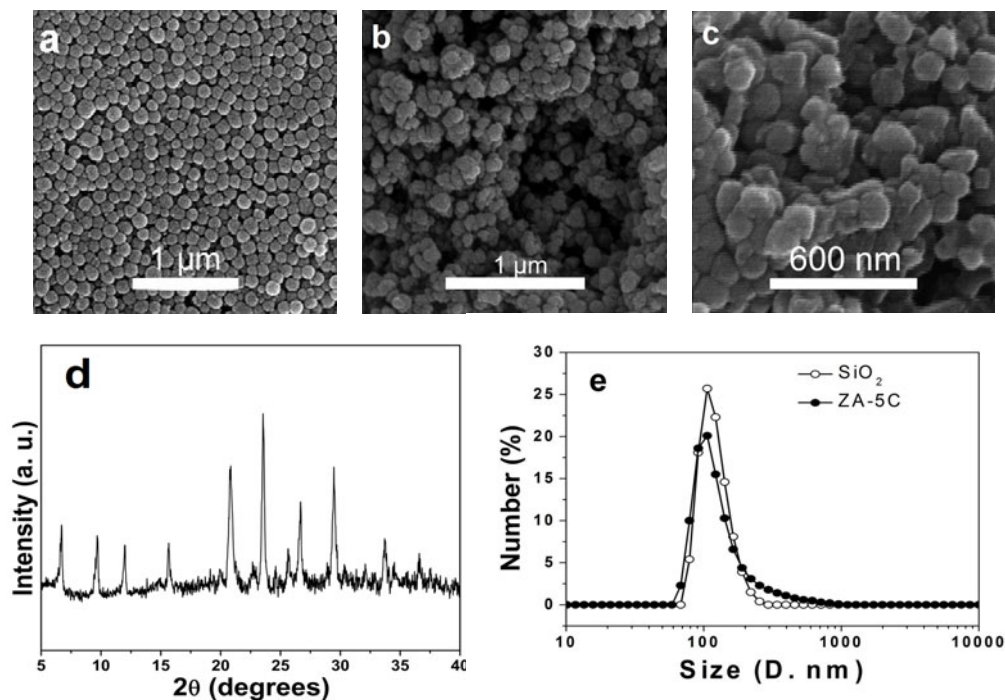

Figure 2. SEM images for (a) silica particles (SNOWTEX ST-ZL), (b) zeolite NaA (ZA-5C) and (c) high magnification of ZA-5C; (d) XRD pattern for ZA-5C and (e) DLS results for silica and ZA-5C. Note: ZA-5C was synthesized from SiO_2-5C under identical hydrothermal conditions (80 °C for 7h) after 5-day aging.

Figure 2a shows the spherical shape of commercial SNOTEX ST-ZL silica samples processing the particle size in the range of 70-240 nm. By comparison, the as-synthesized zeolite NaA nanocrystals (denoted as ZA-5C) exhibit similar morphology and particle size to those of starting silica particles (Fig. 2b). The high magnification SEM image (Fig. 2c) clearly reveals the round cube morphology and uniform particle size of ZA-5C. Their crystal sizes manually measured on the SEM image range from ca. 60 to ca. 250 nm. XRD pattern indicates that only pure zeolite NaA zeolite phase was crystallized (Fig. 2d). Energy-dispersive X-ray spectroscopy (EDXS) detected that the Si/Al ratio of the nano-zeolite bodies rapidly increased in the first six hours, from 1.00:0.58 at 2 h to 1.00:0.71 after 1 h to 1.00:1.01 after 2 h, indicating the rapid incorporation of aluminum ions to form the crystalline zeolite frameworks. The Si/Al molar ratio of final zeolite nanocrystals prepared via 7-hour hydrothermal treatment was detected to be maintained around 1.00:1.01 which is in good agreement with the standard composition of zeolite A. Although the limitations of EDXS in quantifying the aluminum content accurately, the trend of the change in aluminum content should be reliable. Moreover, the chemical analysis results revealing the fast crystallization of zeolite are consistent with the XRD studies.

Dynamic Light Scattering (DLS) studies of the size and size distribution of ZA-5C and starting silica (DDI H_2O diluted) were conducted using a Malvern Instruments (Malvern, UK) Zetasizer Nano

ZS series (ZEN 3600). The particle sizes of starting silica were detected in the range from 70-250 nm, and their mean particle size is around 106 nm (Fig. 2 open circle), which is larger than of 70 - 100 nm in the SNOWTEX ST-ZL specifications. This may be due to the slight agglomeration of silica particles. Zeolite NaA nanocrystals exhibit the mean particle size around 103 nm (Fig. 2 solid circle), which is slightly smaller than that of starting silica [18]. It also shows the size distributions of starting silica and most Zeolite NaA nanocrystals match perfectly. 94.3% quantities of Zeolite NaA nanocrystals possess similar size to that of starting silica (70-250 nm), and 80.1% quantities of which are within 150 nm. 5.7% of relative large particles are still present. However, from SEM investigation, the large particle should arise from zeolite nanocrystals aggregates.

In N_2 analysis, ZA-5C shows that the BET surface area is 24.9 m^2/g, which is much higher than normal micron-sized NaA prepared without porous carbon (~ 6 m^2/g). It is noted that the micropore volume is extremely small (<0.001 cm^3/g), and thus their BET surface area should arise from the external surfaces of zeolite crystals. This indicates that the zeolite NaA nanocrystals synthesized in the present work are well crystallized. Furthermore, the BET surface area of ZA-5C is fairly comparable to that of the starting colloidal silica nanoparticles (24.0 m^2/g), which is consistent with the particle size results obtained with SEM and DSL studies. As a result, the mass ratio of 1 SiO_2: 2 P123: 5 FA appears to be suitable for the formation of continuous mesoporous carbon networks for successful confined conversion of silica nanoparticles into zeolite nanocrystals [18].

Zeolite NaA nanocrystals were successfully crystallized in mesoporous carbon confinement using our novel method. The crystal growth is prohibited within the expected range of confinements. In our system, the synthetic conditions such as aging time and crystallization time show a less influence on the crystal size; while the crystallinity of zeolite nanocrystals can be enhanced by prolongating either of them. These results further support the space-confined growth mechanism and silica templating effect.

Conclusion

Zeolite nanocrystals with duplicated particle size distribution from starting colloidal silica were successfully synthesized without structure-directing agent, seeding crystals and other additives *via* our novel confined space strategy. XRD investigation indicated the capability of this method for the synthesis of pure highly crystalline zeolite nanocrystals. SEM coupled with DSL results doubly confirmed the similar particle size and size distribution of starting colloidal silica and as-synthesized zeolite nanocrystals. It should also be possible to synthesize other types of silica-containing zeolite nanocrystals, such as zeolites X/Y, ZSM-5 and sodalite by altering the composition of the alkaline solution (with or without SDA) and the reaction conditions. The crystal size and size distribution of as-synthesized zeolites could be readily controlled by simply varying those of starting silica particles.

Acknowledgement

References

[1]   Mintova S, Olson NH, Valtchev V, Bein T. Mechanism of zeolite a nanocrystal growth from colloids at room temperature. Science. 1999 Feb;283(5404):958-60.

[2]   Zhou Q, Qiu SL, Pang WQ. Studies on the crystallization mechanism of beta zeolite synthesized with nucleation gel. Chemical Journal of Chinese Universities-Chinese. 2000 Jan;21(1):1-4.

[3]   Mintova S, Olson NH, Senker J, Bein T. Mechanism of the transformation of silica precursor solutions into Si-MFI zeolite. Angew Chem-Int Edit. 2002;41(14):2558-+.

[4]   Murayama N, Yamamoto H, Shibata J. Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. International Journal of Mineral Processing. 2002 Feb;64(1):1-17.

[5]   Gonthier S, Thompson RW. EFFECTS OF SEEDING ON ZEOLITE CRYSTALLIZATION, AND THE GROWTH-BEHAVIOR OF SEEDS.   Advanced Zeolite Science and Applications. Amsterdam: Elsevier Science Publ B V 1994:43-73.

[6]   Boudreau LC, Kuck JA, Tsapatsis M. Deposition of oriented zeolite A films: in situ and secondary growth. Journal of Membrane Science. 1999 Jan;152(1):41-59.

[7]   Xu XC, Yang WS, Liu J, Lin LW. Synthesis and perfection evaluation of NaA zeolite membrane. Separation and Purification Technology. 2001 Oct;25(1-3):475-85.

[8]   Wang HT, Holmberg BA, Yan YS. Homogeneous polymer-zeolite nanocomposite membranes by incorporating dispersible template-removed zeolite nanocrystals. Journal of Materials Chemistry. 2002;12(12):3640-3.

[9]   Huang AS, Lin YS, Yang WS. Synthesis and properties of A-type zeolite membranes by secondary growth method with vacuum seeding. Journal of Membrane Science. 2004 Dec;245(1-2):41-51.

[10]   Mintova S, Mo SY, Bein T. Humidity sensing with ultrathin LTA-type molecular sieve films grown on piezoelectric devices. Chemistry of Materials. 2001 Mar;13(3):901-5.

[11]   Wang ZB, Wang HT, Mitra A, Huang LM, Yan YS. Pure-silica zeolite low-k dielectric thin films. Adv Mater. 2001 May;13(10):746-9.

[12]   Landau MV, Vradman L, Valtchev V, Lezervant J, Liubich E, Talianker M. Hydrocracking of heavy vacuum gas oil with a Pt/H-beta-Al2O3 catalyst: Effect of zeolite crystal size in the nanoscale range. Ind Eng Chem Res. 2003 Jun;42(12):2773-82.

[13]   Robinson SM, Arnold WD, Byers CH. MASS-TRANSFER MECHANISMS FOR ZEOLITE ION-EXCHANGE IN WASTE-WATER TREATMENT. Aiche J. 1994 Dec;40(12):2045-54.

[14]   Yahiro H, Lund A, Aasa R, Benetis NP, Shiotani M. Association forms of NO in sodium ion-exchanged A-type zeolite: Temperature-dependent Q-band EPR spectra. J Phys Chem A. 2000 Aug;104(34):7950-6.

[15]   Chen XB, Yang WS, Liu J, Lin LW. Synthesis of zeolite NaA membranes with high permeance under microwave radiation on mesoporous-layer-modified macroporous substrates for gas separation. Journal of Membrane Science. 2005 Jun;255(1-2):201-11.

[16]   Madsen C, Jacobsen CJH. Nanosized zeolite crystals - convenient control of crystal size distribution by confined space synthesis. Chemical Communications. 1999 Apr(8):673-4.

[17]   Pham-Huu C, Wine G, Tessonnier JP, Ledoux MJ, Rigolet S, Marichal C. BETA zeolite nanowire synthesis under non-hydro thermal conditions using carbon nanotubes as template. Carbon. 2004;42(10):1941-6.

[18]   Y. Huang et al., Micropor. Mesopor. Mater. (2008), doi:10.1016/j.micromeso.2008.07.036.

[19]   Yao JF, Wang HT, Chan KY, Zhang LX, Xu NP. Incorporating organic polymer into silica walls: A novel strategy for synthesis of templated mesoporous silica with tunable pore structure. Microporous and Mesoporous Materials. 2005 Jul;82(1-2):183-9.