Synthesis of Nano Particles of LTA Zeolite by Means of Microemulsion Technique

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ABSTRACT: This mini review article, intends to provide the essential information about microemulsion technique as a reliable approach toward the synthesis of zeolitic nano crystallites. The strategy discussed here provides a unique, effective, and potentially general methodology to the preparation of uniform and high purity nano crystallites of template-free zeolitic materials including LTA, faujasite type and other zeolitic-like materials (i.e. zeotype materials). Microemulsion is a reliable approach for controlled synthesis of uniform nano sized zeolitic particulates. On the other hand, the microwave assisted microemulsion technique has the advantages of short reaction time, producing smaller and more uniform particles with a narrower size distribution and high purity, in comparing to the conventional heating approaches.

KEY WORDS: *Zeolite growth, Microemulsion, Zeolite LTA, Crystal morphology.*

INTRODUCTION

Zeolites are valuable inorganic crystalline materials, which are porous having wide variety of industrial applications due to their unique properties including molecular sieving, ion-exchange and catalytic behaviour. In the recent years, considerable and growing attention has been paid on utilizing zeolitic nano particles or nanozeolites because of their advantages over conventional micron sized materials. Decreasing of zeolitic particle size causes remarkable increasing of external surface areas available for interaction in different reactions. This can be shortened the diffusion path lengths, in which consequently reduces the mass and heat transfer resistances in catalytic and adsorption applications, decreasing of side reactions, enhancing selectivity etc. In recent years, developing of new techniques for synthesis of nano crystalline zeolites in controlled manners have been received tremendous attention. The reduction of particle size of zeolites from micrometer to nanometer scale leads to substantial changes of their properties. Studies have been shown that the particle size and morphology of the zeolitic materials play an important role in their properties and efficiencies as catalysts, adsorbents for separation and ion-exchangers [1, 2].

SYNTHESIS OF ZEOLITIC MATERIALS

So far, numerous hydrothermal techniques were developed by our group or reported in other literatures to synthesis zeolitic nano particles, which usually were carried out by controlling some of the effective parameters including crystallization temperature, type and concentration of organic templating molecules as Structural Directing Agents (SDA), aging and crystallization time, precursors ratio and concentrations etc., in order to increase super saturation condition to dominate the nucleation phenomenon over crystal growth [3-5].

However, it should be mentioned that relatively long aging and synthesis duration, expensive starting materials (particularly organic structural directing agents), lack of reproducibility of the synthesis processes and energy consumption for separation of nano powders by mean of high speed centrifugation are some main issues making the bottom-up chemical synthesis of nanozeolites techno-economically are not viable processes [6]. As an alternative technique, the zeolite particle size may also be reduced mechanically using specially designed ball mills. Although, numerous studies have been revealed that high energy ball milling can be used to produce nano zeolites, however, the crystallinity of the milled zeolites in most of cases were also decreased substantially [7].

At present, zeolite nanocrystals are mostly synthesized under conventional hydrothermal conditions and with the use of organic Structure-Directing Agents (SDA) [8-18]. It is noteworthy that many zeolites (e.g., LTA, FAU), which can be readily synthesized into microcrystals (diameter > 100 nm) without using a template, have interestingly all required template for their synthesis as nano-crystallites. The template approaches have several drawbacks. First, removal of the template is normally carried out by calcination, which in some cases leads to irreversible aggregation of the nanocrystals. Second, the use of template in the synthesis tends to change the Si/Al ratio of the final products that could drastically affect their applications (e.g., air separation). For example, zeolite A, synthesized by using template (tetramethylammonium), has a Si/Al ratio greater than 1, and as a result, after Na^+ exchange, it has a pore size larger than 4 Å [13, 14]. In contrast, template-free synthesis leads to Si/Al < 1. The slight change in pore size, remarkably impacts the air separation capability of zeolite A [19]. And the last but not the least, organic template

materials, which are mostly amine compounds are very expensive. Thus synthesis of zeolite nanocrystals with small uniform diameter and without the use of template is highly desirable.

Plenty of efforts have been made to minimize zeolite crystal size without using a template (i.e. template free approaches) by manipulating the synthesis parameters[20-22]. Confined space synthesis by means of external templating approaches using carbon black[23] and starch[24] as space confinement additives has been developed to produce both templated and template-free zeolite nanocrystals [23, 24]. However, after synthesis, the materials used to provide confined space, have to be burned off at relatively high temperatures (e.g., >400 ℃), which may lead to aggregation of nanocrystallites and lowering the crystallinity of final product.

Water is used as the most common solvent for hydrothermal synthesis of zeolites and molecular sieves in the presence of organic templating agents. The water molecules usually act not only as a solvent but also as: (i) a space filler, (ii) a hydrolyser and reformer of the M-O-M bonds (where M and O denote metal atom and oxygen, respectively), (iii) accelerator of chemical reactions, and (iv) viscosity maintaining agents [25]. All of these nonsolvent influences of water are always kept at the "edge-level" because of its excess quantity relative to the other reactants participating in the reaction. In contrast to the conventional method in which water is a major component, it is of interest to synthesize zeolites and molecular sieves in nonaqueous solvent [26]. Thus, *Bibby & Dale* synthesized silica sodalite in ethylene glycol solvent for the first time. The synthesis of zeolites in several other nonaqueous solvents, e.g., ethylene diamine, triethyleneamine, tetraethylene glycol, etc., has also been reported [27]. Although the synthesis procedure is designated as a nonaqueous type, it is known that a small but definite quantity of water is initially introduced into the system [28].

Microemulsion Approach to Synthesize Zeolites

One promising approach that could be used to control both the size and morphology of zeolite crystals is the utilization of microemulsion system. The microemulsion consists of aqueous domains dispersed in a continuous oil phase. Under appropriate conditions, a variety of reactants can be introduced into the nanometer-sized

aqueous domains for reaction, leading to materials with controlled size and shape. These small aqueous domains can be viewed as nanoreactors for synthesis of zeolite nanocrystals [29, 30]. Generally, microemulsions consist of a surfactant, co-surfactant, oil phase, and water phase [31].

Because microemulsions involve oil–water mixtures, there is significant interfacial tension present in the absence of surfactant. Once surfactant is added to the oil-water system, the interfacial tension begins to drop. Increasing the surfactant concentration continually decreases the interfacial tension until micelles are formed at the Critical Micelle Concentration (CMC). These micelles are nothing more than aggregates of surfactant that, depending on the nature of the solvent in the continuous medium, turn their hydrophobic or lipophobic sections away from that solvent. A co-surfactant, which is typically a straight chained alcohol such as butanol or pentanol, often used to further lower the interfacial tension. By adding the co-surfactant, the shape of the confined phase can be altered by decreasing the interfacial tension. The molecular structure of the surfactant can also lead to different microstructures. There are two balancing or competing factors in using microemulsion as a medium for zeolite growth. On one hand the microemulsion constitutes a confined space that will modulate nucleation and growth (nanoreactor), on the other hand the surfactant will coordinate to the crystallographic faces of the growing crystal and affect the growth rates depending on the crystallographic structure of the surface and the strength of the organic-inorganic interactions. The latter effect should be tunable in a rational manner by changing the chemical nature of the surfactant. Dutta and colleagues first investigated zeolite growth in microemulsion in the early 1990s [32-37]. In 1991 a research group has studied the growth of zeolite A in a microemulsion made up of sodium 1,2-bis(2-ethylhexyloxycarbonyl)-1-ethane sulfonate (AOT), isooctane, and the zeolite phase [34]. Although this work showed that it was possible to grow zeolite in the reverse micellar phase, controlling of the zeolite morphology was not addressed. *Dutta et al.* have also studied zinc-phosphate faujasite analogues grown in microemulsions [33,35,37]. *Yates et al.* have reported the growth of ALPO4-5 in a microemulsion system made up of cetylpyridium chloride, toluene, butanol, and the aqueous phase components[38-40]. *Lee & Shantz*

have studied the growth of silicalite-1 particles in an Igepal, butanol, heptane, zeolite mixture microemulsion [41, 42]. *Manna* has also studied silicalite-1 formation in a bi-continuous AOT-based microemulsion [43].

According to the literatures, non-ionic microemulsions are chosen to synthesize zeolite A due the following reasons: First, low-silica zeolite synthesis mixtures contain a relatively high concentration of alkali cations. This causes that electrostatic forces exist between the ionic surfactant and aqueous ions would be much stronger than other forces in the system. Second, non-ionic microemulsions have been extensively studied [44, 45]. Also, the solubility of nonionic surfactants is a function of the system temperature [45], so it may be possible to change the nature of the final product by changing the temperature of the system. One semi-quantitative indicator of this is the surfactant Phase Inversion Temperature (PIT), where the surfactant changes from water soluble to oil soluble. While the temperatures employed in synthesis typically remain well below this point, the ability to affect the nature of the surfactant (and the microemulsion) through external sources (e.g. temperature) remains an advantage for these non-ionic systems.

Case Studies of Microemulsion Synthesis of LTA

In this section, several different methods for synthesis of LTA zeolite by means of microemulsion approaches will be reviewed.

In a research report [46], zeolite A was synthesized using a molar composition of

$0.22\ Na_2O : 5.0\ SiO_2 : 1.0\ Al_2O_3 : 8.0\ (TMA)_2O : 400\ H_2O$

by means of microemulsion techniques.

To do the synthesis, appropriate amounts of tetramethylammonium hydroxide (25 wt%) was added to an aqueous solution of sodium hydroxide and aluminum isopropoxide with stirring, followed by the addition of aqueous colloidal silica sol (30 wt%). The mixture was sealed and further aged for 24h without stirring for complete dissolving of aluminum isopropoxide.

Microemulsion was prepared by dissolving Cetyl Trimethyl Ammonium Bromide (CTAB) in a mixture of n-butanol and heptane. CTAB, *n*-butanol, and heptane were used as the surfactant, co-surfactant, and the oil phase, respectively.

Subsequently, the pre-weighed starting mixture for the crystallization of LTA was added under stirring to

microemulsion. The final mixture was optically transparent, which indicated the formation of a microemulsion system. The resulting mixture was transferred into a Taflon-lined stainless steel autoclave and heated at 100°C for 6.3 h.(Fig. 1 indicates phase diagram of this experiment).

Another research group was used Igepal surfactants and Lutensol without any purification [47]. The Lutensol AO type surfactants structure is $RO(CH_2CH_2O)nH$, where R = C13/C15-oxo alcohol and n = degree of ethoxylation. Igepal surfactants are nonylphenylethoxylates with ethoxy (EO) numbers of 5 for CO-520, 12 for CO-720, and 40 for CO-890. Fig. 2 shows the structural formula of the two surfactants. Reagent grade butanol and heptane were also used as purchased without further treatments. Sodium aluminate, sodium hydroxide, and tetraethoxysilane were used as received. The composition of the zeolite synthesis mixture was 1 Al_2O_3:4 SiO_2:5.7 Na_2O:190H_2O:16 C_2H_5OH, similar to the composition used by *Zhan et al.* [48] with increased sodium content to favour the formation of zeolite A. The zeolite synthesis mixture was prepared by adding sodium aluminate and sodium hydroxide to water. Upon complete dissolution of that solution, TEOS was added and the mixture stirred for approximately 30 min to allow for complete hydrolysis of the TEOS. This results in a clear and transparent solution. The microemulsions were formed by adding a 2:1 surfactant: butanol (by weight) mixture to a glass test tube. To this mixture, the desired weight of heptane was added followed by the addition of the zeolite mixture described above. For simplicity, the surfactant and co-surfactant were lumped together and the zeolite mixture was treated as one ''phase'' so the mixtures could be visually represented on a ternary phase diagram. The surfactant: butanol ratio by weight is 2:1 unless otherwise noted. Phase diagrams were determined by visual inspection at 333 K unless noted otherwise. Microemulsion compositions will be reported below as (H:S:Z) where ''H'' represents the heptane weight fraction, ''S'' represents the 2:1 surfactant:butanol weight fraction, and ''Z'' represents the zeolite component weight fraction.So 0.1H:0.8S:0.1Z represents an 80 wt.% surfactant/ butanol, 10 wt.% heptane, and 10 wt.% zeolite mixture.(Fig. 3 indicates phase diagram of this experiment).

Zeolite samples grown in oil/water/surfactant mixtures were prepared as follows: fixed amounts of heptane, surfactant, and butanol were mixed together
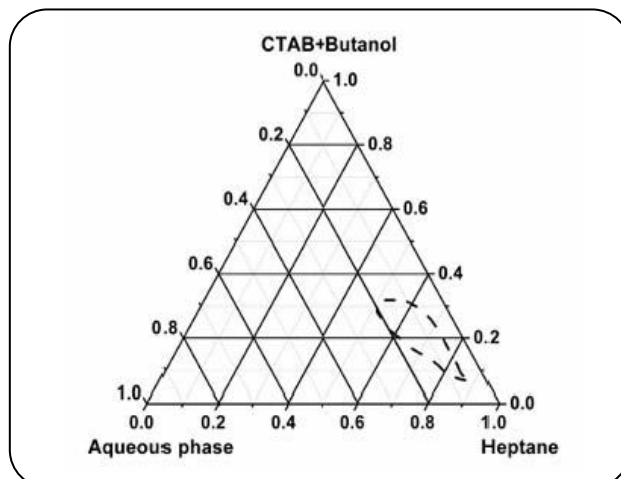

Fig. 1: Phase diagram of microemulsion made from a surfactant phase consisting of CTAB and butanol in a mass ratio of 2:1, heptane, and aqueous phase consisting of synthetic mixture of LTA [46].
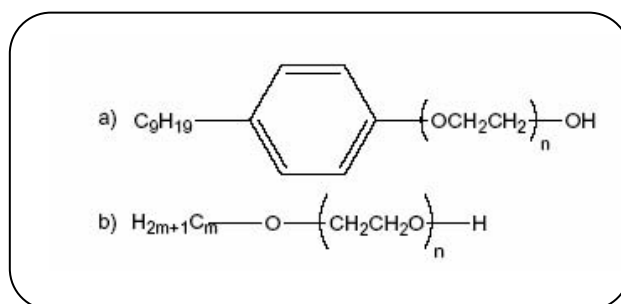

Fig. 2: Non-ionic surfactants of the (a) Igepal CO series and (b) Lutensol AO series. In (b) m = 13–15 [41].
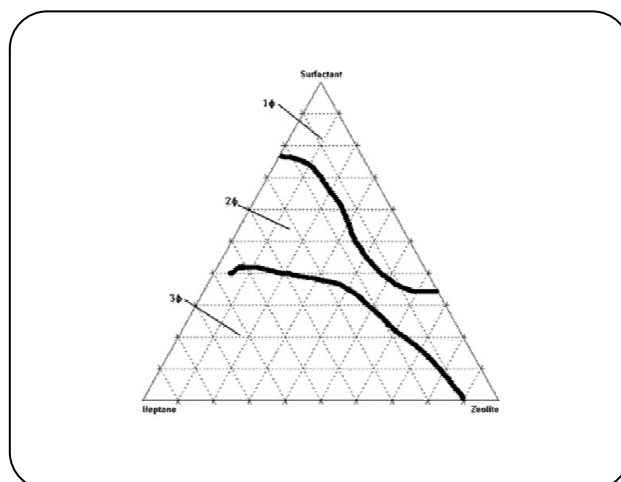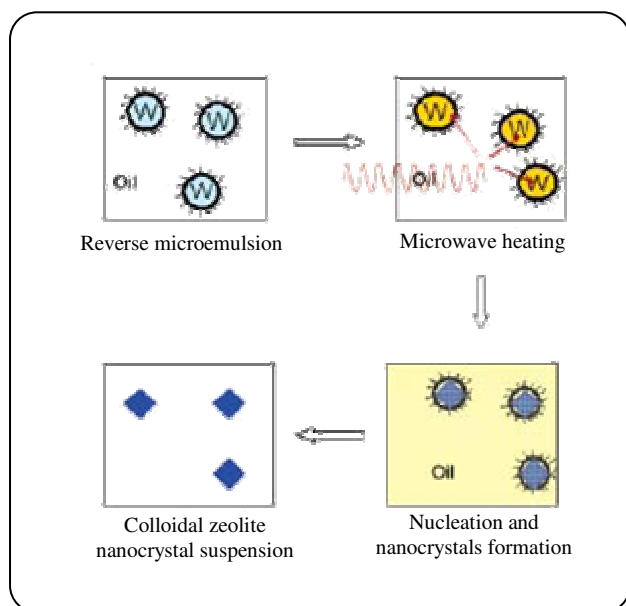

Fig. 3: Phase diagram of microemulsion made from a 2:1 Igepal CO- 720:butanol surfactant mixture, heptane, and zeolite components at 333 K [47].

Fig. 4: Schematic representation of microemulsion-microwave synthetic method [49].

in a Pyrex screw-cap test tube at room temperature and mixed for 1 h. The zeolite solution, prepared as described above was then added. The test tubes were then closed and vigorously shaken for 5 min, at which point they were placed in an oven at the approperiate temperature and allowed to react under quiescent conditions for a given period of time [47].

In another attempt for microwave assisted and microemulsion synthesis of LTA zeolite [49], de-ionized water, sodium hydroxide, and sodium aluminate were added, in that order, and stirred vigorously until the solution became clear. Aqueous colloidal silica (30 wt %) was then added to the solution. The solution became turbid at this time. The final molar composition of the synthesis gel for LTA nano zeolite was 5.85 Na_2O: 2.7 SiO_2:1.00Al_2O_3:182 H_2O. The corresponding weight ratio was 3.56 Na_2O:1.59 SiO_2:1.00 Al_2O_3:32.12 H_2O. The synthesis gel was sealed and aged overnight at room temperature with vigorous stirring.

Microemulsion was prepared by solubilising the synthesis gel prepared above into a mixture of CetylTrimethylAmmonium Bromide (CTAB), n-butanol and cyclohexane, in which CTAB and n-butanol were used as the surfactant and co-surfactant and cyclohexane as the oil phase. In this case, the final mixture was transparent although the zeolite synthesis gel and

the mixture of CTAB, *n*-butanol, and cyclohexane were not transparent before the mixing, indicating that microemulsion was formed in the final mixture. The molar ratios of cyclohexane/CTAB, n-butanol/CTAB, and water (in the synthesis gel)/CTAB were 130, 10, and 5, respectively. The preparation of zeolite nano crystallites was achieved by heating the microemulsion in a microwave oven with a microwave frequency of 2450 MHz. Three different synthesis experiments were carried out including microemulsion with conventional heating, conventional synthesis mixture with microwave heating, and conventional synthesis mixture with conventional heating. The heating temperature of the all experiments was 75 °C. The heating profile was from room temperature to 75 °C within 2 min and then at 75 °C for a controlled amount of time without stirring. The maximum power output of the microwave was adjusted to 600 W. Conventional heating was conducted in a Teflon-lined pressure vessel in a convection oven preset at 75 °C for a desired amount of time without stirring. Schematic representation of the microwave assisted microemulsion synthesis of LTA zeolite is illustrated in Fig. 4.

Based on the literatures, synthesis of LTA nano-crystallites with high crystallinity and narrow particle size distribution (i.e. 100-120nm) and sphere-shaped morphology is achieved in the presence of cationic microemulsions [49]. This achievement reveals that the microemulsion system can accelerate the crystallization process of the LTA. In the formation region of the stable microemulsion, the concentration (weight percent) of the surfactant and co-surfactant can significantly affect the crystallinity and particle size distribution of the resulting LTA crystals. It is found that the reaction time plays an important role in the formation of highly crystallized and uniform sphere-shaped LTA nano crystallites. The control of zeolite nano crystallites with small and uniform size as well as the sphere-morphology from microemulsion system might facilitate new possibilities in their use as seeds for zeolite thin film formation via secondary growth [46].

Furthermore, the reported achievements were show similar trends to those reported by *Lee & Shantz* [41, 42], in which growing of silicalite-1 zeolitic nano particles in the same microemulsion system (Igepal/ butanol/heptane) has been investigated. The aggregation mechanisms seem consistent between the two works, suggesting that

the surfactant structure plays a role in the development of the particle morphology and aggregate size and shape.

Comparisons between those results and what has been reported by Dutta's preliminary results [34] on synthesis of LTA by means of microemulsions technique can also be drawn. In both systems, after considerable heating large cubic crystals on the range of 1–2 µm were formed, although *Dutta et al.* were used the anionic surfactant AOT and isooctane as the oil in those studies. Higher temperatures and longer reaction times were used in that work, but the growth mechanism in that work and this one appear to be similar, namely that small amorphous spherical particles appear at short time scales and grow into the cubic crystals after heating in the microemulsion. By contrast no crystalline material was recovered after 6 h of heating in the sample that did not contain the microemulsion. The samples recovered in these experiments were crystalline and showed well-defined cubic facets. It was also shown that microemulsion composition (specifically surfactant content) played a strong role in the growth kinetics and coalescence (or lack thereof) of the particles [47].

The last but not the least, with the increase of heating time from 20 to 60 min, the zeolite crystals become larger and the crystal size distribution becomes wider. This might be due to the fact that a stable microemulsion is difficult to maintain at elevated temperatures during the crystallization process. It is possible that, with the increase of heating time, some of the water droplets and nano crystallites in the microemulsion become unstable and they merge together. Under these experimental conditions, it is clear that 20 min is the optimal crystallization time to obtain uniform zeolite LTA nano crystallites (40-80 nm) using microwave heating [49]. Microemulsion-microwave method (40-80 nm) produces smaller, more uniform, and purer zeolite nano crystallites than the conventional synthesis mixture and conventional heating method (100-800 nm). It is believed that microwave heating offers faster and more uniform heating than conventional heating and thus leads to more uniform generation and growth of nuclei and avoids the formation of impurity phase.

Reverse microemulsion has advantage over conventional synthesis mixture. The crystals from reverse microemulsion are much smaller than those from conventional synthesis mixture. The surfactant-covered water droplets in reverse microemulsion offer a unique microenvironment for the formation of nanoparticles. They may have possibly served as nanoreactors for nucleation and crystal growth and inhibited the excess aggregation of particles because the surfactants can absorb on the particle surface.

CONCLUSIONS

In summary, in this mini review article, we have discussed the essential information, which are necessary to demonstrate the effectiveness of reverse microemulsion and microwave synthesis method. It is believed that the strategy developed here provides a unique, effective, and potentially general methodology to the preparation of uniform and high purity nano crystallites of template-free zeolites (zeolite Y and X are obvious examples) and other zeolitic-like materials (i.e. zeotype materials). Microemulsion technique can be used as a reliable approach for controlled synthesis of uniform nano sized zeolitic particulates. Furthermore, comparing to the conventional or classical heating by means of electrical oven, microwave heating has the advantages of short reaction time, producing small particles with a narrow size distribution and high purity. The combination of reverse microemulsion and microwave heating has the added advantage that the oil phase in the reverse microemulsion system is transparent to microwave so that the aqueous domains are heated directly, selectively, and rapidly. By contrast, in conventional heating, the heat is transferred from the oil phase to the aqueous domains through conduction so temperature gradient is expected.

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