

## Chapter 2: Introduction to Part I of Thesis

### 1. Introduction

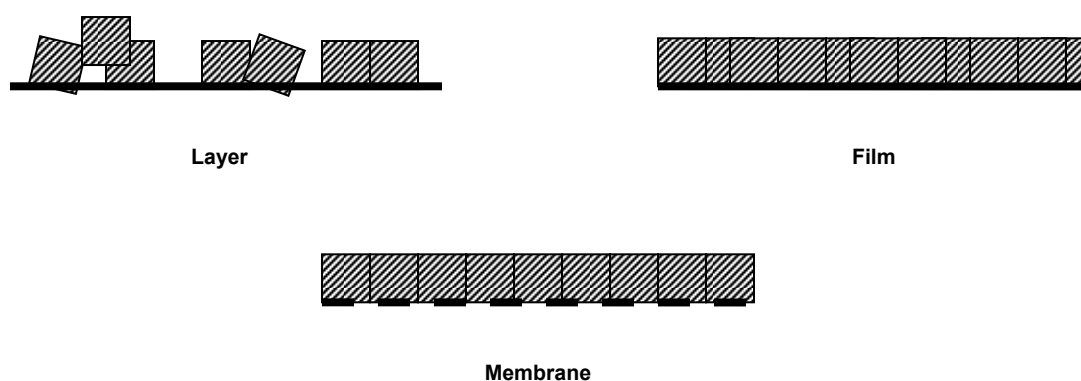
Zeolites and zeolite-based materials offer great potential for the development of nanostructured materials. This is due in large part to their crystallinity, structural symmetry, microporous uniformity, and topological variety, since these properties result in high surface areas, thermal stability, and the ability to sieve molecules based on size- and shape-selectivity.<sup>1</sup> Additionally, zeolites and zeolite-like materials can be synthesized in a range of chemical compositions, producing internal physicochemical properties that can range from acidic to basic and hydrophobic to hydrophilic.<sup>2</sup> Many of these properties can be modified by changing the synthesis conditions, leading to the potential to tailor the final characteristics to the zeolite's application.<sup>3</sup> Consequently, zeolites have been widely used in applications such as gas separation and absorption, catalysis, ion exchange, and have more recently been suggested for use as chemical sensors, membrane reactors, and low dielectric constant ( $k$ ) materials for semiconductors.<sup>1,4,5,6</sup> Many of these applications would benefit from, and in the latter cases require, the development of zeolites in planar form (thin film or membrane).

Planar zeolites are generally classified as nanostructured materials whose lateral dimension is much greater than their thickness. Many zeolite single crystals with a plate- or sheet-like crystal habit are planar; however, these single crystals are typically very small ( $< 1$  mm) and are therefore inappropriate for large-scale applications. Generally, planar zeolite and zeolite-based materials are polycrystalline, and can be categorized as

one of the following three types: layers, films, or membranes (Figure 2.1). Zeolite layers are comprised of individual crystals scattered discontinuously on a surface. Typically, these crystals are not fully intergrown, and are frequently adhered to the surface through electrostatic interactions, rather than through covalent bonding, although this can certainly be done.<sup>7</sup> Layers cannot be self-supported, although their supports can be porous. While molecular sieve layers are of limited use in applications requiring full intergrowth, such as electronic materials, they can be particularly useful in the development of chemical sensors, where their molecular selectivity could improve sensor performance.<sup>8</sup> Zeolite films consist of a continuous coverage of intergrown crystals or crystals imbedded in a composite matrix on the surface of a nonporous support. For the purposes of this chapter, we define films as supported materials, although they may be defined differently elsewhere. The use of a nonporous support restricts the use of zeolite films somewhat; as such, these materials can be used as coatings, whether adsorptive, catalytic, or corrosion-resistant, for applications such as chemical sensors, metal alloys, or low- $k$  dielectrics.<sup>2,4,9</sup> Zeolite membranes, on the other hand, are used for separation processes. Membranes are either self-supported films or films on porous supports that act as a selective barrier to the transport of materials. Self-supported membranes are often referred to as “symmetric membranes”, while supported membranes are “asymmetric”.<sup>10</sup>

The quality of zeolite and zeolite-based films and membranes is determined by the surface coverage, continuity, and the number of defects in the material, which can be evaluated via microscopy techniques (see Section 2.3). For films and membranes, respectively, defects are defined as gaps in the substrate coverage, and transmembrane

pathways much larger than the intracrystalline zeolite pore network.<sup>10</sup> Depending on the application, other requirements for layers, films, and membranes may be imposed. For instance, applications such as chemical sensors require very thin films coating the sensors. Additionally, applications such as catalytic membrane reactors may require membranes with a high degree of selectivity, which could require a specific orientation of the zeolite structure within the membrane.<sup>11,12</sup> Lastly, applications that require thermal cycling, such as thermoelectrics, need film and membrane materials that are well-adhered to their substrates, and do not suffer from cracking or flaking on thermal treatment. For high temperature applications, this is especially a concern. If the coefficients of thermal expansion of the planar zeolite material and the substrate are dissimilar, rapid heating and cooling can lead to cracking and buckling of the planar material, resulting in the destruction of the surface.<sup>11</sup>



**Figure 2.1** Schematic representation of the three categories of nanostructured, planar zeolite and zeolite-based configurations

There are several detailed reviews on the subject of zeolite films and membranes, as well as their applications.<sup>2,10,11,13,14</sup> This chapter provides a brief introduction into the common zeolite and membrane synthesis strategies, and discusses the advantages and disadvantages of each. Section 2 outlines the general process of creating planar zeolites, introducing in turn the selection of a proper support, the various methods of film and membrane production, the suggested models of film and membrane formation, characterization techniques, and lastly, defect elimination. Lastly, Section 3 discusses the necessity of pairing the synthetic technique to the application requirements, which often guides both the choice of synthetic strategy and the development of new strategies.

## **2. Zeolite Film and Membrane Synthetic Strategies**

The synthesis of zeolite films and membranes is in many ways similar to the synthesis of zeolite powders, in that there is often a very specific set of requirements that must be met in order for the zeolite phase of interest to crystallize. Films and membranes, however, have the added requirement of crystallization on a surface. In some cases, this can be as simple as inserting a substrate into the zeolite precursor gel prior to crystallization, while in other cases, it can be as complex as preparing pre-formed zeolite seeds of a specific size in a colloidal suspension, electrochemically modifying a substrate, depositing the seeds on the substrate, and then inserting the substrate into another zeolite precursor gel to carry out a secondary growth procedure that seals the spaces between seed crystals.<sup>15,16</sup> The first step in preparing films and membranes is to determine the type of support needed.

## 2.1 Support Choice and Modification

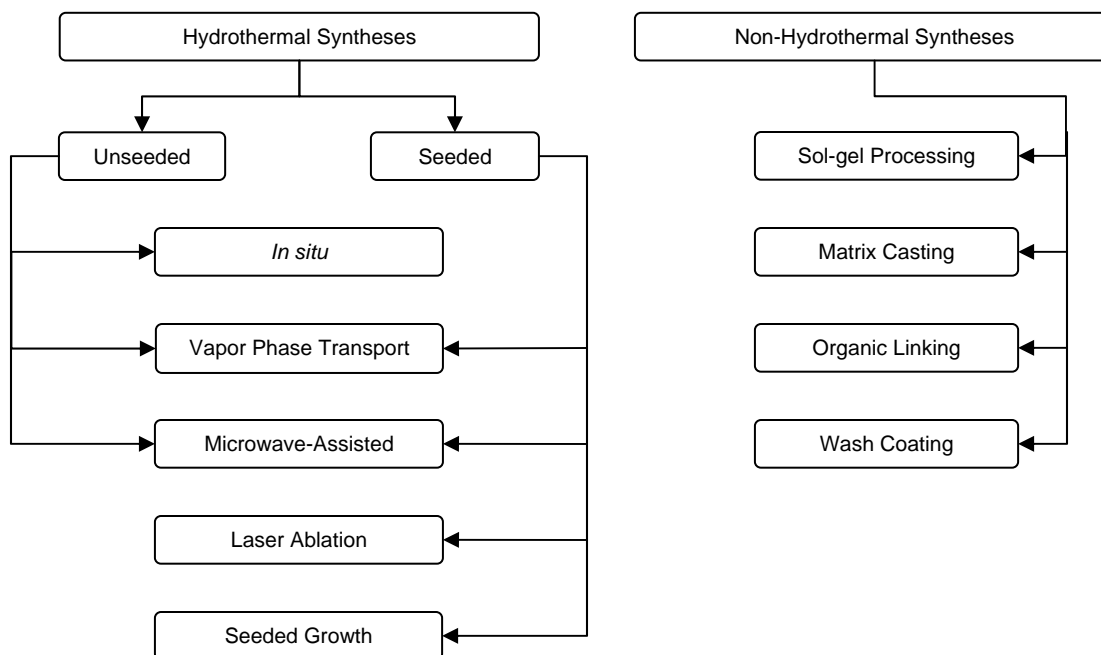
There are myriad possibilities for the choice of substrate for a zeolite film or membrane.<sup>10</sup> For instance, metallic materials such as gold, copper, silver, platinum, and stainless steel have all been used to synthesize zeolite films and membranes, such as zeolite A (LTA topology with an aluminosilicate composition) and zeolite NaY (FAU topology with an aluminosilicate composition with a sodium counter-ion).<sup>17,18</sup> Additionally, ceramic and metal-oxide-based materials, like porous alumina, single-crystal silicon wafers, quartz, and glass, have been used as supports for ZSM-5 (MFI topology with an aluminosilicate composition), silicalite (MFI topology with a pure-silica composition), and Beta (BEA\* topology with either an aluminosilicate or a pure-silica composition).<sup>19,20,21,22,23,24</sup> Lastly, organic polymer supports such as Teflon® and cellulose have been used (and then later removed) to create free-standing, or symmetric, membranes of ZSM-5.<sup>25,26</sup> In many cases, the choice of the support affects the final film or membrane properties. For instance, the substrate can influence the final orientation of the zeolite crystals, the final film thickness, the adhesion of the zeolite crystals to the surface, or the final crystal size.<sup>14</sup>

Substrates may be modified to accommodate the needs of a specific zeolite composition or synthetic technique. The most basic modification of a substrate is cleaning to remove organics that have accumulated on the surface and may prevent zeolite film formation. For instance, single-crystal silicon wafers have a native oxide layer and adsorbed organics on their surface that often need to be removed prior to use as a support. Cleaning may be accomplished through a variety of methods, including dips in aqueous hydrofluoric acid, and piranha solutions, and boiling in Alconox detergent.<sup>27</sup> Chemical

and mechanical polishing techniques may also be used to modify the surface roughness of the substrate, as thin films are less likely to adhere to rough surfaces than smooth.<sup>11</sup> Adhesion of the film to the substrate is generally a function of the hydrophilicity of the surface due to various van der Waals and hydrogen bonding interactions this enables, and can be improved by immersing the substrate in solutions of NaOH, which increases the number of surface hydroxyl groups and therefore the hydrophilicity of the surface. It also increases the number of potential nucleation sites.<sup>11</sup> More complicated techniques involve surface modification, such as the attachment of molecular coupling agents such as thiol alkylsilanes, which are used to either chemically adhere zeolite crystals to the surface, or the functionalization of surface silanols via vapor-phase silylation. Electrophoretic deposition can also be used to attach charged particles from colloidal suspensions to the surface during coating.<sup>11</sup> Lastly, the substrate can be patterned via lithographic techniques to guide zeolite crystallization into defined structures.<sup>28,29,30</sup>

## 2.2 Synthetic Strategies

The synthesis of zeolites in powder form is typically accomplished via hydrothermal or solvothermal conditions under autogeneous pressure at temperatures below 200 °C. Hydrothermal refers to the synthesis of zeolite using water as the gel solvent, whereas solvothermal indicates a non-aqueous (usually organic) solvent for the gel. Films and membranes, however, can be synthesized non-hydrothermally, as well as hydrothermally. The synthetic techniques for hydrothermal and non-hydrothermal film syntheses are often very similar in parts, and many of the synthetic techniques can be used for either category (Figure 2.2).



**Figure 2.2** Synthetic strategies for the formation of zeolite and zeolite-based films and membranes

### 2.2.1 Hydrothermal Techniques

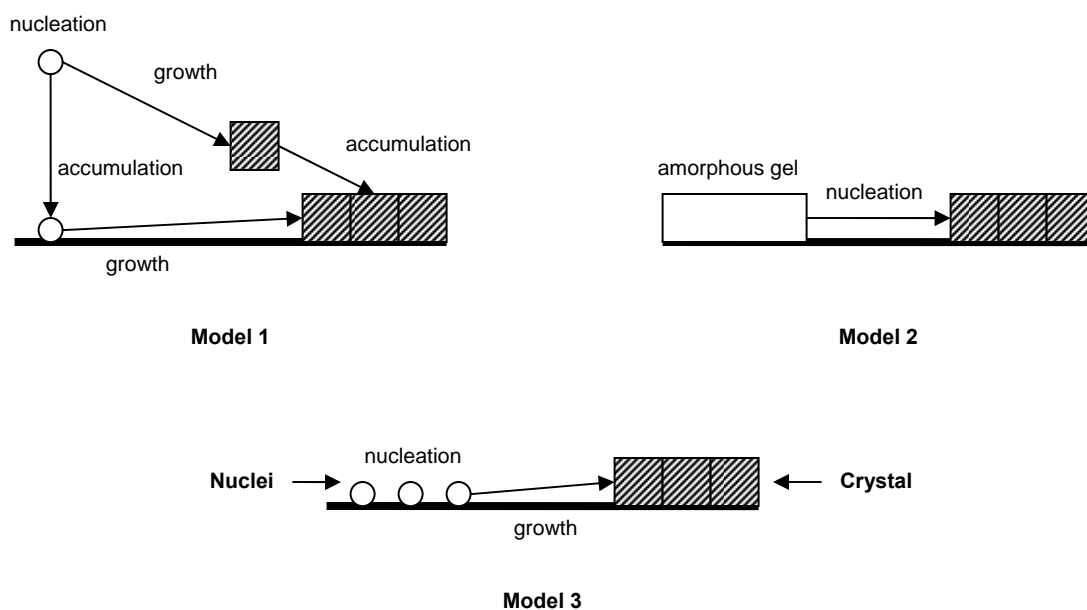
Hydrothermal film and membrane syntheses come in two varieties: seeded and unseeded. Seeded syntheses require the use of pre-formed zeolite crystals, typically nanocrystals of a uniform size, either to attach to the support or to seed the zeolite gel prior to crystallization. The main benefit of seeded syntheses over unseeded syntheses is that the nucleation (at high supersaturation) and growth (at low supersaturation) steps of zeolite crystallization can be decoupled, resulting in the suppression of secondary nucleation.<sup>11</sup> This can also render the effects of the surface on zeolite growth less important. Additionally, seeded methods can also be used to promote the crystallization of a single, pure phase when reaction conditions might tend towards producing a mixed phase, to grow large crystals, or to reduce the severity of reaction conditions, which might be necessary to induce nucleation but not to accommodate crystal growth.<sup>29,31,32,33,34</sup> The

disadvantage of seeded syntheses is that uniform and easily dispersed zeolite seeds must be made, which can be difficult to achieve. For instance, the zeolite particles may clump in solution and form large colloids, as opposed to a uniform suspension. In these cases, significant effort must be made to ensure that the zeolite crystals are well dispersed.<sup>16</sup>

Also, nanocrystals of a uniform size may be difficult to obtain, as this can require stopping the synthesis prior to full crystallization and centrifuging for long times at high speeds to separate the amorphous bulk from the nanocrystals. In these cases, yields may be very low.

Hydrothermal, unseeded zeolite film and membrane syntheses are typically categorized as *in situ* crystallization procedures, referring to the formation of the zeolite film *in situ* during hydrothermal crystallization. In this method, the substrate is directly submerged into the zeolite precursor gel and the zeolite forms on both sides of the surface. Several models have been suggested for the formation of zeolite films via *in situ* procedures (Figure 2.3): (Model 1) homogeneous nucleation in the bulk gel, followed by either growth of the nuclei to crystals and then surface accumulation, or surface accumulation of the nuclei and then growth of the attached nuclei to crystals, (Model 2) diffusion of colloidal material to the surface of the substrate, followed by concentration at the surface and then nucleation of an amorphous gel layer on the surface to intergrown crystals, and (Model 3) direct nucleation at the surface, followed by crystal growth.<sup>2,35,36,37</sup> Any of these models are possible for the formation of zeolite films through *in situ* processes, however, homogeneous nucleation is very common for *in situ* crystallization.<sup>36,37</sup>

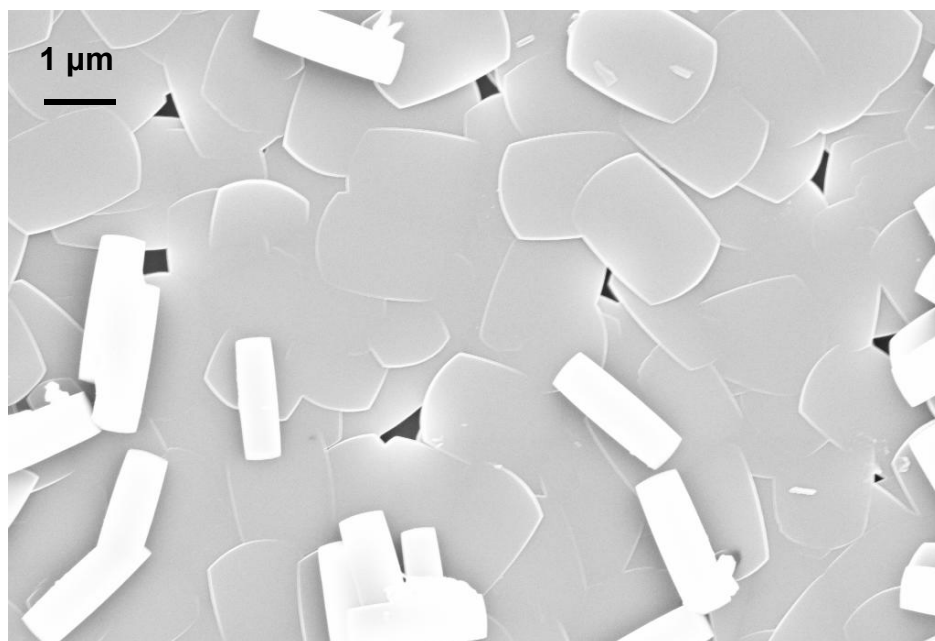




**Figure 2.3** Models of zeolite and zeolite-based film formation for in situ synthetic techniques

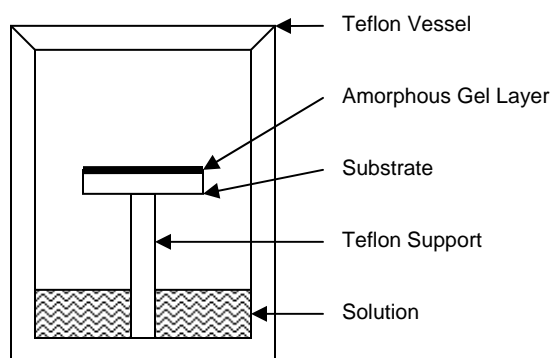
In many *in situ* processes, the substrate itself may be partially consumed, or the gel conditions may lead to leaching of the substrate into the bulk gel.<sup>10</sup> For *in situ* processes which involve accumulation of nuclei or crystals at the substrate from the bulk gel, the accumulation process may be gravitationally or electrostatically driven, as in cases where the substrate has been modified to encourage good adhesion of the resulting film. There are many advantages to *in situ* film synthesis techniques: (1) since the substrate is fully submerged in the zeolite gel during crystallization, the gel can completely coat the surface of even complex surfaces, (2) since the technique involves only the insertion of a substrate, the procedures are much less complicated than other techniques, and (3) since

the synthesis requires no extra steps, the crystallization conditions frequently do not need to be modified to accommodate the film synthesis.<sup>9</sup> However, *in situ* techniques also have drawbacks. For instance, if heterogeneous nucleation occurs (in the bulk gel and at the substrate surface), the resulting polycrystalline film may have layers of scattered crystals on its surface from accumulation of bulk crystals after the film itself has crystallized (Figure 2.4). Additionally, *in situ* procedures call for the immersion of the substrate in, presumably, a clear solution or a dilute gel. Some zeolites, however, require very concentrated conditions to form. This is the case for most fluoride-mediated zeolite syntheses, where the zeolite precursor gel is almost a dry powder. In these cases, *in situ* techniques cannot be applied.



**Figure 2.4** Silicalite (MFI) polycrystalline film grown via *in situ* techniques showing a loose layer of MFI crystals on the surface

For the cases where *in situ* techniques cannot be used, the vapor phase transport method may be used instead (Figure 2.5). In this method, a reactive gel layer is first applied to the substrate by submersion in a parent gel containing alumina, silica, water, and the mineralizing agent, and then the gel layer is crystallized hydrothermally in the presence of the structure-directing agent and water in the vapor phase (the remaining parent gel not used for coating is not crystallized).<sup>2,35,38,39,40,41</sup> More recently, Matsukata and co-workers have extended this approach by incorporating the silica source in the vapor phase, rather than the structure-directing agent and solvent.<sup>42</sup> The vapor phase transport method can be seeded or unseeded, in that the substrate or the precursor gel may be seeded prior to substrate coating. This method is convenient in that it decreases the use of the structure-directing agent, which can be quite expensive, and increases the number of films the reactive gel can make, since the bulk gel itself is not crystallized, but it is also a two-step process that requires the formation of a reactive gel layer, which may not be possible for every zeolite.



**Figure 2.5** Schematic of the vapor phase transport method for film formation

Microwave-assisted crystallization is another hydrothermal synthetic procedure that uses laboratory microwaves to shorten the time required for crystallization. This is primarily a result of the fast heating of the autoclaves inside the microwave.<sup>11</sup> The high energy input also has some unusual effects on the formation of zeolite crystals: since the system heats very quickly to crystallization temperatures, the formation of nuclei is suppressed, leading to the growth of very large crystals. For film syntheses via microwave heating, the synthesis can proceed in a similar fashion to *in situ* crystallization; that is, the substrate may be fully submerged in the precursor gel. Alternatively, the substrate can be dip-coated in the zeolite precursor gel prior to crystallization and aged, which allows nuclei to form in the gel. In either case, the precursor gel or the substrate itself can be seeded to promote film growth. The advantage of this method is the very rapid crystallization time (a matter of hours as opposed to days), but it is limited in that uniform crystal growth is difficult to control.<sup>11</sup>

Lastly, hydrothermal synthesis may be carried out via laser ablation. Laser ablation uses preformed zeolite targets to coat the surface of a substrate with atoms, molecules, and clusters of the zeolitic material at low substrate temperatures.<sup>2</sup> Generally, this forms an amorphous layer of zeolite building-block materials on the surface of the substrate, which are crystallized during the ablation or during subsequent hydrothermal treatments. The main advantage of this method is that a typical zeolite gel is not required, however, the method also tends to result in the formation of zeolite crystals imbedded in an amorphous matrix, rather than a typical polycrystalline zeolite film.

### 2.2.2 Non-Hydrothermal Techniques

Non-hydrothermal, zeolite, and zeolite-based film and membrane synthetic techniques refer to processes of film formation that do not require a hydrothermal crystallization step; instead, these techniques make use of pre-formed zeolite seeds and a variety of binding agents. These techniques are collectively referred to as *ex situ* methods, and can be advantageous if the resulting surface coverage need not be fully intergrown, but rather fully covered, as *ex situ* syntheses allows the separation of the zeolite formation and film formation processes. It is also useful because it is a facile scheme of depositing a film on a surface. However, the final films can have gaps between crystals (thus qualifying the coating as a layer rather than a film), or the presence of a binder matrix in which the crystals are imbedded. For some applications, like low- $k$  dielectrics, this can be favorable, as it can result in very smooth, completely interconnected films.<sup>43</sup> The presence of a permanent binding agent also results in a film with composite properties of the two materials. Lastly, as discussed for the hydrothermally seeded processes, obtaining seeds of appropriate size that can be easily dispersed can be very challenging. In general, non-hydrothermal techniques are a two-step process. First, the zeolite seeds are hydrothermally crystallized (not in the presence of the substrate). Second, the seeds are attached to the surface of the substrate via a binding agent, which can be an organic linker, an electrostatic linker (such as inducing a charge on the substrate), or a gel that contacts the surface. There are four primary processes by which zeolite crystals may be deposited on the surface of a material: sol-gel processing, matrix casting, organic linking, and wash coating.<sup>2,13</sup>

Sol-gel processing refers to the suspension of zeolite crystals in a solvent (the sol), typically tetraethylorthosilicate, followed by the formation of a gel through evaporative processes.<sup>8</sup> The substrate is contacted with the seeds via dip-coating, spin-coating, drop-coating, etc., and the substrate is then dried, hardening the film. In some cases, the sol is actually the original zeolite gel from which the seeds were hydrothermally crystallized. The benefits of this method are the ease with which any three-dimensional substrate can be coated, and the ability to tune the final thickness of the film based on the number of coats. Matrix casting is very similar to sol-gel processing, in that the binding agent is a solution, but here it is usually a polymeric solution, which is useful for its processability into a variety of self-supported shapes. For instance, the polymer / zeolite composite solution could be extruded into fibers, which could be woven into membranes for reverse osmosis water treatment, or it could be used to create flexible self-supported sheets.

Organic linking deposition methods present another interesting method to coat substrates.<sup>2</sup> In this process, the organic linker (generally a silylating agent) is attached to the zeolite crystals in solution, to the surface of the substrate, or to both, resulting in a covalent bond between the crystals and the surface. This method can help improve the dispersability of zeolites in solution, and can result in a substrate covered by only a single layer. However, this method results in a film which can be easily destroyed if the binding agent is removed, for instance, via high temperatures, since the crystals are not actually imbedded in or bonded to the substrate.

Wash coating is the last major method by which seeds can be deposited on a substrate. Here, the seeds are suspended in a binding agent to form a slurry, which is then used to coat the surface of the substrate.<sup>13</sup> The seeds are then bound to the surface via sintering at high temperatures. The primary disadvantage of this route is the high temperature process required for good adhesion of the crystals to the substrate.

### 2.3 Characterization Techniques

Zeolite films and membranes are characterized through a variety of techniques to ensure quality. X-ray diffraction (XRD) is used to determine the crystallinity and zeolite structure of the film. Microscopic techniques, such as scanning electron microscopy (SEM), and energy dispersive spectrometry (EDS), are used to determine film thickness, surface coverage, crystal size, crystal habit, degree of crystal intergrowth, defect quantity and type, and chemical composition of the film. These techniques are especially useful before and after calcination, as they show both that the structure-directing agent has been removed and that the film has not suffered from cracking. Typically, nitrogen adsorption experiments are used to determine the micropore volume and porosity of zeolite powders. However, this method is difficult to use for supported films, because the supports generally do not fit inside the sample tubes. An alternative method for the determination of porosity in thin films is the use of ellipsometric porosimetry, which uses *in situ* ellipsometry to observe the effects of adsorption of various organic vapors on the film via swelling and the change of refractive index.<sup>44</sup> Like nitrogen adsorption for powder samples, this method can determine average pore size, pore distribution, and porosity of the films. However, this method is limited in that only a very few of these setups have been made in the world. Ellipsometry, in general, is also a useful and non-destructive

technique for determining the film thickness of a sample.<sup>45</sup> In order to use this method, however, the films must have a very uniform thickness across the surface (which can be obtained through polishing), and must be reflective. Surface adhesion of the film to the substrate can be measured by laser spallation techniques (although early measurements consisted of the rough “sticky-tape test”, where sticky tape was placed on the film and pulled off to determine how easily the film could be removed).<sup>46</sup> Mechanical testing of the films can also be carried out using standard nanoindentation techniques, which determine the films’ hardness and modulus.<sup>47,48,49</sup> Capacitance testing of the films demonstrates its electronic properties, such as its dielectric constant and response to applied voltages.<sup>50</sup> This characterization method requires high quality (continuous, intergrown, and well-adhered) films with smooth surfaces to obtain consistent measurements using typical parallel-plate capacitance measurements. To obtain smooth, parallel surfaces, a high quality mechanical polisher is often needed, especially for film synthesis methods that do not directly yield a smooth surface (i.e., most hydrothermal syntheses). The use of these techniques, individually or in combination, demonstrates the type, quality, and physical properties of the resulting films. Other techniques, such as catalytic testing and separation ability, may also be applied if the end-use of the film or membrane requires it.

#### 2.4 Defect Elimination

Zeolite films and membranes often have defects, discovered during characterization, which must be removed prior to their end use. For instance, cracks formed during calcination, or holes formed during crystallization, can often be sealed by soaking the



sample in a silica-containing gel and drying it, resulting in areas of the film with amorphous materials. Alternatively, the surface can be sealed using chemical vapor deposition techniques, such as vapor phase silylation, which can attack surface silanol groups (site defects in the crystal structure). This can also be used to attenuate the hydrophilicity of the film, since silanols promote water adsorption. When post-synthetic techniques cannot be used to fix the defects, defect elimination becomes an iterative process where the film preparation method itself must be adjusted to prevent defect formation. This can result in a change of substrate, the modification of a substrate, or changes in the crystallization or deposition conditions.

### **3. Development of New Synthetic Techniques**

The choice of an appropriate film or membrane preparation technique is crucial to the development of a high-quality planar zeolite for a given application. If the application requires an ultra-thin film composed completely of intergrown zeolites, without the presence of a binder, a hydrothermal method such as vapor phase transport may be easiest. However, if the presence of a binder will not affect the end-use, a non-hydrothermal method such as sol-gel processing via spin-coating may be an easier choice. The zeolite crystallization conditions must also be taken into consideration, as must the choice of crystal size. If the film needs to be composed of very large crystals, seeded syntheses, which suppress nucleation, may be most appropriate. If the zeolite crystallizes at very concentrated gel conditions, an *in situ* synthesis would be inappropriate as the substrate cannot be submerged in the gel. In each case, the factors to consider are the end requirements of the film, the nature of the support, the zeolite gel

composition, the final zeolite topology, and the necessary crystallization conditions, such as aging time, crystallization time, and crystallization temperature. By examining these factors, it is generally possible to identify a synthetic technique that is appropriate for film preparation. In situations where this is not the case, new film and membrane preparation methods must be developed. It is through this process of pairing and modifying synthetic techniques that novel synthesis concepts are introduced, and the field of zeolite and zeolite-based nanostructures extended.

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