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Investigation into the Crystallization of Molecular Sieve DNL-6

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Abstract

Crystallization of DNL-6, a silicoaluminophosphate (SAPO) based molecular sieve with the RHO topology was investigated under both the hydrothermal synthesis (HTS) and dry-gel conversion (DGC) conditions. Crystallization of DNL-6 under the HTS conditions is rather fast. But a combination of crystallization under the DGC conditions and reducing reaction temperature slow down the reactions, allowing for capturing intermediates. Under the DGC conditions, DNL-6 crystallizes through a semi-crystalline layered phase. The nature of this intermediate is aluminophosphate (AIPO) rather than SAPO with most P atoms having a local environment of $P(-O-Al)_3(OH)$. The surfactant (cetyltrimethylammonium chloride) used for synthesis appears to be part of the layered intermediate. Si is directly incorporated in the DNL-6 framework via SM II mechanism when the semi-crystalline AIPO phase is transforming to DNL-6 with the assistance of a very small amount of water. Both the structure directing agent and the surfactant play a role in the formation of DNL-6 as they were found within the final synthesized products. SEM data shows that hydrothermal synthesis produces a much more crystalline product. The facts that the semi-crystalline layered phase was also observed in the powder X-ray diffraction patterns of the solid samples obtained under the HTS conditions and that the evolution of the local structure around P and Al in the intermediate phases are similar imply that under the reaction conditions employed in the present study, the formation pathways of DNL-6 under the HTS and DGC conditions appear to have some similarities.

Keywords

DNL-6, silicoaluminophosphate, dry-gel conversion, hydrothermal synthesis, molecular sieves

1. Introduction

Microporous materials such as zeolites, aluminophosphates (AlPO_4s) and silicoaluminophosphates (SAPOs) based molecular sieves are extensively used in a wide variety of disciplines and have multiple applications due to their exceptional thermal stability, highly selective sorption ability, and excellent catalytic properties.¹⁻³ Much of the research on microporous materials has focused on adsorption properties, catalytic capabilities and their crystallization mechanisms.⁴⁻⁷

Understanding the formation of the microporous materials is important for designing new materials, and controlling their morphology, particle size and surface properties in order to meet industrial needs. The most common method for preparing microporous materials is hydrothermal synthesis (HTS). Since crystallization is carried out in an autoclave at elevated temperature and pressure,^{5,8} *in-situ* characterization of the crystallization process is challenging. Therefore, despite a number of *in-situ* approaches which have been developed,⁹⁻¹⁴ vast majority of the studies in the crystallization of microporous materials have been carried out involving the use of *ex-situ* methods to characterize the solids obtained during the crystallization process.¹⁵ One of the limits of HTS is the rapid reaction rates which can hinder the ability to collect intermediate samples. Consequently, a shift in research has focused on reducing the amount of water used in synthesis in order to retard the reaction rate and obtain intermediates. Examples include using the approaches such as solvent-free synthesis and dry-gel conversion (DGC).¹⁶⁻¹⁸ It has been widely accepted that the formation pathways of molecular sieve under the DGC

conditions are fundamentally similar to those under the HTS conditions because the dry-gel powder typically contains 20-40% water by weight.^{5,19-21}

It should be pointed out that DGC has been recongnized as a good alternative approach for studying crystallization because it can simplify the reaction systems by confining all the reactive species in the solid phases. A small amount of water is physically separated from the dry gel, preventing the situation where the reactive species in solution are in direct contact with solid gel from occurring. Most importantly, the amount of water from vapor and occluded in the gel is not enough to dissolve the solids. Thus, the crystallization under DGC conditions is not due to gel dissolution.^{21,22} The lack of bulk water can effectively slow down the reactions by preventing a liquid phase and therefore limiting mass transport. This feature allows for dry-gel conversion to be utilized to capture intermediates under a more favorable circumstance.²³⁻²⁵ Previous work using the DGC method has been used to study the crystallization of zeolites, AlPO_4s and SAPOs.²⁵⁻²⁹ The differences and similarities in crystallization under DGC and HTS conditions have been discussed in the literature.^{5,19}

The DGC synthesis can be further classified as: (1) steam-assisted conversion (SAC) with the initial dry gel containing the structure directing agent (SDA) being separated from a small amount of water in a reaction vessel; (2) vapor-phase transport (VPT) where a small amount of SDA solution is put at the bottom of the reaction vessel.⁵ In the present study, only SAC method was used, and the SAC is referred to as the DGC.

One SAPO based molecular sieve of recent interest is DNL-6 that was first discovered at Dalian National Laboratory.³⁰ This sieve has RHO topology that has two secondary building units

(SBUs): double-8-rings (d8R) and LTA cages (see Figure 1). DNL-6 is a promising acidic catalyst for the methanol-to-olefin reaction,³¹⁻³⁴ as this sieves can have high concentration of Bronsted acidic sites,³⁵ and an excellent material for CO₂ separation.³⁶ There have been reports in the literature on synthesis of DNL-6 and Rho topology zeolites and zeolite analogs under the HTS, DGC and aminothermal conditions^{30,32,36-38} and different SDAs have been used to prepare DNL.^{30,39} Under HTS conditions, reports have shown that DNL-6 can crystallize in a single day however, it is challenging to synthesize pure phase DNL-6. Slightly varying the Si content or the amount of templating agent leads to the formation of SAPO-34 with CHA topology or a completely amorphous material.³⁰ Previous work also examined the role of the surfactant used in the synthesis of DNL-6.⁴⁰ At the present time, the formation of DNL-6 is still not understood completely on a molecular level.

Figure 1. RHO topology with alternating double-8-rings and LTA cages

In this study, we examined the formation of DNL-6 under both the DGC and HTS conditions. A combination of using DGC method and reducing reaction temperature slow down the crystallization, allowing capture of the intermediates that are difficult to obtain under the HTS conditions. The intermediate phases are characterized by powder X-ray diffraction (PXRD), solid-state NMR (SSNMR), scanning electron microscopy (SEM). The results provide new insights into the understanding of the formation of DNL-6.

2. Experimental

The hydrothermal synthesis of DNL-6 was performed according to literature procedures.³⁰ The initial HTS and DGC compositions ($\text{Al}(\text{O-}i\text{-Pr})_3\text{:H}_3\text{PO}_4\text{:SiO}_2\text{:CTACl:DEA:H}_2\text{O}$) were 1.00:0.93:0.20:0.096:1.00:55.8, respectively. For the hydrothermal synthesis, 4.02 g (0.0197 mol) of aluminum isopropoxide (Sigma Aldrich) was dissolved in 18 mL of water and was mixed with 1.78 g (0.0184 mol) of 85% phosphoric acid (Caledon Laboratory Chemicals) and left to stir for 15 minutes. After being stirred, 0.24 g (0.004 mol) of fumed silica, particle size 5 to 50 nm, (Caledon Laboratory Chemicals) was slowly added and left to stir for 30 minutes. After stirring, 2.44 g (0.0019 mol) of a 25% w/w solution of the surfactant, cetyltrimethylammonium chloride (CTACl), (Sigma Aldrich) was added, followed by 1.44 g (0.0197 mol) of the SDA, diethylamine (DEA) (Alfa Aesar), and stirred for 2 hours. The final product was then placed into a Teflon container and put inside a stainless steel autoclave. The autoclave was heated in an oven at 200°C for 24 hours to yield the final crystalline product. The product was then washed repeatedly with water and methanol followed by calcination, in a furnace at 600°C for four hours.

The synthesis of DNL-6 under the dry-gel (SAC) conditions involves the following. After mixing DEA and CTACl, the gel was stirred for 5 hours followed by freeze-drying overnight. The resulting powder was then placed in a small Teflon cup, which was put into a larger Teflon container with a small of water at the bottom at a ratio of 1 g dry gel : 0.3 mL water. Water and the dry-gel were never in contact prior to heating. The crystallization was initially carried out at 200 °C. However, only amorphous materials were obtained. The temperature was then lowered to 160°C and the autoclaves were heated for up to 10 days. The washing process was the same as in the hydrothermal route.

Powder X-ray diffraction (PXRD) was used as a fingerprinting method to determine if the desired structure was synthesized. The PXRD patterns were acquired by a Rigaku diffractometer using Co K α radiation ($\lambda = 1.7902 \text{ \AA}$). All the samples were scanned between 5° - 45° at a scan rate of 10°/min, with a 0.02° increment rate.

SSNMR spectra were acquired for four different nuclei, ^{27}Al , ^{31}P , ^{29}Si and ^{13}C . All the spectra were acquired on a Varian Infinity Plus 400 spectrometer operating at a magnetic field strength of 9.4 T. The resonance frequencies for ^{27}Al , ^{31}P , ^{29}Si and ^{13}C are 104.3, 161.92, 79.46, and 100.5 MHz, respectively. Each sample was placed in a ZrO_2 rotor and spun at the magic-angle with a spinning rate of 8 kHz. ^{27}Al spectra were referenced using 1 M $\text{Al}(\text{NO}_3)_3$ ($\delta_{\text{iso}} = 0.0 \text{ ppm}$). ^{31}P spectra were referenced using $\text{NH}_4\text{H}_2\text{PO}_4$ (secondary reference of 85% H_3PO_4 , 0.81 ppm). ^{29}Si was referenced using tetrakis(trimethylsilyl)-silane (TTMSS) (secondary of TMS, 9.1 ppm). ^{13}C was referenced using adamantane (secondary of TMS, 38.56 ppm). ^{31}P magic-angle spinning (MAS) NMR spectra were obtained using a recycle delay of 60 seconds (s) and a pulse tip angle of 45°

corresponding to a pulse length of 1.83 μs . ^{27}Al MAS NMR spectra were attained with a pulse delay of 1 s and a pulse tip angle of 45° corresponding to a pulse length of 1.10 μs . ^{29}Si MAS NMR spectra were acquired with a pulse delay of 60 s and a pulse tip angle of 60° . A 90° pulse length was 1.75 μs . ^{13}C cross-polarization (CP) experiments were acquired with a pulse delay of 10 s and ^1H 90° pulse angle was 5 μs and a contact time of 3 ms.

3. Results and Discussion

PXRD is used as a finger printing method for identifying microporous materials, but information can also be gained by analyzing the intermediate crystalline structures during the crystallization process. Figures 2 and 3 show the PXRD patterns obtained under the HTS and DGC conditions, respectively. The PXRD pattern of the HTS sample obtained after one hour (h) of heating has no diffraction peaks present, indicating that the sample is completely amorphous. The earliest diffraction peaks were seen at roughly 3 h after the crystallization began, however, these peaks are extremely weak at this stage. At 9.5 h more defined peaks start to appear at 2θ values of $\sim 6^\circ$, $\sim 9^\circ$, and 25° , indicating that some long-range ordering starts developing in the dry gel. It is important to note that the peak at about 6° is not part of the final powder pattern of DNL-6. This peak can be attributed to a layered phase that occurs during the nucleation phase.²⁹ This diffraction peak at 6° slowly disappear as the crystallization continues and disappears completely at 24 h. No SAPO-34, a competing phase, was observed. All the diffractions seen in the XRD pattern of the 24 h sample belong to DNL-6.

Figure 2. Powder XRD patterns of DNL-6 synthesized by the HTS method a) $t = 1$ h to $t = 13$ h; b) $t = 1$ d

Figure 3. Powder XRD patterns of DNL-6 synthesized by the DGC method

In the PXRD patterns of the DGC samples (Figure 3), it can be seen that the initial dry-gel is completely amorphous, indicating that even after prolonged stirring, no long-range ordering

exists in the sample without being treated at the elevated temperatures and pressures. At 8 h, a reflection is first seen at near 6° along with a broad reflection near 25° . Both these reflections continue to grow in intensity as the crystallization continues. The low-angle peak at 6° indicates that a layered phase is formed in the early stage of the crystallizations. The fact that this peak remains relatively broad throughout the entire crystallization period suggests it is semi-crystalline in nature. A similar situation has been observed in the crystallization of several SAPO- and AlPO_4 -based molecular sieves under DGC conditions.^{19,21,41,42} The fact that the peaks belonging to the semi-crystalline phase is also seen in the hydrothermal synthesis suggests that the first stages of induction and nucleation are similar for the HTS and DGC under the conditions employed. The first set of peaks that can be assigned to DNL-6 start to appear after 4 days (d). During the HTS, the early peaks originating from DNL-6 appeared in a time frame of hours opposed to days, suggesting that the crystallization under DGC conditions at a lower temperature is much slower. The crystallinity of the DNL-6 continues to increase from 4 d to 10 d. For the 10 day sample, crystalline DNL-6 product becomes predominate. However, although much weaker, the peak at 6° remains after 10 d, indicating that the layered intermediate still exists. Layered AlPO materials often have lower thermal stability than SAPO molecular sieves, therefore, in order to remove this impurity phase, the final product was subjected to calcination at 600°C . Indeed, the low-angle reflection disappears in the corresponding PXRD pattern, indicating that the layered material no longer exists upon calcination. Judging from the PXRD pattern, there are also amorphous materials present in the calcined sample.

Figure 3 shows that the intensity of the peak at 6° decreases relative to the DNL-6 reflections as the crystallization time increases, indicating that the molecular sieve is formed

through a conversion of a layered intermediate. Since not enough water in the system to dissolve the layered material the transformation likely occurred through direct conversion from a semi-crystalline intermediate to DNL-6 with the assistance from the water molecules both occluded in the dry gel and in vapor phase.^{29,41} The low-angle peak is at around 6° , indicating a relatively large basal spacing. The result implies that the surfactant is part of the layered material. A more conclusive evidence of existing surfactant comes from ^{13}C NMR spectrum which will be discussed later. As mention before, the layered intermediate phases were previously reported in the crystallization of different AlPO_4s and SAPOs.^{21,22,28,43,44} The low-angle peak of the layered intermediate observed in the formation of $\text{AlPO}_4\text{-5}$ disappears after washing, indicating that it is held together by weak van der Waals forces and hydrogen bonding.²¹ In the case of DNL-6, the reflections remain even after extensive washing. This indicates that the semi-crystalline layered material must contain certain structural units that are held firmly by covalent Al-O-P bonds and these units are directly carried into the DNL-6 structure without bond breaking and reforming. A recent work has determined the single crystal structure of a layered material that can be directly transformed to $\text{AlPO}_4\text{-5}$ by DGC.⁴⁵

Figure 4 shows selected SEM images of the HTS and DGC samples. The SEM images of the initial gels of both DGC and HTS samples suggest that they are amorphous. The SEM image of the 24 h HTS sample displays large crystals with well-defined truncated rhombic dodecahedron as reported in the literature.³⁶ The image of the 10 d DGC sample shows crystals covered by the amorphous/semi-crystalline materials, which is consistent with the PXRD pattern, and ^{31}P and ^{27}Al NMR data (see discussion below). The elemental composition of DNL-6 can be seen in Table 1. The DNL-6 prepared under HTS conditions has 16% Si. However, the data of the 10 d DGC

sample do not represent true composition of the DNL-6, as the DN-6 crystals are coated by the semicrystalline intermediate/amorphous materials and EDX is a surface technique.

Figure 4. Micrographs taken of DNL-6 being synthesized after a) 1 h by DGC, b) 10 d by DGC, c) 1 h by HTS, d) 24 h by HTS.

Table 1. Elemental composition (molar basis) of DNL-6 from EDX analysis.

method	Time	Si	Al	P	P/Al	(Si + P)/Al
DGC	10 days	0.20	0.60	0.21	0.34	0.67
HTS	24 hours	0.16	0.50	0.34	0.69	1.00

To follow the evolution of the short-range ordering around P and Al, probe Si incorporation and monitor the behavior of the SDA and surfactant during the crystallization, solid-state NMR (SSNMR) experiments were carried out on both the HTS and DGC intermediate phases. The evolution of the framework and the P, Al and Si local environments as a function of

crystallization time can be followed by ^{31}P , ^{27}Al and ^{29}Si MAS NMR. DNL-6 framework has a single Si, Al and P sites corresponding to $\text{Si}(4\text{Al})$, $\text{Al}(\text{OP})_4$ and $\text{P}(\text{OAl})_4$. However, a penta-coordinated Al environment, $\text{Al}(\text{OP})_4(\text{OH}_2)$ due to interactions with either water or a template molecule within the pores was also observed.³⁰

The ^{31}P MAS NMR spectra of the samples obtained as a function of crystallization time under the HTS conditions are shown in Figure 5. The spectrum of the initial solids (1 h sample) exhibits a very broad resonance centered at around -10 ppm with a breadth of ~50 ppm, which suggests that vast majority of the sample are amorphous materials and the local P structure is disordered. Superimposed with the broad resonance are two very weak peaks: one slightly sharper resonance was observed at 0 ppm and the other appearing as a broad shoulder at roughly -19 ppm. The weak signal at around 0 ppm is due to unreacted phosphates and the peak at -19 ppm is due to a layered phase (see discussion below). The spectra of the 3 and 5 h samples are rather similar: the resonance at 0 ppm disappears as all the free phosphates have been consumed; the shoulder peak at -19 ppm has evolved into a well-defined sharp peak. A careful inspection of the PXRD patterns of the 3 and 5 h samples reveals that there is a very weak reflection at around $\sim 6^\circ$, indicating the formation of the layered phase. Thus, the -19 ppm can be assigned to the P site in the layered intermediated.^{21,46} The sharpness of this peak indicates the ordered local environment in this phase. The nature of the -19 ppm resonance in the layered phases found in the crystallization of AlPO_4 and SAPO based molecular sieves have been extensively investigated and the P species was identified as $\text{P}(\text{OAl})_3(\text{OH})$.^{15,21,41,47}

After 8 h, a new resonance appeared at -29 ppm. It first emerged as a very broad shoulder and grew with time. This resonance correlates to $P(-O-Al)_4$ species of crystalline DNL-6 as it coincides with the emergence of DNL-6 reflections in the PXRD pattern.³⁰ As the resonance at -29 ppm continues to grow, the broad amorphous peak and the resonance at -19 ppm of the layered intermediate decrease. At 13 h, the resonance at -19 ppm in the ^{31}P MAS NMR spectrum and the 6° reflection in the PXRD pattern disappeared completely. At 24 h the reaction continues to completion as the -29 ppm resonance dominates the spectrum, indicating that the vast majority of the phosphorous are now part of the framework.

The ^{31}P MAS spectra of the DGC samples as a function of crystallization time (Figure 6) exhibit a trend similar to that seen for the HTS, except the evolution of the spectra is much slower. Similar to the HTS, the 1 h spectrum of the DGC contains the same broad amorphous resonance along with the two peaks at around 0 ppm and -19 ppm. After 4 h, these two peaks become more visible. The resonance at -19 ppm continues to increase in intensity over a four-day period. Starting at 4 d a small resonance is visible at -30 ppm, indicating the formation of DNL-6. The $P(-O-Al)_4$ resonance increases in intensity from 4 d to 10 d while the resonance at -19 ppm decreases. However, for the DGC method after 10 d both appreciable amounts of amorphous material and layered intermediate remain. This observation is consistent with that in the PXRD pattern. The ^{31}P MAS NMR spectra suggest that both the HTS and DGC follow the similar crystallization pathways, except that the crystallization rates are different.

The ^{27}Al MAS NMR spectra are shown in Figure 7. The spectrum of the 1 h HTS sample displays two resonances after 1 h into the synthesis. The stronger resonances centered at -4 ppm corresponds to $\text{Al}(\text{-O-P})_4(\text{OH}_2)_2$ octahedral environment.⁴⁸ The second resonance is located at 44 ppm, corresponding to tetrahedral $\text{Al}(\text{-O-P})_4$. Both belong to aluminum species in the amorphous materials.[49] Between 3 h and 9.5 h, the spectra do not change significantly, which is consistent

Figure 5. ^{31}P MAS SSNMR spectra of DNL-6 intermediates synthesized by HTS.

Figure 6. ^{31}P MAS SSNMR spectra of DNL-6 intermediates synthesized by DGC.

with the PXRD patterns. At 11 h, a new resonance starts to emerge between the above-mentioned two resonances. The chemical shift of this new resonance is indicative of penta-coordinated aluminum $\text{Al}(\text{-O-P})_4(\text{OH}_2)$.⁴⁷ The appearance of this peak coincides with the observation in the PXRD patterns (Figure 1) where the early DNL-6 reflections start to emerge between 9 h and 11.5 h. Therefore, the penta-coordinated aluminum corresponds to the aluminum in the DNL-6 formed that is coordinated to the water inside the pores.³⁰ The signal at

25 ppm due to penta-coordinated Al can be seen unambiguously in the deconvoluted spectrum of 24 h sample (Figure 7). At 24 h the resonance at -4 ppm still exists. The corresponding ^{31}P MAS spectrum (Figure 5) is dominated by the resonance at -30 ppm due to DNL-6, indicating the amount of impurity is small. Therefore, the strong octahedral Al peaks cannot be fully attributed to residual amorphous and/or layered materials. As many AlPO_4 and SAPO-based materials have octahedral Al, $\text{Al}(-\text{O-P})_4(\text{OH}_2)_2$, we suggest the DNL-6 prepared may also have octahedral Al. As discussed later, some mesopores also exist in the DNL-6 prepared due to the use of surfactant. The presence of mesopores leads to the larger portion of octahedral Al. In the spectra of the DGC samples (Figure 8), the same resonances at -5 ppm and 45 ppm are seen at the start of the reaction, indicating $\text{Al}(-\text{O-P})_4(\text{OH}_2)_2$ and $\text{Al}(-\text{O-P})_4$, respectively. After 4 d, the PXRD patterns for the DGC show DNL-6 reflections, however no resonance that belongs to penta-coordinated water exists. It appears that under the DGC conditions, as-made DNL-6 only have tetrahedral and octahedral Al in the framework.

^{29}Si MAS NMR was employed to gain information on the Si substitution. ^{29}Si MAS NMR spectrum of the 8 h HTS sample (Figure 9) shows no Si signal in the solids at all. Unlike other SAPOs such as SAPO-5, SAPO-34^{19,28} where the Si species in the initial gel and the gel obtained in the early stage of the crystallization are simply unreacted silica. Their ^{29}Si MAS spectra often have a single resonance position at around -110 ppm due to unreacted silica. In the present case,

Figure 7. ^{27}Al MAS SSNMR spectra of DNL-6 intermediates synthesized by HTS method.

Figure 8. ^{27}Al MAS SSNMR spectra of DNL-6 intermediates synthesized by DGC.

the fumed silica with very fine particles was used as silicon source. In the early stage of the crystallization, vast majority of fumed silica still remain suspended in the solution and were separated from the solids by centrifugation. A similar situation is also reported for SAPO-37.⁵¹ The lack of Si signals in the ^{29}Si MAS spectra clearly suggests that the solids obtained at early stage are AlPO in nature. After 11 h, a weak resonance emerges at -90.5 ppm, which corresponds to $\text{Si}(-\text{O}-\text{Al})_4$.^[52] The emergence of the -90.5 ppm peak corresponds to the PXRD pattern which shows that the formation of the DNL-6 has begun, and also coincides with the appearance of the resonance corresponding to $\text{P}(\text{O}-\text{Al})_4$ in the framework in the ^{31}P MAS spectrum. Therefore, the -90.5 ppm peak can be assigned to the $\text{Si}(-\text{O}-\text{Al})_4$ in the DNL-6 framework which indicates that Si atoms are being incorporated into the DNL-6 framework. After the 24 h, the reactions have nearly gone to completion and more Si atoms have been incorporated in the DNL-6 framework as the signal of the peak increases in intensity. Besides -90.5 ppm peak no other resonances have emerged, indicating that there is only a single Si species present as acidic center and no silicon islands are formed within the DNL-6 framework under the synthetic conditions used in this study.

^{29}Si MAS spectra of the samples obtained under the DGC conditions are similar to those of the HTS samples (Figure 10). The spectra of the 4 h and 4 d samples both exhibit no signal at all for the same reason discussed earlier. There is a resonance at -90.3 ppm appearing after 10 days due to the Si in the framework. However, the intensity of this peak is relatively weak, suggesting that the Si content is likely low. Again, seeing only one resonance at -90.3 ppm indicates that Si

must be incorporated into the framework in the same SM II fashion as the HTS, albeit at a slower rate. The Si only starts to be incorporated in the framework once the DNL-6 starts forming.

Figure 9. ^{29}Si MAS SSNMR spectra of DNL-6 intermediates by HTS

Figure 10. ^{29}Si MAS SSNMR spectra of DNL-6 intermediates by DGC.

^{13}C CP MAS NMR experiments were carried out to probe the role of the SDA and surfactant in crystallization. As carbon is not part of the DNL-6 framework, any carbon signal observed in the ^{13}C CP MAS spectra must be due to either the SDA or surfactant. Since CTACl and DEA have distinctively different ^{13}C chemical shifts, they are distinguishable. All the samples were washed prior to performing ^{13}C SSNMR experiments to ensure that any carbon signal can only be attributed to CTACl or DEA occluded within the framework.

The ^{13}C CP MAS spectra of the HTS samples are shown in Figure 11.^{56,57} After 1 h, all the observed resonances are due to the surfactant and no signals due to DEA was observed. The ^{27}Al , ^{31}P , and PXRD data all indicate that no DNL-6 exists at this point. Thus, the surfactant must be present in the amorphous solids. Since the sample was washed extensively, observing the peaks

due to surfactant suggests that the surfactant is held tightly in the solids. Thus, it may play a role in organizing the structure of the intermediate solids which eventually converts to DNL-6. At 11 h, two new weak resonances belonging to DEA can be seen and the timing of the appearance of these resonances coincides with the emergence of the DNL-6 reflections in the PXRD pattern, suggesting that the signals originate from the DEA molecules occluded inside the DNL-6 framework. After 24 h of heating, the intensity of the DEA resonances increases significantly as the sample are mainly DNL-6 crystals.

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Figure 11. ^{13}C MAS CP SSNMR spectra of DNL-6 intermediates synthesized by HTS method (1, green = DEA; 2, blue = CTACl). Signal assignments are based on references 50 and 51.

The ^{13}C spectra of the DGC samples are illustrated in Figure 12. Unlike the situation in the HTS, the spectrum of the 1 h DGC sample exhibits a sharp peak due to DEA. Also, a close inspection of the spectrum reveals that although extremely weak and broad, a resonance due to DEA can be recognized at around 43 ppm. For the 10 d sample, the intensities of the peaks due to the DEA are stronger, but the signals due to the surfactant dominate. This is likely due to the fact that there is a significant amount of the layered intermediate in the sample, meaning the surfactant is involved in the formation of this material. Since the surfactant is seen in the both HTS and DGC final products, it cannot be completely ruled out that the DNL-6 prepared may have some mesopores as the surfactant CTACl can be used to prepare LTA zeolite with the same alpha-cages found in DNL-6.⁵⁵

Figure 12. ^{13}C MAS CP SSNMR spectra of DNL-6 intermediates synthesized by DGC (1, green = DEA; 2, blue = CATCl).

4. Summary

Based on the information gathered, a few comments can be made on the DNL-6 crystallization. Previous work suggested that under HTS conditions, DNL-6 can crystallize directly from a liquid phase with the amorphous species being gradually dissolved, providing nutrients.³⁰ The DGC results presented in this study indicates an alternative route may exist as DNL-6 can also be formed via the conversion of the layered materials. Since the amount of water available in the DGC (specifically SAC) process is not sufficient to dissolve the layered intermediate, water can only assist in the bond breaking and reforming in the solids, leading to the conversion of the layered phase to form DNL-6 without being completely dissolved in a liquid phase. In this process, the role of water is similar to that in bulk liquid phase synthesis. The role of the surfactant in the

crystallization was investigated previously.⁴⁰ The literature finding suggests that although the presence of cationic surfactant is not essential for DNL-6 formation, the surfactant does affect the crystal morphology and phase purity by inhibiting the formation of competing SAPO-34. Our DGC results seem to suggest that the surfactant molecules are part of the structure of the layered intermediate as it is known that mesostructured AlPO lamellar and tubular materials can be prepared using cationic surfactants.^{56,57} It is also likely that the DNL-6 formed may have some mesopores trapping the surfactant. Unlike the HTS, a small amount of DEA was seen in the early stage of the crystallization, which implies that some structural units trapping the DEA molecules may exist. Si incorporation occurs at the later stage of the crystallization and the Si substitution is through the SM II mechanism.

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Tables:

Table 1. Elemental composition (molar basis) of DNL-6 from EDX analysis.

method	Time	Si	Al	P	P/Al	(Si + P)/Al
DGC	10 days	0.20	0.60	0.21	0.34	0.67
HTS	24 hours	0.16	0.50	0.34	0.69	1.00

Figure Captions:

Figure 1. RHO topology with alternating double-8-rings and LTA cages

Figure 2. Powder XRD patterns of DNL-6 synthesized by the HTS method a) $t = 1$ h to $t = 13$ h; b) $t = 1$ d

Figure 3. Powder XRD patterns of DNL-6 synthesized by the DGC method

Figure 4. Micrographs taken of DNL-6 being synthesized after a) 1 h by DGC, b) 10 d by DGC, c) 1 h by HTS, d) 24 h by HTS.

Figure 5. ^{31}P MAS SSNMR spectra of DNL-6 intermediates synthesized by HTS.

Figure 6. ^{31}P MAS SSNMR spectra of DNL-6 intermediates synthesized by DGC.

Figure 7. ^{27}Al MAS SSNMR spectra of DNL-6 intermediates synthesized by HTS method.

Figure 8. ^{27}Al MAS SSNMR spectra of DNL-6 intermediates synthesized by DGC.

Figure 9. ^{29}Si MAS SSNMR spectra of DNL-6 intermediates by HTS

Figure 10. ^{29}Si MAS SSNMR spectra of DNL-6 intermediates by DGC.

Figure 11. ^{13}C MAS CP SSNMR spectra of DNL-6 intermediates synthesized by HTS method (1, green = DEA; 2, blue = CTACl). Signal assignments are based on references 50 and 51.

Figure 12. ^{13}C MAS CP SSNMR spectra of DNL-6 intermediates synthesized by DGC (1, green = DEA; 2, blue = CTACl).

TOC:

Dry-gel conversion

Hydrothermal synthesis

Draft