

ULTRAFAST LASER SYNTHESIS OF NANOPOROUS ZEOLITE A

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By
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ULTRAFAST LASER SYNTHESIS OF NANOPOROUS ZEOLITE

A

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July 2025

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ABSTRACT

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Zeolites are microporous aluminosilicate self-assembled nanocrystals. Zeolite A is the first commercially synthesized zeolite, which has cubic unit cell that consist of alumina and silica tetrahedra together with the extraframework cations like Na^+ , K^+ , Ca^{2+} . Zeolite A has been widely studied zeolite in the literature owing to the properties like high porosity, high surface area ($\sim 600 \text{ m}^2/\text{g}$), and high chemical and thermal stability, and high ion exchange capacity. All of these properties make Zeolite A used in various industrial applications like CO_2 adsorption, wastewater treatments, biosensor applications, etc.

Although zeolites have a wide range of industrial uses, they have still been extensively investigated in academia as well. Accordingly, various zeolite synthesis methods have been developed, but all have limitations. While conventional hydrothermal synthesis offers benefits such as high-quality discrete crystals, ease of use, safety, and industrial scalability, it lacks precise control over nucleation and growth. A method that combines these advantages with the ability to produce defect-free crystals using low-energy photons within a short reaction time has not been developed yet. To address this, we introduce a new method for synthesizing zeolites (TPA-silicalite-1, zeolite Y, zeolite A, and hierarchical ZSM-5) using ultrafast laser energy deposition. In this approach, energy is deposited on a timescale comparable to the polymerization reactions that drive crystal formation.

In this thesis study, we further investigate the ultrafast laser pulses on the synthesis mechanism and crystalline structure of nanoporous zeolite A. Utilizing

a femtosecond laser at 1040 nm wavelength, we achieved controlled energy deposition in the precursor suspension, accelerating the reaction via multiphoton absorption and laser-induced flows for nearly uniform-sized zeolite A crystals (~ 260 nm). Through the controlled deposition of energy, this method achieves rapid crystallization of Zeolite A with high crystallinity (90-100%) and a narrower particle size distribution compared to the crystals synthesized via the conventional hydrothermal method. Comprehensive characterizations, including Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDXS), X-Ray Diffraction (XRD), High Resolution Transmission Electron Microscopy (HR-TEM), Selected Area Electron Diffraction (SAED), Thermo-gravimetric Analysis (TGA), Brauener-Emmet-Teller (BET), and Fourier Transformed Infrared (FTIR) Spectroscopy, revealed that the laser-synthesized zeolites exhibit structural integrity and quality comparable to conventionally synthesized counterparts. Moreover, CO_2 adsorption capacity analysis was carried out to evaluate the gas capture performance and practical applicability of Zeolite A synthesized via the ultrafast laser synthesis method.

The ultrafast laser synthesis method was successfully repeated over 80 times to enable various characterizations. This novel technique offers a rapid and alternative approach to synthesizing zeolites with precise control over structural and functional properties.

Keywords: Ultrafast laser, laser-induced flows, zeolite A, nucleation & growth, CO_2 adsorption.

ÖZET

NANO-GÖZENEKLİ ZEOLİT A’NIN ULTRAHIZLI LAZER İLE SENTEZİ

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Zeolitler, mikro gözenekli, kendiliğinden birleşen alüminosilikat nanokristallerdir. Zeolit A, alümina ve silika tetrahedrallerden oluşan kübik birim hücreye ve Na^+ , K^+ , Ca^{2+} gibi ekstra-çerçeve katyonlarına sahip ilk ticari olarak sentezlenen zeolittir. Zeolit A, yüksek gözeneklilik, yüksek yüzey alanı ($\sim 600 \text{ m}^2/\text{g}$), yüksek kimyasal ve termal kararlılık ve yüksek iyon değişim kapasitesi gibi özellikleri nedeniyle literatürde yaygın olarak incelenen bir zeolittir. Tüm bu özellikler, Zeolit A’nın CO_2 adsorpsiyonu, atık su arıtımı, biyosensör uygulamaları vb. gibi çeşitli endüstriyel uygulamalarda kullanılmasını sağlar.

Zeolitlerin endüstriyel kullanım alanları geniş olsa da, akademi dünyasında da kapsamlı araştırmalar yapılmaktadır. Bu doğrultuda, çeşitli zeolit sentez yöntemleri geliştirilmiş olsa da, hepsinin kendine özgü sınırlamaları bulunmaktadır. Geleneksel hidrotermal sentez, yüksek kaliteli ayrı kristaller, kullanım kolaylığı, güvenlik ve endüstriyel ölçeklenebilirlik gibi avantajlar sunsa da, çekirdeklenme ve büyüme üzerinde hassas bir kontrolden yoksundur. Bu avantajları, düşük enerjili fotonlar kullanarak kısa bir reaksiyon süresi içinde kusursuz kristaller üretme yeteneğiyle birleştiren bir yöntem henüz geliştirilmemiştir. Bu sorunu ele almak için, ultra hızlı lazer enerji biriktirme yöntemi kullanarak zeolitleri (TPA-silikalit-1, zeolit Y, zeolit A ve hiyerarşik ZSM-5) sentezlemek için yeni bir yöntem sunuyoruz. Bu yaklaşımda, enerji, kristal oluşumunu sağlayan polimerizasyon reaksiyonlarına benzer bir zaman ölçeğinde (femtosaniye-pikosaniye) biriktirilir.

Bu tez çalışmasında, nano gözenekli zeolit A’nın sentez mekanizması ve kristal yapısı üzerinde ultra hızlı lazer darbelerinin etkilerini araştırdık. 1040 nm dalga

boyunda bir femtosaniye lazer kullanarak, öncül süspansiyonda kontrollü enerji birikimi elde ettik, tekdüzeye yakın boyutlu zeolit A kristalleri için (~ 260 nm) çoklu foton emilimi ve lazerle indüklenen akışlar yoluyla reaksiyonu hızlandırdık. Kontrollü enerji birikimi sayesinde, bu yöntem, geleneksel hidrotermal yöntemle sentezlenen kristallere kıyasla yüksek kristal yapıya (%90-100) ve daha dar bir parçacık boyutu dağılımına sahip Zeolit A'nın hızlı kristalleşmesini sağlar. Taramalı Elektron Mikroskobu (SEM), Enerji Dağıtıcı X-Işını Spektroskopisi (EDXS), X-Işını Kırınımı (XRD), Yüksek Çözünürlüklü Geçirgen Elektron Mikroskobu (HR-TEM), Seçilmiş Alan Elektron Kırınımı (SAED), Termo-gravimetrik Analiz (TGA), Brauner-Emmet-Teller (BET) ve Fourier Dönüşümlü Kızılötesi (FTIR) Spektroskopisi dahil olmak üzere kapsamlı karakterizasyonlar, lazerle sentezlenen zeolitlerin geleneksel olarak sentezlenen muadilleriyle karşılaştırılabilir yapısal bütünlük ve kaliteye sahip olduğunu ortaya koydu. Ayrıca, ultra hızlı lazer sentez yöntemiyle sentezlenen Zeolit A'nın gaz yakalama performansını ve pratik uygulanabilirliğini değerlendirmek için CO_2 adsorpsiyon kapasitesi analizi gerçekleştirilmiştir.

Ultra hızlı lazer sentez yöntemi, çeşitli karakterizasyonlara olanak sağlamak için 80'den fazla kez başarıyla tekrarlanmıştır. Bu yeni teknik, yapısal ve işlevsel özellikler üzerinde hassas kontrol sağlayan zeolitlerin sentezlenmesine hızlı ve alternatif bir yaklaşım sunmaktadır.

Anahtar sözcükler: Ultrahızlı lazer, lazer-indüklü akış, zeolit A, çekirdeklenme ve büyüme, CO_2 adsorpsiyonu.

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Chapter 1

Introduction

Zeolites are crystalline microporous (pore sizes less than 2 nm) aluminosilicates with highly ordered pore structure and large surface area.^[1, 2, 3] They were first discovered by Swedish mineralogist Axel Fredrik Cronstedt in the 18th century.^[2] They were named by combining the Greek words “zeo” (to boil) and “lithos” (stone) because zeolites lose their water content and foam when heated.^[4] Today, zeolites are divided into three primary classes: natural, synthetic and hypothetical. Natural zeolites form over time through the chemical interaction between volcanic ash and alkaline groundwater, leading to the gradual formation of crystalline structures. Synthetic zeolites were synthesized to be commercialized in 1950s for the first time and they offer a wide range of applications thanks to their controlled properties. On the other hand, hypothetical zeolites, which have not yet been synthesized experimentally, are important structures that shed light on future applications in terms of theoretically possible pore geometries and cage structures. Currently, more than 40 zeolite species found in nature. 260-type frameworks of zeolites are synthesized experimentally according to the International Zeolite Association (IZA) and IZA represents different framework structures with a three-letter code (e.g. Linde Type A as LTA, Faujasite as FAU, etc.).^[5] Millions of hypothetical zeolite frameworks are obtained computationally.^[5, 6, 7, 8]

The basic structure of zeolites is formed by the bonding of SiO_4^{4-} and AlO_4^{5-} tetrahedra units to each other via oxygen atoms from their corners. The inclusion of Al^{3+} ions in the structure causes the cage to be negatively charged; this charge is usually balanced by alkali or alkaline earth cations such as Na^+ , K^+ , Ca^{2+} , etc. Generally zeolites synthesized via conventional hydrothermal synthesis method with the empirical formula;^[4, 9, 10]

$$M_x^{n+}[(AlO_2)_x(SiO_2)_y].zH_2O \quad (1.1)$$

where M is an alkali or alkaline earth metal that has valance n to neutralize the charged zeolite. The frameworks of zeolites consist of primary building units (PBUs), secondary building units (SBUs) and composite building units (CBUs). PBUs of zeolites are $(AlO_4)^-$ and (SiO_4) tetrahedra. These PBUs make Si, Al-O-Si, Al bonds by sharing oxygens with adjacent tetrahedra to form a simple geometric shapes which are named as SBUs.^[4, 9, 10]

The SBUs can be single rings, double rings or more complex. Currently, 23 different forms of SBUs are known to exist. Furthermore, zeolites may contain CBUs like double n-rings, cages and cavities. Rings are the most common CBUs. The size of the rings which is determined by number of tetrahedra of a ring limits the pore size in zeolites as shown in **Figure 1.1**.^[9, 10] The resulting porous structure brings with it many important properties such as high surface area, ion exchange capacity due to charge balancing cations, adsorption and molecular sieving ability due to molecular size pores, high thermal and chemical stability, etc. These properties are the fundamental factors that determine the diversity of not only the structures of zeolites but also their functions.^[1, 11]

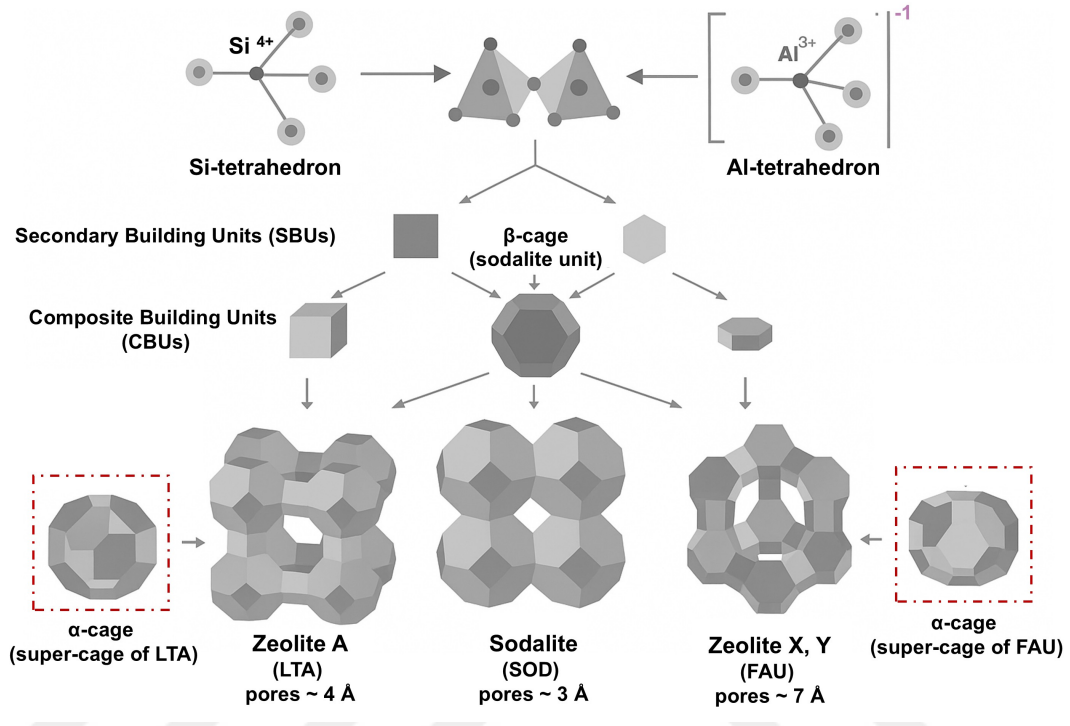


Figure 1.1: From primary building units to different zeolite frameworks composition. Adapted from the reference [12].

Thanks to these special structural and chemical properties that they possess, zeolites are widely used as catalysts in the petrochemical industry,^[13, 14] as adsorbents in agriculture,^[15] as gas separators in environmental technologies,^[16] as ion exchange agents in detergents,^[17] as controlled release providers in drug delivery and medicine,^[18] and in recent years as functional materials in optoelectronics and energy storage.^[19, 20] Having such a wide application potential has increased the scientific interest in synthesis and structural control of zeolites both theoretically and experimentally.

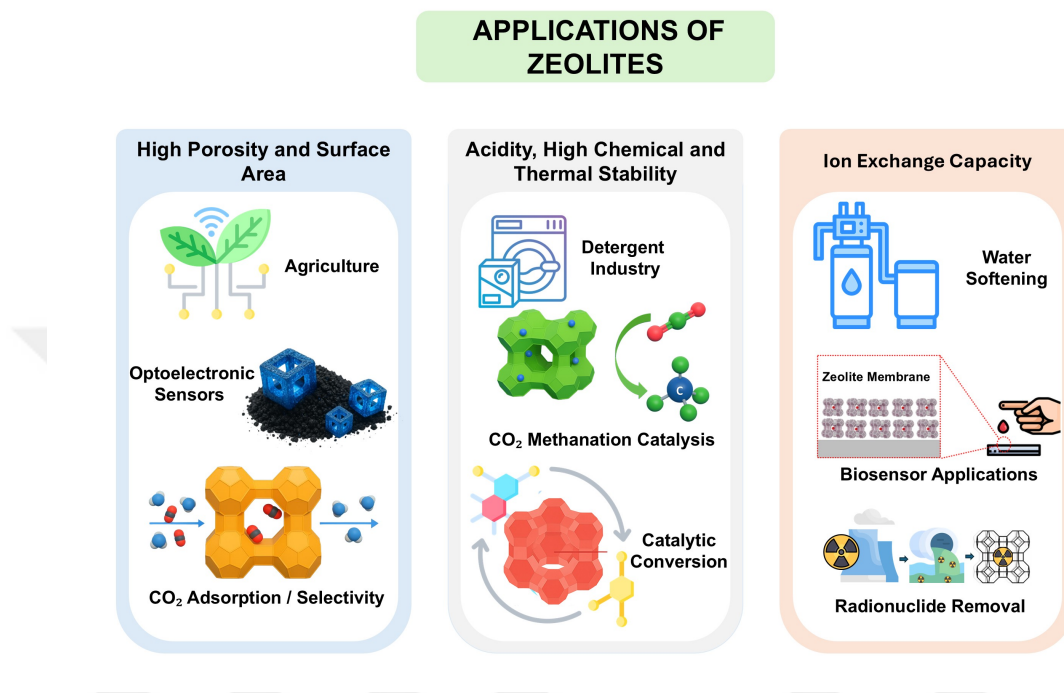


Figure 1.2: General properties of zeolites and their areas of use in different applications.

A thorough understanding of the crystallization mechanism of nanocrystals such as zeolite is essential to gain control over the unique properties and effective functionalities of the nanocrystal to be formed. Zeolite crystallization consists of sequential phases of nucleation and growth. Nucleation mechanisms in aqueous solutions are divided into two main category; primary and secondary nucleation. Primary nucleation is driven by the solution itself (homogeneous nucleation) or extraneous material in the solution (heterogeneous nucleation).^[21, 22] Secondary nucleation has a lower activation energy than primary nucleation and is triggered by the presence of parent crystals of the same phase. To facilitate the production and release of secondary nuclei, secondary nucleation requires fluid motion to physically damage (micro-attrition) the parent crystals.^[22] However, induced fluid motion (e.g. stirring with high fluid velocities, high agitation rates) is not present in many zeolite synthesis systems. Furthermore, the settling of crystals is

generally not sufficient to cause secondary nucleation, and secondary nucleation due to ageing is thought to have poor effect on crystallization.^[5, 21, 22]

The crystal growth phase following nucleation is the process in which the building blocks around the nuclei accumulate and form larger and more regular crystals. This growth kinetics varies depending on various parameters such as batch composition, pH, temperature, stirring speed and ageing time of the precursor suspension. In order to understand these mechanisms and accelerate crystallization, various alternative synthesis methods and pathways/procedures have been developed.^[11, 23, 24, 25, 26] Moreover, modeling studies developed in recent years have provided important information to understand zeolite crystallization from both kinetic and thermodynamic perspectives and have established a theoretical basis for early oligamerization reactions of zeolites.^[21, 22, 27, 28]

Although various synthesis methods have been developed for synthesizing zeolites, each comes with its own set of limitations.^[11, 23] A synthesis method has not yet been developed that combines the benefits of hydrothermal synthesis, such as the production of high-quality, discrete crystals and user-friendliness, with the advantages of alternative methods, such as accelerated zeolite crystallization and improved control over nucleation and growth.^[11, 23, 24] As a proof-of-concept study, we demonstrated that ultrafast lasers (femtosecond) can be utilized to assemble zeolites with the aforementioned advantages.^[29] Moreover, this novel method effectively addresses the disadvantages of hydrothermal synthesis, such as long synthesis times and imprecise control over nucleation and growth, and the challenges associated with other techniques, such as unwanted defect formation and safety concerns associated with high-energy light source equipment.^[23, 24] We have demonstrated that it is possible to study the sequential evolution of the synthesis process of TPA-Silicalite-1 zeolites from early oligomers to fully grown crystals using this novel synthesis approach.^[29]

In this thesis work, we extend our novel ultrafast laser synthesis method to Na-form zeolite A (LTA framework, Na-LTA), which exhibits a more intricate

crystallization mechanism than simple TPA-Silicalite-1, such as both having both SiO_2 and Al_2O_3 tetrahedra in the framework, and sodium ions (Na^+) as extra-framework cations. The effect of ultrafast pulses on zeolite A crystals obtained by ultrafast laser synthesis method comprehensively examined and discussed regarding structural properties, defect site analysis, and adsorption behavior in detail. In Chapter 2, zeolite A and their well-known synthesis methods will be introduced in detail, and ultrafast laser synthesis method will be discussed in detail. In Chapter 3, the experimental set-up, mass composition and energy deposition calculations, procedures and characterization methods used in the experiments will be explained in detail. In Chapter 4, the structural and functional properties of zeolite A synthesized via ultrafast laser synthesis are given and discussed in comparison with the properties of zeolites synthesized via the conventional hydrothermal synthesis method with different characterization methods. In Chapter 5, the thesis will be summarized and future perspective will be given.

Chapter 2

Background

2.1 Zeolite A

Zeolite A (Linde Type A, LTA) is the first commercially synthesized zeolite by Donald W. Breck and his colleagues in the Union Carbide R&D laboratories in the 1950s then commercialized by the Linde company.^[30] Zeolite A has a highly symmetric cubic unit cell (Fm3c space group, $a = 24.6 \text{ \AA}$) which consists of silica and alumina tetrahedra together with the extra-framework cations such as sodium (Na^+), potassium (K^+), and calcium (Ca^{2+}). It is characterized by the chemical formula;^[31, 32]

$$|(Na_{12}(H_2O)_{278}|_8[Al_{12}Si_{12}O_{48}]_8 \quad (2.1)$$

which is its most common hydrated sodium form (Na-LTA).^[5] These sodium ions can be exchanged with other cations. Depending upon the exchangeable cation in the zeolite A structure it is also commonly termed Zeolite 3A or K-LTA if the ion is exchanged with K^+ , Zeolite 4A or Na-LTA if the ion is exchanged with Na^+ , or Zeolite 5A or Ca-LTA if the ion is exchanged with Ca^{2+} .^[33, 32]

Zeolite A, like other zeolites, consists of SiO_4 and AlO_4^- tetrahedral units. However, Zeolite A is the zeolite with the lowest silica content framework with a Si/Al ratio of 1.0. In zeolite A, a negative charge is formed for each AlO_4^- tetrahedra. This charge is balanced by extra-framework Na^+ ions. This makes LTA one of the zeolite types with the highest cation charge density.^[33, 32]

Zeolite A has three fundamental structural units (see **Figure 2.1**). The first is the D4R (Double 4-ring) consisting of four-membered ring pairs, which is the building block that connects the sod-cages in the framework. The second is the sodalite-cage (β -cage) consisting of 4- and 6-membered rings containing 24 T-atoms. The third is the α -cage (supercage, LTA cage) consisting of 4-, 6- and 8-membered rings containing 48 T-atoms. The zeolite framework is connected to each other by sodalite cages and D4R units, forming large supercages. These supercages are ~ 4.2 Å in diameter and allow the diffusion of gases, ions or molecules.^[34]

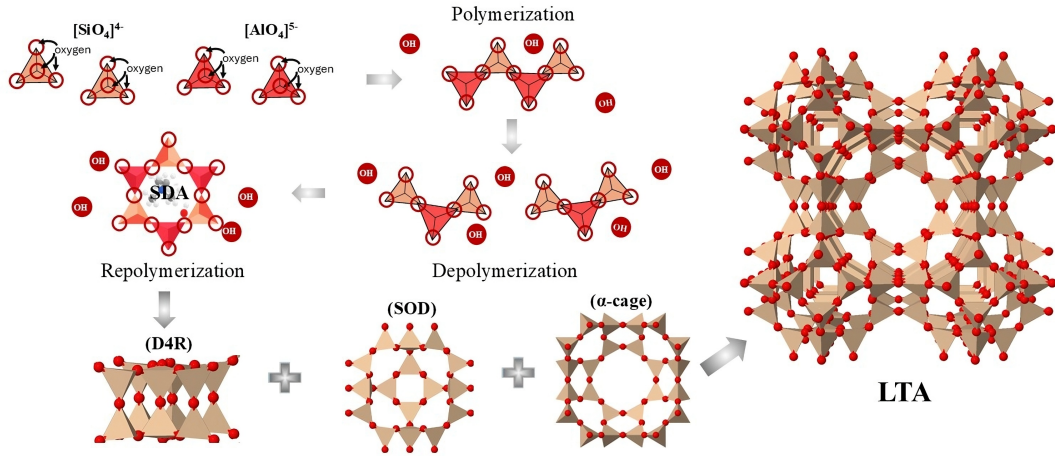


Figure 2.1: Schematic representation of Zeolite A crystallization.

2.1.1 Nucleation and Growth of Zeolite A

Classical nucleation theory (CNT) argues that crystals form directly from monomers and that the process is driven by the decrease in free energy.^[35, 36] This model is based on ideal assumptions such as “burst nucleation”, but it is insufficient to explain all physical systems.^[36] Therefore, alternative approaches such as the Finke-Watzky model and Ostwald ripening have been developed; however, they also cannot provide explanations at the molecular level.^[36] Non-classical nucleation pathways suggest the existence of more complex precursor species and multi-step processes. These pathways argue that crystallization occurs not only by the accumulation of monomers but also by nanoparticle aggregation and organization.^[35, 36, 37] Rimer et.al. (2014) claim that both classical (attachment of individual molecules) and non-classical (direct attachment of metastable precursors) growth mechanisms are observed together in the crystal growth of zeolite silicalite-1, which is widely used for mechanistic studies of zeolites.^[37] However, the early reactions at the nucleation stage (silica oligomerization reactions) occur in a very short time (femtosecond-picosecond time scale), it is difficult to observe these processes directly.^[28, 36]

The crystallization processes of aluminosilicate zeolites like Zeolite A are more complicated than those of pure silicate zeolites (e.g. silicalite-1) due to many equilibrium interactions between the various aluminosilicate species. The crystallization studies on Zeolite A are pioneered by the work of Mintova et al. (1999) who provided a deep mechanistic understanding of the RT synthesis and nucleation of templated nano-zeolite A.^[38]

The crystallization pathway of Zeolite A in colloidal precursor solution is visualized in **Figure 2.2**. *(i)* By adding TMAOH to the amorphous gel, the pH increases and densification and gelation are promoted. *(ii)* The formed amorphous gel particles act as nucleation microenvironments. *(iii)* Initial crystallites nucleate within these gels at one crystal per gel particle. *(iv)* Over time (3–7 days at RT), the gel is consumed and transforms into a single dense crystal particle.

(v) Finally, the crystal retains its external size but internally becomes regular and grows by Ostwald ripening.^[38]

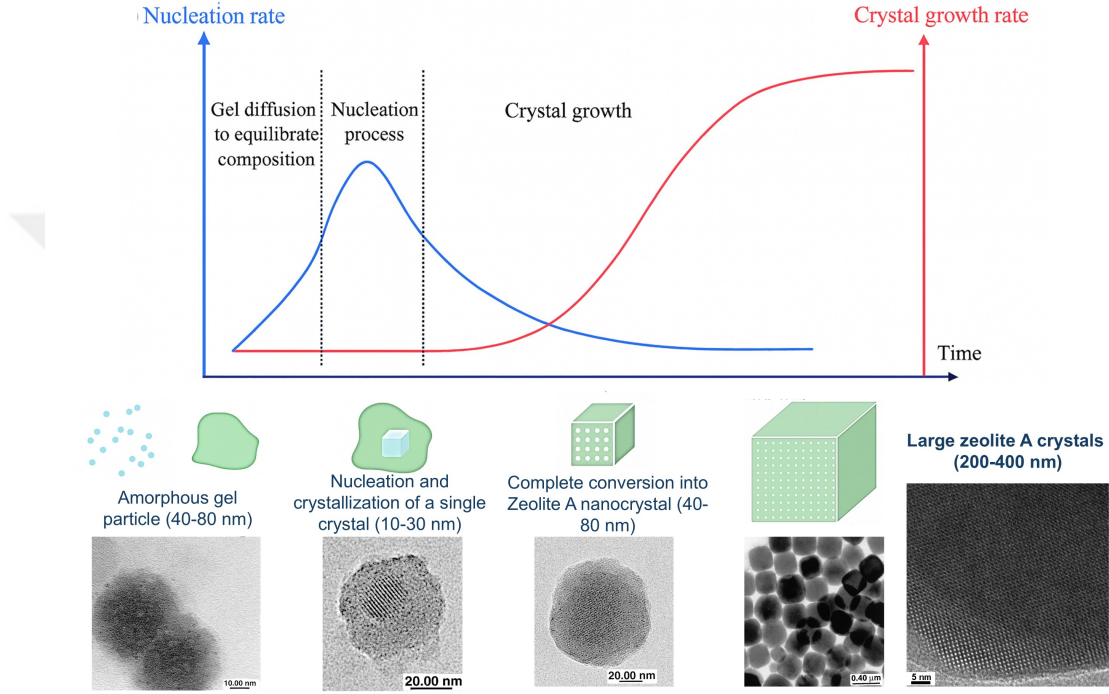


Figure 2.2: Schematic representation of nucleation and crystallization rates, and HR-TEM images to show how a single crystal is generated from amorphous gel, and converted into nano-crystal. Adapted from references [38, 39].

The tetrahedral units in the zeolite A precursor suspension form 4-membered rings (4R) and isolated D4Rs around the extra-framework cations like Na^+ and water in the precursor by polymerization/depolymerization reactions and form isolated D4Rs. The formation of these isolated D4Rs even at pre-nucleation (induction time) was observed by in situ Small-Angle and Wide-Angle X-ray Scattering (SAXS/WAXS) methods.^[40] Then, the increase in the band in the region $500\text{-}650\text{ cm}^{-1}$ with heating in Fourier Transformed Infrared (FTIR) Spectroscopy indicated that the isolated D4Rs transformed into framework-integrated D4Rs.^[40] This suggests that the isolated D4Rs acted as early structural motifs,

probably merging into larger precursor particles and becoming integral parts of the final LTA framework. During nucleation, it was observed by Nuclear Magnetic Resonance (NMR) and UV-Raman Spectroscopy that six-membered rings (6R) were formed around the TMA^+ as a organic structure directing agent.^[41] After nucleation, both sodalite (β) cages and α -cages appear in the ^{29}Si NMR spectroscopy.^[41] This suggests that nucleation in Zeolite A starts with D4R and growth occurs by binding D4R and sodalite cages to each other, and LTA framework is formed as shown in **Figure 2.3-a**.

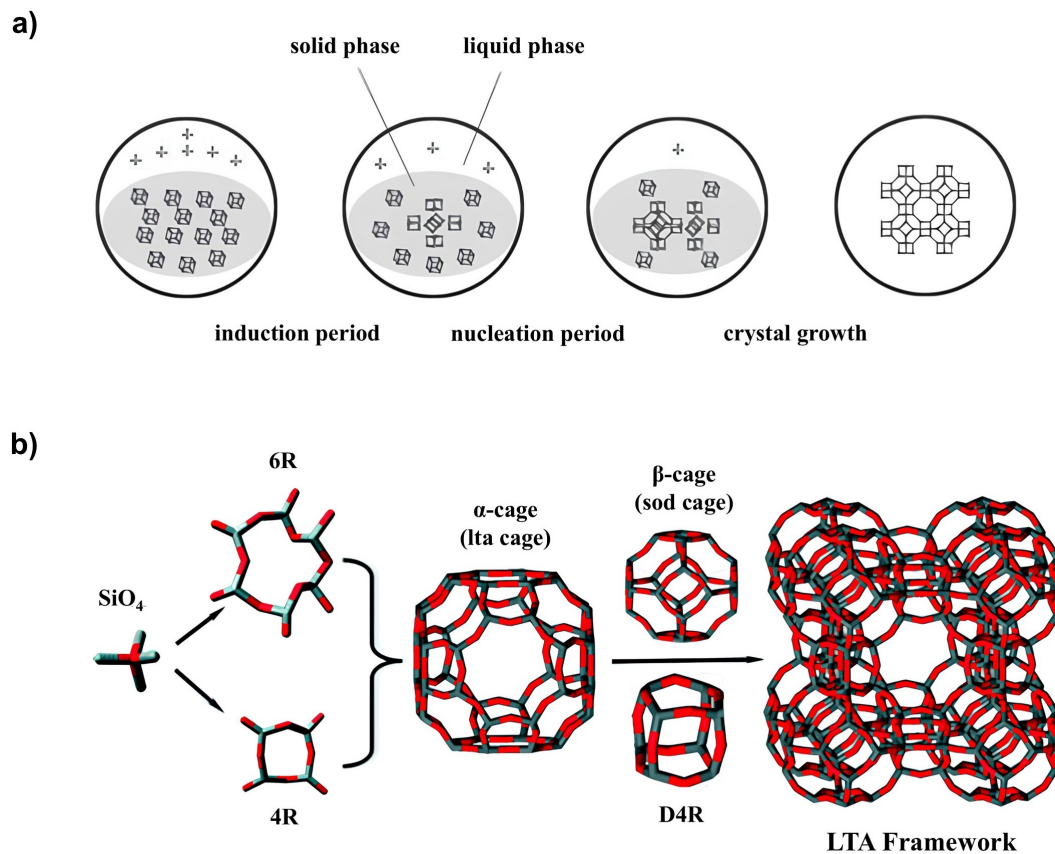


Figure 2.3: a) Schematic representation of nucleation and crystallization of Zeolite A starting from D4R. Adapted from reference [41]. b) Schematic representation of nucleation and crystallization of zeolite A starting from α -cage. Adapted from reference [39].

However, using a charge density mismatch synthesis approach, Hong et al. (2013) claim that nucleation for zeolite LTA starts with the formation of α -cage, not with smaller sod or D4R cages. [34] Crystallization proceeds with sod-cage and then D4R-cage structure. According to this theory, energy calculations show that α -cage + sod-cage structures are more stable than α + D4R structures. [34] Also consistent with other studies, this study also suggests that the absence of Na^+ or TMA^+ inhibits crystallization; both are crucial for the initiation of crystallization. The crystallization pathway of this theory consists of 3 steps as illustrated in **Figure 2.3-b**: (i) Formation of α -cages via TMA^+ and Na^+ directing, (ii) growth of sod-cages around α -cages, (iii) formation of D4R-cages to connect sod units to the LTA framework. [34]

2.1.2 Active Sites of Zeolite A

Zeolite A typically has a Si/Al ratio of approximately 1, and the presence of a high amount of Al^{3+} ions in the framework creates a negative charge on each Al^{3+} tetrahedral SiO_4 lattice, which is balanced by exchangeable cations (usually Na^+) located within the pore system. Therefore, the structure of Zeolite A is highly ionic in character and contains a large number of cationic active sites. [42]

The most prominent component of the active sites of Zeolite A are exchangeable cations that balance the negative charges in the structure. These cations are localized in specific regions of the zeolite lattice and play a critical role in adsorption and ion exchange properties. [42, 43] Crystallographically, three main cation positions have been identified in Zeolite A as shown in **Figure 2.4**. Site I is located around the 6R near the center of the sodalite cages. Since these positions are narrow and difficult to access, these cations are less reactive. Site II is located in the immediate vicinity of the entrance opening of the large α -cage. Cations in this position have high adsorption capacity due to easy access of gas molecules (especially CO_2). In Site III, cations are located around the 4R of D4R. These cationic positions determine the physical adsorption capacity of

Zeolite A by establishing electrostatic interactions with the adsorbent molecules. In particular, Na^+ and K^+ ions form strong interactions with high quadrupole moment molecules such as CO_2 , providing high selectivity.[31, 42, 43]

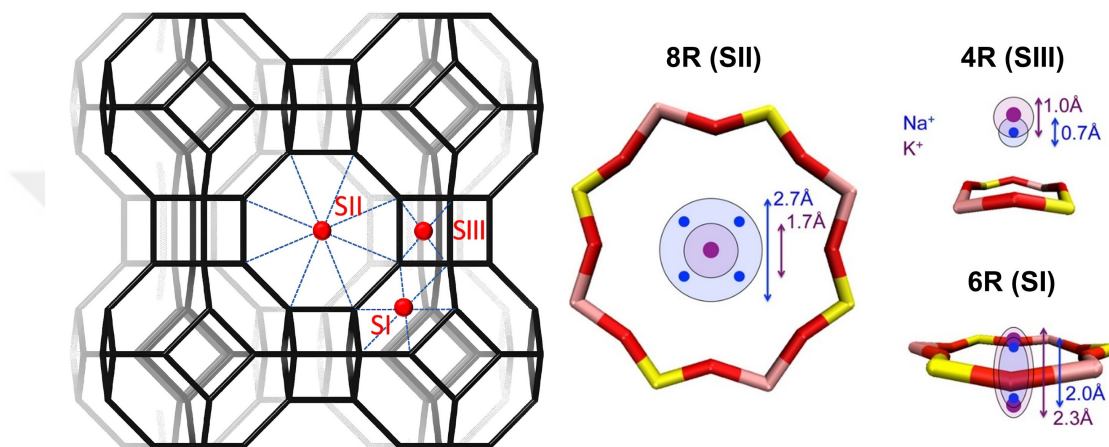


Figure 2.4: Cation sites of LTA zeolite. Site I lies close to the 6R, site II is located in the window of the 8R, and site III is located above the 4R. Adapted from references [42, 44].

If the negative charge on the aluminosilicates lattice is compensated by a proton, the resulting material provides Brønsted acidity for various acid-catalyzed organic transformations.[45] However, Zeolite A does not exhibit significant Brønsted acidic properties in its natural state (Na-A form), since it does not contain any bridging -OH groups carrying protons (H^+). However, Brønsted acidic sites can be formed when Na^+ ions are replaced by H^+ through ion exchange.[46] These sites are formed as Si-OH-Al bridges connected to AlO_4 tetrahedra and have high acidic strength.[47] However, due to the low Si/Al ratio (~ 1) of Zeolite A, a high density of negative charges is formed, which makes it difficult to stabilize H^+ ions. Therefore, Zeolite A in the H-A form is less stable in terms of thermal stability and is rarely preferred in practice.[47] Zeolites with higher silica content (e.g. ZSM-5) have more advantageous Brønsted acidic properties. Therefore, high silica LTA zeolites have been widely studied experimentally and computationally.[48, 49, 50]

During thermal activation, dehydroxylation of the bridging OH groups results in the formation of framework or non-framework species with Lewis acidic characteristics.^[45] Lewis acidic sites are very weakly present in Zeolite A in its natural state. However, cations such as Na^+ can act as weak Lewis acids.^[46, 51] Although these cations have the capacity to attract electron pairs, they provide insufficient acidity for most Lewis acidic reactions. However, these weak Lewis acidic centers can interact weakly with polar molecules (e.g. water, ammonia).^[46, 51]

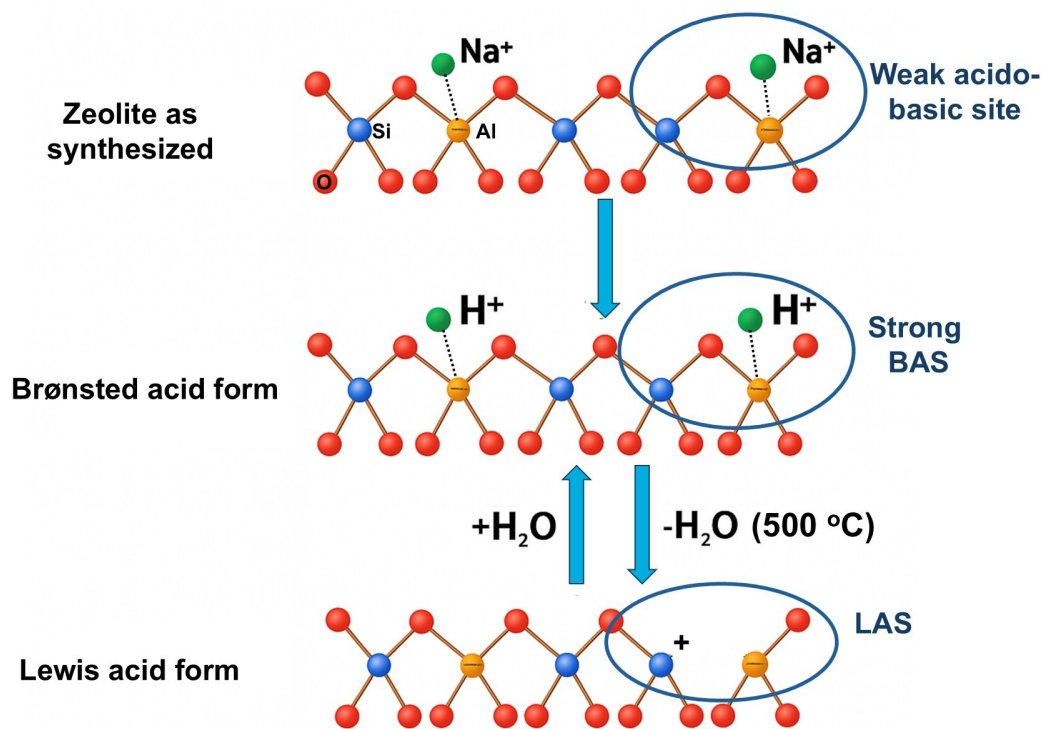


Figure 2.5: Schematic representation of Brønsted and Lewis acid form of zeolite. Adapted from reference [52].

All these cationic and acidic sites enable zeolite A to create strong electrostatic fields inside the pore; therefore, Si/Al ratio is a critical parameter, and low Si/Al value leads to higher Al content and increased ion exchange capacity and protonic acidity. Cations provide effective interaction with polar gas molecules such as

CO₂ by forming adsorption centers. Therefore, Zeolite A shows remarkable CO₂ adsorption capacity and is widely studied in the literature.^[42, 43, 44, 53, 54] In this thesis, CO₂ adsorption capacity of zeolite A synthesized via the ultrafast laser and hydrothermal synthesis method is investigated in Chapter 4.8.

2.2 Zeolite Synthesis Methods

2.2.1 Conventional Hydrothermal Synthesis Method

Conventionally, zeolites are synthesized using the hydrothermal synthesis method, which is carried out by controlled crystallization of amorphous aqueous precursor suspension in a stainless steel autoclave under the temperature between 50-270°C and autogenous pressure over an extended period of time.^[11, 55] Conventional hydrothermal synthesis requires precursor suspension preparation and ageing step in which silica and alumina sources (e.g. tetraethylorthosilicate and aluminum isopropoxide) are mixed in a basic medium (pH > 12) and prepared precursor suspension is kept steady or stirred at room temperature or higher temperature for a certain period of time.^[23, 55] The effects of this step on the direction of the zeolite nucleation process have been discussed in many studies. In short, zeolite synthesis is highly sensitive to kinetic factors such as aging, order of mixing, chemical composition, stirring speeds etc.^[56, 57, 58] Later, the precursor suspension is kept in a teflon-lined autoclave at moderate temperatures for hours or days and hydrothermal crystallization occurs. In the hydrothermal crystallization process, energy is deposited on the precursor suspension in the form of thermal energy.^[55] Heat provides the activation energy for chemical reactions to initiate the nucleation and growth of zeolite crystals, however, conductive heating prevents control over crystallization. Finally, the zeolite crystals formed are separated by centrifugation, washed with pure water to decrease the pH into neutral range and then dried to obtain powder product. The pore-forming organic structure directing agent (OSDA) can be removed by high-temperature treatment, i.e.,

calcination.[11, 23, 55]

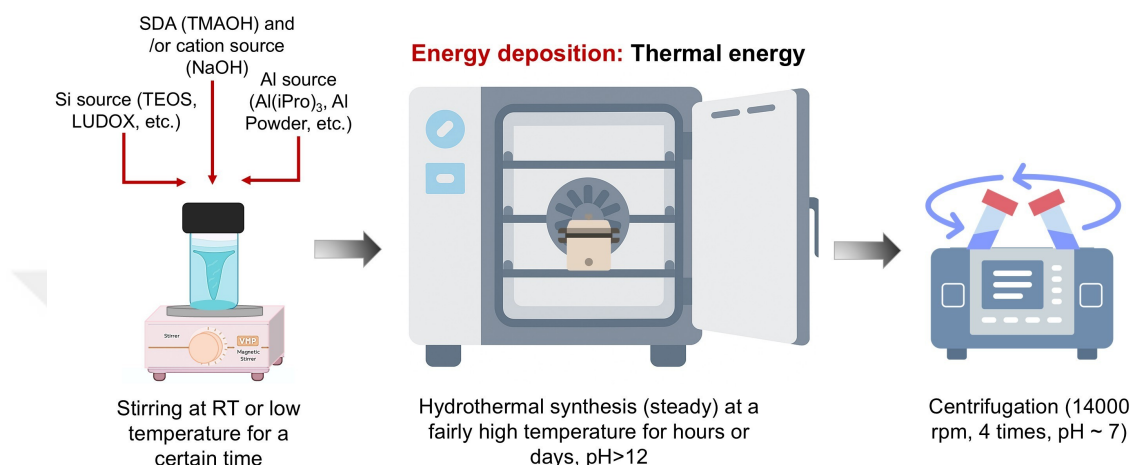


Figure 2.6: Schematic representation of conventional hydrothermal synthesis procedure including agitation, hydrothermal treatment, and centrifugation.

Conventional hydrothermal method provides discrete zeolite crystals and good product quality, such as high crystallinity, high wt. % yield, less defect formation etc. While the method is relatively easy, safe, efficient, and industrially scalable, it is a time-consuming method.[11, 23, 24] Moreover, conventional heating and the requirement of fairly high/moderate temperatures and autogenous pressures make the hydrothermal synthesis method suffer from limited control over the crystallization process. Therefore, various alternative methods have been developed and proposed to accelerate the synthesis and have precise control over the crystallization of zeolites.[23, 24]

2.2.2 Microwave-assisted Synthesis Method

The microwave-assisted synthesis is one of the most common alternative methods to accelerate zeolite synthesis. In microwave-assisted synthesis, microwaves

interact with polar molecules (like water) or ions (like OH^-) in the precursor suspension, allowing the microwave method to be used on both gel-like and aqueous precursors.^[11, 23, 24, 26, 59, 60] Microwave's low-energy photons are insufficient for breaking chemical bonds and do not affect the activation energy for nucleation. However, ionic conduction and these dipole interactions convert electromagnetic energy into heat through rapid rotation and molecular friction in an alternating electromagnetic field which is called dielectric heating (see **Figure 2.7**).^[26, 59]

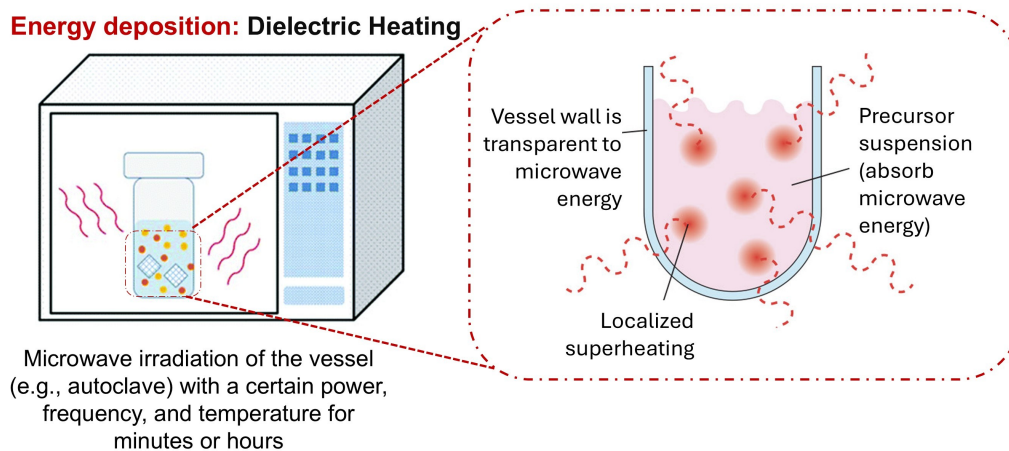


Figure 2.7: Schematic representation of microwave synthesis by dielectric heating. Adapted from references [24, 61].

This method reduces the reaction time from days to hours or even minutes. However, agglomeration in zeolite crystals can occur since microwaves generate localized hot spots in the precursor suspension (Figure 2.7). Moreover, because long synthesis times cause structural degradation, while short synthesis times result in low crystal yield and poor crystallinity, the optimum synthesis time is limited to a narrow window, making it difficult to consistently control product quality.^[59] Besides, the short penetration depth of microwaves is also an issue for scaling up the synthesis.^[26, 59, 60] Furthermore, this method generally requires a multi-step procedure or is used as pretreatment for hydrothermal synthesis of zeolites to accelerate the synthesis time requires subsequent hydrothermal synthesis.^[11, 23, 24]

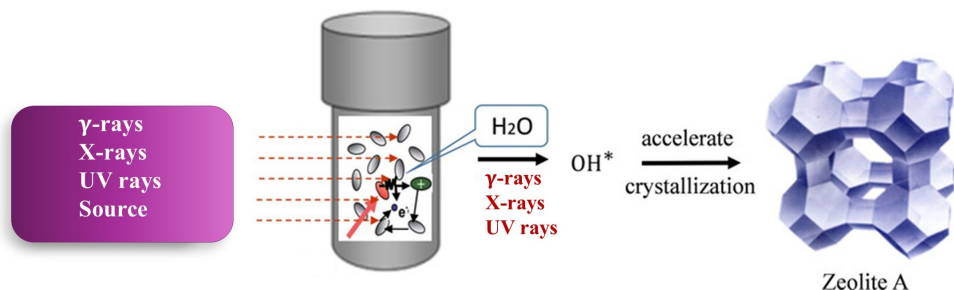
2.2.3 High Energy Irradiation-based Synthesis Methods

As an alternative to hydrothermal and microwave-assisted synthesis methods, irradiation-based synthesis methods provide highly reactive hydroxyl radicals ($\cdot\text{OH}$) to accelerate silica polymerization reactions, and high-energy light sources such as UV,^[62] gamma ray,^[25] and high-energy e-beam^[63] are used in these methods.

In irradiation-based zeolite synthesis methods, including ultraviolet light, gamma ray and high-energy electron beam irradiation, hydroxyl radicals are generated using high-energy photons or electrons (**Figure 2.8-a**).^[25, 62, 64] The photons of ultraviolet and gamma ray have enough energy to break the bonds of H_2O molecules to form reactive hydroxyl radicals. These radicals lower the activation energies of the reactions. DFT calculations show that $\cdot\text{OH}$ break O-Si-O bonds more effectively than OH ions (OH^-), which leads to polymerization/depolymerization and nucleation of the zeolite by breaking and promoting the O-Si-O bonds as shown in the **Figure 2.8-b**.^[62, 64]

This synthesis method accelerates nucleation and provides control over crystallization. However, like other high-energy light source methods, they lead to the formation of unintended irregular mesoporosity, which limits the applicability of the methods for nano-sized zeolites.^[23, 24, 25, 64] Moreover, excessive radiation might damage the crystal structure and specialized radiation equipment is required. These methods have radiation exposure-based health risks, especially in gamma irradiation.^[23, 24, 25, 62]

a) **Energy deposition: Highly energetic photon exposure**



b) **accelerated crystallization via highly reactive hydroxyl radicals**

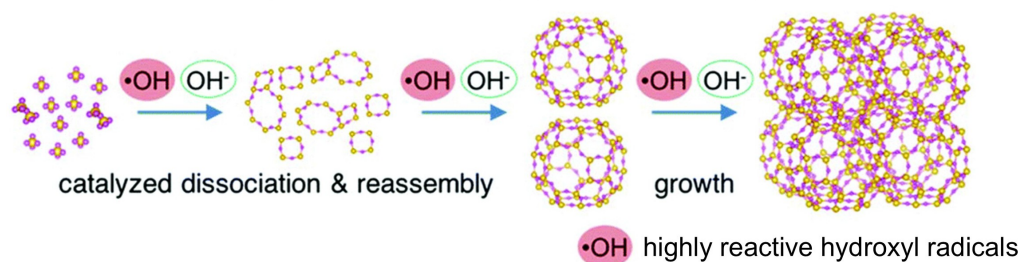


Figure 2.8: a) Schematic illustration of high energy photon irradiation-based synthesis methods. Adapted from reference [25]. b) Schematic illustration of the accelerated nucleation and crystallization of sodalite via highly reactive hydroxyl radicals. Adapted from reference [24].

Recently, Mintova, et.al. (2025) observed in situ the ultra-fast crystallization of RHO type nanozeolites by means of $\cdot\text{OH}$ radicals generated by triggering the radiolysis of water using electron beam (e-beam) irradiation using transmission electron microscopy (TEM). This study is consistent with previous UV/gamma studies. Unlike UV/gamma studies, instantaneous nucleation occurred within seconds and this study provides in situ observation of the crystallization path.^[65]

2.3 Ultrafast Laser Synthesis Method

As mentioned above in detail, although hydrothermal, microwave-assisted, and irradiation-based (UV, gamma, and e-beam) methods have been developed for zeolite synthesis, each has different limitations. Although the hydrothermal method can be applied on an industrial scale, it is time-consuming and does not offer precise control over nucleation, while the microwave method accelerates the process but has limited temperature uniformity and product quality. Irradiation-based techniques accelerate reactions with reactive hydroxyl free radicals, but excessive radiation can damage the crystal structure and require special equipment.

Our group presented the ultrafast laser synthesis method as a new energy deposition approach based on femtosecond laser pulses with low-energy photons to overcome these limitations.^[29] Processes such as plasma, shock waves, cavitation bubbles and laser-induced flows are triggered in a transparent liquid medium by ultrafast laser pulses and result in rapid and controlled crystallization of zeolites, such as Silicalite-1, ZSM-5, Zeolite Y and Zeolite A. In order to understand this method in detail, first ultrafast lasers, then multiphoton absorption, which is a characteristic feature of ultrafast laser-material interaction, and as a result laser-induced optical breakdown and the subsequent cascade of events will be explained in this section.

2.3.1 Ultrafast Lasers

Ultrafast lasers are laser systems that produce extremely short light pulses with pulse durations (τ) in the femtosecond (10^{-15} s) and picosecond (10^{-12} s) range. These systems can produce very high peak power ($P_{peak} = E_{pulse}/\tau$) despite having low average power (**Figure 2.9-a**), unlike conventional long-pulse (nanosecond) lasers and continuous-wave (CW) lasers.^[66, 67] In conventional nanosecond

or continuous wave lasers, since energy transfer occurs over longer time intervals, significant thermal build-up occurs in the lasered area, resulting in melting, vaporization or environmental damage. The extremely short pulse durations of ultrafast lasers ensure that the energy transferred by the light into the material is absorbed without thermal dissipation (**Figure 2.9-b**), enabling processing with high spatiotemporal resolution and minimal damage at moderate average temperatures.^[66, 67]

The effectiveness of ultrafast lasers depends on the laser parameters such as wavelength, pulse duration, and repetition rate which are shown in Figure 2.9-a. Wavelength (λ) is a fundamental quantity that determines the energy of a photon and is defined by the relationship $E = hc/\lambda$.^[68, 69] Short wavelengths carry high-energy photons, while long wavelengths provide deeper penetration. In ultrafast lasers, near-infrared (NIR, 700–1100 nm) wavelengths are generally preferred because this range provides an optical window with low scattering and absorption for sensitive environments like biological tissues.^[70, 71] The pulse duration (τ) plays a critical role in defining the peak power of the laser pulses. The shorter the pulse duration (such as femtosecond picosecond), the same energy can be transferred in a much shorter time period, resulting in a dramatic increase in peak power. In this way, nonlinear processes such as multi-photon absorption can be triggered with low average powers. Repetition rate determines how many pulses the laser produces per second and is expressed in Hz or MHz. High repetition rates (>1 MHz) create risk of thermal accumulation on the material, while at low repetition rates (<1 kHz), thermal effects are negligible.^[68, 69, 72]

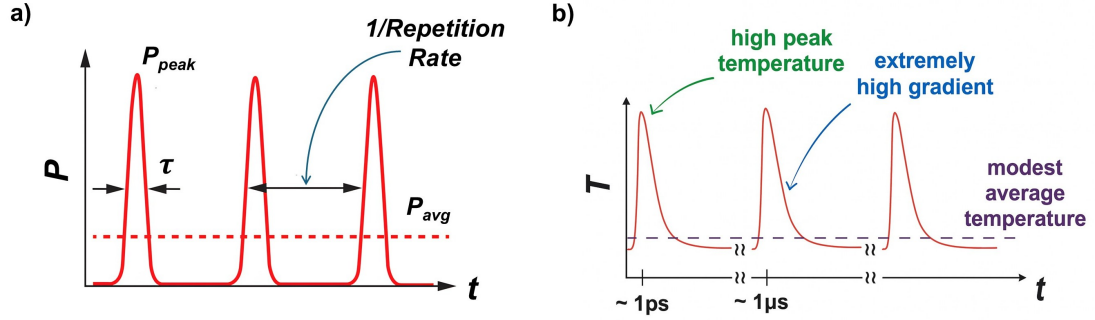


Figure 2.9: a) A demonstrative plot of the average power P_{avg} and peak power P_{peak} for a laser with pulse duration τ . Adapted from the reference [73]. b) A representative plot of the temperature profile generated by each pulse by ultrafast lasers. Adapted from the reference [29].

The interactions of ultrafast lasers with gases and solids have been extensively studied due to their connection with atmospheric propagation of high-power lasers and their minimal thermal accumulation. The minimal thermal accumulation offers significant advantages in areas such as tissue ablation without thermal damage in dentistry,^[74] minimally invasive corneal incisions in ophthalmic surgery,^[75] and silicon ablation in semiconductors.^[76] On the other hand, the interaction of ultrafast lasers with liquids is a complex scientific problem. This is due to the sequence of interconnected events that occur during laser irradiation (such as plasma formation and bubble dynamics), and how energy is absorbed and transferred. As a result, progress in understanding ultrafast laser-liquid interactions has been relatively less explored.^[77, 78]

Nowadays, the aqueous laser-induced breakdown has become popular in the scientific community, especially in terms of nanomaterial synthesis,^[69, 79] pulsed cellular microsurgery and micromanipulation,^[80] and in-situ monitoring and analysis of aqueous samples.^[81, 82] Thanks to the ultrashort pulse durations in the femtosecond range, ultrafast lasers can transfer energy to a confined local volume within the liquid before thermal dissipation begins. Because the energy

is concentrated both spatially (localized) and temporally (within fs), the intensity is extremely high. This high intensity triggers nonlinear optical effects and leads to the dominance of nonlinear optical processes (like multiphoton absorption and avalanche ionization) on molecules of the liquid. The laser-induced plasma generated during this interaction process can lead to molecular dissociation, resulting in subsequent chemical changes.^[83] Therefore, ultrafast lasers allow for more molecular-level in situ investigation compared to other conventional techniques.^[81, 84]

Experimental and theoretical studies of aqueous laser-induced breakdown have focused on the following domains:^[85] The multi-photon absorption threshold for optical breakdown in aqueous media, the properties and time evolution of the resulting plasma, and the cavitation and shock wave phenomena that follow plasma breakdown. First, the concept of multiphoton absorption, which initiates optical breakdown, will be explained.

2.3.2 Multiphoton Absorption

Multiphoton absorption (MPA) is a nonlinear optical process that develops beyond classical linear optical absorption and occurs under high-intensity laser light (MW/cm^2 - GW/cm^2).^[83, 85] In linear absorption, the energy of a single photon is sufficient for an electron to transition to a higher energy level. In MPA, however, this transition requires the simultaneous absorption of multiple photons (usually two or three) since the interacted dielectric material is transparent to the laser wavelength (**Figure 2.10**). While the energy of each photon alone is not sufficient to cross the energy gap, when they act together, they enable the transition through virtual intermediate states.^[83, 85, 86]

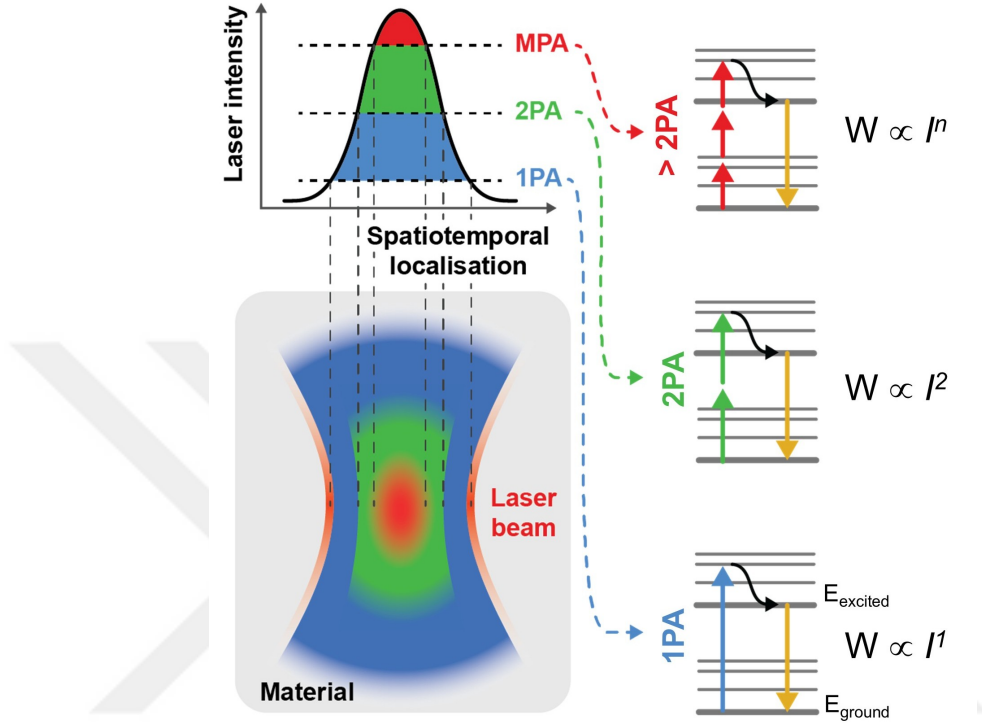


Figure 2.10: Schematic illustration of multiphoton absorption by an ultrafast laser. Adapted from the reference [29].

MPA is achieved with ultrashort laser pulses in the time scale of femtoseconds (fs) and picoseconds (ps). These pulses can operate at low average power despite having high peak irradiance. This is because the probability of MPA depends strongly on the intensity of the laser beam. Therefore, MPA provides energy transfer localized in the center of the focused laser light as shown in the Figure 2.10.[83, 85]

Laser-induced breakdown is a process that causes plasma formation in dense matter (solid, liquid or gas) under the effect of laser beam.[83, 85] This process is triggered either by direct multi-photon ionization or by a chain process called "avalanche ionization".[85, 86] Avalanche ionization proceeds by generating more free carriers as a result of laser excitation of free carrier seeds (such as electrons)

in the medium. For this, some free electrons must be present in the medium beforehand. However, in some cases (for example, very pure media or very short-pulsed lasers), these free electrons are not present. In this case, the necessary electrons are created with MPA. Under this condition, the threshold value of MPA is the minimum light intensity required for the system to undergo optical breakdown.^[77, 85, 86]

The multiphoton absorption (MPA) threshold depends on the photon energy, the ionization potential of the medium, laser wavelength, pulse duration, and intrinsic material constants. At ultrashort pulse durations (femtosecond regime), the time required for avalanche or cascade ionization to build up becomes insufficient, making multiphoton ionization the dominant mechanism for laser-induced breakdown in transparent media.^[86]

2.3.3 Nonlinear Optical Breakdown in Aqueous Medium

Laser-induced breakdown (LIB) in liquid media usually starts with a plasma process which is triggered by the absorption of electromagnetic energy in an optically transparent medium (e.g. pure water) to form free electrons. The chain of physical events that occur in the liquid during LIB includes plasma formation, plasma expansion, shock wave generation, and the formation of cavitation bubbles.

Laser-induced breakdown (LIB) in liquid media begins when the laser light reaches a sufficient intensity (MPA threshold) in the focal volume of the liquid to overcome the dielectric strength of the medium, as shown in **Figure 2.11**. This interaction, which typically occurs at nanometer wavelengths and on picosecond to femtosecond time scales, is first initiated by plasma formation. In the stage following the formation of the plasma, the plasma volume under high temperature and pressure begins to expand suddenly. This expansion is adiabatic and sends a shock wave with supersonic speeds against the surrounding liquid.^[85, 86]

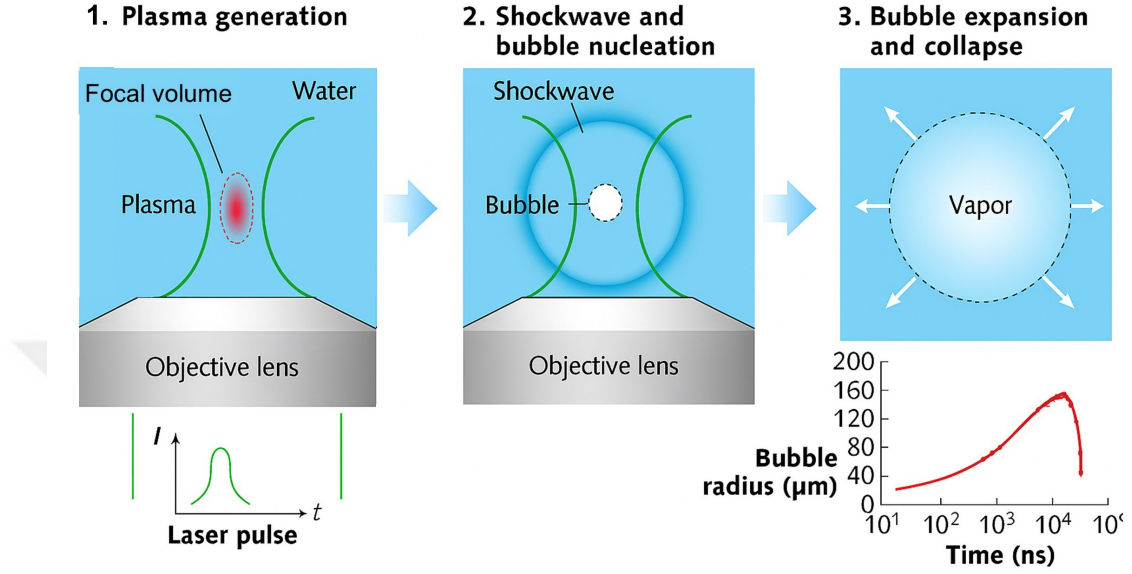


Figure 2.11: Depiction of the creation of laser-induced cavitation bubbles from the laser-induced plasma. Adapted from the reference [87].

The shock wave spreads outward as a pressure wave around the plasma and creates large pressure gradients in the medium in a short time. The speed of this shock front is initially well above the speed of sound and gradually fades and turns into an acoustic wave. This shock wave causes the liquid surrounding the plasma volume to compress and causes sudden volumetric changes. When the laser pulse ends, the plasma loses its energy and cools rapidly, and the plasma disappears as a result of the recombination of ions and electrons. However, during this time, the surrounding liquid may have been vaporized by the thermal energy of the plasma; this large volume region in the vapor phase forms the core of the cavitation bubble (Figure 2.11) with two characteristics; transient high-temperature (10^4 K) and ultrafast cooling (10^8 K/s).^[85, 88]

A cavitation bubble is a suddenly expanded vapor space in a liquid. The high internal pressure and temperature resulting from plasma expansion push the surrounding liquid outward. Thus, the cavitation bubble expands rapidly.

When the internal pressure of the bubble drops below the static pressure of the surrounding liquid, i.e. when the gas inside cools and its density decreases, the bubble enters the collapse phase.^[85]

Thermal gradients ($\sim 10^6 \text{K mm}^{-1}$) on the surface, especially when the laser is focused on the liquid–gas or liquid–solid interface (i.e., symmetry-breaking), disrupt the surface tension and stimulate Marangoni flow.^[89, 90] Marangoni flow arises from temperature-dependent changes in surface tension and causes the liquid to flow from a hot region of low surface tension to a cold region of high surface tension. Such convective flows usually form circular or vortical structures on length scales ranging from a few microns to hundreds of microns.^[89] This process can be amplified by thermocapillary effects caused by laser-induced heating, both on the surface and throughout the volume. In addition, sudden pressure changes during the collapse of cavitation bubbles can transform these flows, leading to quite complex microdynamic patterns.^[89, 91]

In this thesis study, Zeolite A crystals (LTA framework type) was synthesized using femtosecond laser (300 fs) to provide energy flux. The use of transparent precursor suspension and glass vial-insert enables the multiphoton absorption at 1040 nm wavelength. As a result of this interaction, various physical processes such as plasma formation, cavitation bubbles, shock waves and laser-induced convective flows occur. These processes play a critical role in zeolite crystal formation by triggering energy transfer and chemical reactions. The experimental setup used in the synthesis, the applied procedures and energy deposition calculations are presented in Chapter 3; and the details regarding the synthesis mechanism are presented in Chapter 4.1 in detail.

Chapter 3

Methods

3.1 Experimental Set-up

Zeolite A syntheses are carried out in vial (Isolab, N13 vial, 4 mL)-inserts (Restek, WISP-48, 500 μL) that function as closed systems for femtosecond laser (Spectra Physics, Spirit One, 1040–8 SHG) irradiation. The laser's central wavelength is set to 1040 nm and pulse repetition rate is set to 200 kHz. Through an optical path, the laser beam is directed into the reaction vial, which is suspended in air by attaching a sample holder to the cap of vial. Immediately after the beam is coming out of the laser, it follows the optical path by hitting on a mirror that directs it to beam expander. Then, it is directed to a half-wave plate and beam splitter enabling beam attenuation for power regulation. Lastly, the beam passes through a 1-inch convex lens with a focal length of 5 cm and focuses on the glass-liquid interface. The beam diameter was measured to be approximately 9 μm using the Thorlabs beam profiler.

3.2 Mass Composition Calculations

3.2.1 Chemicals

The chemicals used in this project as follows:

- Tetraethylorthosilicate (TEOS, 98%, Sigma Aldrich),
- Aluminum isopropoxide ($\text{Al}(\text{iPro})_3$, >98 %, Sigma Aldrich),
- Tetramethylammonium hydroxide (TMAOH, 25 wt. %, Sigma Aldrich),
- Deionized distilled water (DDI H_2O , resistivity = 18.2 $\text{M}\Omega$),
- Sodium hydroxide (NaOH, 99%, Merck).

N13 vials and their compatible inserts were purchased from ISOLAB and Restek Corporation, respectively.

3.2.2 Calculations

In order to prepare a precursor suspension corresponding to a specific molar formula, the amounts of all chemical components to be included in the precursor suspension must be carefully calculated in terms of weight units (grams). In these calculations, the molar ratio and density of each compound are taken into account. In this study, the $\text{Al}(\text{iPro})_3$: 3.09 TEOS: 7.36 TMAOH: 0.33 NaOH: 192.41 H_2O molar formula was used for the synthesis of Zeolite A and the molar composition of the precursor suspension was calculated according to this molar formula as in Table 3.1.

Table 3.1: Molar composition of chemicals required to form the precursor suspension of the zeolite A.

Chemicals	1 mol $Al(iPro)_3$	3.09 mol TEOS	7.36 mol TMAH (25 wt %)	0.33 mol NaOH	192.41 mol H_2O
1 $Al(iPro)_3$	1 mol -1 mol				
3.09 TEOS		3.09 mol - 3.09 mol			
7.36 (TMAH + 15.19 H_2O)			7.36 mol - 7.36 mol		192.41 mol -111.8 mol
0.33 NaOH				0.33 mol - 0.33 mol	
80.16 H_2O					80.16 mol - 80.16 mol

The amount of water contained in the suspension during the synthesis process is a fundamental parameter that directly affects the alkalinity of the system. Alkalinity plays a decisive role on the crystal growth rate and the average size of the formed zeolite crystals.^[29]

For this zeolite A molar formula in the above, the required mass amounts are determined by multiplying the molar ratio of each compound by its density. By preserving these mass ratios as in the Table 3.2, the precursor suspension required for the synthesis of Zeolite A can be prepared.

Table 3.2: Mass composition of chemicals required to form the precursor suspension of the zeolite A.

Compound Formula	Moles	FW (g/mol)	Mass (g) ^a	Density (g/mL)	Volume ^b (mL)	Volume (%)
Al(iPro) ₃	1.00	208.42	208.42	1.035	201.372	4.027
TEOS	3.09	212.58	656.87	0.933	704.04	14.078
TMAOH · 15.19 H ₂ O	7.36	364.57	3683.46	1.016	2640.98	52.808
NaOH	0.33	40.40	13.30	1.13	11.80	0.236
H ₂ O	80.16	18.00	1442.88	1.00	1442.88	28.852

^aMass = Moles × Formula Weight.

^bVolume = Mass / Density.

The volumetric ratios, molarities and weight contributions of the compounds in the prepared precursor suspension solution are summarized in Table 3.3 to develop a systematic synthesis approach and to calculate pulse energy deposition values in the Chapter 3.5.

Table 3.3: Molarities of compounds in the precursor suspension of zeolite Na-LTA.

Compound Formula	Moles	MW (g/mol)	Mass (g) ^a	Molarity (mol/L solution) ^b
Al_2O_3	0.50	101.96	50.98	0.100
SiO_2	3.09	60.08	183.85	0.612
TPAOH	7.36	91.154	670.89	1.472
Na_2O	0.165	61.98	10.23	0.033
H_2O	192.41	18.00	3463.38	38.482

^aMass = Moles $\times$ MW (molecular weight).

^bMolarity = Moles / Volume of solution (5.001 L).

3.3 Synthesis Procedure

Zeolite As are synthesized from the precursor suspension with molar composition: $Al(iPro)_3$: 3.09 TEOS: 7.36 TMAOH: 0.33 NaOH: 192.41 H_2O . To prepare precursor suspension, DI water (0.95 g) is added to TMAOH (2.17 g, 25 wt%) and agitated for 20 min. Subsequently, $Al(iPro)_3$ (0.17 g) is slowly added to the mixture and stirred with a magnetic stirrer for 1 hour. TEOS (0.53 g) is then added, and the mixture is stirred for 2 hours. In a separate beaker, NaOH (0.01 g) and DI water (0.23 g) are mixed and added dropwise to the final mixture. Lastly, the final mixture is aged at room temperature for 15 hours under stirring. After aging, 400 μ L of the precursor suspension is placed in an oven at 100 °C for 8

hours for hydrothermal treatment. Another 400 μL of the precursor suspension in the vial insert is ultrafast laser-treated (Spectra-Physics, 200 kHz repetition rate, 5 W average power) for 4 hours. After ultrafast laser treatment, the samples are separated into precipitated and supernatant parts. Precipitated parts are washed four times with DI water to lower the pH to ~ 7 by centrifugation (14000 rpm, 7 min, Eppendorf Centrifuge 5420), and dried overnight at 45 $^{\circ}\text{C}$.

3.4 Energy Deposition Calculations

It is important to know how much of the laser power the precursor suspension absorbs in order to calculate energy deposition values. Therefore, 400 μL of Zeolite A precursor suspension, which has a blurry-transparent color and was prepared by the molar formula and procedure described in Section 3.3, was used. The usual synthesis conditions were provided for energy absorption experiments. First, a repetition rate of 200 kHz was used and data were collected for power ranging from 1 Watt to 6 Watt (see **Appendix A**). After the first bubble formation, the output power was recorded. The average power absorption was calculated in the same way as our previous work.^[29]

In the glass vial–glass insert–precursor suspension system, the laser beam passes through multiple media (glass, air, suspension) with different refractive indices, experiencing various optical effects such as reflection, scattering, and absorption at each interface and medium as shown in the **Figure 3.1**. The laser beam first hits the glass vial and undergoes Fresnel reflection at the air–glass vial interface because of different refractive indices (n_1 and n_2). It then transmits the air gap and hits the glass insert, where it is reflected again at the glass insert–suspension interface in a similar manner (n_2 and n_3). In the glass insert–precursor suspension interface, where the laser light focuses, not only linear absorption but also nonlinear processes such as multi-photon absorption. It causes significant

losses in light power. The liquid medium, on the other hand, causes light scattering. After exiting the suspension, the laser beam follows the glass-air transition again with similar reflections, ultimately reaching the power meter.

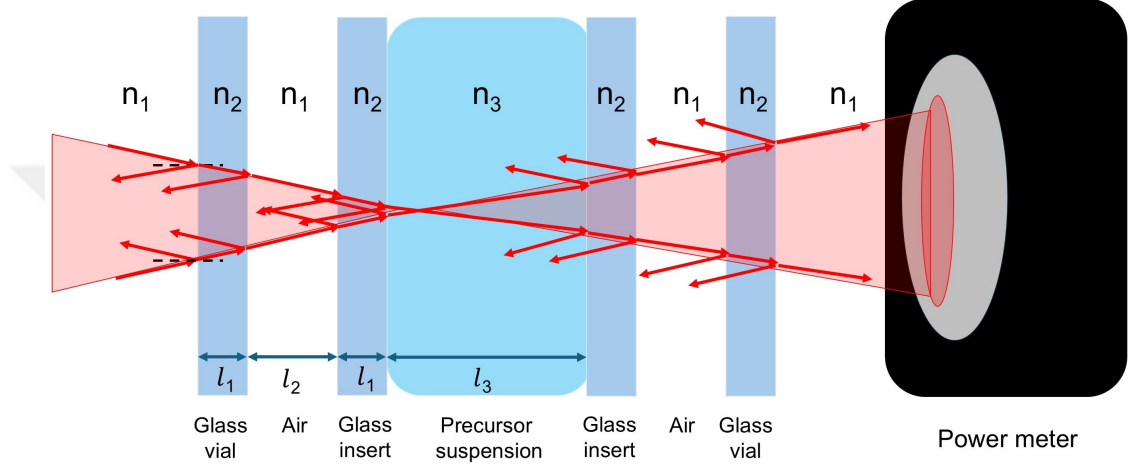


Figure 3.1: Illustration of the transmitted laser light through the vial-insert-precursor suspension system and its power loss due to the reflection, absorption, and scattering by the medium and interfaces.

Therefore, to roughly calculate the power losses that occur in the glass vial–glass insert–precursor suspension system, five different measurements were performed. These measurements were performed to calculate the power loss in the system due to: (i) light reflection by the air–glass vial interface, (ii) light reflection by the air–glass insert interface, (iii) light absorption and scattering by the glass insert, (iv) light reflection by the glass insert–water interface, and (v) light absorption and scattering by water.

In the first measurement to estimate the power loss due to the air–glass vial interface, 5.4 W laser power is passed through the glass vial (IsoLab, N13 vial) and the power meter measured the laser power as 4.75 W after passing through the glass vial. The transmittance of the front glass of the vial, which the laser first passes through, is T_1 , and the transmittance of the back glass, which it then

passes through before reaching the power meter, is T_2 . Since the laser is not focused on the glass vial, the transmittance of the front and back glass of the vial can be taken as equal, i.e., $T_1 = T_2$. Thus, T_1 can be estimated as:

$$5.4 \text{ W} \times T_1 \times T_2 = 4.75 \text{ W} , \text{ where } T_1 = T_2 \quad (3.1)$$

$$T_1 = \sqrt{\frac{4.75 \text{ W}}{5.4 \text{ W}}} = 0.938 \quad (3.2)$$

the transmittance of the one thin glass vial wall is 93.8 %.

In the second measurement to estimate the power loss due to the air-glass insert interface, 5.4 W laser power is passed through the glass insert (Sentez Lab, 500 μL) too and the power meter measured the laser power as 4.54 W after passing through the glass insert. The transmittance of the front glass of the insert, which the laser first passes through, is T_3 , and the transmittance of the back glass, which it then passes through before reaching the power meter, is T_4 . Since the laser is not focused on the glass insert as in the first measurement, the transmittance of the front and back glass of the insert can be taken as equal too, i.e., $T_3 = T_4$. Therefore, T_3 can be estimated as:

$$5.4 \text{ W} \times T_3 \times T_4 = 4.54 \text{ W} , \text{ where } T_3 = T_4 \quad (3.3)$$

$$T_3 = \sqrt{\frac{4.54 \text{ W}}{5.4 \text{ W}}} = 0.917 \quad (3.4)$$

the transmittance of the one thin glass insert wall is 91.7 %.

In the third measurement to estimate the power loss due to the light absorbed and scattered by glass insert, 5.4 W laser power is focused on the glass insert and the power meter measured the laser power as 3.85 W. Since the laser is focused on the glass insert, and the transmittance of the front and back glass of the insert

is known, the total ratio of the light absorbed and scattered by the glass insert (A_1) can be estimated as:

$$5.4 \text{ W} \times T_3 \times T_4 \times (1 - A_1) = 3.85 \text{ W} , \text{ where } T_3 = T_4 = 0.917 \quad (3.5)$$

$$(1 - A_1) = \frac{3.85 \text{ W}}{5.4 \text{ W} \times 0.917^2} = 0.848 \quad (3.6)$$

Hence, the total ratio of the light absorbed and scattered by the glass insert, A_1 , is estimated as 15.2 %.

In the fourth measurement to estimate the power loss due to the glass insert-water interface, 5.4 W of laser power was passed through the glass insert and the DI water inside it, and the power meter measured the laser power as 4.5 W after passing through the glass insert and the water inside. Because the refractive indices of the glass insert and water are close to each other and the fluctuations in the measured laser power are within the error range, the transmittance of the glass insert-water interface (T_5) was theoretically calculated and used as 0.996.

In the fifth measurement to estimate the power loss due to the light absorbed and scattered by the glass insert-water interface, 5.4 W of laser power was focused on the glass insert-water interface and the power meter measured the passed laser power as 2 W. Since the transmittance of the front and back glass of the insert, and transmittance of water are known, the total ratio of the light absorbed and scattered by the glass insert-water interface (A_2) can be estimated as:

$$5.4 \text{ W} \times T_3 \times T_4 \times T_5 \times (1 - A_2) = 2 \text{ W} , \text{ where } T_3 = T_4 = 0.917 \text{ and } T_5 = 0.996 \quad (3.7)$$

$$(1 - A_2) = \frac{2 \text{ W}}{5.4 \text{ W} \times 0.917^2 \times 0.996} = 0.442 \quad (3.8)$$

Therefore, the total ratio of light absorbed and scattered by the glass insert-water interface, A_2 , is estimated to be 55.77%. According to the third measurement, the total ratio of light absorbed and scattered by the glass insert, which was 15.2%, increased to 55.77% with the inclusion of water, although both have similar refractive indexes. This indicates that in this system using fully transparent glass and water, there is more power loss due to scattering than absorption.

To find the average input power on the precursor solution, transmittance of the interfaces should be included, like:

$$P_{in} = 5.4 \text{ W} \times T_1 \times T_3 \times T_5 \times (1 - A_2) \quad (3.9)$$

$$P_{in} = 5.4 \text{ W} \times 0.938 \times 0.917 \times 0.996 \times 0.442 = 2.045 \text{ W} \quad (3.10)$$

The output power from the system was detected via a power meter and was equal to 0.53 Watt for the same reference synthesis. To find the average output power from the precursor solution, loss from the interfaces should be included, like:

$$P_{out} = 0.53 \text{ W} / (T_2 \times T_4 \times T_5) \quad (3.11)$$

$$P_{out} = 0.53 \text{ W} / (0.938 \times 0.917 \times 0.996) = 0.618 \text{ W} \quad (3.12)$$

Then, the average power absorbed by the precursor solution is the difference of the average input power on the precursor and the average output power from the precursor.

$$P_{in} - P_{out} = 1.427 \text{ W} \quad (3.13)$$

Hence, approximately 26.4% of incident laser beam is absorbed by this precursor suspension.

Since we know the molarity of silica (SiO_2) and alumina (Al_2O_3) in the precursor solution from the Table 3.3, we can calculate the energy incident per mole of silica and alumina. However, to do this, the interaction volume, where zeolite polymerization reactions, nucleation, and crystal growth take place, need to be determined. The interaction volume can be estimated by assuming a Gaussian irradiance distribution for the ultrafast laser beam and modeling it as a cylinder, with the cylinder's diameter equal to the laser spot size and its height equal to the confocal parameter.

The confocal parameter is twice the Rayleigh length, which is the distance along the direction of the beam from the point where the beam is the narrowest (called the beam waist) to the point where the cross-sectional area of the beam has doubled as expressed in the equation:^[92]

$$z_R = \frac{\pi\omega_0^2}{\lambda} \quad (3.14)$$

where ω_0 is the radius of the beam waist (half of the spot size which was measured to be $9 \mu\text{m}$ by using a Thorlabs beam profiler), and λ is the wavelength of the laser light (1040 nm). Then, the Rayleigh length is:

$$z_R = \frac{\pi(4.5 \times 10^{-6} \text{ m})^2}{(1040 \times 10^{-9} \text{ m})} = 61.1 \mu\text{m} \quad (3.15)$$

Hence interaction volume is:

$$V_i = \frac{4}{3}\pi\omega_0^2 z_R = \frac{4}{3}\pi(4.5 \times 10^{-6} \text{ m})^2(61.1 \times 10^{-6} \text{ m}) = 5.18 \times 10^3 \mu\text{m}^3 \quad (3.16)$$

In almost all of the syntheses, precursor suspension in the vial insert was $400 \mu\text{L}$. That's why, $400 \mu\text{L}$ is taken as total volume and mol of silica (SiO_2) and alumina (Al_2O_3) distributed within the interaction volume is:

$$n_{\text{SiO}_2} = (7.77 \times 10^{-6} \text{ mm}^3) \frac{0.612 \text{ mol SiO}_2}{10^{-6} L} \quad (1 \text{ mm}^3 = 10^{-6} L) \quad (3.17)$$

$$n_{SiO_2} = 4.755 \times 10^{-6} \mu\text{mol} = 4.755 \text{ pmol SiO}_2 \quad (3.18)$$

$$n_{Al_2O_3} = (7.77 \times 10^{-6} \mu L) \frac{0.1 \text{ mol Al}_2\text{O}_3}{10^{-6} L} \quad (3.19)$$

$$n_{Al_2O_3} = 0.777 \times 10^{-6} \mu\text{mol} = 0.777 \text{ pmol Al}_2\text{O}_3 \quad (3.20)$$

The interaction energy represents the interaction of each laser pulse with the molecules in the interaction volume. The energy deposited by the laser into the precursor suspension within the interaction volume can be determined by dividing the energy of each laser pulse by the number of moles of silica and alumina in the interaction volume.

$$\text{Pulse Fluence (J/cm}^2\text{)} = \frac{\text{Pulse Energy (J)}}{\text{Spot area (cm}^2\text{)}} \quad (3.21)$$

Since approximately 26.4% of incident laser power is absorbed by the precursor suspension (i.e., 1.32 W), pulse energy can be estimated as:

$$\text{Pulse Energy} = \frac{P_{\text{average}}}{\text{Repetition Rate}} = \frac{1.32 \text{ W}}{200 \text{ kHz}} = 6.6 \times 10^{-6} \text{ J} \quad (3.22)$$

$$\text{Pulse Fluence (J/cm}^2\text{)} = \frac{6.6 \times 10^{-6} \text{ J}}{6.36 \times 10^{-7} \text{ cm}^2} = 10.38 \text{ J/cm}^2 \quad (3.23)$$

$$E_i = \frac{\text{Pulse Energy}}{n_{SiO_2} \text{ or } n_{Al_2O_3}} \quad (3.24)$$

Previously, we have calculated the pulse energy of the laser with the reference laser parameters (Rep. rate = 200 kHz, average laser power = 5 W, reaction time = 4 hours) as 6.6 μ J and mols of silica and alumina from Equation(3.18) and Equation(3.20). Hence, the interaction energy is:

$$E_{i, SiO_2} = \frac{6.6 \mu J}{4.755 \text{ pmol SiO}_2} = 1.39 \text{ MJ/mol SiO}_2 \quad (3.25)$$

$$E_{i,Al_2O_3} = \frac{6.6\mu J}{0.777 \text{ pmol } Al_2O_3} = 8.5 \text{ MJ/mol } Al_2O_3 \quad (3.26)$$

3.5 Characterization Methods

3.5.1 Scanning Electron Microscopy

The morphology of the Zeolite A crystals was analyzed by scanning electron microscopy (SEM, FEI Quanta 200F, 30 kV accelerating voltage, 15 nm Au/Pd coated). The samples were prepared by centrifuging the aqueous solutions of zeolites collected immediately after synthesis, dropping one drop onto a stub and drying overnight. To prevent charging, 15 nm Au/Pd was coated on SEM stubs with zeolite samples by Gatan 682 Precision Etching Coating device. The particle size was determined by taking an average of at least 300-400 zeolite particles per sample from several SEM images through Image J software.

Si/Al ratios of the Zeolite A crystals (no coating) were determined by Energy-dispersive X-ray spectroscopy (EDXS) with Genesis Apex 4 EDAX coupled with Quanta FEI 200F SEM at 10 kV voltage.

3.5.2 X-Ray Diffraction

X-ray diffraction patterns of the powder Zeolite LTA were measured by Malvern Panalytical X'Pert Pro Multipurpose X-ray diffractometer with Cu K α radiation (operating at 45 kV, 40 mA) in the 2θ range of 5°-50°. In order to make quantitative comparison for relative crystallinity % from XRD patterns, 2 mg of zeolite powder was used in each XRD measurement.

3.5.3 High-Resolution Transmission Electron Microscopy

In order to reveal the crystalline nature of zeolite A synthesized via the ultrafast method, high-resolution transmission electron microscopy (HR-TEM) analysis was performed. HR-TEM images were recorded through TECNAI G2 20 S TWIN Transmission Electron Microscope by FEI company at a high tension of 200 kV. The zeolite A powder samples have been dispersed in ethanol and dropped on copper TEM grids. Moreover, selected area electron diffraction (SAED) pattern is acquired.

3.5.4 Thermo-gravimetric Analysis

Thermogravimetric-differential thermal analysis (TG-DTA) for thermal stability analysis, zeolitic water, and organic structure directing agent (TMA) contents determination was performed using SDT650 TGA-DSC (at 25° - 900° C temperature range, heating rate of 5° C/min). Differential thermal analysis (DTA) was obtained by taking the differential of TGA graphs using OriginLab Software.

3.5.5 Brauenner-Emmet-Teller Analysis

The Brunauer-Emmett-Teller (BET) method was applied to determine the total surface area of the Na-LTA crystals was determined by utilizing the Quantachrome Autosorb IQ2 MP Gas Sorption system (employing N₂ adsorption-desorption isotherm at 77.3 K). Before measurement, the sample underwent outgassing at 300°C for 16 hours. BET and V-t methods are used to obtain total surface area and micropore surface area, respectively. The Barrett-Joyner-Halenda (BJH) and Density Function Theory (DFT) methods determined micropore volume and pore size distribution.

3.5.6 Fourier Transformed Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy was used to examine the functional groups and characteristic fingerprint vibrations of the Zeolite A samples synthesized via both ultrafast laser and hydrothermal method. Measurements were performed using a Bruker TENSOR 37 spectrometer in transmission mode. During sample preparation, Zeolite A powder was first finely ground and then homogeneously mixed with spectroscopically pure potassium bromide (KBr) at a 1:100 weight ratio. This mixture was pressed for 3–5 minutes using a Carver 4350L hydraulic press under approximately 8 tons of pressure, resulting in transparent pellets. FTIR measurements were performed in the mid-IR region, covering the 4000–400 cm^{-1} range, with a spectral resolution of 4 cm^{-1} . The background spectrum was taken from the empty hole under the same conditions and was automatically subtracted from the sample spectrum during measurement. All analyses were performed at ambient conditions.

3.5.7 CO_2 Adsorption Analysis

CO_2 capture measurements were conducted using the CatLab-2, a fully automated catalyst characterization system by Specson Instruments. It is equipped with five Bronkhorst Mass Flow Controllers and a fixed-bed quartz tubular reactor, connected to an SRS RGA 200 mass spectrometer for real-time gas analysis. To capture CO_2 , 100 mg of each zeolite A synthesized via ultrafast laser and conventional hydrothermal method is placed inside a quartz reactor, and each sample undergoes thermal activation before adsorption tests. This involves heating the sample to 350°C with an argon flow for 2 hours, cooling to ambient temperature, and stabilizing under continuous argon flow for 60 minutes. A mixture containing 2% CO_2 in argon gas is introduced into the reactor at a flow rate of 20 sccm, maintaining room temperature and pressure for 3 hours. The mass spectrometer continuously tracks the m/z 44 signal, providing real-time data for dynamic

breakthrough curves.



Chapter 4

Result & Discussion

4.1 Zeolite Synthesis Mechanism

The Zeolite A precursor suspension prepared by the procedure described in Chapter 3.1 is placed in the experimental setup described in Chapter 3.4 to perform the synthesis. The synthesis begins by focusing a near-infrared femtosecond laser beam at the glass-liquid interface of the insert in which the precursor suspension placed. The laser pulses are absorbed in this region through multiphoton absorption, creating a extremely "hot zone" in a small-volume. This hot zone, which acts as an "ultrafast reactor," triggers silica polymerization/depolymerization reactions as shown in **Figure 4.1**.

Multiphoton absorption also initiates optical breakdown, leading to the formation of a transient plasma. This plasma significantly increases the local density of reactive species. The sudden expansion of the plasma when the pulse ends and the high temperature difference between the hot zone and the surrounding liquid cause the formation of cavitation bubbles in the precursor suspension. When these bubbles collapse, they emit shock waves, increasing the mixing and homogeneity of the medium. These thermal gradients and shock waves then give rise

to a strong convective flows.

Moreover, the symmetry breaking and the temperature gradients created by focusing the laser at the glass-liquid interface trigger the Marangoni convection. The laser creates localized temperature gradients both at the surface and within the regions of the liquid where the laser light can penetrate, and these gradients further enhance convection due to thermocapillary effects. The resulting high-speed convective flows transport the building blocks and clusters assembled in the precursor suspension from the hot zone to the surrounding bulk liquid (Figure 4.1). This heat and mass transfer creates a dynamic synthesis environment that supports crystal growth.

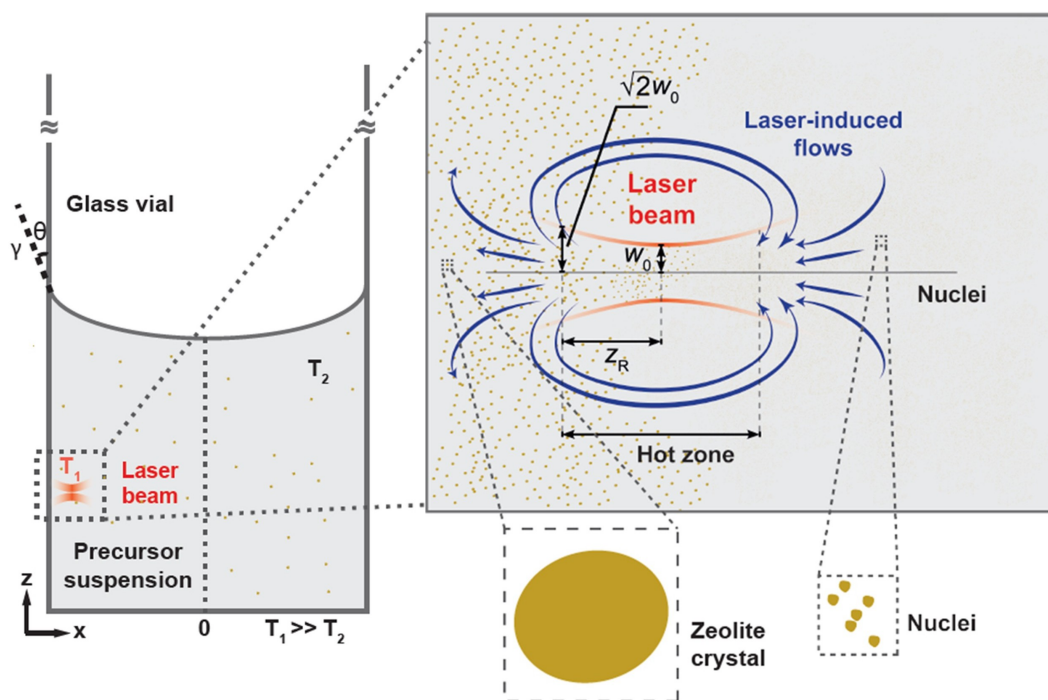


Figure 4.1: Schematic showing the working mechanism of a small ultrafast reactor in which zeolite crystals are produced at the glass-liquid interface. Adapted from the reference [29].

As explained in detail in our recent article, the small reactor volume allows

the average temperature throughout the system to remain low.^[29] This allows a large temperature difference to be maintained between the hot zone and the surrounding liquid and supports the continuity of the convective flows. All of these interactions support the laser-driven assembly process, enabling the rapid and controlled nucleation and growth of zeolite crystals.

4.2 Morphology and Particle Size Distribution Analysis

To investigate the morphology and particle size distribution of Zeolite A synthesized via both ultrafast laser and hydrothermal methods scanning electron microscopy (SEM) analysis was performed. The SEM images of zeolite A nanocrystals synthesized by both methods show discrete, and fully crystalline structures. A cubic crystal morphology is expected for zeolite A crystals in the literature.^[5, 32, 38] Although the average size of the crystals < 300 nm, sharp corners typical of micron-sized crystals are observed in SEM images of zeolite A crystals synthesized by ultrafast laser method in **Figure 4.2** while the rounding of corners observed in nano-sized crystals is observed in SEM images of zeolite A crystals synthesized by hydrothermal method.^[57, 93] The apparent differences in the morphology of crystals synthesized by these two methods is attributed to the fact that the mass and heat transfer in the ultrafast laser method is quite different from that in the hydrothermal method.

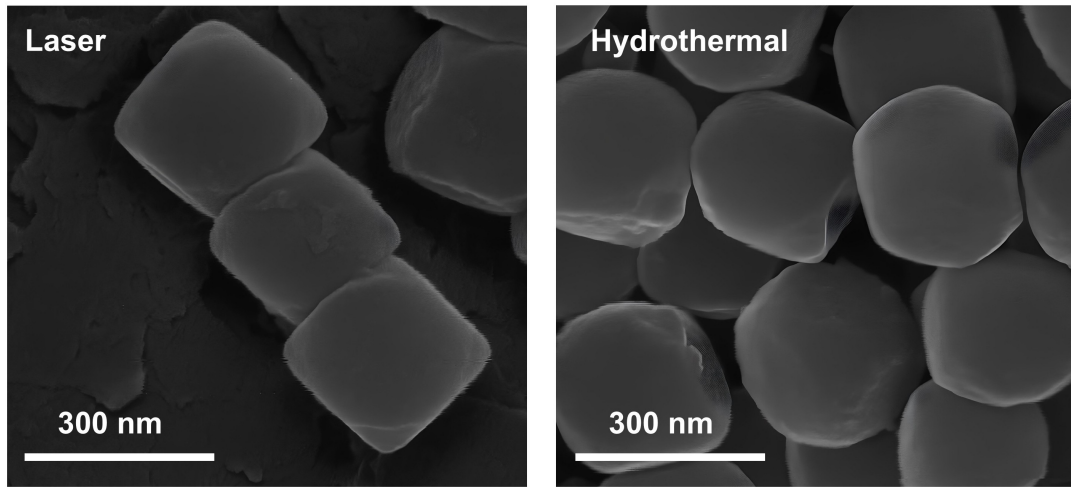


Figure 4.2: SEM images of zeolite A synthesized via ultrafast laser method (laser) and hydrothermal method (hydrothermal).

The laser induced-flows driven heat and mass transfer also play a critical role in achieving a narrow particle size distribution. These effects are clearly observable in the SEM images (**Figure 4.3-a** and **Figure 4.3-b**); while the zeolite A crystals synthesized via the ultrafast laser method are more regular and uniform, more variation in size and morphology is observed in the crystals synthesized via the hydrothermal method. This difference is also evident in the quantitative particle size distribution analysis in **Figure 4.3-c** and **Figure 4.3-d**. The zeolite A crystals synthesized via the ultrafast laser method and hydrothermal method have analyzed through ImageJ software to obtain particle size distribution.

According to this quantitative analysis, the average size (mean) $\pm$ standard deviation (σ) of zeolite A crystals synthesized by ultrafast laser method is 259.4 ± 42 nm, while the average size (mean) $\pm$ standard deviation (σ) of crystals synthesized by hydrothermal method is $247.3 \text{ nm} \pm 57 \text{ nm}$. According to the results, the zeolite crystals synthesized via ultrafast laser are roughly 10 nm larger. However, as can be understood from the coefficient of variation (CV (%))

$= (\text{Standard deviation}/\text{mean}) \times 100$) values and gaussian fit in the Figure 4.3-c) and Figure 4.3-d), the laser-induced synthesis mechanism provides a narrow particle size distribution and makes the crystal growth more controlled.

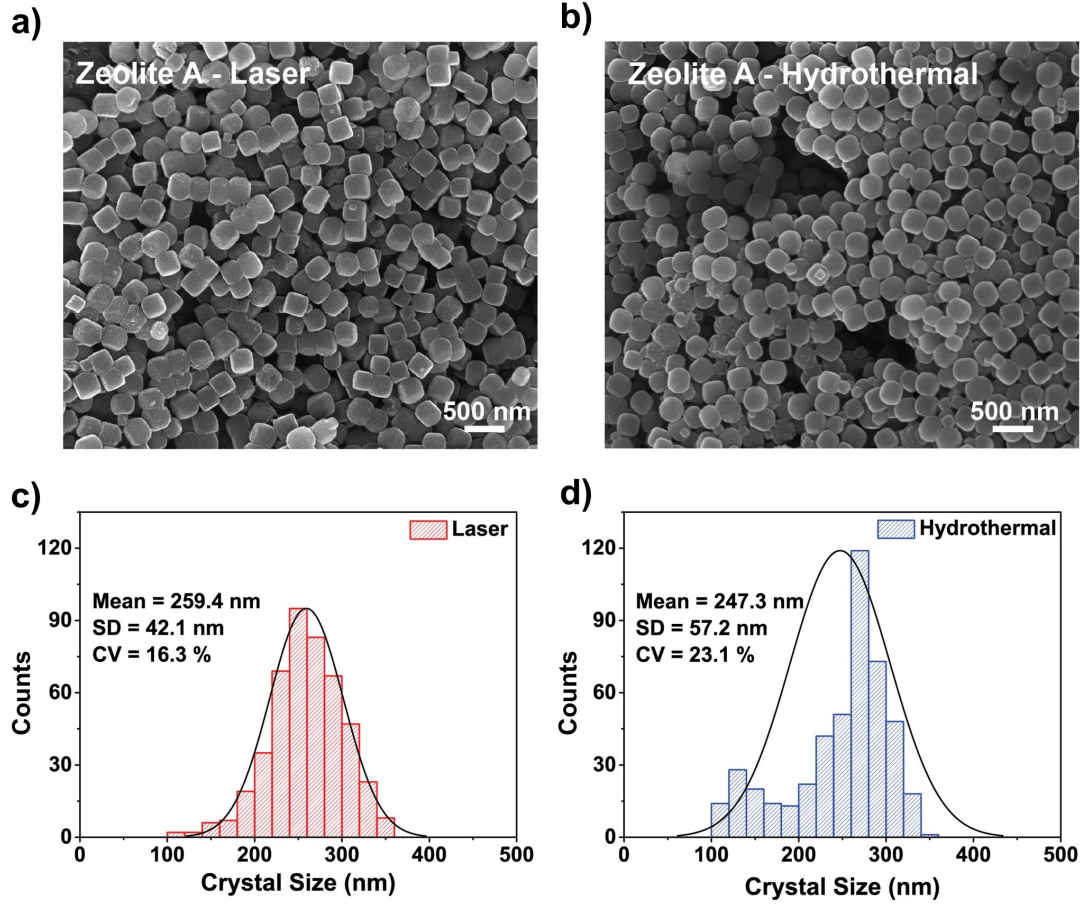


Figure 4.3: (a) SEM image and (c) particle size distribution analysis of the zeolite A synthesized via ultrafast laser method; and (b) SEM image and (d) particle size distribution analysis of zeolite A synthesized via hydrothermal method.

The most prominent effect of the laser-induced synthesis mechanism on zeolite crystals was explained in the previous section. Accordingly, we can hypothesize that all nuclei are formed at similar time intervals due to the continuous and balanced transfer of precursors to the hot zone by laser-induced high-speed convective flows (see **Figure 4.4**). Since the subsequent growth phase occurs on

the basis of synchronous nucleation and balanced mass transfer, etc., the uniform crystal sizes are obtained. Furthermore, laser-induced flows continuously transfer precursors to the nuclei (Figure 4.4), preventing local supersaturation and ensuring that growth is limited to existing crystals. Thus, the growth process proceeds in a controlled manner, and the resulting zeolite particles exhibit a narrower size distribution as observed in the Figure 4.3.

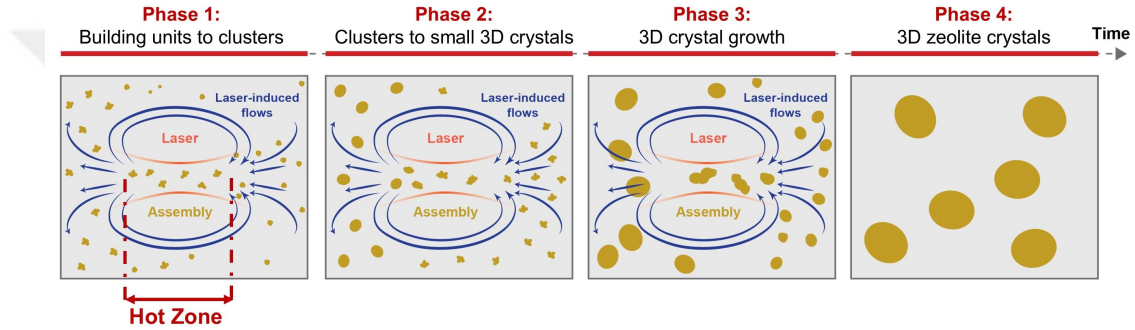


Figure 4.4: Schematic representation of the effect of laser-induced flows on the nuclei formation and growth of the zeolite crystals. Adapted from the reference [29].

During the optimization of synthesis parameters, after the color change from transparent precursor to milky began—indicating the start of the growth process—SEM images revealed that the nanoparticles grew in a direct attachment manner. In the SEM images in **Figure 4.5**, Zeolite A crystals have a characteristic cubic morphology. In addition, numerous small (> 15 nm) spherical nanoparticles are noticeable on the crystal surfaces and around them. This suggests that during the growth stage of Zeolite A synthesized via ultrafast laser method, the direct attachment of metastable aluminosilicate nanoparticles to the crystal surface was observed. This growth mechanism, involves the diffusion of precursor particles from solution, attachment to the crystal surface, and subsequent reorganization and integration into the crystal lattice,^[37, 39] which is consistent with our previous observations for TPA-Silicalite-1.^[29]

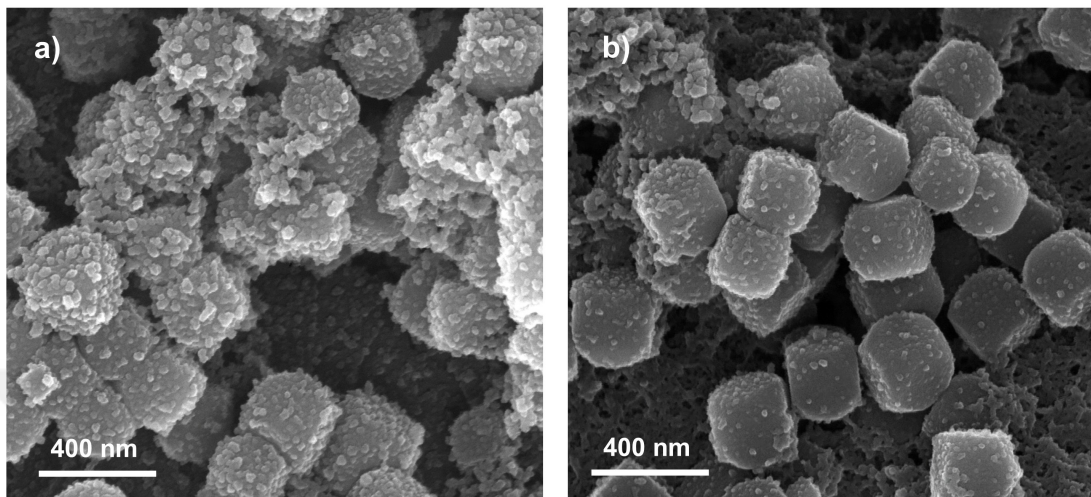


Figure 4.5: SEM images of zeolite A crystals in the growth process synthesized via ultrafast laser method.

In ultrafast laser synthesis, high energy density and rapid local heating enable the formation of a large number of nanoparticles from reactive species in the suspension in a short time. Laser-induced convective flows carry these precursor particles to the hot zone and direct them to the crystal surfaces. Therefore, the particles observed densely on the surfaces are not only residues of formation, but also active building blocks of growth. In addition, these flows contribute to the narrow size distribution and morphological control by ensuring that growth is simultaneous.

4.2.1 Si/Al Ratio Calculation from EDXS Analysis

The Si/Al ratio in zeolites is an important parameter that directly affects the composition of the crystal framework, and thus the acidic properties, ion exchange capacity and thermal stability.^[32, 94, 95] The change in this ratio generally depends on the synthesis conditions, especially the organic structure-directing agents (OSDA) used. For example, the syntheses using organic templates such as

tetramethylammonium (TMA^+), generally result in a $\text{Si}/\text{Al} \sim 2$ ratio.^[94, 96, 97] In contrast, in template-free (OSDA-free) syntheses, the Si/Al ratio is around 1.

The elemental chemical composition of LTA type zeolites synthesized via both ultrafast laser and hydrothermal method was analyzed using Energy Dispersive X-Ray Spectroscopy (EDXS) and the results are obtained by taking average of 8 different measured spectrum (see **Appendix B** for the spectrum) of calcined Zeolite A synthesized via both methods. The Si/Al ratio of ultrafast laser-synthesized zeolite A is determined as 1.61 and hydrothermally synthesized zeolite A as 1.59.

4.3 X-Ray Diffraction Analysis and Crystallinity Calculations

The main characterization of synthesized samples by the ultrafast laser method has been carried out by X-ray diffraction (XRD) pattern analysis. **Figure 4.6** illustrates XRD patterns for the zeolite A samples synthesized by hydrothermal (red) and ultrafast laser methods (green), and the reference pattern for zeolite A obtained from the International Zeolite Association (IZA) web page (blue).^[5]

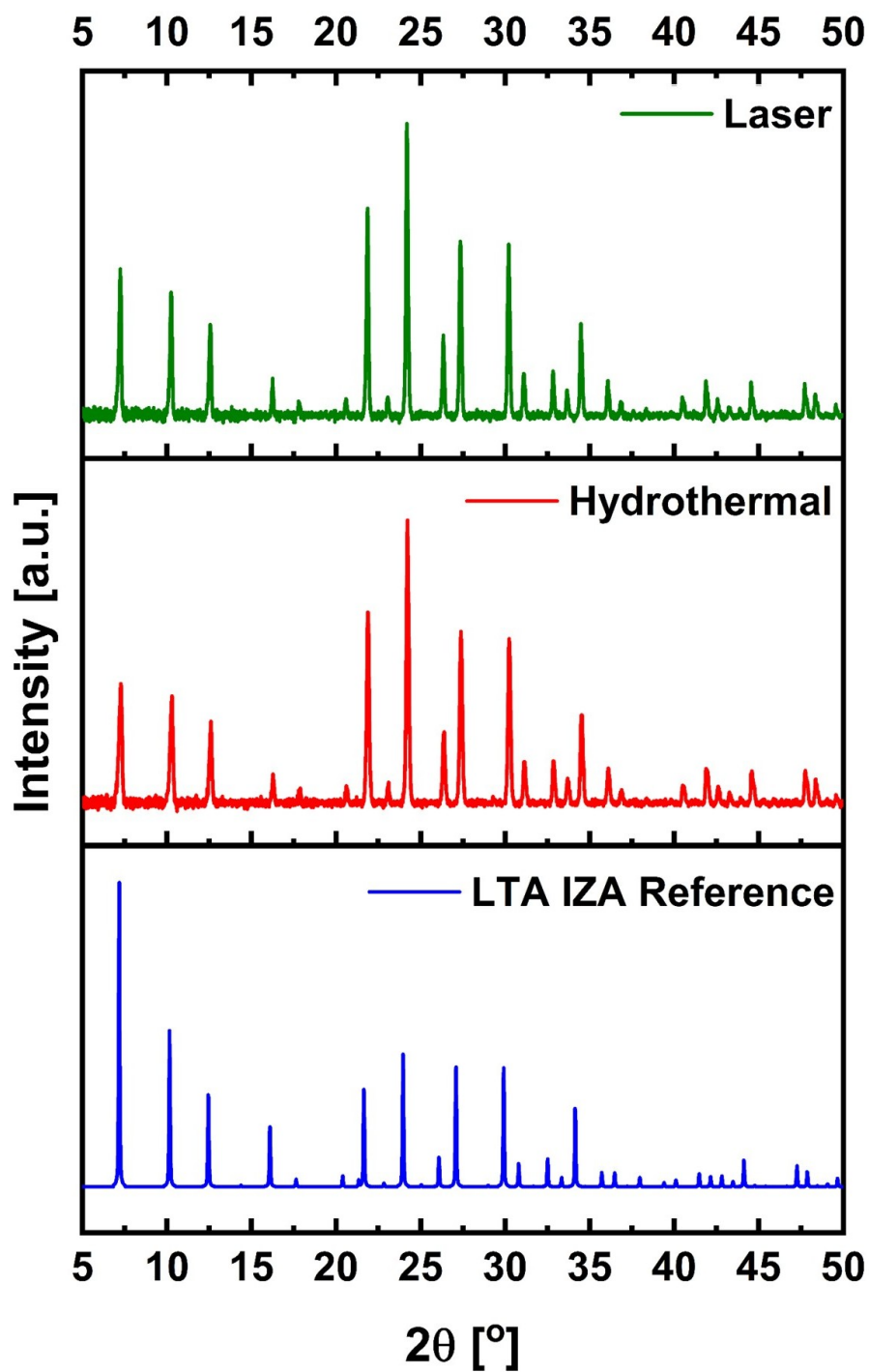


Figure 4.6: XRD patterns of microporous zeolite A crystals synthesized via laser and hydrothermal synthesis methods. Reference XRD patterns are obtained from the IZA.^[5]

The organic structure directing agent (OSDA) used in zeolite A synthesis is tetramethylammonium hydroxide (TMAOH), which dissociates into TMA^+ and OH^- ions in aqueous medium. Oligomerization of silica and alumina molecules around TMA^+ ion gives the final structure of zeolite A.^[94] TMA^+ ions are present within the framework until removal through calcination, where the sample is heated up to high temperatures ($\sim 500^\circ\text{C}$) for 3 hours to remove OSDA, but the zeolite framework remains as it is. This process affects X-ray diffraction patterns as well, where in the case of a sample that is not calcined, signal intensity is lowered for some planes because of organic OSDA filling the pores. Peak intensities representing (200), (220), and (222) planes (see Figure 4.6 and **Figure 4.7**) are lower for not calcined samples (hydrothermal and laser) compared to the calculated powder pattern obtained from IZA.^[5]

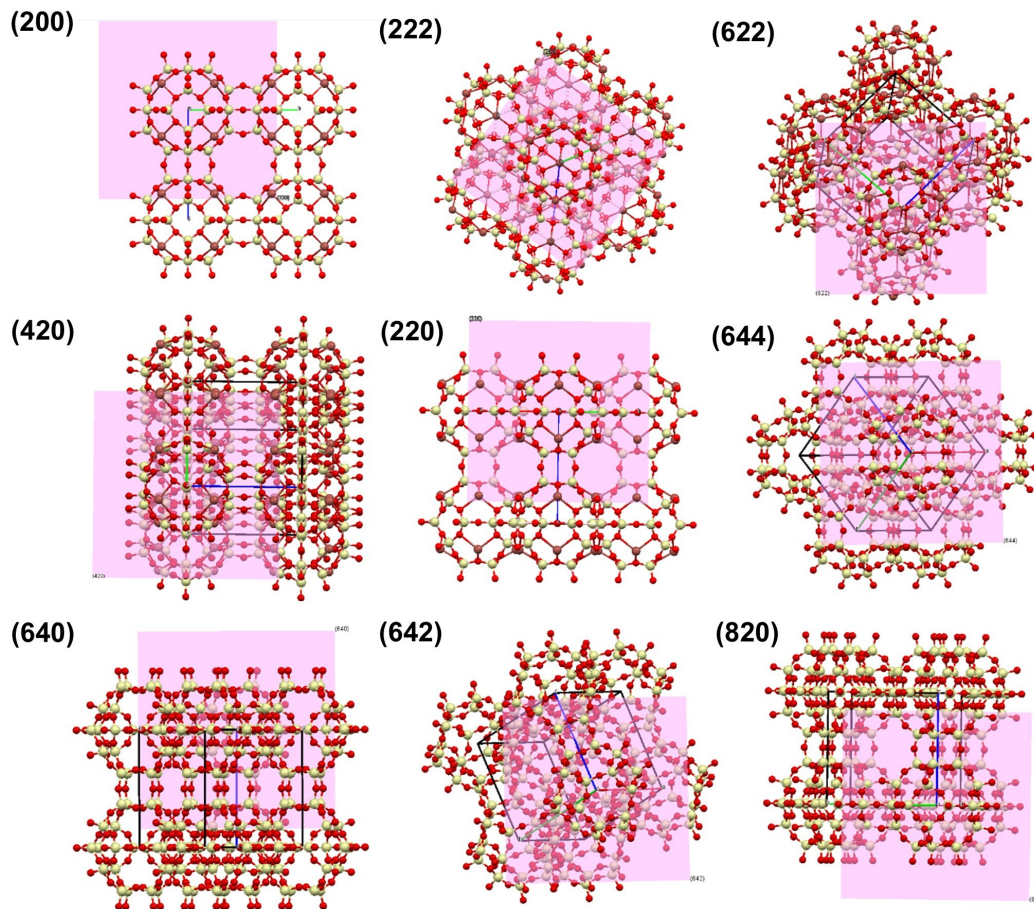


Figure 4.7: Characteristic planes of Zeolite LTA unit cells representing peaks in the XRD pattern. The 3D drawing of the unit cell and planes are obtained from the Mercury Software.

The characteristic peaks of zeolite A at $2\theta^\circ$ are 7.18° , 10.17° , 12.46° , 16.11° , 21.67° , 24.0° , 26.11° , 27.11° , 29.94° , and 34.18° that are reported in the literature.^[98] The miller indices corresponding to these angles are (200), (220), (222), (420), (600), (622), (640), (642), (820) and (664).^[98]

To estimate the percent crystallinity using the XRD pattern, the sum of the relative intensities of the 5 most intense peaks of the zeolite A synthesized via ultrafast laser method was divided by the sum of the relative intensities of 5 most

intense peaks of the zeolite A synthesized via hydrothermal method XRD pattern (**Table 4.1**).

$$\frac{\sum I_{\text{relative}} \text{ of 5 most intense peaks of the Zeolite A (laser)}}{\sum I_{\text{relative}} \text{ of 5 most intense peaks of the Zeolite A (hydrothermal)}} = \text{Cryst. \%} \quad (4.1)$$

In order to compare the relative intensities, identical amounts of powder samples synthesized via both methods were weighed, and XRD analyses were subsequently performed. Since the relative crystallinity of laser-synthesized Zeolite A was calculated as 106.8% by using Table 4.1, the values were normalized by setting this value to 100%, and the crystallinity of other samples was scaled accordingly.

Table 4.1: Relative intensities of most intense five peaks of Zeolite A

Characteristic Peaks	I_{relative} (Hydrothermal)	I_{relative} (Laser)
7.2	71.186	89.347
10.2	55.937	66.940
24.25	97.150	100.000
27.36	65.797	67.188
30.22	100.000	93.194

In **Figure 4.8**, XRD patterns from independent Zeolite A syntheses via ultrafast laser method performed under the same reaction conditions at different time intervals (1 week, 1 month, and 3 months apart) were compared, and it was observed that the crystal structure was successfully formed in each synthesis, with no detectable impurity phases. Crystallinity % was determined as 100%,

97.5%, 93%, and 99% for Trials 1, 2, 3, and 4, respectively. These results demonstrate that the method is reproducible, with no significant variation in synthesis performance over time.

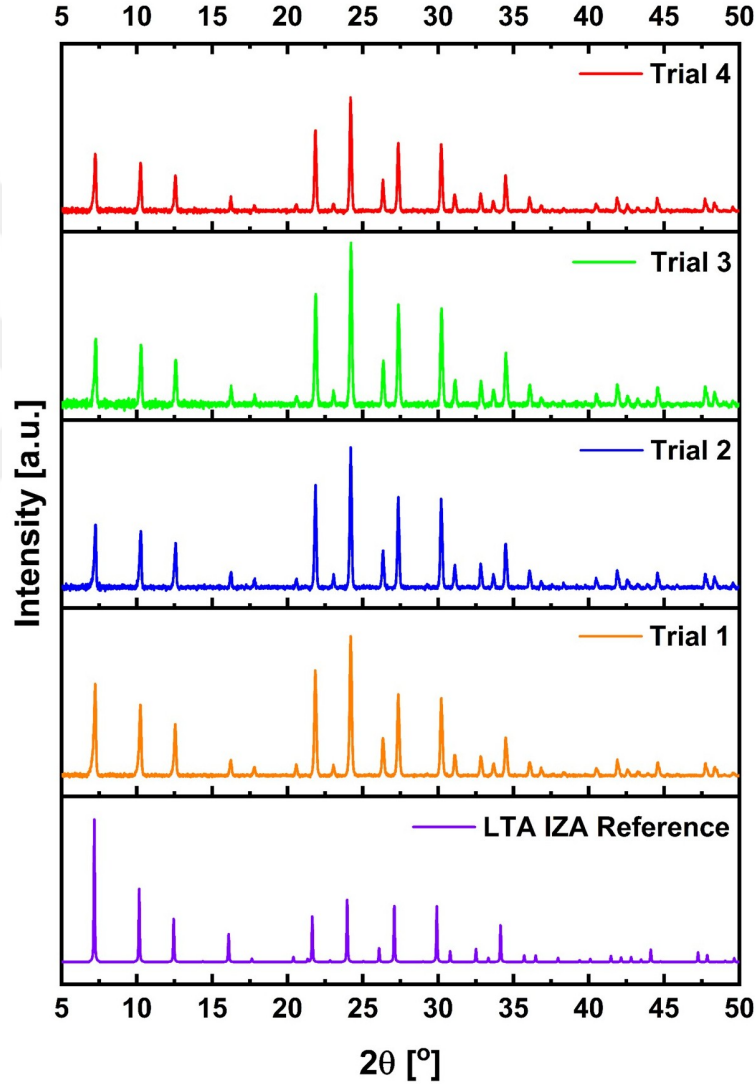


Figure 4.8: XRD patterns of Zeolite A synthesized via ultrafast laser method, where the reference experiment (Trial 1, 100 % crystallinity) was repeated after 1 week (Trial 2, 97.5 % crystallinity), 1 month (Trial 3, 93 % crystallinity) and 3 months (Trial 4, 99 % crystallinity). They are compared to the reference LTA XRD pattern from the IZA’s webpage.^[5]

4.4 High-Resolution Transmission Electron Microscopy Analysis

Fully crystalline (crystallinity relative to hydrothermal sample $> 100\%$ from XRD estimation in Equation 4.1 and Table 4.1) zeolite A synthesized via the ultrafast laser method, was suspended in ethanol and sonicated for five minutes before a drop of the resulting solution was placed on a copper TEM grid covered with carbon for High-Resolution Transmission Electron Microscopy (HR-TEM) investigation. Regular atomic planes called lattice fringe were also observed in the obtained HR-TEM images as in the **Figure 4.9**). While these fringes are characteristically seen in materials with a crystalline structure, a clear and periodic fringe structure is not observed in materials with an amorphous structure.^[99] Thus, the lattice fringes observed in the HR-TEM images, in addition to XRD investigations, confirm the highly crystalline nature of zeolite A synthesized via ultrafast laser method.

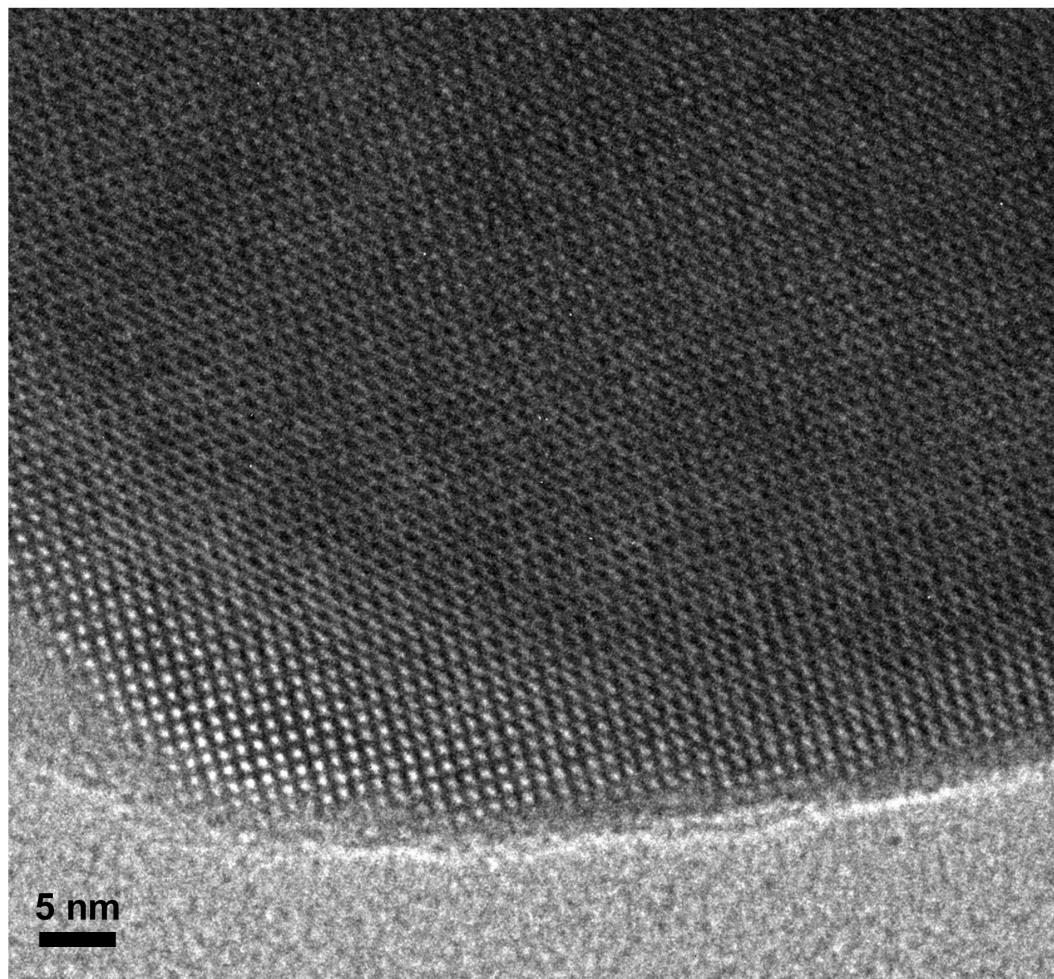


Figure 4.9: High-resolution transmission electron microscopy of lattice fringes of single zeolite A crystal.

Figure 4.10 also shows the diffraction spots observed in the selected area electron diffraction (SAED) pattern of Zeolite A synthesized by ultrafast laser method. SAED technique allows the crystal structure of the material to be analyzed directly under the electron microscope. If the diffraction pattern is in the form of dots (spots), this indicates the presence of an oriented crystal; while rings indicate an amorphous structure or a polycrystalline structure consisting of very small crystallites.^[99] Therefore, observation of spot patterns confirms that

the Zeolite A crystal synthesized via ultrafast laser contains well-oriented crystal regions.

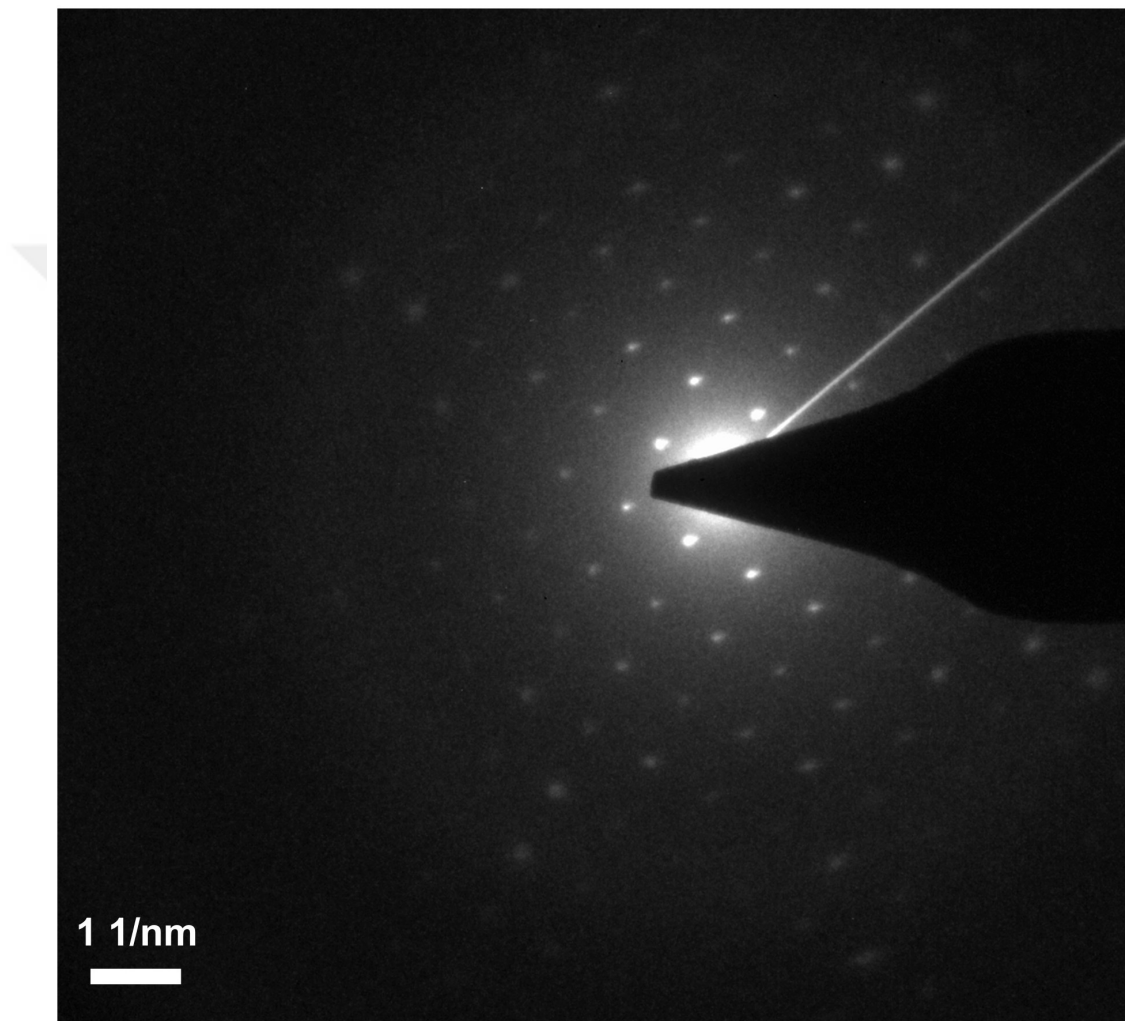


Figure 4.10: Diffraction spots of single zeolite A crystal synthesized via ultrafast laser in selected area electron diffraction (SAED).

4.5 Thermo-gravimetric and Differential Thermal Analysis

Thermogravimetric analysis (TGA), a widely used technique for zeolite characterization, provides information on physical and chemical properties by monitoring the mass of a sample over time under controlled temperature increases.^[100] It reveals phase transitions within a material by evaluating thermal events such as evaporation, sublimation, adsorption/desorption, and decomposition. When combined, TGA and differential thermogravimetric analysis (DTA) provide comprehensive data on the thermal stability, water and template content, and structural integrity of zeolites.^[100] DTA is obtained by taking the derivative of the TGA curve with respect to temperature and provides a highly accurate representation of mass loss events at different temperature ranges and at what rates. This allows overlapping or sequential decomposition processes (such as water loss and organic template removal) to be more clearly separated and interpreted.^[100]

For zeolite A synthesized via ultrafast laser method, TGA and DTA analyses are critical to verify the efficiency of the synthesis and the application potential of the material. Zeolite A, with its low Si/Al ratio, exhibits high hydrophilicity and can accommodate significant amounts of water in its pores. The removal of these water molecules from the framework with increasing temperature can be observed as significant mass losses in TGA results (see **Figure 4.11** and **Figure 4.12**). Furthermore, due to the organic tetramethylammonium (TMA) used as a structure-directing agent in the synthesis, additional mass losses are expected at certain temperature ranges.

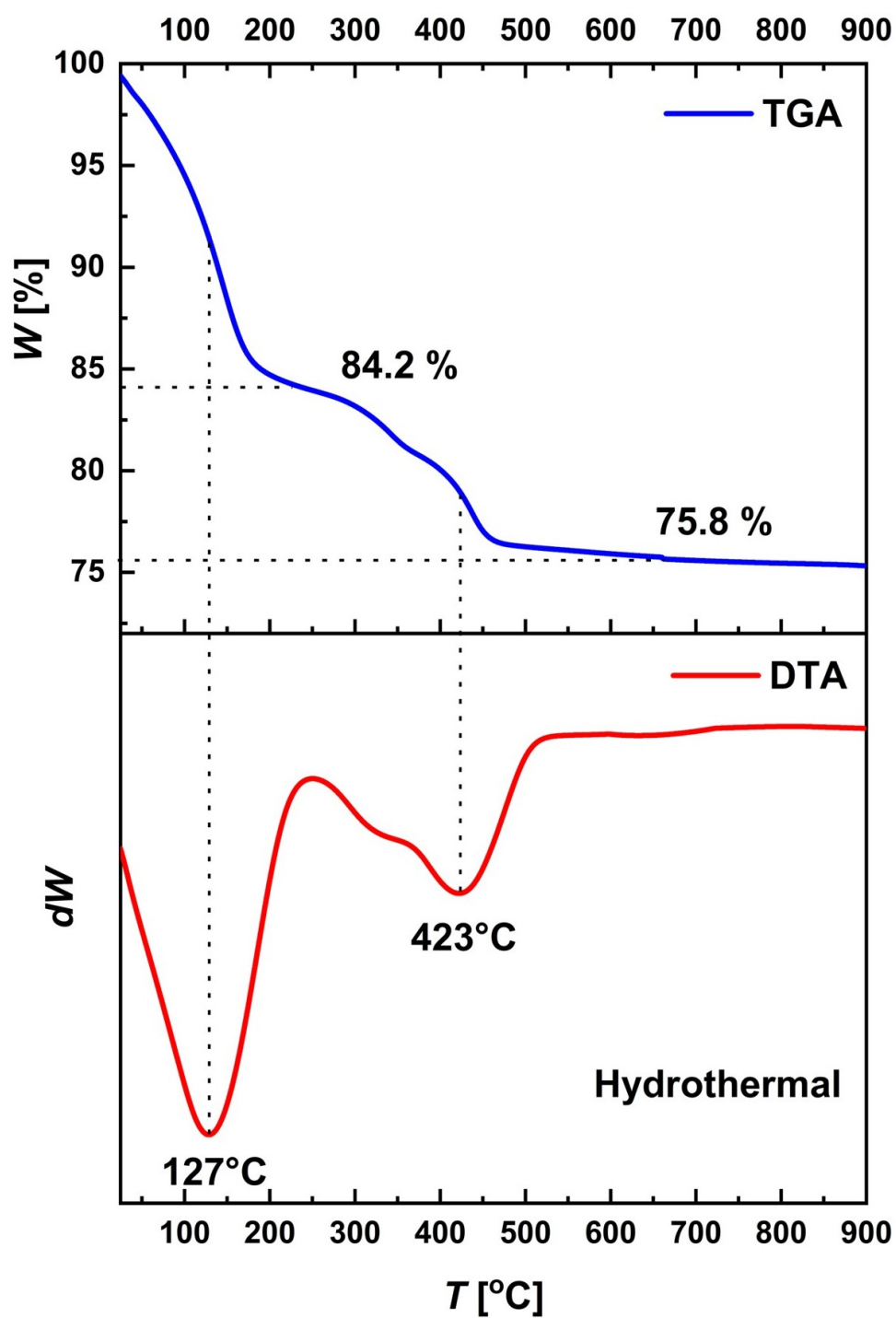


Figure 4.11: Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) plots of uncalcined zeolite A synthesized via conventional hydrothermal method.

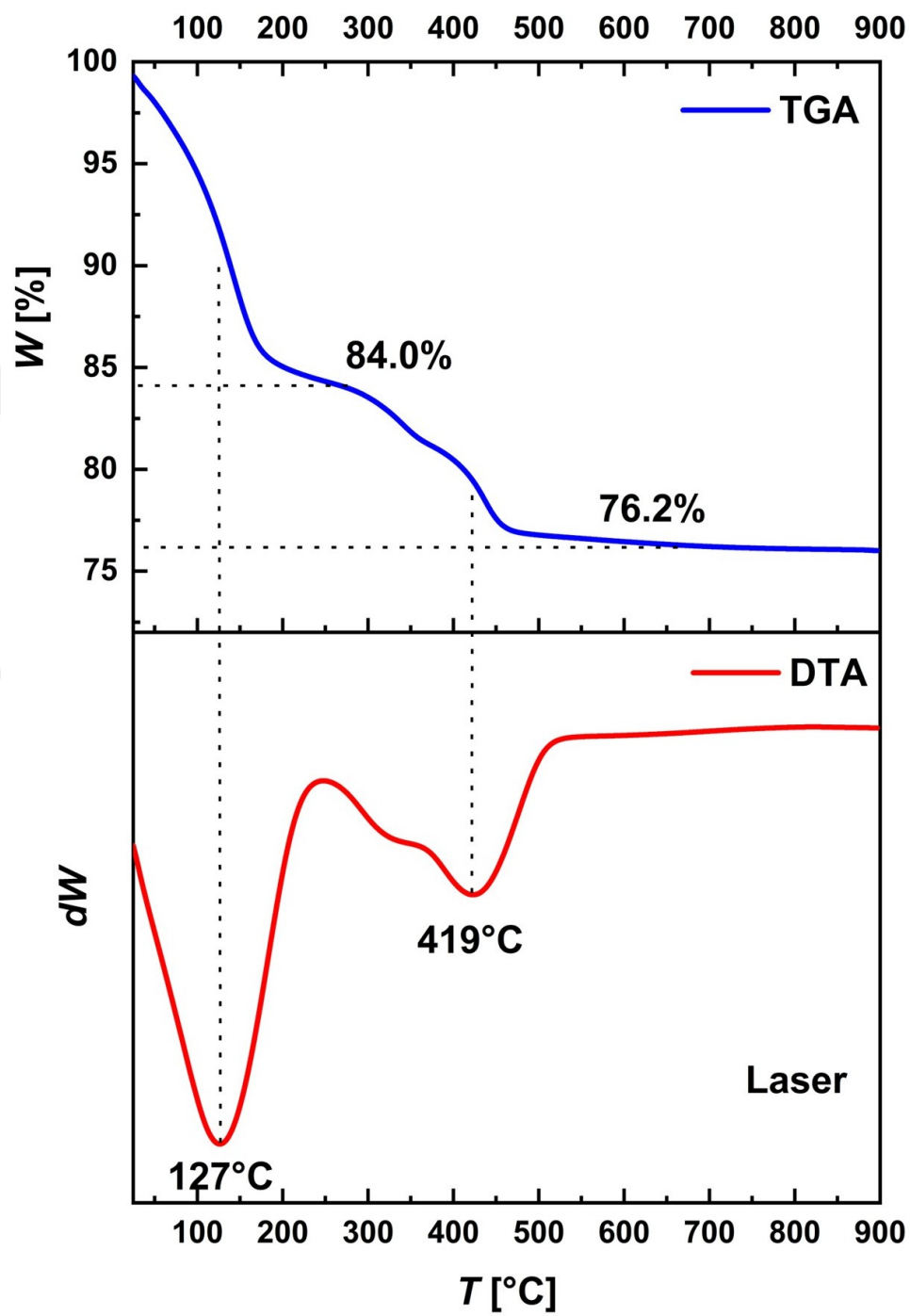


Figure 4.12: Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) plots of uncalcined zeolite A synthesized via ultrafast laser method.

The thermal behaviour of Zeolite A samples produced via hydrothermal and ultrafast laser methods are comparable with the the Zeolite A crystals in the literature.^[101, 102] TGA analyses of Zeolite A samples synthesized via the hydrothermal method in the Figure 4.11 and ultrafast laser-assisted method in the Figure 4.12 show similar weight loss trends. In the hydrothermal synthesized sample, the weight decreases from 100% to 84.2% in the temperature range of 100-200 °C due to water loss in the pores, while the weight decreases up to 75.8% in the temperature range of 400–500 °C due to the removal of the organic structure directing agent TMA. Similarly, the Zeolite A sample synthesized via the ultrafast laser method decreases to 84.0% between 100–200 °C and stabilizes at 76.2% at 500 °C. These data reveal that both methods exhibit comparable thermal behavior, with only minor variations in the ultimate weight retention at higher temperatures.

4.6 Brunauer-Emmett-Teller (BET) Analysis

Brunauer-Emmett-Teller (BET) analysis is commonly used method to measure the specific surface area of porous materials like zeolites.^[103, 104, 105] BET theory is typically applied to multilayer adsorption systems that use chemically inert gases and calculates the specific surface area by the amount of gas adsorbed on the surface.^[103, 106] The total BET surface area is obtained by using the linear region of adsorption isotherm.^[106] According to the classification by the International Union of Pure and Applied Chemistry (IUPAC), adsorption isotherms are divided into six basic types (Types I–VI) as in the **Figure 4.13**, and the shape of these isotherms provides significant information on the pore size and distribution of the pore structure of the material.^[103, 105, 107]

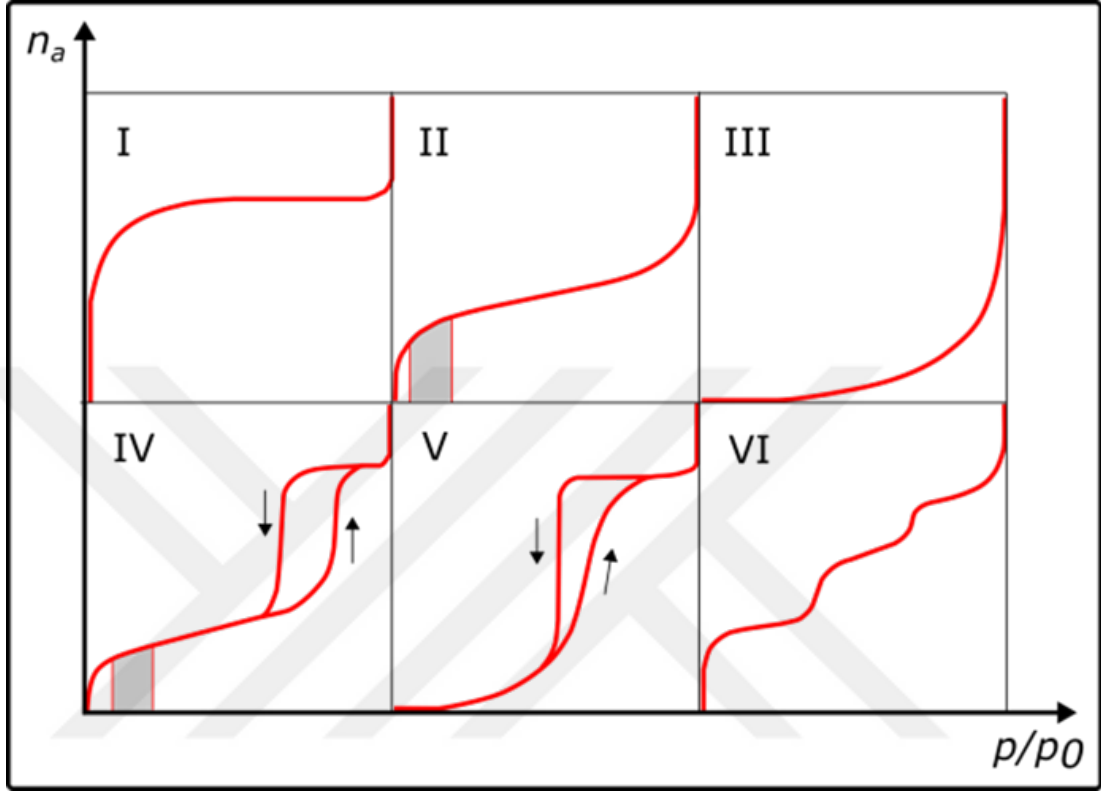


Figure 4.13: IUPAC classification of adsorption isotherms of absorbed volume versus relative pressure graphics. The Type I isotherm represents microporous (≤ 2 nm) structures, Types II–III represent macroporous systems, and Types IV–V represent mesoporous (2–50 nm) materials. Type VI is a rare phenomenon indicating layer by layer adsorption. Adapted from the reference [108].

Moreover, to calculate the micropore area and micropore volume, t-plot (V-t method) and BJH (Barrett-Joyner-Halenda) methods have developed.[103, 105, 109] While t-plot calculates the micropore contribution by comparing the adsorption isotherm with the reference isotherm, BJH method is often preferred for mesoporous materials. Pore size distribution are obtained using the density functional theory (DFT) model which allows for more accurate analysis, particularly for complex microporous structures, such as, zeolites, by taking into account molecular interactions and pore geometry.[103, 105]

The results of the BET analysis, which was carried out to investigate the specific surface area and porosity of zeolite A crystals synthesized by ultrafast laser method and to evaluate the effects of ultrafast laser method on the synthesis and to reveal the application potential of the synthesized zeolite A, are summarized in **Table 4.2**. For comparison, the same analysis was performed for zeolite A crystals synthesized via the conventional hydrothermal method.

Table 4.2: Results of BET analysis of zeolite A synthesized via both ultrafast laser synthesis and conventional hydrothermal synthesis methods.

Sample	BET Surface Area (m ² /g)	Micropore Surface Area (m ² /g)	External Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)
Zeolite A (UFLS*)	675.006	614.876	60.130	0.277	0.231
Zeolite A (CHS**)	648.389	610.012	38.377	0.272	0.232

* UFLS stands for ultra-fast laser synthesis.

** CHS stands for conventional hydrothermal synthesis.

The BET surface area is obtained from the BET method.

The micropore area, micropore volume and external surface area are obtained by the t-plot method.

Total pore volume is obtained by DFT method.

4.6.1 Specific Surface Area

Specific surface area is a critical parameter because it directly affects surface-related properties of zeolites, such as adsorption capacity, ion exchange capacity,

and catalytic activity.^[103, 105] A higher specific surface area indicates more active sites are available, which in turn determines the material's adsorption performance. In the literature, the expected BET specific surface area for nano-sized Zeolite A (LTA framework) is in the range of 400–700 m²/g.^[50, 54, 105, 110, 111]

The results in the Table 4.2 shows that the BET surface area of zeolite A synthesized by ultrafast laser and conventional hydrothermal methods were 675.006 m²/g and 648.389 m²/g, respectively, which both match the specific surface area range of zeolite A and shows a highly porous structure. The BET plot for zeolite A in **Figure 4.14** and **Figure 4.15** typically resembles a Type I isotherm, which is one of the six main adsorption isotherm types that are classified by the IUPAC in Figure 4.13.

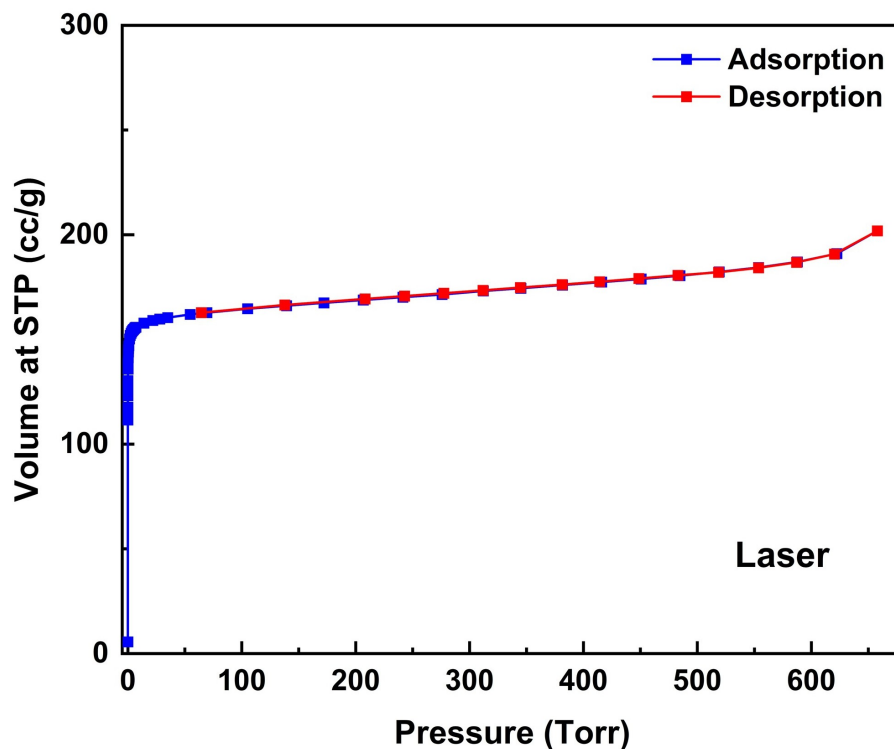


Figure 4.14: Brunauer-Emmett-Teller (BET) adsorption-desorption isotherm of Zeolite A synthesized via ultrafast laser method.

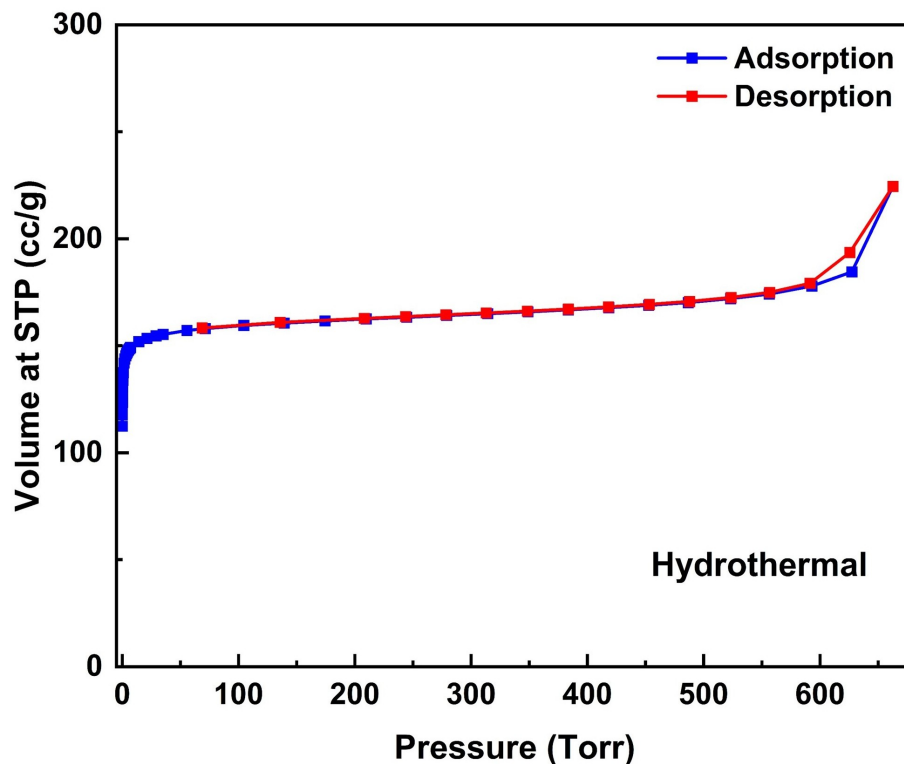


Figure 4.15: Brunauer-Emmett-Teller (BET) adsorption-desorption isotherm of Zeolite A synthesized via conventional hydrothermal method.

4.6.2 Micropore Surface Area and Volume

Micropore surface area and volume are critical parameters that directly impact the adsorption capacity, selectivity, and diffusion properties of zeolites.^[105] A high micropore volume allows for the retention of more molecules, while a large micropore surface area increases the number of active sites, increasing the efficiency of surface reactions. The micropore surface area of Zeolite LTA (microporous) in the literature is expected to be an approximate value to the BET surface area, and the total pore volume is expected to be in the range of 0.20-0.29 cm³/g.^[50, 54, 105, 110, 111]

The results of the V-t method showed that the micropore surface area is 614.876 m²/g and 610.012 m²/g, the external surface area is 60.130 m²/g and 38.377 m²/g, and the micropore volume is 0.231 cm³/g and 0.232 cm³/g for samples synthesized via ultrafast laser and conventional hydrothermal method. The similarity between the results of samples are due to the fact that the micropore surface area and pore volume are usually measured at a high relative pressure, typically $p/p_0 = 0.99$ in the V-t method, assuming the pores are completely filled with adsorbate.^[103, 105] Zeolite A crystals synthesized via both methods have microporous structures, as indicated by the high micropore area and micropore volume from the t-plot analysis by V-t method. The sharp increase in the relative pressure for samples synthesized via both methods reflects the high affinity of the micropores for nitrogen adsorption.^[103, 105]

In addition to the micropore volume obtained by the V-t method, the micropore volume was also calculated using density functional theory (DFT), an approach that takes into account the full isotherm.^[103] Based on DFT analysis, the micropore pore volume for zeolite A synthesized via the ultrafast laser method was found to be 0.277 cm³/g, and the micropore pore volume for zeolite A synthesized via the conventional hydrothermal method was 0.272 cm³/g. These results obtained by DFT analysis are consistent with the values reported in the literature for nano-sized Zeolite A samples.^[54]

4.6.3 Pore Size Distribution

The pore size distribution was evaluated further by DFT approach. According to **Figure 4.16**, the half-pore width was found to be 2.998 Å. This indicates that most of the pores in this zeolite sample are molecular in size, which is consistent with the structure of zeolite A.^[5]

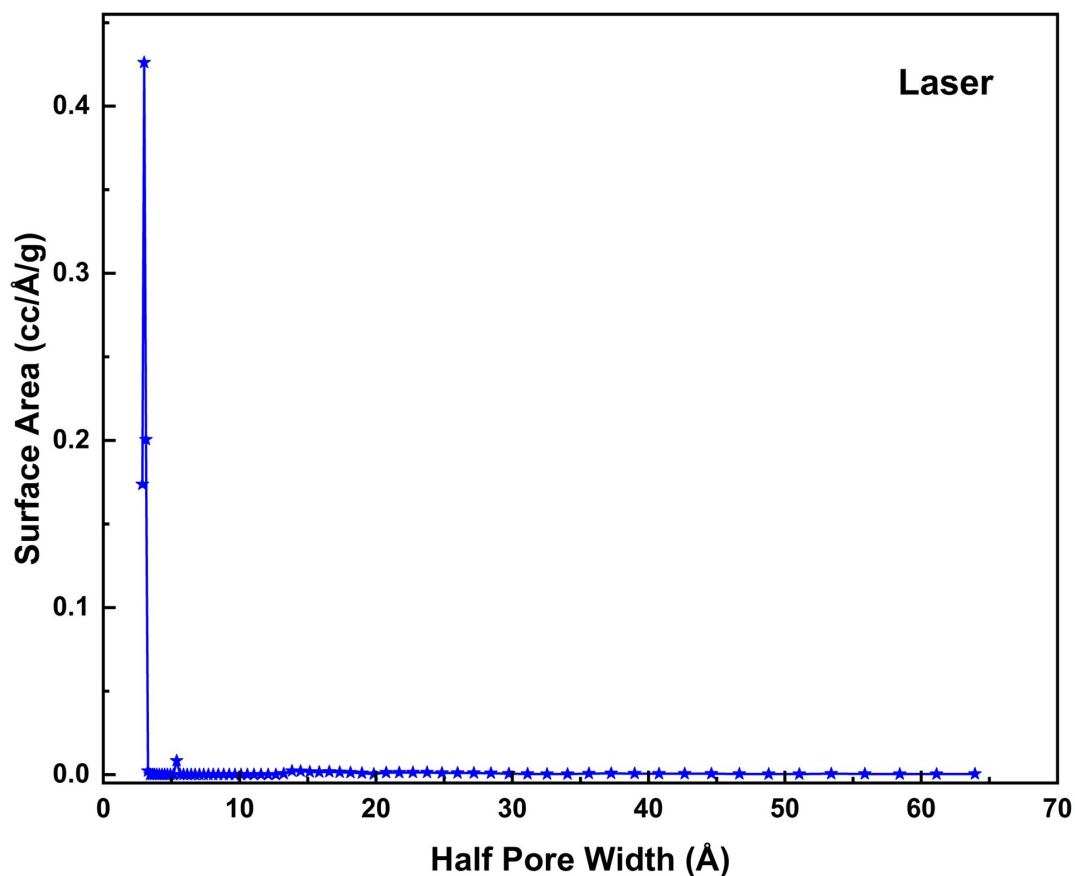


Figure 4.16: Pore size distribution of zeolite A synthesized via ultrafast laser method, obtained from BET isotherm.

However, according to the DFT results and **Figure 4.17**, the pore width of the sample synthesized via the hydrothermal method was 4.297 Å, which is higher than expected in the literature.^[5] This deviation can be attributed to the fact that, although the microporous Zeolite A synthesized via the hydrothermal method exhibits a Type I isotherm (see Figure 4.15), the desorption curve does not perfectly overlap with the adsorption curve at around 625 Torr, leading to a deviation in the calculated pore width.

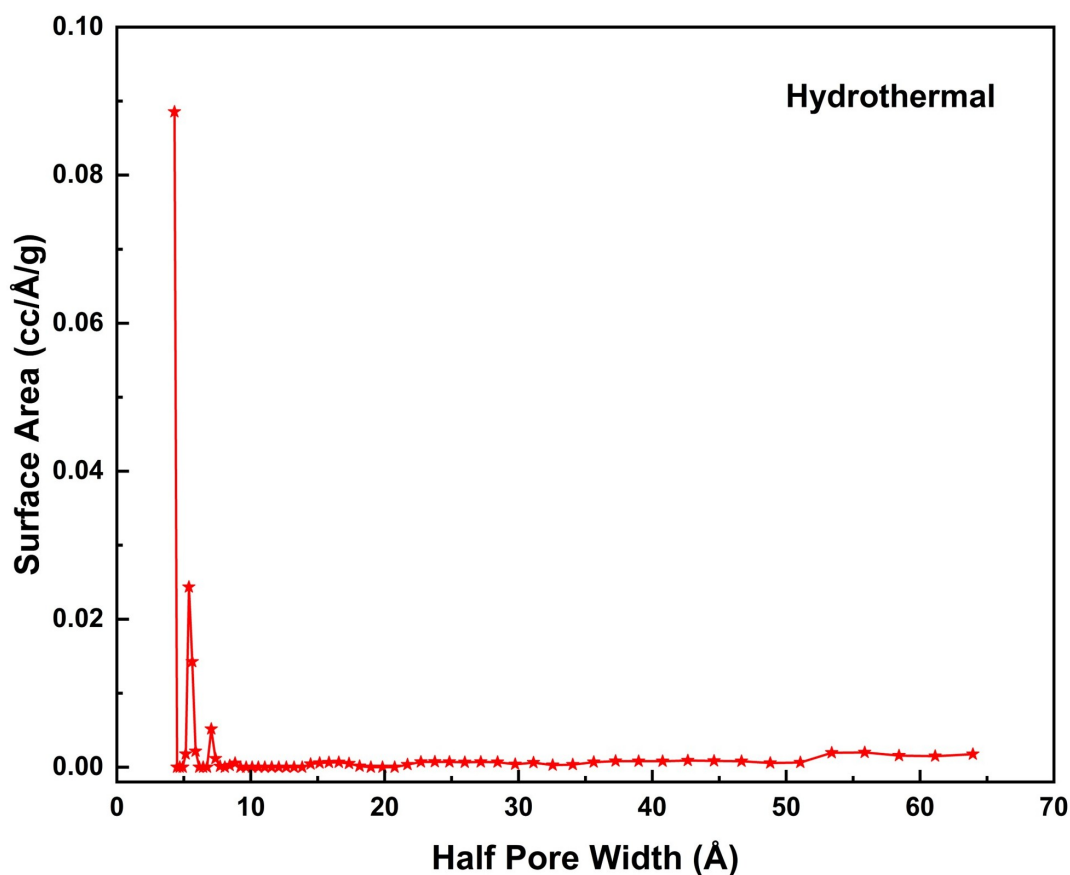


Figure 4.17: Pore size distribution of zeolite A synthesized via conventional hydrothermal method, obtained from BET isotherm.

4.7 Vibrational Structure Analysis with in FTIR Spectroscopy

The structural vibrations of zeolites produce characteristic vibrational bands in the mid- and far-infrared regions.^[112] These vibrations are divided into two types: external and internal vibrations of the tetrahedra, the structural units of the zeolite.^[5, 112] Since every zeolite consists of tetrahedra, some of the resulting

IR bands are structure-sensitive while others are not.^[112, 113] Internal tetrahedral vibrations were determined in the ranges of 1250 - 920 cm^{-1} (asymmetric stretching), 720 - 650 cm^{-1} (symmetric stretching), and 500 - 420 cm^{-1} (T-O bending, T indicates the tetrahedral framework atom, which typically represents silicon (Si) or aluminum (Al) within the structure.). In addition, external linkages were associated with bands in the ranges of 650 - 500 cm^{-1} (double ring vibrations), 420 - 300 cm^{-1} (pore opening vibrations), 1150 - 1050 cm^{-1} (asymmetric stretching), and 820 - 750 cm^{-1} (symmetric stretching).^[113] Furthermore, a band at 1650 cm^{-1} was related to interstitial bonded water (adsorbed water), while a broad band between 3000 - 3700 cm^{-1} was attributed to intra- and intermolecular hydrogen bonding.^[5, 113] Since the internal tetrahedral vibrations of all aluminosilicate zeolites generally give bands in almost the same position, their sensitivity to structure is not as sensitive as the positions of the external linkage bands. Thus, in this thesis, all bands will be examined, with a focus on the structure-sensitive bands and the hydroxyl band.

The result of the FTIR analyses of calcined Zeolite A synthesized via conventional hydrothermal and ultrafast laser methods in **Figure 4.18** shows similar characteristic vibrational band positions. In both samples, the 471 cm^{-1} band corresponds to bending (rocking) vibrations occurring in the T-O-T (Si-O-Al or Si-O-Si) bonds. The band around 571 cm^{-1} represents vibrations associated with double four-membered rings (D4R), a characteristic structural units of LTA framework. The 685 cm^{-1} band indicates T-O-T bending vibrations. Furthermore, the 1037 cm^{-1} band represents Si-O-T asymmetric stretching of internal tetrahedral vibrations of LTA. It was also observed that the intensity of the external Si-O-T asymmetric stretching band around 1120 cm^{-1} increased in zeolite A synthesized via ultrafast laser method compared to its hydrothermally synthesized counterpart. These findings indicate that the characteristic vibrational bands of zeolite A crystals synthesized via both methods and the results are consistent with the literature.^[114, 115, 116]

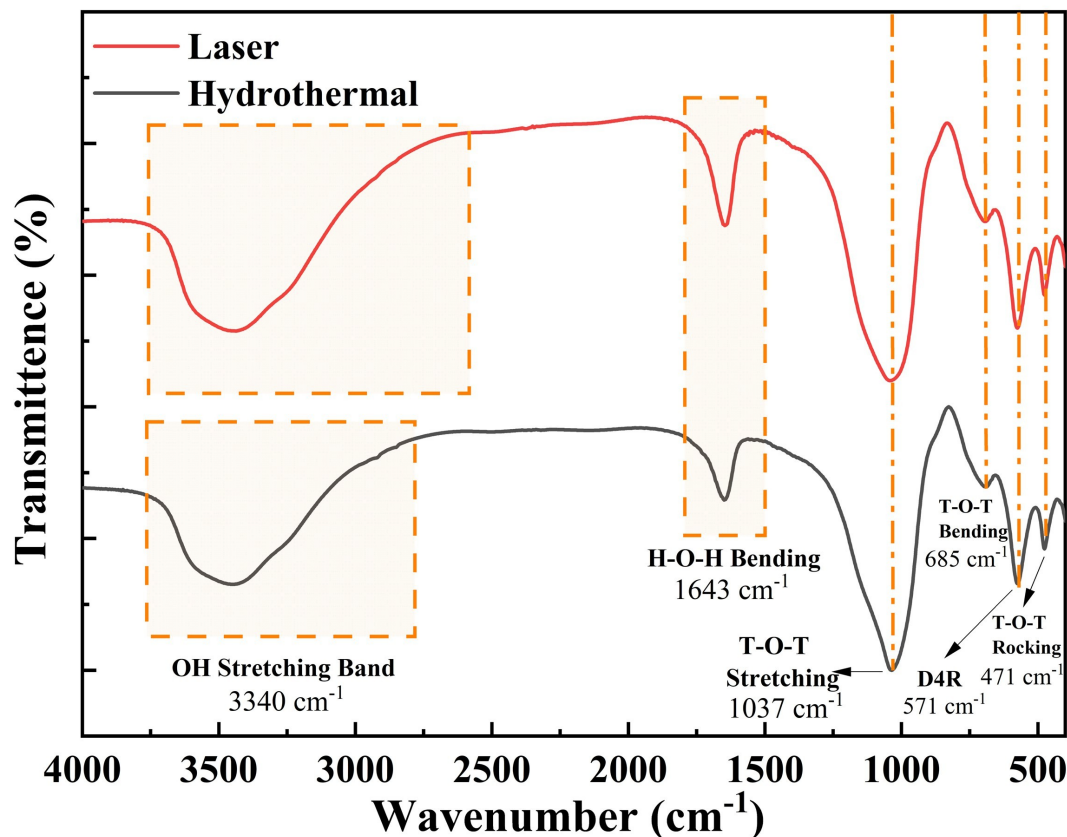


Figure 4.18: Fourier transform infrared (FTIR) spectrum of calcined zeolite A crystals synthesized via conventional hydrothermal method and ultrafast laser method in transmission mode.

The broad band between 3000-3700 cm^{-1} is attributed to intra- and inter-molecular hydrogen bonding.^[5, 113, 114] Hydroxyl groups attached to the zeolite surface can significantly change the chemical properties of the structure. There are 5 types of hydroxyl groups defined in the literature.^[112] These are; (i) Silanol groups at the ends of the lattice, and give vibrational bands around 3740 cm^{-1} , (ii) Hydroxyl groups at defect sites (known as hydroxyl nests), and give vibrational bands around 3720 cm^{-1} , OH groups attached to extra-framework T

atoms, give vibrational bands around 3680 cm^{-1} , OH groups attached to multivalent cations that balance the negative charge of the framework, give vibrational bands around $3580\text{--}3520\text{ cm}^{-1}$, bridging OH groups (such as $\equiv\text{Al}(\text{OH})\text{Si}\equiv$ groups), which have Brønsted acidic properties, give vibrational bands around $3600\text{--}3650\text{ cm}^{-1}$ as depicted in the **Figure 4.19**.^[112, 113, 117]

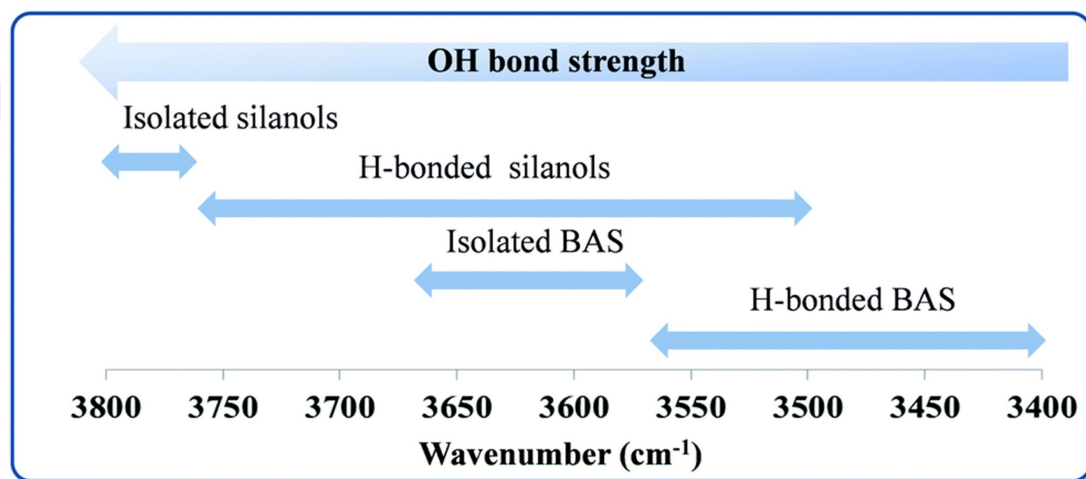


Figure 4.19: Bands related to OH stretching in zeolites' FTIR Spectroscopy. Adapted from the reference [117].

Although these peaks appear as a single peak in the FTIR spectrum (see Figure 4.18), deconvolution was applied to this peak to analyze the individual components. The centers of these peaks are seen to be at 3250 cm^{-1} , 3430 cm^{-1} and 3580 cm^{-1} . The vibrational band around 3700 cm^{-1} was not observed in FTIR spectrum of Zeolite A crystals synthesized via both methods. This indicates that synthesized zeolite A crystals have no isolated silanol, whose band is around $3700\text{--}3800\text{ cm}^{-1}$.^[117]

The OH stretching band around $3000\text{--}3700\text{ cm}^{-1}$ has slight differences and broadened in FTIR spectrum of zeolite A synthesized via ultrafast laser method. To investigate the broad band around $2800\text{--}3800\text{ cm}^{-1}$ for analysis of the defect site and hydroxyl groups of zeolite A crystals without the effect of water, it is

necessary to conduct in-situ FTIR analysis in which system is heated up to remove adsorbed water from the pores of the zeolite.

4.8 CO₂ Adsorption Capacity

While zeolites do not possess the extremely high surface areas found in metal-organic frameworks (MOFs) (1000 to 10000 m²/g,^[118, 119] they still offer considerable CO₂ adsorption capacity at low pressures (<5 bar) and room temperature, making them attractive materials for CO₂ capture applications.^[42, 43] Zeolite A's 3-types of active sites and high ion exchange capacity make it one of the most experimentally and computationally investigated zeolites in the literature.^[42, 43, 44] Zeolite A is a small-pore zeolite (i.e., 0.4 nm).^[5] A notable feature of Zeolite A in terms of CO₂ adsorption, as previously mentioned in Chapter 2.1.2, is its three distinct extra-framework cation sites. Site II lies within the 8R windows that open into the alpha-cage and facilitates strong electrostatic interactions with CO₂. The oxygen atoms of CO₂ molecules can interact with extra-framework cations (Na⁺) in the active sites of zeolite A, and the interaction of one oxygen atom with one extra-framework cation is the simplest interaction (see **Figure 4.20-A**). DFT and Monte Carlo simulations indicate that CO₂ interacts simultaneously with multiple cation sites of Zeolite A.^[42, 44] Specifically, the bridging mechanism is most commonly observed mechanism in which one oxygen of CO₂ interacts with a cation in Site II, while the other oxygen interacts with a cation in Sites I or III as shown in the Figure 4.20-D and Figure 4.20-E. This double bonding results in high electrostatic stabilization, increasing adsorption capacity. Moreover, CO₂ molecules can form carbonate like species (Figure 4.20-B and Figure 4.20-C), however, this type of interaction is less observable.^[42, 54]

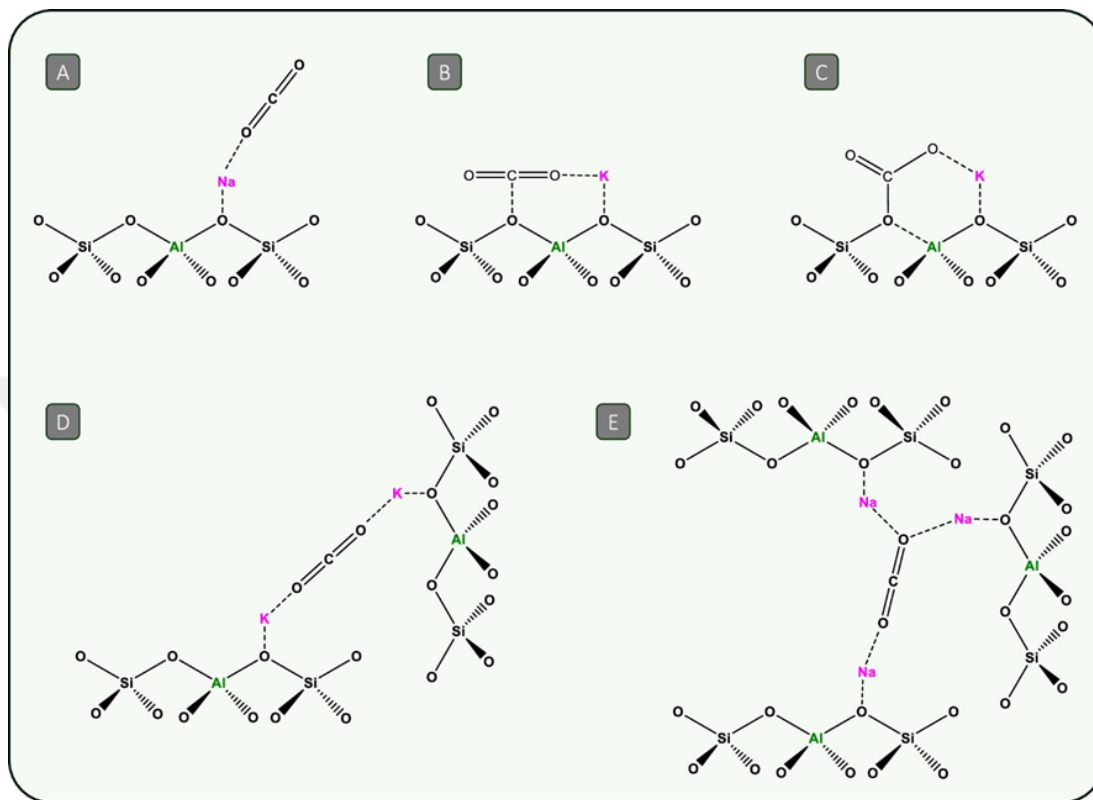


Figure 4.20: The interaction mechanisms of CO_2 molecules with active sites of zeolites. Adapted from the reference [42].

In the current thesis, CO_2 adsorption analysis was performed to investigate the adsorption capacity performance of Zeolite A synthesized with ultrafast laser method. Initially, thermal activation treatment was performed before the adsorption measurements. This initial-heat treatment ensures complete removal of physically adsorbed water molecules from the pores of the Zeolite A, thus ensuring full accessibility of the pore space to CO_2 molecules (see **Appendix D** for details).

Secondly, the CCA, the area under the CO_2 breakthrough curve obtained by the mas spectrometer in the experiment, is calculated. This area was calculated for each measurement using OriginLab Software, and the graphs and calculations are included in Appendix D. The actual adsorption is calculated as the ratio of

this area to the calibration area (S) and normalized by the mass of the adsorbent:

$$\text{Captured CO}_2 = \frac{\text{CCA}}{S} \times \frac{1 \text{ g}}{m} \quad (4.2)$$

where m is the mass of the adsorbent and it is 0.1 g in our work. In the calculations, the sample weight was accepted as less than 0.1 g based on TGA analysis due to the amount of water removed from the pores.

When CCA is found by subtracting the area under the breakthrough curve of the laser or hydrothermal sample from the area under the breakthrough curve of the "blank test", the CO₂ adsorption capacity for the laser sample is calculated as **2.44 mmol/g** and the CO₂ adsorption capacity for the hydrothermal sample as **1.87 mmol/g**. In order to better understanding for this distinct difference in the CO₂ adsorption capacity between zeolite A sample synthesized via ultrafast laser method and hydrothermal method, further breakthrough curve analysis is needed.

4.8.1 Breakthrough Curve Analysis

In breakthrough curve analysis, breakthrough curve shape, breakthrough delay, and saturation time are crucial to understand the pore structure and adsorption kinetics of the material. **Figure 4.21** shows the breakthrough curve, the CO₂ signal captured over time by the mass spectrometer for hydrothermal and laser samples^[42, 120]. The curve is horizontal when the adsorbent is actively capturing CO₂. As the CO₂ signal begins to be detected, the curve begins to rise and reaches a saturation point.

4.8.1.1 Shape of the Breakthrough Curve

The shape of the breakthrough curve provides important information about the adsorption kinetics. The shape of the curve's slope indicates how rapidly adsorption occurs. The more steeper the curve indicates fast mass transfer, thus fast adsorption kinetics.^[42, 43] A shallower slope may indicate broad range of pore size, thus slower adsorption kinetics.

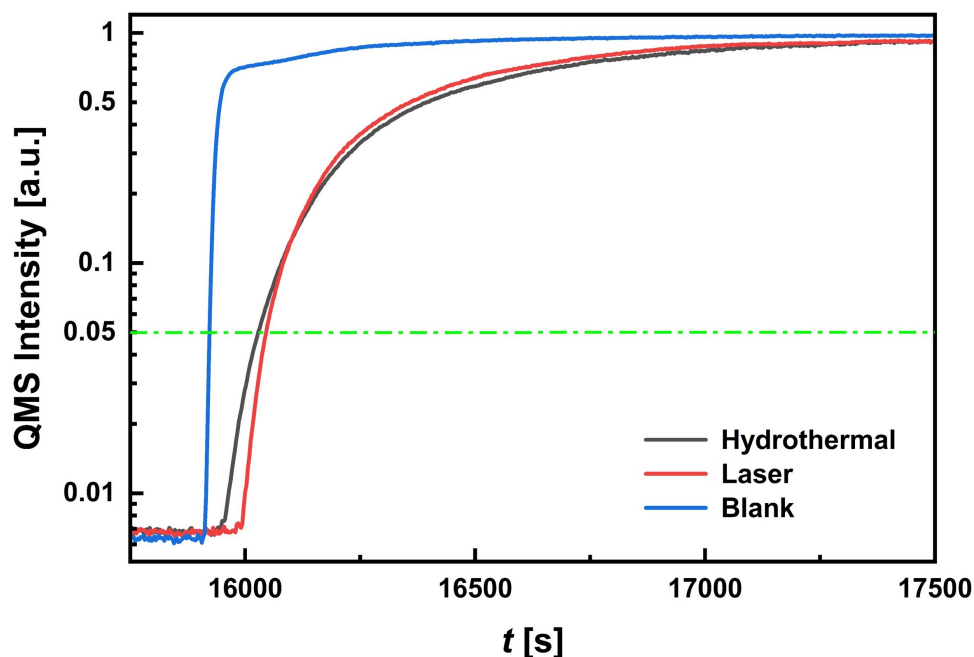


Figure 4.21: Plot of dynamic breakthrough curves of blank test (blue), zeolite A synthesized via ultrafast laser method (red), and conventional hydrothermal method (gray). Green dashed line is the breakthrough point where outlet CO₂ concentration is 0.05 of the inlet CO₂ concentration.

It is visually apparent that the breakthrough curve of the laser sample has a steeper slope than the hydrothermal sample in the Figure 4.21. Slope analysis using OriginPro Software revealed that the breakthrough curve of the laser sample was approximately 10% higher than the hydrothermal sample. This difference,

the steeper curve of the laser sample, clearly demonstrates that the adsorption kinetics of the laser sample are slightly faster than the hydrothermal sample. The reason for this may be that the laser sample has a narrower pore size distribution than the hydrothermal sample, as can be seen from the pore size distribution analysis performed in Chapter 4.6.3.

4.8.1.2 Breakthrough Delay

Breakthrough delay is the time from the moment CO_2 gas is introduced into the system until the first CO_2 signal is detected by the mass spectrometer. During this time, CO_2 molecules diffuse into the pores of the adsorbent material and bind to the active surface sites.^[42] The absence of detectable CO_2 at the outlet indicates that the adsorbent is still effectively capturing CO_2 molecules. Therefore, a long breakthrough delay generally indicates a high adsorption capacity or strong adsorption interactions.^[42, 121] Conversely, a short delay may suggest that the adsorbent has a low capacity or weak interaction with CO_2 .

On the other hand, in the literature, breakthrough delay is defined as the time interval in which the outlet gas concentration reaches 0.05 of the inlet concentration.^[122, 123, 124, 125] This is because there needs to be a certain point in terms of distinguishability from background noise and comparability with the literature. Therefore, in this analysis, the breakthrough delay was estimated based on the breakthrough point where the CO_2 concentration in the outlet gas reached 5% (see **Figure 4.22**).

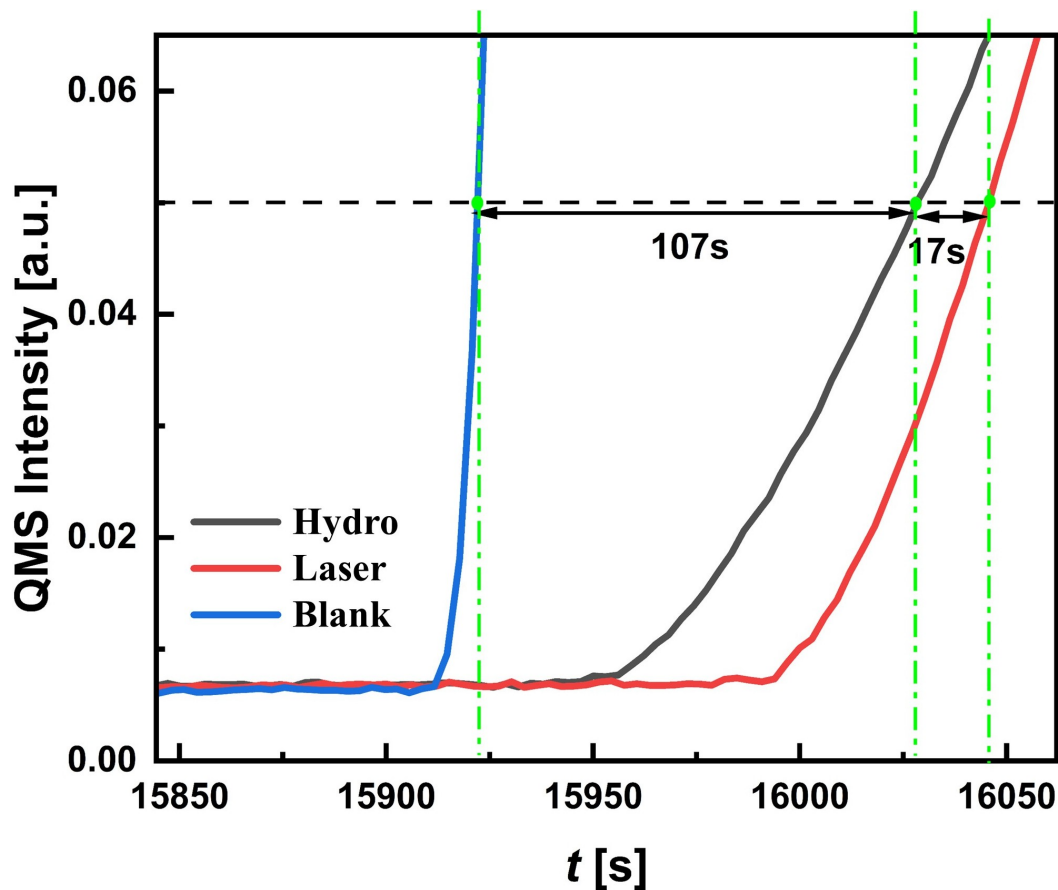


Figure 4.22: Zoomed plot of dynamic breakthrough curves in the Figure 4.21. The black dashed line is the breakthrough point and the green dashed lines are guide lines to see which time the breakthrough point corresponds to.

The breakthrough delay at the breakthrough point shown in Figure 4.22 is 124 seconds for the laser sample and 107 seconds for the hydrothermal sample. In fact, the time interval between the hydrothermal and laser samples (46 s) when the CO₂ signal is first detected is much more pronounced, however, the time interval at the breakthrough point (17 s) also provides sufficient information to infer the CO₂ adsorption capacity of the samples and their interaction with CO₂.

4.8.1.3 Saturation Time

Longer saturation time usually implies a higher adsorption capacity and larger pore volume.^[121, 126, 127] Conversely, a short saturation time can imply that the adsorbent has a low capacity or weak interaction with the adsorbate, so that it becomes saturated quickly and adsorbing halts. According to the saturation time analysis through OriginLab Software, saturation time of the hydrothermal sample is 40 minutes shorter than the saturation time of the laser sample (see **Figure 4.23**).

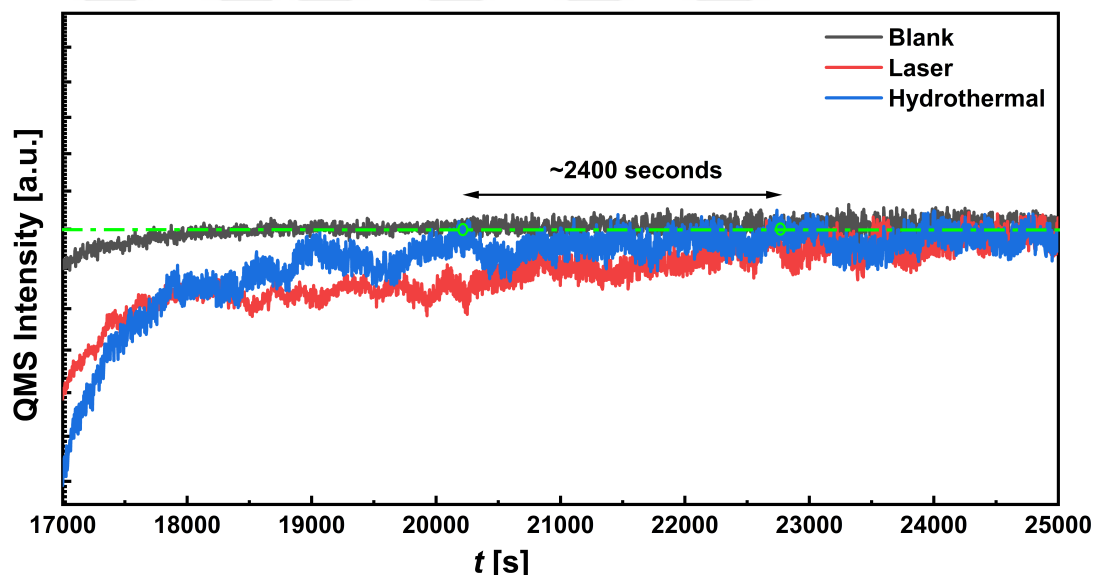


Figure 4.23: Zoomed plot of the plateau of the dynamic breakthrough curves in the Figure 4.21. The green dashed line is the saturation line ($C_{in}=1.0$) and the green circles are the points when the samples reach the saturation point.

Overall, the zeolite A crystals synthesized via ultrafast laser method exhibits a higher CO_2 adsorption capacity (2.44 mmol/g) compared to its hydrothermally synthesized counterpart (1.87 mmol/g). dynamic breakthrough curve analyses reveal that the laser sample has a steeper slope ($\sim 10\%$), meaning faster adsorption kinetics. The differences in breakthrough time (17 s) and saturation time (40 min)

indicate significant differences in the interaction behavior of the two samples with CO₂ and differences in the number of active sites due to the difference in BET surface area and external surface area (see Chapter 4.6). Based on these results, it can be concluded that the zeolite A synthesized via ultrafast laser method has a higher CO₂ adsorption capacity than the zeolite A synthesized via conventional hydrothermal method, and that the laser sample exhibits a stronger interaction with CO₂.



Chapter 5

Conclusion & Future Outlook

In this thesis, the ultrafast laser synthesis method was used as a novel method for synthesis of relatively complex zeolite A (LTA framework) synthesis, and the effect of ultrafast laser pulses on the morphological, structural, thermal, and adsorptive properties of synthesized zeolite A was investigated in detail. The ultrafast laser beam was focused onto the precursor suspension, triggering multiphoton absorption, local plasma formation, and the cascade of events (shock waves, cavitation bubbles, and laser-induced flows generation). This allowed the formation of discrete, cubic, highly crystalline (90 - 100%), and Zeolite A crystals with uniform size distribution in a shorter reaction time (4 hours vs. 8 hours), with low-energy photons.

The Zeolite A crystals were synthesized via ultrafast laser synthesis method over 80 times, proving the repeatability of this method. No impurity phases, such as Zeolite P and sodalite were observed in the XRD analysis of these syntheses, and the crystals were highly crystalline (90 - 100 %) compared to those of zeolite A synthesized via the conventional hydrothermal method. In addition, distinct lattice fringes in the HR-TEM analysis and diffraction spots of the SAED analysis also confirm the highly crystalline nature of Zeolite A synthesized via the ultrafast laser method.

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA), used to evaluate thermal properties, show that synthesized zeolite A via an ultrafast laser method has similar thermal behavior to Zeolite A samples synthesized via conventional hydrothermal methods and reported in the literature. Brunauer–Emmett–Teller (BET) analysis indicates that zeolite A crystals synthesized via ultrafast laser method have higher specific surface area ($675.006 \text{ m}^2/\text{g}$ vs. $648.389 \text{ m}^2/\text{g}$), and uniform pore size distribution (half pore width = $2.998 \text{ \AA}$).

Fourier transform infrared (FTIR) analysis, which was performed to investigate the effect of ultrafast laser pulses on the characteristic vibrational bands of zeolite A crystals synthesized via ultrafast laser method, is consistent with the control sample (hydrothermally synthesized) and the literature. The ultrafast laser synthesis has apparent effects on the broad band of the FTIR spectrum of zeolite A around $3000\text{--}3700 \text{ cm}^{-1}$. However, to reach a more precise conclusion and analyze defect sites, characterizations such as in-situ FTIR and Si^{29} NMR should be performed.

Furthermore, CO_2 adsorption capacity measurements revealed that Zeolite A crystals synthesized via ultrafast lasers exhibited higher adsorption capacities (2.44 mmol/g) than samples obtained via hydrothermal methods (1.87 mmol/g). Dynamic breakthrough curve analyses show that Zeolite A synthesized via ultrafast laser method has an approximately 10% steeper breakthrough curve, a longer breakthrough delay and reaches saturation later compared to its hydrothermally synthesized counterpart indicating stronger and more effective interactions with CO_2 molecules. The higher CO_2 adsorption capacity of the Zeolite A synthesized via ultrafast laser method can be attributed to its higher BET surface area and uniform pore size distribution.

5.1 Future Outlook

The novel ultrafast laser synthesis method stands out as a promising method due to its time efficiency but also for control over crystallization, enables zeolite synthesis with low-energy photons. Since ultrafast laser synthesis method can initiate reactions with spatiotemporally controlled energy delivery, in-situ characterization, such as in-situ Raman or in-situ FTIR can be adapted to reveal synthesis mechanism further. Moreover, the direct attachment growth mechanism observed in SEM images of Zeolite A and early nucleation of Zeolite A can be studied in detail using advanced structural characterization techniques such as SAXS/WAXS. Future studies could focus on investigating the scalability (gram scale) of this method and integrating advanced spectroscopic techniques for real-time monitoring of the synthesis process.

Bibliography

- [1] G. A. Ozin, A. Kuperman, and A. Stein, “Advanced zeolite, materials science,” *Angewandte Chemie International Edition in English*, vol. 28, no. 3, pp. 359–376, 1989.
- [2] A. Cronstedt, “Natural zeolite and minerals,” *Svenska Vetenskaps Akademiens Handlingar Stockholm*, vol. 17, p. 120, 1756.
- [3] S. Lopez-Orozco, A. Inayat, A. Schwab, T. Selvam, and W. Schwieger, “Zeolitic materials with hierarchical porous structures,” *Advanced Materials*, vol. 23, no. 22-23, pp. 2602–2615, 2011.
- [4] C. Vercaemst, *Isomeric olefinic periodic mesoporous organosilicas: an emerging class of versatile nanomaterials*. PhD thesis, Ghent University, 2009.
- [5] International Zeolite Association (IZA), “Iza structure commission.” <http://www.iza-structure.org/>, 2025. Accessed: 2025-06-21.
- [6] W. Yan and J. Yu, “Our journey in zeolite science,” *Microporous and Mesoporous Materials*, vol. 358, p. 112368, 2023.
- [7] V. A. Blatov, G. D. Ilyushin, and D. M. Proserpio, “The zeolite conundrum: why are there so many hypothetical zeolites and so few observed? a possible answer from the zeolite-type frameworks perceived as packings of tiles,” *Chemistry of Materials*, vol. 25, no. 3, pp. 412–424, 2013.

- [8] B. A. Helfrecht, G. Pireddu, R. Semino, S. M. Auerbach, and M. Ceriotti, “Ranking the synthesizability of hypothetical zeolites with the sorting hat,” *Digital Discovery*, vol. 1, no. 6, pp. 779–789, 2022.
- [9] S. M. Auerbach, K. A. Carrado, and P. K. Dutta, *Handbook of zeolite science and technology*. CRC press, 2003.
- [10] M. Moshoeshoe, M. S. Nadiye-Tabbiruka, and V. Obuseng, “A review of the chemistry, structure, properties and applications of zeolites,” *Am. J. Mater. Sci*, vol. 7, no. 5, pp. 196–221, 2017.
- [11] X. Meng and F.-S. Xiao, “Green routes for synthesis of zeolites,” *Chemical reviews*, vol. 114, no. 2, pp. 1521–1543, 2014.
- [12] A. Miteva and V. Stoyanova, “Zeolites application in terrestrial and space industry—a review,” *Aerospace Research in Bulgaria*, vol. 32, pp. 209–223, 2020.
- [13] Y. Chai, W. Dai, G. Wu, N. Guan, and L. Li, “Confinement in a zeolite and zeolite catalysis,” *Accounts of Chemical Research*, vol. 54, no. 13, pp. 2894–2904, 2021.
- [14] A. Corma, M. J. Díaz-Cabañas, J. Martínez-Triguero, F. Rey, and J. Rius, “A large-cavity zeolite with wide pore windows and potential as an oil refining catalyst,” *Nature*, vol. 418, no. 6897, pp. 514–517, 2002.
- [15] K. Ramesh and D. D. Reddy, “Zeolites and their potential uses in agriculture,” *Advances in agronomy*, vol. 113, pp. 219–241, 2011.
- [16] S. Mintova and T. Bein, “Nanosized zeolite films for vapor-sensing applications,” *Microporous and Mesoporous Materials*, vol. 50, no. 2-3, pp. 159–166, 2001.
- [17] T. Nawaz and S. Sengupta, “Silver recovery from laundry wastewater: the role of detergent chemistry,” *ACS Sustainable Chemistry & Engineering*, vol. 6, no. 1, pp. 600–608, 2018.

- [18] L. Bacakova, M. Vandrovцова, I. Kopova, and I. Jirka, “Applications of zeolites in biotechnology and medicine—a review,” *Biomaterials science*, vol. 6, no. 5, pp. 974–989, 2018.
- [19] R. Núñez-González, M. Xiao, J. Antúnez-García, J. L. Ponce-Ruiz, A. Reyes-Serrato, V. Petranovskii, F. N. Murrieta-Rico, and N. Rakov, “First-principles study of optical properties of linde-type a zeolite,” *physica status solidi (b)*, vol. 260, no. 12, p. 2300378, 2023.
- [20] M. Borja and P. K. Dutta, “Storage of light energy by photoelectron transfer across a sensitized zeolite–solution interface,” *Nature*, vol. 362, no. 6415, pp. 43–45, 1993.
- [21] J. Cejka, A. Corma, and S. Zones, *Zeolites and catalysis: synthesis, reactions and applications*. John Wiley & Sons, 2010.
- [22] H. G. Karge and J. Weitkamp, “Molecular sieves,” *Science and Technology*, vol. 1, 1999.
- [23] A. Deneyer, Q. Ke, J. Devos, and M. Dusselier, “Zeolite synthesis under non-conventional conditions: reagents, reactors, and modi operandi,” *Chemistry of Materials*, vol. 32, no. 12, pp. 4884–4919, 2020.
- [24] Z. Liu, J. Zhu, T. Wakiyara, and T. Okubo, “Ultrafast synthesis of zeolites: breakthrough, progress and perspective,” *Inorganic Chemistry Frontiers*, vol. 6, no. 1, pp. 14–31, 2019.
- [25] X. Chen, M. Qiu, S. Li, C. Yang, L. Shi, S. Zhou, G. Yu, L. Ge, X. Yu, Z. Liu, *et al.*, “Gamma-ray irradiation to accelerate crystallization of mesoporous zeolites,” *Angewandte Chemie International Edition*, vol. 59, no. 28, pp. 11325–11329, 2020.
- [26] G. A. Tompsett, W. C. Conner, and K. S. Yngvesson, “Microwave synthesis of nanoporous materials,” *Chemphyschem: a European journal of chemical physics and physical chemistry*, vol. 7, no. 2, pp. 296–319, 2006.

- [27] D. Lesthaeghe, P. Vansteenkiste, T. Verstraelen, A. Ghysels, C. E. Kirschhock, J. A. Martens, V. V. Speybroeck, and M. Waroquier, “Mfi fingerprint: How pentasil-induced ir bands shift during zeolite nanogrowth,” *The Journal of Physical Chemistry C*, vol. 112, no. 25, pp. 9186–9191, 2008.
- [28] X.-Q. Zhang, T. T. Trinh, R. A. van Santen, and A. P. Jansen, “Mechanism of the initial stage of silicate oligomerization,” *Journal of the American Chemical Society*, vol. 133, no. 17, pp. 6613–6625, 2011.
- [29] S. Galioglu, M. Hagverdiyev, M. M. Doğan, Ö. Yavuz, Ü. S. Nizam, G. Makey, A. Şura, M. Laçın, B. A. Kurç, P. Elahi, *et al.*, “Ultrafast laser synthesis of zeolites,” *Advanced Materials*, p. 2415562, 2025.
- [30] D. Breck, W. Eversole, and R. Milton, “New synthetic crystalline zeolites,” *Journal of the American Chemical Society*, vol. 78, no. 10, pp. 2338–2339, 1956.
- [31] S. a. M. de Lucena, J. C. A. Oliveira, D. V. Gonçalves, L. M. Lucas, P. A. Moura, R. G. Santiago, D. C. Azevedo, and M. Bastos-Neto, “Lta zeolite characterization based on pore type distribution,” *Industrial & Engineering Chemistry Research*, vol. 61, no. 5, pp. 2268–2279, 2022.
- [32] F. Collins, A. Rozhkovskaya, J. G. Outram, and G. J. Millar, “A critical review of waste resources, synthesis, and applications for zeolite lta,” *Microporous and mesoporous Materials*, vol. 291, p. 109667, 2020.
- [33] J. Pan, B. Wang, S. Liu, S. Liu, and W. Yan, “Synthesis and application of lta zeolite for the removal of inorganic and organic hazardous substances from water: A review,” *Molecules*, vol. 30, no. 3, p. 554, 2025.
- [34] M. B. Park, Y. Lee, A. Zheng, F.-S. Xiao, C. P. Nicholas, G. J. Lewis, and S. B. Hong, “Formation pathway for lta zeolite crystals synthesized via a charge density mismatch approach,” *Journal of the American Chemical Society*, vol. 135, no. 6, pp. 2248–2255, 2013.

- [35] M. D. Oleksiak, J. A. Soltis, M. T. Conato, R. L. Penn, and J. D. Rimer, "Nucleation of fau and lta zeolites from heterogeneous aluminosilicate precursors," *Chemistry of Materials*, vol. 28, no. 14, pp. 4906–4916, 2016.
- [36] A. J. Mallette, K. Shilpa, and J. D. Rimer, "The current understanding of mechanistic pathways in zeolite crystallization," *Chemical Reviews*, vol. 124, no. 6, pp. 3416–3493, 2024.
- [37] A. I. Lupulescu and J. D. Rimer, "In situ imaging of silicalite-1 surface growth reveals the mechanism of crystallization," *Science*, vol. 344, no. 6185, pp. 729–732, 2014.
- [38] S. Mintova, N. H. Olson, V. Valtchev, and T. Bein, "Mechanism of zeolite a nanocrystal growth from colloids at room temperature," *Science*, vol. 283, no. 5404, pp. 958–960, 1999.
- [39] J. Grand, H. Awala, and S. Mintova, "Mechanism of zeolites crystal growth: new findings and open questions," *CrystEngComm*, vol. 18, no. 5, pp. 650–664, 2016.
- [40] W. Fan, M. Ogura, G. Sankar, and T. Okubo, "In situ small-angle and wide-angle x-ray scattering investigation on nucleation and crystal growth of nanosized zeolite a," *Chemistry of Materials*, vol. 19, no. 8, pp. 1906–1917, 2007.
- [41] L. Ren, C. Li, F. Fan, Q. Guo, D. Liang, Z. Feng, C. Li, S. Li, and F.-S. Xiao, "Uv-raman and nmr spectroscopic studies on the crystallization of zeolite a and a new synthetic route," *Chemistry–A European Journal*, vol. 17, no. 22, pp. 6162–6169, 2011.
- [42] D. G. Boer, J. Langerak, and P. P. Pescarmona, "Zeolites as selective adsorbents for co2 separation," *ACS Applied Energy Materials*, vol. 6, no. 5, pp. 2634–2656, 2023.

- [43] Z. Tao, Y. Tian, W. Wu, Z. Liu, W. Fu, C.-W. Kung, and J. Shang, “Development of zeolite adsorbents for co₂ separation in achieving carbon neutrality,” *npj Materials Sustainability*, vol. 2, no. 1, p. 20, 2024.
- [44] A. Mace, K. Laasonen, and A. Laaksonen, “Free energy barriers for co₂ and n₂ in zeolite naka: an ab initio molecular dynamics approach,” *Physical Chemistry Chemical Physics*, vol. 16, no. 1, pp. 166–172, 2014.
- [45] G. Busca, “Acidity and basicity of zeolites: A fundamental approach,” *Microporous and Mesoporous Materials*, vol. 254, pp. 3–16, 2017.
- [46] M. Huang, A. Auroux, and S. Kaliaguine, “Crystallinity dependence of acid site distribution in ha, hx and hy zeolites,” *Microporous Materials*, vol. 5, no. 1-2, pp. 17–27, 1995.
- [47] S. H. Ahn, Q. Wang, Y. Wang, Y. Chu, F. Deng, and S. B. Hong, “Identifying crystallographically different si-oh-al brønsted acid sites in lta zeolites,” *Angewandte Chemie International Edition*, vol. 61, no. 24, p. e202203603, 2022.
- [48] T. Lemishko, M. Jiménez-Ruiz, F. Rey, S. Valencia, T. Blasco, A. Vidal Moya, and G. Sastre, “Inelastic neutron scattering study of the aluminum and brønsted site location in aluminosilicate lta zeolites,” *The Journal of Physical Chemistry C*, vol. 122, no. 21, pp. 11450–11454, 2018.
- [49] T. Lemishko, S. Valencia, F. Rey, M. Jimenez-Ruiz, and G. Sastre, “Inelastic neutron scattering study on the location of brønsted acid sites in high silica lta zeolite,” *The Journal of Physical Chemistry C*, vol. 120, no. 43, pp. 24904–24909, 2016.
- [50] H. Xu, P. Lu, G. Fu, J. Miao, J. Zhao, R. Ding, L. Zhao, Z. Lang, X. Yang, and V. Valtchev, “The strong sda/framework interactions and acidity study of high-silica lta-type zeolites,” *Microporous and Mesoporous Materials*, vol. 360, p. 112724, 2023.

- [51] T. Sun, J. Wei, C. Zhou, Y. Wang, Z. Shu, J. Zhou, and J. Chen, “Facile preparation and enhanced photocatalytic hydrogen evolution of cation-exchanged zeolite lta supported tio₂ photocatalysts,” *International Journal of Hydrogen Energy*, vol. 48, no. 37, pp. 13851–13863, 2023.
- [52] L. Hong, J. Zang, B. Li, G. Liu, Y. Wang, and L. Wu, “Research progress on the synthesis of nanosized and hierarchical beta zeolites,” *Inorganics*, vol. 11, no. 5, p. 214, 2023.
- [53] E. Jaramillo and M. Chandross, “Adsorption of small molecules in lta zeolites. 1. nh₃, co₂, and h₂o in zeolite 4a,” *The Journal of Physical Chemistry B*, vol. 108, no. 52, pp. 20155–20159, 2004.
- [54] M. Palomino, A. Corma, F. Rey, and S. Valencia, “New insights on co₂-methane separation using lta zeolites with different si/al ratios and a first comparison with mofs,” *Langmuir*, vol. 26, no. 3, pp. 1910–1917, 2010.
- [55] C. S. Cundy and P. A. Cox, “The hydrothermal synthesis of zeolites: history and development from the earliest days to the present time,” *Chemical reviews*, vol. 103, no. 3, pp. 663–702, 2003.
- [56] C. S. Cundy and P. A. Cox, “The hydrothermal synthesis of zeolites: Precursors, intermediates and reaction mechanism,” *Microporous and mesoporous materials*, vol. 82, no. 1-2, pp. 1–78, 2005.
- [57] S. Yu, S. Kwon, and K. Na, “Synthesis of lta zeolites with controlled crystal sizes by variation of synthetic parameters: Effect of na⁺ concentration, aging time, and hydrothermal conditions,” *Journal of Sol-Gel Science and Technology*, vol. 98, pp. 411–421, 2021.
- [58] X. Qinhuo and Y. Aizhen, “Hydrothermal synthesis and crystallization of zeolites,” *Progress in Crystal Growth and Characterization of Materials*, vol. 21, no. 1-4, pp. 29–70, 1991.

- [59] S. Głowniak, B. Szczęśniak, J. Choma, and M. Jaroniec, “Advances in microwave synthesis of nanoporous materials,” *Advanced Materials*, vol. 33, no. 48, p. 2103477, 2021.
- [60] M. Nüchter, B. Ondruschka, W. Bonrath, and A. Gum, “Microwave assisted synthesis—a critical technology overview,” *Green chemistry*, vol. 6, no. 3, pp. 128–141, 2004.
- [61] CEM Corporation, “Theory of microwave chemistry.” https://cem.com/pt/microwave-chemistry/theory?___store=pt&___from_store=en, 2025. Accessed: 2025-06-27.
- [62] G. Feng, P. Cheng, W. Yan, M. Boronat, X. Li, J.-H. Su, J. Wang, Y. Li, A. Corma, R. Xu, *et al.*, “Accelerated crystallization of zeolites via hydroxyl free radicals,” *Science*, vol. 351, no. 6278, pp. 1188–1191, 2016.
- [63] J. Chen, M. Zhang, J. Shu, M. Yuan, W. Yan, P. Bai, L. He, N. Shen, S. Gong, D. Zhang, *et al.*, “Electron beam irradiation-induced formation of defect-rich zeolites under ambient condition within minutes,” *Angewandte Chemie International Edition*, vol. 60, no. 27, pp. 14858–14863, 2021.
- [64] T. H. Novita and G. T. Kadja, “Hydroxyl radicals-mediated zeolite crystallization: impacts on the kinetics, crystal morphologies, and catalytic application,” *Journal of Porous Materials*, vol. 31, no. 2, pp. 403–421, 2024.
- [65] C. Sidhoum, A. Amedlous, C. Sanchez, O. Ersen, and S. Mintova, “Ultra-fast crystallization of nanozeolite via hydroxyl radicals generated by electron-beam-induced radiolysis,” *Small Science*, p. 2500089, 2025.
- [66] M. V. Shugaev, C. Wu, O. Armbruster, A. Naghilou, N. Brouwer, D. S. Ivanov, T. J.-Y. Derrien, N. M. Bulgakova, W. Kautek, B. Rethfeld, *et al.*, “Fundamentals of ultrafast laser–material interaction,” *Mrs Bulletin*, vol. 41, no. 12, pp. 960–968, 2016.

- [67] K. C. Phillips, H. H. Gandhi, E. Mazur, and S. Sundaram, “Ultrafast laser processing of materials: a review,” *Advances in Optics and Photonics*, vol. 7, no. 4, pp. 684–712, 2015.
- [68] J. D. Pickering, *Ultrafast lasers and optics for experimentalists*. IOP Publishing, 2024.
- [69] J. Theerthagiri, K. Karuppasamy, S. J. Lee, R. Shwetharani, H.-S. Kim, S. K. Pasha, M. Ashokkumar, and M. Y. Choi, “Fundamentals and comprehensive insights on pulsed laser synthesis of advanced materials for diverse photo-and electrocatalytic applications,” *Light: Science & Applications*, vol. 11, no. 1, p. 250, 2022.
- [70] G. M. Peavy, “Lasers and laser–tissue interaction,” *Veterinary Clinics: Small Animal Practice*, vol. 32, no. 3, pp. 517–534, 2002.
- [71] V. Venugopalan, N. Nishioka, and B. Mikić, “Thermodynamic response of soft biological tissues to pulsed infrared-laser irradiation,” *Biophysical Journal*, vol. 70, no. 6, pp. 2981–2993, 1996.
- [72] X. Jia and X. Zhao, “Thermal accumulation at kilohertz repetition rates inside fused silica under ultrafast laser irradiation,” *Optics letters*, vol. 45, no. 13, pp. 3390–3393, 2020.
- [73] E. Optics, “Basics of ultrafast lasers,” n.d. Accessed: 2025-07-02.
- [74] H. K. Soong and J. B. Malta, “Femtosecond lasers in ophthalmology,” *American journal of ophthalmology*, vol. 147, no. 2, pp. 189–197, 2009.
- [75] C. Kerse, H. Kalaycıoğlu, P. Elahi, B. Çetin, D. K. Kesim, Ö. Akçaalan, S. Yavaş, M. D. Aşık, B. Öktem, H. Hoogland, *et al.*, “Ablation-cooled material removal with ultrafast bursts of pulses,” *Nature*, vol. 537, no. 7618, pp. 84–88, 2016.
- [76] J. Bonse, S. Baudach, J. Krüger, W. Kautek, and M. Lenzner, “Femtosecond laser ablation of silicon–modification thresholds and morphology,” *Applied Physics A*, vol. 74, pp. 19–25, 2002.

- [77] P. K. Kennedy, “A first-order model for computation of laser-induced breakdown thresholds in ocular and aqueous media. i. theory,” *IEEE journal of quantum electronics*, vol. 31, no. 12, pp. 2241–2249, 2002.
- [78] Y. Chen, Y. Hu, Y. Wang, Y. Jiang, A. Chen, and M. Jin, “Dynamics of femtosecond laser-driven liquid jets,” *Physics of Fluids*, vol. 36, no. 9, 2024.
- [79] V. Korede, N. Nagalingam, F. M. Penha, N. van der Linden, J. T. Padding, R. Hartkamp, and H. B. Eral, “A review of laser-induced crystallization from solution,” *Crystal Growth & Design*, vol. 23, no. 5, pp. 3873–3916, 2023.
- [80] V. Venugopalan, A. Guerra III, K. Nahen, and A. Vogel, “Role of laser-induced plasma formation in pulsed cellular microsurgery and micromanipulation,” *Physical review letters*, vol. 88, no. 7, p. 078103, 2002.
- [81] A. Stolow, A. E. Bragg, and D. M. Neumark, “Femtosecond time-resolved photoelectron spectroscopy,” *Chemical reviews*, vol. 104, no. 4, pp. 1719–1758, 2004.
- [82] O. Samek, D. C. Beddows, J. Kaiser, S. V. Kukhlevsky, M. Liska, H. H. Telle, and A. J. Whitehouse, “Application of laser-induced breakdown spectroscopy to in situ analysis of liquid samples,” *Optical Engineering*, vol. 39, no. 8, pp. 2248–2262, 2000.
- [83] G. S. He, L.-S. Tan, Q. Zheng, and P. N. Prasad, “Multiphoton absorbing materials: molecular designs, characterizations, and applications,” *Chemical reviews*, vol. 108, no. 4, pp. 1245–1330, 2008.
- [84] C. Xie, R. Meyer, L. Froehly, R. Giust, and F. Courvoisier, “In-situ diagnostic of femtosecond laser probe pulses for high resolution ultrafast imaging,” *Light: Science & Applications*, vol. 10, no. 1, p. 126, 2021.
- [85] P. K. Kennedy, D. X. Hammer, and B. A. Rockwell, “Laser-induced breakdown in aqueous media,” *Progress in quantum electronics*, vol. 21, no. 3, pp. 155–248, 1997.

- [86] J. Noack and A. Vogel, “Laser-induced plasma formation in water at nanosecond to femtosecond time scales: calculation of thresholds, absorption coefficients, and energy density,” *IEEE journal of quantum electronics*, vol. 35, no. 8, pp. 1156–1167, 2002.
- [87] L. Staff, “Pulsed laser-induced cavitation: Ultrafast bubbles enable novel nano-/microfluidic systems,” 2023. Accessed: 2025-07-04.
- [88] B. Yan, Q. Gu, W. Cao, B. Cai, Y. Li, Z. Zeng, P. Liu, Z. Ke, S. Meng, G. Ouyang, *et al.*, “Laser direct overall water splitting for h₂ and h₂o₂ production,” *Proceedings of the National Academy of Sciences*, vol. 121, no. 9, p. e2319286121, 2024.
- [89] E. Vela, M. Hafez, and S. Régnier, “Laser-induced thermocapillary convection for mesoscale manipulation,” *International Journal of Optomechatronics*, vol. 3, no. 4, pp. 289–302, 2009.
- [90] G. Makey, S. Galioglu, R. Ghaffari, E. D. Engin, G. Yıldırım, Ö. Yavuz, O. Bektaş, Ü. S. Nizam, Ö. Akbulut, Ö. Şahin, *et al.*, “Universality of dissipative self-assembly from quantum dots to human cells,” *Nature Physics*, vol. 16, no. 7, pp. 795–801, 2020.
- [91] S. Ilday, G. Makey, G. B. Akguc, Ö. Yavuz, O. Tokel, I. Pavlov, O. Gülseren, and F. Ö. Ilday, “Rich complex behaviour of self-assembled nanoparticles far from equilibrium,” *Nature communications*, vol. 8, no. 1, p. 14942, 2017.
- [92] M. Hagverdiyev, “Femtosecond laser assisted synthesis of silicate-1 zeolite,” Master’s thesis, Bilkent Universitesi (Turkey), 2022.
- [93] S. Mintova, B. Fieres, and T. Bein, “Crystal growth of nanosized lta zeolite from precursor colloids,” in *Studies in Surface Science and Catalysis*, vol. 142, pp. 223–229, Elsevier, 2002.
- [94] J. Li, M. Gao, W. Yan, and J. Yu, “Regulation of the si/al ratios and al distributions of zeolites and their impact on properties,” *Chemical Science*, vol. 14, no. 8, pp. 1935–1959, 2023.

- [95] J. Antúnez-García, D. Galván, V. Petranovskii, F. N. Murrieta-Rico, R. I. Yocupicio-Gaxiola, M. G. Shelyapina, and S. Fuentes-Moyado, “The effect of chemical composition on the properties of lta zeolite: A theoretical study,” *Computational Materials Science*, vol. 196, p. 110557, 2021.
- [96] Y. Bouizi, J.-L. Paillaud, L. Simon, and V. Valtchev, “Seeded synthesis of very high silica zeolite a,” *Chemistry of materials*, vol. 19, no. 4, pp. 652–654, 2007.
- [97] J. Yu, “Synthesis of zeolites,” in *Studies in surface science and catalysis*, vol. 168, pp. 39–103, Elsevier, 2007.
- [98] M. M. Treacy and J. B. Higgins, *Collection of simulated XRD powder patterns for zeolites fifth (5th) revised edition*. Elsevier, 2007.
- [99] W. Zhou and H. F. Greer, “What can electron microscopy tell us beyond crystal structures?,” *European Journal of Inorganic Chemistry*, vol. 2016, no. 7, pp. 941–950, 2016.
- [100] G. Pál-Borbély, “Thermal analysis of zeolites,” *Characterization II*, pp. 67–101, 2005.
- [101] N. M. Musyoka, L. F. Petrik, E. Hums, A. Kuhnt, and W. Schwieger, “Thermal stability studies of zeolites a and x synthesized from south african coal fly ash,” *Research on Chemical Intermediates*, vol. 41, no. 2, pp. 575–582, 2015.
- [102] A. Iqbal, H. Sattar, R. Haider, and S. Munir, “Synthesis and characterization of pure phase zeolite 4a from coal fly ash,” *Journal of Cleaner Production*, vol. 219, pp. 258–267, 2019.
- [103] S. Lowell, J. E. Shields, M. A. Thomas, and M. Thommes, *Characterization of porous solids and powders: surface area, pore size and density*, vol. 16. Springer Science & Business Media, 2012.

- [104] Y.-S. Bae, A. O. Yazaydin, and R. Q. Snurr, "Evaluation of the bet method for determining surface areas of mofs and zeolites that contain ultra-micropores," *Langmuir*, vol. 26, no. 8, pp. 5475–5483, 2010.
- [105] S. Valencia and F. Rey, *New Developments in Adsorption/Separation of Small Molecules by Zeolites*. Springer, 2020.
- [106] S. Brunauer, P. H. Emmett, and E. Teller, "Adsorption of gases in multi-molecular layers," *Journal of the American chemical society*, vol. 60, no. 2, pp. 309–319, 1938.
- [107] M. Muttakin, S. Mitra, K. Thu, K. Ito, and B. B. Saha, "Theoretical framework to evaluate minimum desorption temperature for iupac classified adsorption isotherms," *International Journal of Heat and Mass Transfer*, vol. 122, pp. 795–805, 2018.
- [108] A. J. Connelly, "Bet surface area," 2017. Accessed: 2025-07-15.
- [109] J. De Boer, B. Lippens, B. Linsen, J. Broekhoff, A. Van den Heuvel, and T. J. Osinga, "Thet-curve of multimolecular n2-adsorption," *Journal of colloid and interface science*, vol. 21, no. 4, pp. 405–414, 1966.
- [110] E. Khoramzadeh, M. Mofarahi, and C.-H. Lee, "Equilibrium adsorption study of co2 and n2 on synthesized zeolites 13x, 4a, 5a, and beta," *Journal of Chemical & Engineering Data*, vol. 64, no. 12, pp. 5648–5664, 2019.
- [111] W. Chen, G. Song, Y. Lin, J. Qiao, T. Wu, X. Yi, and S. Kawi, "Synthesis and catalytic performance of linde-type a zeolite (lta) from coal fly ash utilizing microwave and ultrasound collaborative activation method," *Catalysis Today*, vol. 397, pp. 407–418, 2022.
- [112] D. Barthomeuf, "Spectroscopic investigations of zeolite properties," in *Zeolite Microporous Solids: Synthesis, Structure, and Reactivity*, pp. 193–223, Springer, 1992.
- [113] H. E. Robson, *Verified synthesis of zeolitic materials*. Gulf Professional Publishing, 2001.

- [114] M. K. Król and P. Jeleń, “The effect of heat treatment on the structure of zeolite a,” *Materials*, vol. 14, no. 16, p. 4642, 2021.
- [115] A. Koleżyński, A. Mikuła, and M. Król, “Periodic model of lta framework containing various non-tetrahedral cations,” *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 157, pp. 17–25, 2016.
- [116] W. Mozgawa, W. Jastrzębski, and M. Handke, “Vibrational spectra of d4r and d6r structural units,” *Journal of Molecular Structure*, vol. 744, pp. 663–670, 2005.
- [117] I. C. Medeiros-Costa, E. Dib, N. Nesterenko, J.-P. Dath, J.-P. Gilson, and S. Mintova, “Silanol defect engineering and healing in zeolites: opportunities to fine-tune their properties and performances,” *Chemical Society Reviews*, vol. 50, no. 19, pp. 11156–11179, 2021.
- [118] H. Furukawa, K. E. Cordova, M. O’Keeffe, and O. M. Yaghi, “The chemistry and applications of metal-organic frameworks,” *Science*, vol. 341, no. 6149, p. 1230444, 2013.
- [119] A. G. Slater and A. I. Cooper, “Porous materials. function-led design of new porous materials.,” *Science (New York, NY)*, vol. 348, no. 6238, pp. aaa8075–aaa8075, 2015.
- [120] A. Samanta, A. Zhao, G. K. Shimizu, P. Sarkar, and R. Gupta, “Post-combustion co2 capture using solid sorbents: a review,” *Industrial & Engineering Chemistry Research*, vol. 51, no. 4, pp. 1438–1463, 2012.
- [121] P. Pasabeyoglu, E. Deniz, G. Moumin, Z. Say, and B. Akata, “Solar-driven calcination of clays for sustainable zeolite production: Co2 capture performance at ambient conditions,” *Journal of Cleaner Production*, vol. 477, p. 143838, 2024.
- [122] M. K. Al Mesfer and M. Danish, “Breakthrough adsorption study of activated carbons for co2 separation from flue gas,” *Journal of Environmental Chemical Engineering*, vol. 6, no. 4, pp. 4514–4524, 2018.

- [123] M. K. A. Mesfer, M. Danish, M. I. Khan, I. H. Ali, M. Hasan, and A. E. Jery, “Continuous fixed bed co₂ adsorption: breakthrough, column efficiency, mass transfer zone,” *Processes*, vol. 8, no. 10, p. 1233, 2020.
- [124] F. Raganati, M. Bellusci, F. Leardi, F. Varsano, and P. Ammendola, “CaL-20 obtained by mechanochemical synthesis for temperature swing adsorption co₂ capture: A thermodynamic and kinetic study,” *Chemical Engineering Journal*, vol. 506, p. 159966, 2025.
- [125] P. Murge, S. Dinda, and S. Roy, “Zeolite-based sorbent for co₂ capture: preparation and performance evaluation,” *Langmuir*, vol. 35, no. 46, pp. 14751–14760, 2019.
- [126] M. M. Lozinska, E. Mangano, J. P. Mowat, A. M. Shepherd, R. F. Howe, S. P. Thompson, J. E. Parker, S. Brandani, and P. A. Wright, “Understanding carbon dioxide adsorption on univalent cation forms of the flexible zeolite rho at conditions relevant to carbon capture from flue gases,” *Journal of the American Chemical Society*, vol. 134, no. 42, pp. 17628–17642, 2012.
- [127] L. Hauchhum and P. Mahanta, “Carbon dioxide adsorption on zeolites and activated carbon by pressure swing adsorption in a fixed bed,” *International Journal of Energy and Environmental Engineering*, vol. 5, no. 4, pp. 349–356, 2014.

Appendix A

Average Absorbed Power Measurements for Zeolite A

Zeolite A molar formula in the Chapter 3.3 was used to prepare precursor suspension. Precursor aged for 16 hours and has blurry-transparent color. 400 μl of precursor solution was used for the Power Absorption Experiment. Firstly, a 200 kHz repetition rate was used, then a 500 kHz and 1 MHz repetition rates were used. Data for power from 1 Watt to 6 Watt was collected for each. After first bubble formation, the output power was recorded in the **Table A.1**, **Table A.2**, and **Table A.3**.

Table A.1: Laser parameters of power absorption measurements of zeolite A for 200 kHz repetition rate.

Avg Laser Power Incident (W)	Avg Laser Power Passed (W)	Avg Power Absorbed (W)	Pulse Repetition Rate (kHz)	Pulse Energy (μJ)	Pulse Duration (fs)	Spot Size (μm)	Area (cm^2)	Peak Power (MW)	Pulse Fluence (Jcm^{-2})	Max Laser Power (%)	Bubble Formation and Color Change
1	-	-	200 kHz	-	300	9	6.36×10^{-7}	-	-	16	No
1.5	-	-	200 kHz	-	300	9	6.36×10^{-7}	-	-	23	No
2	-	-	200 kHz	-	300	9	6.36×10^{-7}	-	-	31	No
2.5	0.4	0.56	200 kHz	2.79	300	9	6.36×10^{-7}	9.33	4.40	39	Little
3	0.55	0.59	200 kHz	2.95	300	9	6.36×10^{-7}	9.83	4.64	46	Yes
3.5	0.62	0.72	200 kHz	3.58	300	9	6.36×10^{-7}	12.00	5.66	54	Yes
4	0.63	0.91	200 kHz	4.55	300	9	6.36×10^{-7}	15.17	7.15	62	Yes
4.5	0.55	1.21	200 kHz	6.05	300	9	6.36×10^{-7}	20.17	9.51	69	Yes
5	0.53	1.43	200 kHz	7.15	300	9	6.36×10^{-7}	23.83	11.24	77	Yes
5.5	0.5	1.68	200 kHz	8.40	300	9	6.36×10^{-7}	28.00	13.21	84	Yes
6	0.4	1.99	200 kHz	9.95	300	9	6.36×10^{-7}	33.17	15.64	92	Yes

Table A.2: Laser parameters of power absorption measurements of zeolite A for 500 kHz repetition rate.

Average Laser Power Incident (W)	Average Laser Power Passed (W)	Average Power Absorbed (W)	Pulse Repetition Rate (kHz)	Pulse Energy (μJ)	Pulse Duration (fs)	Spot Size (μm)	Area (cm^2)	Peak Power (MW)	Pulse Fluence (Jcm^{-2})	Max Laser Power (%)	Bubble Formation and Color Change
1	-	-	500 kHz	-	300	9	6.36×10^{-7}	-	-	16	No
1.5	-	-	500 kHz	-	300	9	6.36×10^{-7}	-	-	24	No
2	-	-	500 kHz	-	300	9	6.36×10^{-7}	-	-	32	-
2.5	-	-	500 kHz	-	300	9	6.36×10^{-7}	-	-	40	-
3	0.65	0.47	500 kHz	0.94	300	9	6.36×10^{-7}	3.13	1.48	47	Little
3.5	0.61	0.73	500 kHz	1.46	300	9	6.36×10^{-7}	4.87	2.30	55	Yes
4	0.55	1.00	500 kHz	2.00	300	9	6.36×10^{-7}	6.67	3.14	63	Yes
4.5	0.46	1.31	500 kHz	2.62	300	9	6.36×10^{-7}	8.73	4.12	70	Yes
5	0.53	1.43	500 kHz	2.86	300	9	6.36×10^{-7}	9.53	4.50	77	Yes
5.5	0.58	1.58	500 kHz	3.16	300	9	6.36×10^{-7}	10.53	4.97	85	Yes
6	0.7	1.64	500 kHz	3.28	300	9	6.36×10^{-7}	10.93	5.16	93	Yes

Table A.3: Laser parameters of power absorption measurements of zeolite A for 1MHz repetition rate.

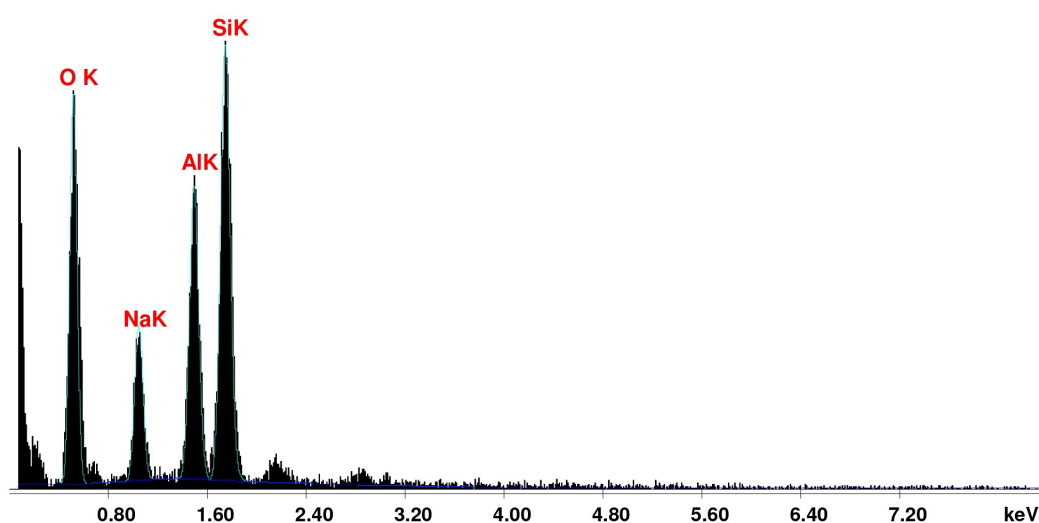
Average Laser Power Incident (W)	Average Laser Power Passed (W)	Average Power Absorbed (W)	Pulse Repetition Rate (kHz)	Pulse Energy (μJ)	Pulse Duration (fs)	Spot Size (μm)	Area (cm^2)	Peak Power (MW)	Pulse Fluence (Jcm^{-2})	Max Laser Power (%)	Bubble Formation and Color Change
1	-	-	1 MHz	-	300	9	6.36×10^{-7}	-	-	17	No
1.5	-	-	1 MHz	-	300	9	6.36×10^{-7}	-	-	25	No
2	0.4	0.35	1 MHz	0.35	300	9	6.36×10^{-7}	1.17	0.55	33	Very Little
2.5	0.44	0.51	1 MHz	0.51	300	9	6.36×10^{-7}	1.70	0.80	41	Little
3	0.54	0.60	1 MHz	0.60	300	9	6.36×10^{-7}	2.00	0.94	48	Little
3.5	0.56	0.78	1 MHz	0.78	300	9	6.36×10^{-7}	2.60	1.23	56	Little
4	0.61	0.93	1 MHz	0.93	300	9	6.36×10^{-7}	3.10	1.45	64	Yes
4.5	0.54	1.22	1 MHz	1.22	300	9	6.36×10^{-7}	4.07	1.92	71	Yes
5	0.59	1.36	1 MHz	1.36	300	9	6.36×10^{-7}	5.53	2.14	79	Yes
5.5	0.52	1.65	1 MHz	1.65	300	9	6.36×10^{-7}	5.50	2.60	86	Yes
6	0.59	1.77	1 MHz	1.77	300	9	6.36×10^{-7}	5.90	2.78	95	Yes

Appendix B

Energy Dispersive X-Ray Spectroscopy Results of Zeolite A

Energy Dispersive X-Ray Spectroscopy (EDXS) analysis was performed to determine the elemental composition and Si/Al ratio of Zeolite A samples synthesized via the ultrafast laser method and the conventional hydrothermal method. Spectra were taken from seven different points on the surface of the samples, which were pressed as powder onto the SEM stub for both methods, and the average of these values was calculated. This approach was chosen to evaluate the homogeneity of the samples and to obtain a more representative composition by minimizing potential local variations. The Si/Al ratio was obtained by comparing the atomic % of the Si and Al atoms in the spectra in **Figure B.1** and **Figure B.2**.

c:\edax32\genesis\genspc.spc
 Label:Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)
 kV:15.0 Tilt:0.0 Take-off:14.4 Det TypeSDD Apollo X Res:136 Amp.T:0.8
 FS : 521 Lsec : 7 12-Feb-2025 08:36:04



Weight % by Element

Filename	O K	NaK	AlK	SiK
genspc.spc	41.50	11.63	16.95	29.93

Atomic % by Element

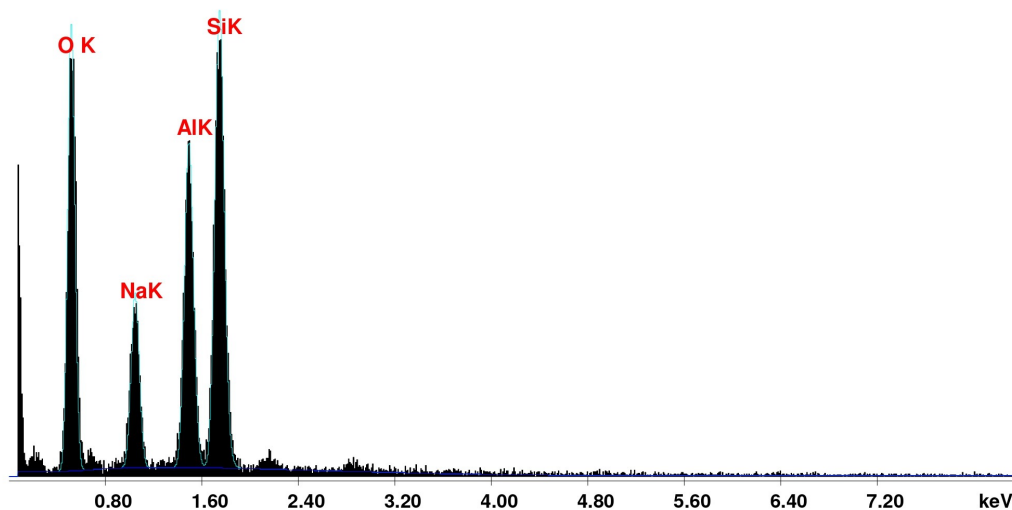
Filename	O K	NaK	AlK	SiK
genspc.spc	54.11	10.55	13.10	22.23

K-Ratio

Filename	O K	NaK	AlK	SiK
genspc.spc	0.1352	0.0453	0.0961	0.1599

Figure B.1: One of the the Energy Dispersive X-Ray (EDX) spectrum of the Zeolite A crystals synthesized via ultrafast laser method as an representative spectrum.

c:\edax32\genesis\genspc.spc
Label:Chlorite (Nrm.%= 38.86, 20.96, 34.83, 1.14, 3.84, 0.28)
kV:15.0 Tilt:0.0 Take-off:14.4 Det TypeSDD Apollo X Res:136 Amp.T:0.8
FS : 802 Lsec : 14 12-Feb-2025 08:44:31



Weight % by Element

Filename	O K	NaK	AlK	SiK
genspc.spc	42.29	11.91	17.14	28.66

Atomic % by Element

Filename	O K	NaK	AlK	SiK
genspc.spc	54.88	10.75	13.19	21.18

K-Ratio

Filename	O K	NaK	AlK	SiK
genspc.spc	0.1400	0.0460	0.0963	0.1517

Figure B.2: One of the Energy Dispersive X-Ray (EDX) spectrum of the Zeolite A crystals synthesized via conventional hydrothermal method as an representative spectrum.

Appendix C

Details of the CO₂ Adsorption Analysis

Prior to measurements, a thermal activation treatment was carried out to eliminate water molecules from the pores, guaranteeing that CO₂ molecules could fully enter the pore space. As observed from thermogravimetric analysis (TGA) in Chapter 4.5, the water retention of zeolite A crystals synthesized via the ultra-fast laser method and the hydrothermal method is quite similar. Similar results are also observed in **Figure C.1**, however, there is a broadening in the water signal of the hydrothermal sample compared to the laser sample. Due to a technical problem during the measurement, the laser sample underwent thermal treatment and was exposed to CO₂ gas twice. Therefore, the difference in water signal between the two samples is due to the weight loss of the laser sample between the experiments and containing less water compared to the hydrothermal sample.

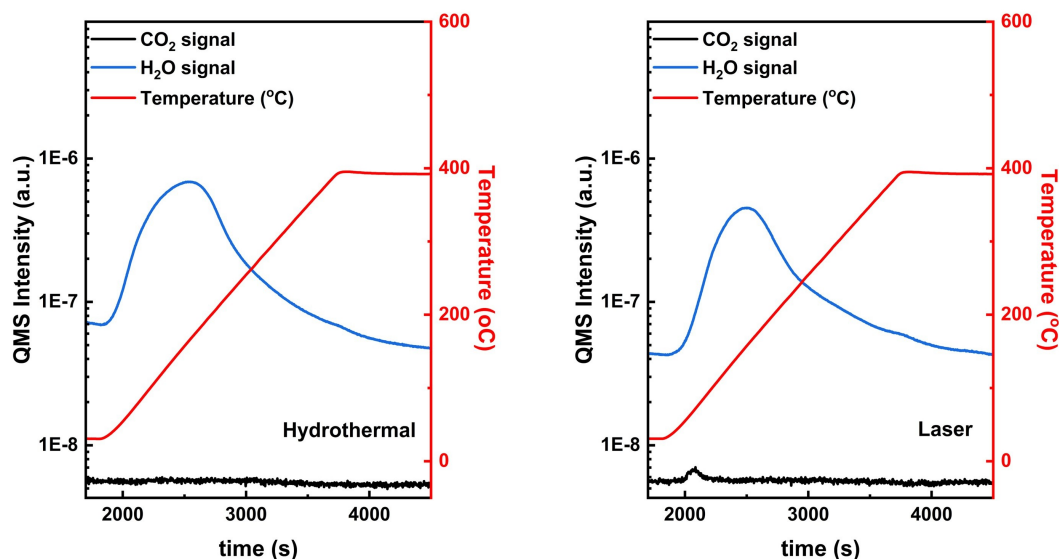


Figure C.1: Initial heat treatment result for zeolite A synthesized via ultrafast laser method (laser) and conventional hydrothermal method (hydrothermal). The plots include the CO₂ signal, the water (H₂O) signal, and the temperature (°C).

Since the CO₂ adsorption measurement was repeated twice for the zeolite A synthesized via ultrafast laser, a small CO₂ peak was observed at the beginning of the heat treatment. This peak indicates that CO₂ remaining from the previous adsorption-desorption cycle was retained in the pores. In contrast, since the hydrothermally synthesized Zeolite A had not been exposed to any CO₂ flow beforehand, no CO₂ peak was observed during the heat treatment.

Following thermal activation, the samples were exposed to a mixture of 2% CO₂ in argon gas at 1 bar and 20 sccm flow rate at room temperature for 3 hours. During this time, dynamic breakthrough curves were obtained by continuously monitoring the m/z 44 signals (i.e., CO₂ signal) with a mass spectrometer. The lack of a signal detection for a certain period despite the introduction of CO₂ gas into the system indicates that CO₂ is diffusing into the pores of the adsorbent and is being retained. During the period when this signal is not observed, CO₂ is adsorbed by the adsorbent in the active sites; when the signal begins to increase,

the system reaches saturation. Therefore, the area under the breakthrough curve provides quantitative information about the adsorption capacity.

To quantitatively calculate the CO₂ adsorption capacity, the system was first calibrated. For this purpose, a "blank test" was conducted under the same experimental conditions with an empty reactor containing no adsorbent, and system-induced lag times were determined. This process is critical to isolate the effect of the adsorbent alone. Firstly, the calibration area (S), which is the theoretical signal area obtained by introducing CO₂ at a constant flow rate under known flow conditions, is determined:

$$S = \frac{P \cdot V_{\text{total}}}{R \cdot T} \quad (\text{C.1})$$

where P is the atmospheric pressure, V_{total} is the total calibration volume, R is the ideal gas constant, and T is the temperature. The calibration volume is the amount of CO₂ introduced into the system without adsorbent during the experiment:

$$V_{\text{total}} = \text{Time (min)} \times \text{Flow rate (cm}^3/\text{min)} \times \frac{\% \text{CO}_2}{100} \quad (\text{C.2})$$

When the parameter values used in the experiment are included, the calibrated volume is calculated as:

$$V_{\text{total}} = 10 \text{ min} \times 20 \frac{\text{cm}^3}{\text{min}} \times \frac{2}{100} = 4 \text{ cm}^3 \quad (\text{C.3})$$

When we put this volume value into Equation C.1, the calibrated area value is:

$$S = \frac{1 \times 4 \times 10^{-3}}{0.082057 \times 298.15} \approx 1.635 \times 10^{-4} \text{ mol} = 0.1635 \text{ mmol} \quad (\text{C.4})$$

Secondly, the CCA, the area under the CO₂ breakthrough curve obtained by the mas spectrometer in the experiment, is calculated. This area was calculated for each measurement using OriginLab Software (see Figure C.2, Figure C.3 and Figure C.4). The actual adsorption is calculated as the ratio of this area to the calibration area and normalized by the mass of the adsorbent:

$$\text{Captured CO}_2 = \frac{\text{CCA}}{S} \times \frac{1 \text{ g}}{m} \quad (\text{C.5})$$

where m is the mass of the adsorbent and it is 0.1 g in our work. Nevertheless, it is important to consider the weight of the hydrothermal sample (0.0842 g) and the laser sample (0.0672 g) due to the weight losses during the experiment for laser sample and the amount of water removed from the pores.

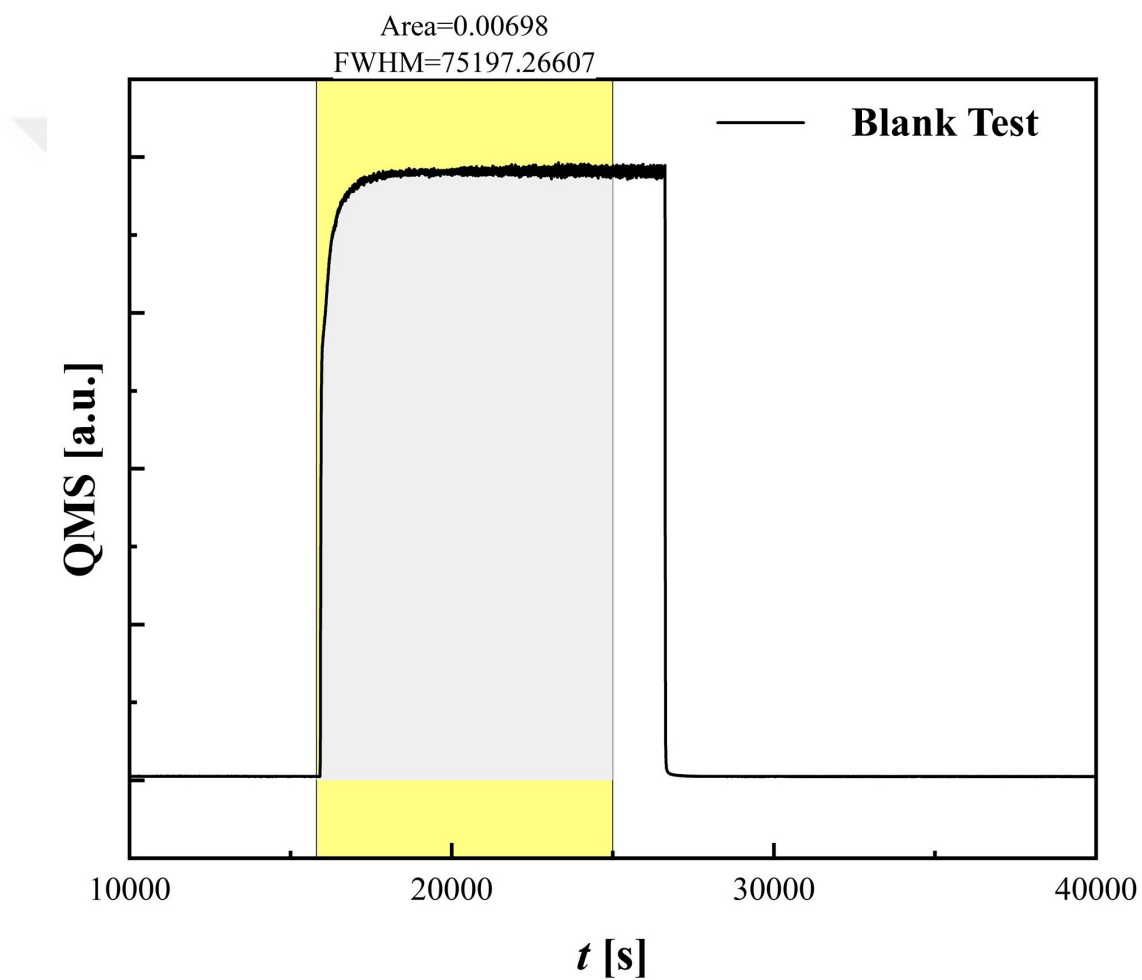


Figure C.2: The area under the CO₂ breakthrough curve of blank test calculated by using OriginLab Software.

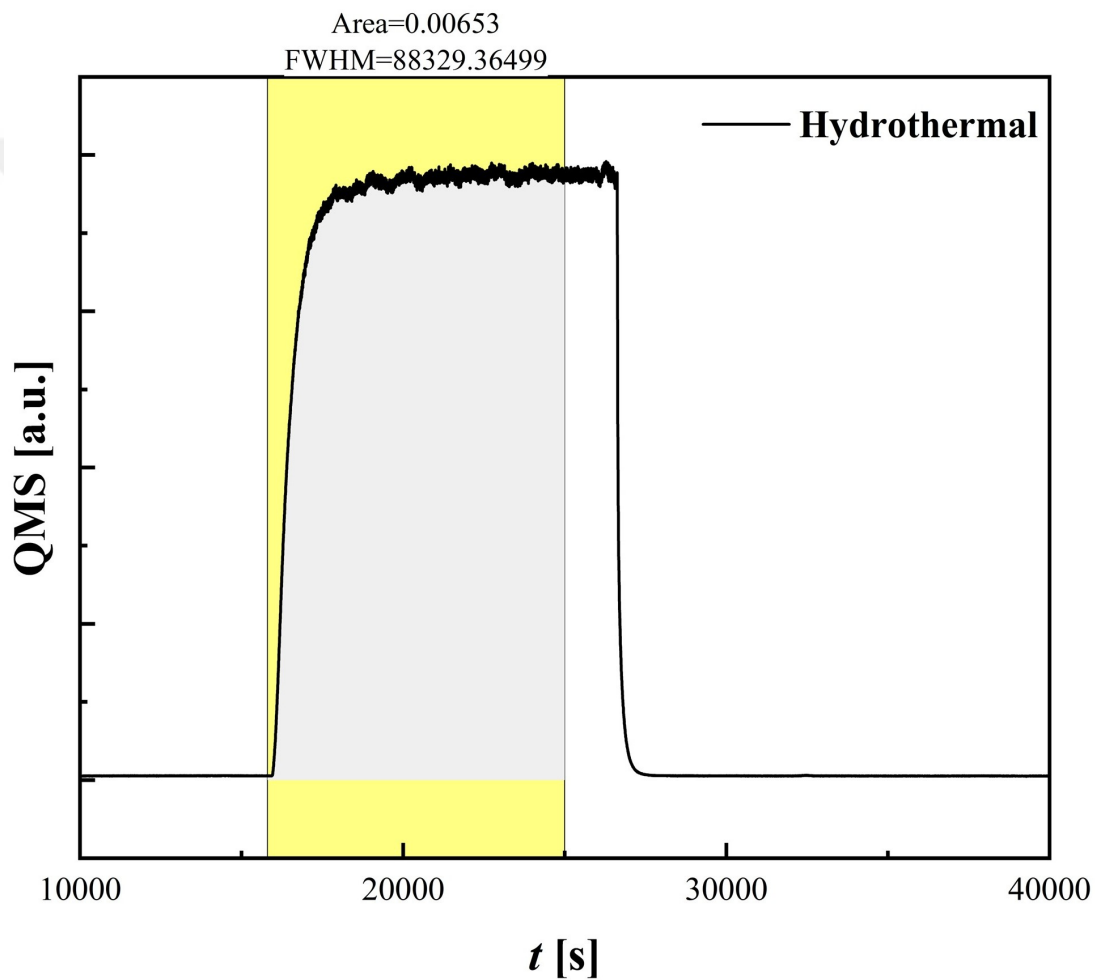


Figure C.3: The area under the CO₂ breakthrough curve of Zeolite A crystals synthesized via conventional hydrothermal method calculated by using OriginLab Software.

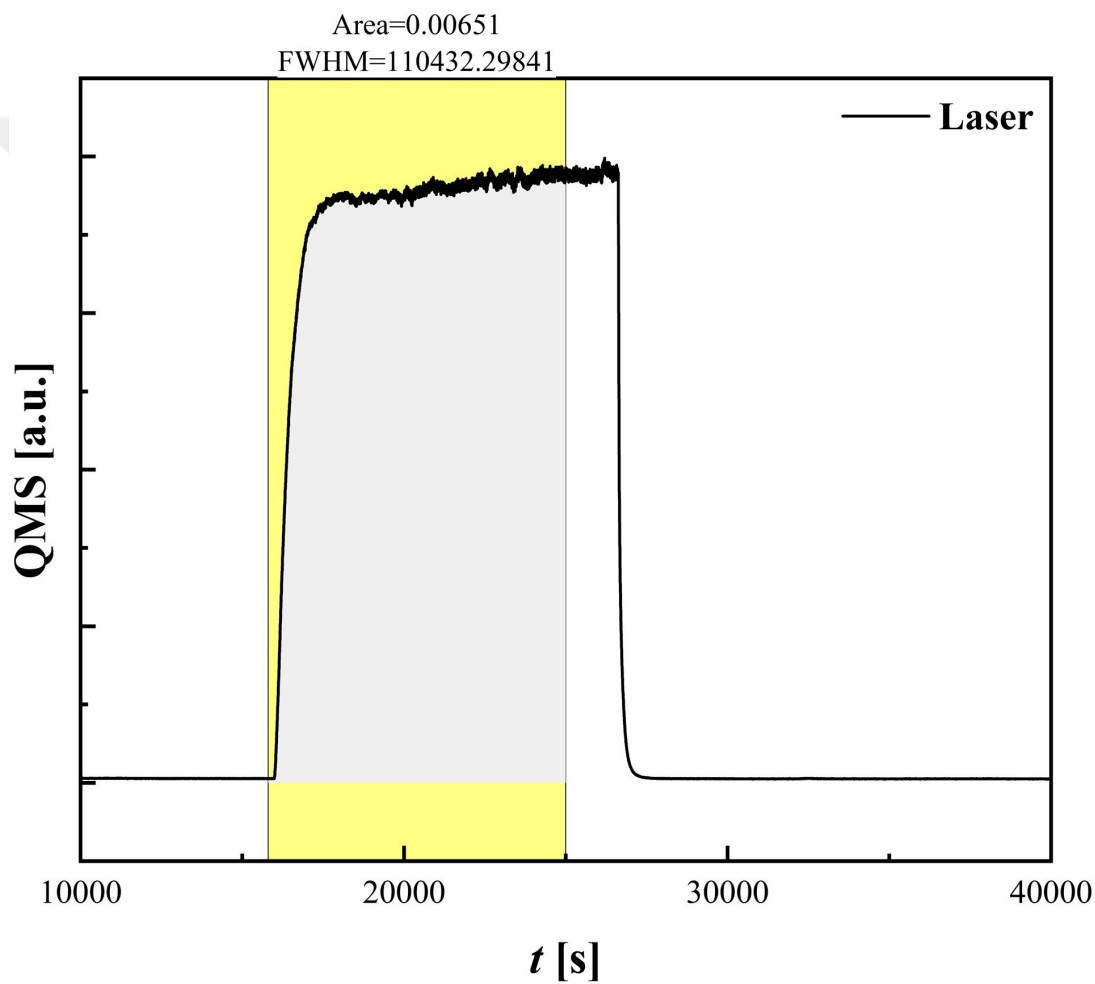


Figure C.4: The area under the CO₂ breakthrough curve of Zeolite A crystals synthesized via ultrafast laser method calculated by using OriginLab Software.