Journal of Colloid and Interface Science 422 (2014) 45–53

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

An emulsion-based droplet hydrothermal synthesis method for the production of uniform sized zeolite nanocrystals

Pankaj Sharma, Moon Hee Han, Churl Hee Cho *

Graduate School of Green Energy Technology, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 305-764, Republic of Korea

ARTICLE INFO

Article history:
Received 29 November 2013
Accepted 12 February 2014
Available online 20 February 2014

Keywords:
Emulsion
Droplet based
Nanocrystal
Crystalline
Narrow distribution

ABSTRACT

A droplet based new hydrothermal synthesis method for nano-zeolite synthesis in bulk amount with uniform size, shape and morphology is presented. The proposed process addresses the limitation and shortcomings of droplet based microfluidic reactors and conventional hydrothermal methods. The process has been designed on the concept of mixing two immiscible solutions at high speed which then produces nano/submicron size droplets. Confinement within the droplet provides uniform heat transfer, enhanced mass transfer to growing crystal, chaotic advection within droplet facilitate rapid mixing, prevent the contact between growing crystals etc. Fine-tuned nano-cubic LTA zeolite crystals of size ~100 nm with uniform morphology and size distribution were prepared. Just within 4 h of reaction time (aging + crystallization) well shaped cubic crystals with high crystallinity and size uniformity can be synthesized by the proposed synthesis process. Diffraction and electron microscopic studies reveal the high phase purity and size uniformity of as-synthesized LTA zeolite particles.

1. Introduction

During last few decades, many efforts have been made and still many are ongoing to produce nanostructured inorganic materials with maximum possible uniformity in their size and shape. High isomorphism in zeolite materials is desired because of their greater application in reaction, separation, medicine, optoelectronics, sensors, and energy materials due to the high surface to volume ratio and short length of mass transfer. The reported crystal growth theories reveal that in inorganic material syntheses there are mainly two mechanisms by which crystal growth takes place. The first growth mechanism is solution mediated transport, which generally observed in dilute or clear solution synthesis [1]. The second growth mechanism is aggregation/step growth (aggregation of primary nanoparticles/crystallites resulting in large crystalline units, and addition of nanoparticles to a crystalline center/growing crystal) [2–5]. The aggregation/step growth mechanism mainly observed in high concentration, supersaturated and heterogeneous reaction mixtures. Therefore, if our target is to synthesize nanosize zeolite particles of size less than 100 nm with narrow particle distribution then we must have to find out a ways to control or restrict the solution transformation to growing crystals and aggregation of primary particles. This could only be possible if we can isolate the initially formed primary amorphous gel particle during crystallization.

In recent years microemulsions, microreactors and microfluidic devices have been proposed for the synthesis of nanoscale inorganic materials with uniform morphology and narrow particle size distributions (PSD) [6–12]. More recently, the droplet based microfluidic devices or segment flow reactors have been developed to overcome the limitations of laminar or continuous flow microfluidic devices [10]. In particular, droplet assisted microfluidic devices provide homogeneous heating, dispersion and rapid mixing of reactants by chaotic advection in the droplet. Unfortunately, there are only a few papers which report synthesis of zeolite particles with a diameter of less than 100 nm with high uniformity in size. To date, Kim and his research group reported the synthesis of ZSM-5 and zeolite A nanocrystals in droplet and ionic liquid assisted microfluidic reactors [13,14]. In their studies, the microfluidic reactors were assembled on a microchip using fine capillaries of inner diameter of few micrometers. Furthermore, the flow rate in these droplet based microfluidic reactors is quite low (2–8 μL min^{-1}) [13,14]. So, the main drawback in microfluidic reactors is the slow production rate. For large scale production this synthesis process may not hold good. The only possible way to produce large amount using the droplet based microfluidic reactors is to set up large number of production units, because there is no possibility to increase the flow rate and capillaries diameter. If we will increase the capillary diameter then we cannot attain the desired droplet of volume in nanoliter or microliter. On the other hand,

* Corresponding author. Fax: +82 42 822 3334.
E-mail addresses: sharmapankaj47@yahoo.com (P. Sharma), choch@cnu.ac.kr (C.H. Cho).

http://dx.doi.org/10.1016/j.jcis.2014.02.013
0021-9797/

we cannot change the flow rate also as each zeolite material has an optimum crystallization time. In addition to these limitations of droplet based microfluidic reactor, the other drawback is non-applicability of this process in heterogeneous, viscous aluminosilicate precursor gel based hydrothermal synthesis.

Therefore, in order to overcome these limitations of droplet based microfluidic reactors and to synthesize nanosize LTA zeolites with narrow particle size distribution, we have proposed a new droplet based hydrothermal synthesis method. The basic idea behind the proposed method is to use the concept of mixing of two immiscible solutions at high rotating speed which leads to the production of nano/submicron droplets. Furthermore, aqueous/oil viscosity, interfacial tension, and rate of energy dissipation on these small divided volumes of low density zeolite precursor solution on vigorous mixing helps in the generation of spherical droplets [15]. The droplets formed in the proposed hydrothermal method have all the characteristics, applications and features, which were served by droplet formed in microfluidic reactor. Further, these droplets provide high dispersion and mixing throughout the synthesis process, as the formation and deformation of droplets took place continuously.

2. Experimental

Nano-LTA zeolite cubic crystals were synthesized using molar ratio $1.8Al_2O_3$:$11.25SiO_2$:$13.4(TMA)_2O$:$1.2NaOH$:$700H_2O$, which is considered to be an ideal molar concentration of LTA zeolite synthesis from clear solution as reported in the literature [1]. Preparation of clear zeolite precursor solution was achieved by mixing calculated amount of tetramethylammonium silicate solution (15–20 wt%, ⩾99.99%, Aldrich), tetramethylammonium hydroxide pentahydrate (98%, Alfa Aesar), deionized water (DIW) and NaOH (97%, Junsei Chemical Co. Ltd.) at room temperature. After mixing this resultant solution for 1 h, aluminum isopropoxide (⩾98%, Aldrich) was added to it. This resultant reaction mixture was stirred continuously until aluminum isopropoxide completely dissolved to obtain the final clear solution. The zeolite reaction mixture of

Table 1
Detailed reaction conditions and sample code for each as-synthesized LTA zeolite.

Code	Aging temperature[d] (°C)	Aging time (h)	Crystallization temperature[d] (°C)	Crystallization time (h)
LTA-1[a]	25	2	85	2
LTA-2[a]	25	2	85	4
LTA-3[a]	25	2	85	5
LTA-4[a]	25	4	85	2
LTA-5[a]	25	4	85	4
LTA-6[a]	25	4	85	5
LTA-7[a]	25	4	50	24
LTA-8[a]	25	4	50	48
LTA-9[a,b]	25	24	85	24
LTA-10[a,b]	25	24	85	6
LTA-11[c]	25	2	85	5
LTA-12[c]	25	4	85	5

[a] Crystallization of reaction mixture was made in 250 mL glass containing pre-heated Fluorinert FC-40 solution (by proposed droplet based synthesis).
[b] Dilution of reaction mixture has been done by adding 50 mL deionized water to it.
[c] Crystallization of reaction mixture have been carried out by direct heating (simple hydrothermal process).
[d] Temperature variation of ±2 °C was observed during synthesis.

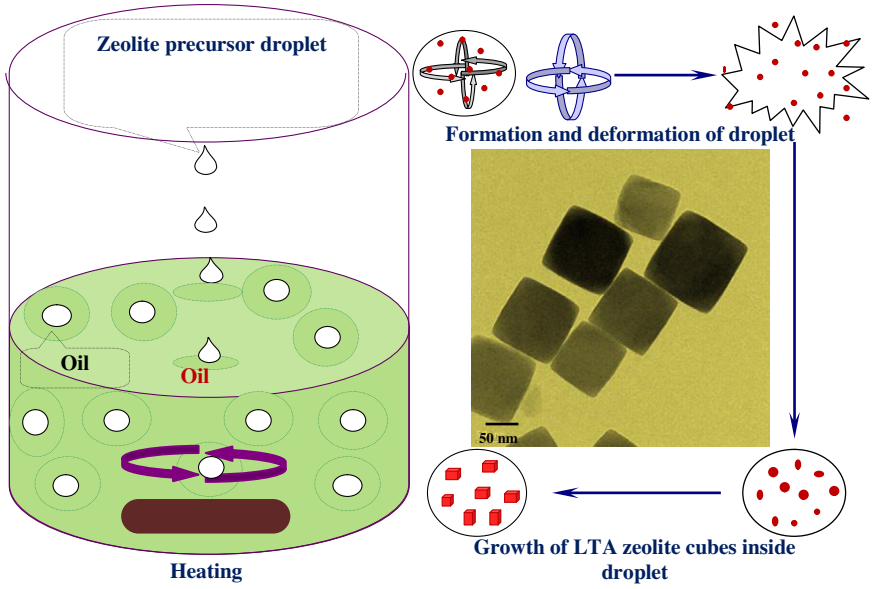

Fig. 1. Schematic illustration of our droplet based synthesis process. The clear zeolite precursor solution was added drop wise to preheated FC-40 oil solution. When zeolite solution was added to this immiscible FC-40 oil with continuous magnetic stirring then it forms droplets. The FC-40 forms a thin lubricant layer around the zeolite solution droplet. The droplet undergoes three dimensional rotation and when these droplets reach the surface it breaks down and particle gets dispersed in the solution. Then, again formation of droplet took place which contains grown zeolite particles.