

## Modification of zeolite L (LTL) morphology using diols, $(\text{OH})_2(\text{CH}_2)_{2n+2}\text{O}_n$ ( $n = 0, 1, \text{ and } 2$ )

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### ABSTRACT

We report an alternative route to modify the morphology and the size of zeolite L (LTL) crystals using diols as co-solvents in the hydrothermal condition. Among the investigated diols, only triethylene glycol (TEG) acts as an efficient organic solvent in facilitating the LTL formation. The powder X-ray diffraction (PXRD) patterns exhibit the co-existence of LTL phase with other zeolite phases (T, W, and others), manifesting the syntheses of LTL crystals are sensitive to the presence of organic solvents in the synthesis gel. Our systematic approach demonstrates that the formation of these impurity phases can be greatly suppressed using TEG under: (i) shorter synthesis duration (<2 days) at higher synthesis temperature (180 °C); (ii) higher co-solvent content at lower synthesis temperature (150 °C), and (iii) moderate aging time (17.5–22 h). LTL crystals with high crystallinity and high purity are attained using TEG as the co-solvent in the precursor solution hydrothermally treated at 150 °C for 6 days. It is noticed that the addition of TEG molecules hampers the growth of cancrinite columns along the *c*-axis in the high water content environment. SEM images show that the dimensions of the LTL crystals are both 1.5–1.8 μm in diameter and in length, yielding the aspect ratio of about 1. This work provides an alternative synthetic protocol to tune the morphology of LTL crystals using TEG as a co-solvent.

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### 1. Introduction

Zeolites are crystalline aluminosilicates whose frameworks demonstrate well-defined microporous channels [1,2]. The functionality and the molecular screening capability of their frameworks equip themselves well in industries as catalysts, membranes, and among others [3–5]. Recent developments have opened another avenue of zeolite applications in fields of sustainable energy and of biomedicines [6–8]. It is noted that the success of their diverse applications are highly correlated with the morphology and the size of zeolite crystals [9–11]. For instance, the selectivity and the product distribution of aromatic alkylation reactions and of fluid catalytic cracking processes are dependent on the particle size and morphology, due to the diffusion limitation in zeolite porous framework [10,12]. These industrial applications have inspired research developments of synthesis protocols to tune the morphology and the size of zeolite crystals systematically [13–15]. Fundamentally, the developments of synthesis protocols could be established through understanding zeolite crystallization mechanisms [16,17]. Experimentally, the development of synthesis protocols has been achieved to tune the size and the morphology of zeolite crystals through adjusting synthesis variables (compositions of synthesis gels, synthesis temperature, and synthesis duration), through

adopting various synthesis methods (hydrothermal vs. microwave), and through adding organic compounds and/or co-solvents.

The synthetic zeolite L (LTL) was first invented by Breck and Acara in the 1960s [18]. Its framework structure was later refined by Barrer and Villiger [19]. The LTL framework features with one-dimensional channels by associating 6 cancrinite columns with oxygen bridges, resulting in the 12-membered-ring pore structure (space group  $P6/mmm$ ,  $a = 1.84$  nm, and  $c = 0.75$  nm). The diameter of pore size is about 7.1 Å. The cancrinite columns are formed by cancrinite cages and double 6-rings (D6R) along the *c*-axis [19–21]. Due to its unique one-dimensional pore structure, zeolite L has attracted intense research attention in catalyst [22–26] and in sustainable energy [27–29]. It has been observed that the successful implementation in either areas is strongly correlated to the size and the shape of zeolite L [25,27].

Many studies have reported strategies to tune the size and the morphology of LTL crystals by varying the composition of synthesis gels, the silica content, the water content, the mineralizing agent content, the synthesis duration, and the synthesis temperature [30–35]. Wortel reported the attainment of cylindrical crystals whereas a high water content ( $\text{H}_2\text{O}/(\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{SiO}_2) > 8$ ) was employed in the synthesis gel composition [36]. Moreover, Calzaferri's group demonstrated that the fluorescent trapping efficiency was greatly improved when the aspect ratio of LTL crystals was inferior to one [27,37]. The group also reported a synthesis protocol of tuning LTL crystal size from 30 to 3000 nm by varying

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the contents of H<sub>2</sub>O and mineralizing agent, by changing the sources of silica and alumina, and by using the synthesis conditions [33]. A similar study was reported by Yoon's group using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as the alumina source, a higher synthesis temperature, and a longer synthesis duration [38]. Larlus and coworkers also reported that the influence of water content on the aspect ratio of LTL crystals [32], in which the morphology of LTL crystals was tuned from a coin-like shape to a cylindrical shape with the increase of water content. In addition, the authors investigated the effect of aging time on the size of LTL crystals, which they reported that the longer aging time, the smaller the particle size. It is noteworthy that scanning electron microscope (SEM) has been extensively utilized to characterize the shape of LTL crystals. The purity of those LTL phases was scarcely reported.

Recently, Shantz's group reported the tuning of LTL crystal morphology in the presence of microemulsion, in which the aspect ratio was recorded between 5–10 and above [39]. Takahashi's group published a method to tune the morphology of LTL crystals by incorporating alkanolamine to the precursor solution [40]. The results from their experiments allowed attaining a well-defined clam-like morphology with a diameter of 1500 nm and a thickness of 300 nm. Furthermore, Brent et al. added crown ethers as the space filler to alter the LTL crystal growth behavior along the *c*-axis [41]. Based on previous studies [42,43], the authors indicated that the addition of crown ethers in the zeolite precursor solution, especially 21-crown-7 ether, yielded a change in the size of zeolite L crystals while the hexagonal cylindrical morphology of LTL crystals still remained.

Solvothermal syntheses have been applied in zeolite syntheses [44,45]. For instance, Bibby and Dale used ethylene glycol in the "non-aqueous" gel composition as the solvent to attain pure silica sodalite crystals [46]. The authors indicated that the spatial effect played a significant role for an organic compound being a successful solvent in zeolite precursor solution. Xu's group reported the successful syntheses of silicalite-1, ZSM-39, and ZSM-48 using organic solvents such as ethylene glycol, glycerol and butyl alcohol, along with organocations [47]. It was noticed that the balance and selection between organocations and solvents were significant for the formation of crystalline materials. Chen et al. investigated the effect of co-solvents on the crystallization of Si-MFI crystals using ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) [48,49]. With the assistance of microwave heating, the addition of co-solvents affected the growth behavior of discrete MFI crystals more favorable in the *c*-axis.

We have recently reported an alternative route to tune LTL morphology towards a disk-like shape by incorporating ethanol (EtOH) as the co-solvent in the synthesis gel [50]. In this work, we systematically investigate the co-solvent effect by selecting ethylene glycol (EG) as the co-solvent, which has an extra OH group compared with EtOH. Diethylene glycol (DEG) and triethylene glycol (TEG) are chosen as co-solvents to investigate the effect of backbone length. Our study indicates that only TEG can serve as an efficient co-solvent for the formation of LTL crystals. This study provides an alternative approach in the tuning of zeolite L crystals.

## 2. Experimental

### 2.1. Synthesis of zeolites

Ludox<sup>®</sup> HS-40 and aluminum sulfate octadecahydrate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O) were purchased from Sigma–Aldrich. Potassium hydroxide (KOH, Baker), ethylene glycol (EG, C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, Alfa Aesar), diethylene glycol (DEG, C<sub>4</sub>H<sub>10</sub>O<sub>3</sub>, Alfa Aesar), and triethylene glycol (TEG, C<sub>6</sub>H<sub>14</sub>O<sub>4</sub>, Alfa Aesar) were purchased from VWR Inc. All chemicals were used as received. Zeolite L was synthesized following the

published procedure [38]. The same procedure was subsequently modified to synthesize zeolite L crystals using a co-solvent. The products were labeled as RL–S–C–T–D, whereas S = EG, DEG, or TEG; C = 30 or 80; T = 150 or 180; D = 1, 3, 6, or 15. For example, the synthesis of zeolite L with a gel composition of 1 Al<sub>2</sub>O<sub>3</sub>:20 SiO<sub>2</sub>:10.9 K<sub>2</sub>O:1000 H<sub>2</sub>O:30 C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> at 150 °C for 6 days was labeled as RL-EG-30-150-6. Its synthesis is described as follows. The alumina–potassium solution was prepared by dissolving 2.01 g of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O and 3.69 g of KOH in 35.50 g of de-ionized water, and was stirred until the mixture turned transparent. The silica solution was prepared by mixing 9.05 g of Ludox<sup>®</sup> HS-40 with 13.83 g of de-ionized water. While stirring, about 5.62 g of C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> was added dropwise to the silica solution. The silica–H<sub>2</sub>O–C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> solution was slowly added to the alumina–potassium solution. The zeolite precursor gel solution was subsequently aged at room temperature for 16 h. The aged solution was transferred into a Teflon-lined stainless steel autoclave for the hydrothermal synthesis at 150 °C for 6 days statically. At the end of the designated time, the autoclave was cooled down to room temperature. The solid product was rinsed using copious amounts of de-ionized water, and was subsequently dried at room temperature overnight prior to further characterizations.

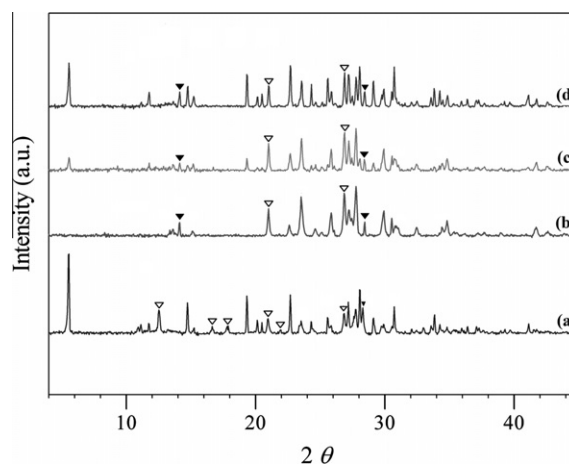
### 2.2. Characterization

The powder X-ray diffraction (PXRD) patterns were acquired using a Bruker D8 Advance instrument (Cu K $\alpha$ 1 with Ge monochromator) operated at 40 kV and 40 mA. The powder X-ray diffraction (PXRD) patterns were recorded in the range of  $2\theta = 4\text{--}45^\circ$  with a step size of 0.04° and 25 s per step. Scanning electron microscope (SEM, Model JSM-6380 LV) was applied to obtain the morphology and the dimensions of zeolite L crystals.

## 3. Results and discussion

### 3.1. Effect of diol identity

For investigating the diol identity effect, a series of syntheses are performed using the molar gel composition of 1 Al<sub>2</sub>O<sub>3</sub>:20 SiO<sub>2</sub>:10.9 K<sub>2</sub>O:1000 H<sub>2</sub>O:30 (OH)<sub>2</sub>(CH<sub>2</sub>)<sub>2n+2</sub>O<sub>n</sub> (*n* = 0, 1, and 2). The synthesis published by Lee et al. is reproduced as the benchmark [38], whose gel composition is 1 Al<sub>2</sub>O<sub>3</sub>:20 SiO<sub>2</sub>:10.9 K<sub>2</sub>O:1030 H<sub>2</sub>O. Fig. 1 shows the powder X-ray diffraction (PXRD)



**Fig. 1.** Powder XRD patterns of LTL crystals attained at 180 °C for 3 days using 1 Al<sub>2</sub>O<sub>3</sub>:20 SiO<sub>2</sub>:10.9 K<sub>2</sub>O:1000 H<sub>2</sub>O:30 (OH)<sub>2</sub>(CH<sub>2</sub>)<sub>2n+2</sub>O<sub>n</sub> (*n* = 0, 1, and 2). (a) LTL synthesized without using any co-solvent; (b) C<sub>2</sub>H<sub>6</sub>O<sub>2</sub> (RL-EG-30-180-3); (c) C<sub>4</sub>H<sub>10</sub>O<sub>3</sub> (RL-DEG-30-180-3); (d) C<sub>6</sub>H<sub>14</sub>O<sub>4</sub> (RL-TEG-30-180-3). The empty triangles represent peaks of zeolite W. The solid triangles represent peaks of cancrisilite.

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