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Industrial Zeolite Molecular Sieves

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Abstract

Zeolite molecular sieves are used in industrial applications since more than 60 years, mainly as highly efficient adsorbents for separation processes in gas or liquid phase. Zeolite molecular sieves may be applied in powder form, preferably in static applications, but to a much larger extent as shaped material in both static and dynamic (flowing media) applications. Many shaping technologies for molecular sieves have been developed over the last decades, reflecting the different requirements for molecular sieves in different applications. This review deals with the influence of the applied zeolite synthesis and shaping methods for hydrophilic zeolite molecular sieves (procedures, materials, recipes) on the potential industrial applications; thereby considering powders, binder-containing shapes as well as binderless shapes (including compact structures such as honeycombs, multi-channel, and foam-like structures). Due to new challenges from the market, more specialized, tailor-made types of zeolite molecular sieves are required. Such a higher specialization can be achieved by applying new types of zeolites or zeolite-like materials, modified synthesis and/or post synthesis treatments, and by modified, to the needs of the application adjusted shaping processes.

Keywords: zeolite, molecular sieve, adsorption, fixed bed, compact zeolite bodies

1. Introduction

Zeolite molecular sieves are used in industrial applications since more than 60 years, mainly as highly efficient adsorbents for separation processes in gas or liquid phase. The current market volume for molecular sieves (especially for zeolites for adsorption applications) is 150.000–200.000 t with a sales volume of 450–550 Mio. USD with an annual growth forecast up to 2020 of 3–5% [1–3]. Growth drivers are environmental protection and conservation of resources (deeper processing of crude oil, using of coal and natural gas (especially from off-shore and

shale gas deposits coming [4–6]) as raw material for petrochemical products in the so-called coal-to-liquid (CTL) or gas-to-liquid (GTL) processes) [7–9].

Zeolite molecular sieves can be applied in powder form, preferably in static applications. During the polyurethane production, zeolite 3A powder is mixed with the polyol component to enable exclusion of moisture and prevent the chemical reaction of water with the isocyanate component [10]. To support the material handling, and to avoid, for example, dust formation molecular sieve beads are used in non-regenerative applications, too. Dry sealing plug or small dry bags filled with zeolite A (or silica) [11, 12] to guaranty a dry transport or storage of humidity sensitive goods such as electronical products, leather ware, or pharmaceuticals are common [11, 12]. The application of zeolite 3A in insulating glass panes is well-known, too. By putting the adsorbent material as desiccant in the perforated spacer between the two or three window panes moisture condensation between the panes (fogging) is prevented [13]. Refrigerant drying [14, 15] is also a static adsorption process, where in the coolant circuit formed, water and acidic components are removed [14, 15].

Besides the mentioned application examples, shaped zeolite molecular sieve material in flowing media is used to a much larger extent. For instance, the purification of technical hydrogen (removal of nitrogen and carbon monoxide) on zeolite 5A [16], the pre-purification of raw air on zeolite NaX [17] for the cryogenic air separation or the adsorptive oxygen enrichment, for example, on zeolite type 5A [18] or LiX [19, 20] should be mentioned in this place. Applied technologies for purification and drying of natural gas are operating with zeolite molecular sieves [21] of zeolite 5A and/or NaX type [22]. In petro chemistry applications especially in steam cracking plants, light hydrocarbons are separated by low temperature rectification. To avoid ice crystal and gas hydrate formation, cracked gases have to be dried to a residual water content <1 ppm [23]. Zeolite molecular sieves of type 3A meet the requirements for that complex process [22]. For the sake of completeness, the principle of the simulating moving bed (SMB) should also be mentioned. This practically continuous liquid phase adsorption process is based on the countercurrent extraction principle [24]. The so-called Molex process, where paraffin mixtures (zeolite molecular sieve of type 5A [25, 26]) are separated, and the so-called Parex processes, where *p*-xylen is separated from C₈ aromatic mixture (zeolite molecular sieve of type KY or BaX [27]) are known SMB processes. Furthermore, the dehydration of preferably bio-ethanol above the azeotropic point to more than 99.5% on zeolite 3A is common practice [28, 29]. Besides the mentioned examples, the use of zeolite molecular sieves in automotive applications such as drying of brake air in rail vehicles, trucks, or busses is also a well-known application. To avoid corrosion or freezing caused by humidity, such pneumatically working braking systems are equipped with zeolite 4A molecular sieve or silica gel-containing desiccant cartridges [22].

Another field for the application of zeolite molecular sieves is the utilization of the adsorption heat during the adsorption process. Different applications such as building heating [30–32] or enhanced household devices such as dish washers [33, 34] based on the thermo-chemical energy properties of zeolites are introduced into the market.

The above-mentioned examples clearly demonstrate the demand for zeolite molecular sieves with special properties depending on the different requirements in the application.

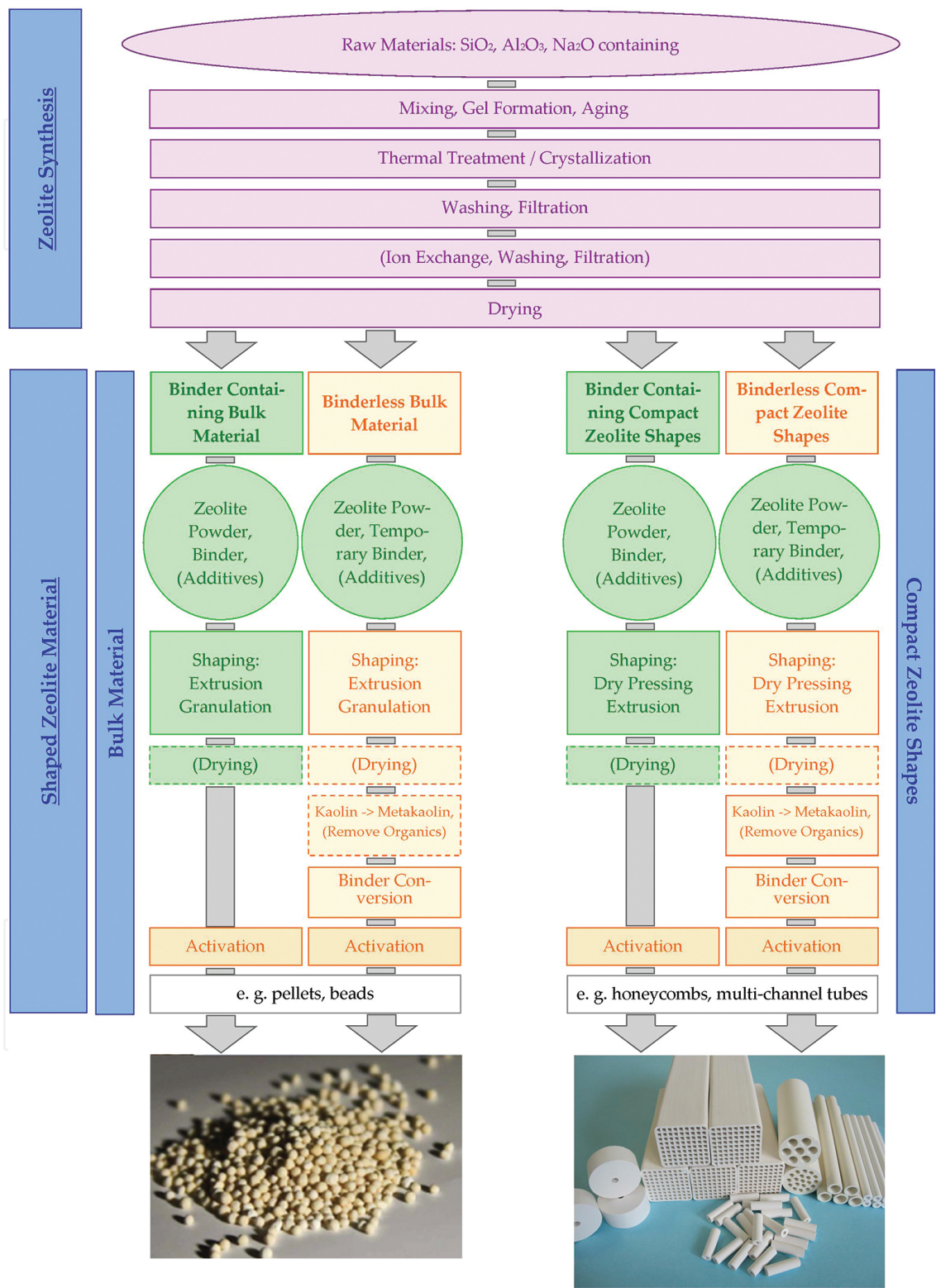


Figure 1. Overview of the manufacturing of different zeolite molecular sieves (figure compact zeolite bodies [35]).

Many synthesis and shaping technologies for molecular sieves were developed over the last decades. Within the following descriptions, the influence of the applied synthesis and shaping methods for hydrophilic zeolite molecular sieves of zeolite A, X, and NaY on their properties, and thus, on their potential applicability in industrial adsorption processes is discussed. The procedures, materials, and recipes for the manufacturing of zeolite powders, binder-containing shapes as well as binderless shapes are described. Also compact structures such as honeycombs and multi-channel tubes are considered.

Figure 1 summarizes different manufacturing procedures and materials dealt with in this review.

2. Zeolite powder with different particle sizes

Within the manufacturing of synthetic zeolite molecular sieves, the synthesis of the related zeolite powder is first step. There are two different principles for the synthesis of aluminum-rich zeolites in industrial processes:

- Manufacturing of highly pure crystalline zeolite powders from a synthesis gel and
- Conversion of natural minerals into zeolite matter.

Usually, in the industrial production of zeolite A, X, and NaY, the sodium form is manufactured (except the zeolite LSX synthesis [36]). Therefore, different raw materials as silicon source such as silicic acid, colloidal silica, sodium silicate, or silica gel [37] are used. Possible alumina sources are alumina trihydrate, sodium aluminate, activated alumina, gamma alumina. Sodium may be obtained from sodium hydroxide which controls simultaneously the pH value [37]. A convenient way to prepare such a reactant mixture is to pour under more or less intensive stirring an aqueous solution containing the aluminum source and sodium hydroxide into an aqueous solution containing the silica source. After gel formation and generating a homogeneous mixture, the mixture is heated up to maximal 120°C at atmospheric pressure or moderate overpressure [37]. After crystallization, the zeolite suspension is filtered at temperatures between room temperature and reaction temperature [37], for example, in a filter press [38] or a centrifuge [39, 40] or a vacuum belt filter [40]. The zeolite crystals are washed directly on the filter device till a pH value between 9 and 12 [37] is achieved. If desired, the zeolite powder in its (virgin) sodium form can be ion exchanged or otherwise modified. For example, the filter cake can be suspended in a suitable salt solution and stirred at a suitable temperature. Alternatively, the exchange step is done in a column [41] or directly on the filter press [42] with a suitable salt solution at a suitable temperature. After the ion-exchange procedure is completed, the zeolite is washed as described above. Afterwards, the filter cake is dried in a direct or indirect heated thermal treatment process, as, for example, spray drying, spin flash drying, or long gap mill drying [40, 43]. The dried zeolite powder is processed in the following steps. The mother liquor from the filtration step can usually (at least to a certain extent) be reused in the following zeolite synthesis batch [37, 44].

The manufacturing of zeolites by conversion of minerals is not really a commonly used process. In several papers which deal with the synthesis of zeolite A, X, and NaY from minerals, kaolin or metakaolin is used as aluminum source [45–47]. A disadvantage of such procedures is the presence of impurities in the applied minerals [45], but some advantages (simple treatment of the mother liquor and a nearly waste-free production) support the application of that synthesis method especially in the case of zeolite NaY [46].

The properties of zeolite molecular sieves can be influenced by the properties of the starting zeolite powder. For instance, the hydrothermal stability or desorption characteristics of FAU vary with the chemical composition, especially the aluminum content [48]. The particle size, particle size distribution, and the surface characteristics of single zeolite crystals affect the adsorption properties as well as the mechanical stability of zeolite molecular sieves. By varying the synthesis gel composition, time, or temperature or by adding additives to the synthesis gel, the mentioned properties of the zeolite powder can be changed [49, 50]. Depending on the intended applications, the particle size distribution is adjusted. Besides the described classical gel synthesis [51] resulting in particles of about 5 μm , microparticles (particle size of approx. 1 μm) and nanoparticles (particle sizes between 50 and 100 nm) can be achieved via new synthesis routes [52].

3. Binder-containing zeolite molecular sieves

In dynamic adsorption processes, where the adsorbent has to be regenerated frequently, the fluid dynamics (e.g., the pressure drop over the fixed bed of molecular sieves) has to be taken into account. Therefore, the zeolite has to be applied in a suitable particle size (usually in the form of shaped mechanically stable macroscopic particles such as beads/spheres or extrudates/cylinders).

Because pure zeolite powder does not exhibit binding properties, an appropriate binder needs to be applied to form the above-mentioned macroscopic particles. **Figure 2** shows the main principles for the manufacturing of conventional binder-containing zeolite molecular sieves (bulk material).

The zeolite component is the main component of the pre-mixture and can be applied as dried zeolite powder (occasionally as filtercake). Usually, the zeolite component is modified (as described above, e.g., ion exchanged or dealuminated) prior to the shaping step. Besides the zeolite component a binder material is put into the pre-mixture. Mineral binders such as bentonite, attapulgite, or kaolin are common [53, 54] as well as synthetic binders such as alumina, silica [54, 55], or a mixture thereof [56]. The type of binder material to be applied depends on the shaping procedure and on the final application of the zeolite molecular sieve. Bentonite (montmorillonite) for example is commonly used for extrusion [57, 58], attapulgite for beading [59]. It should be noted that (natural) mineral binders may contain impurities (e.g., catalytically active heavy metals), which could cause undesired side reactions in the final application. If necessary, additives such as shaping aids (e.g., mineral oil, PVA, starch derivate solutions [60]) are put into the pre-mixture to make the shaping process most effective. Such

mainly organic compounds are burnt out in subsequent thermal treatment steps. In order to create a defined secondary pore system (see below) thermally or chemically, removable spacers (e.g., cellulose fibers or soluble salts) are added to the pre-mixture. In most of the bulk zeolite molecular sieves, a binder content of around 20% (anhydrous basis) is used. But also lower (down to around 5%) and higher (above 30%) binder amounts are described [59].

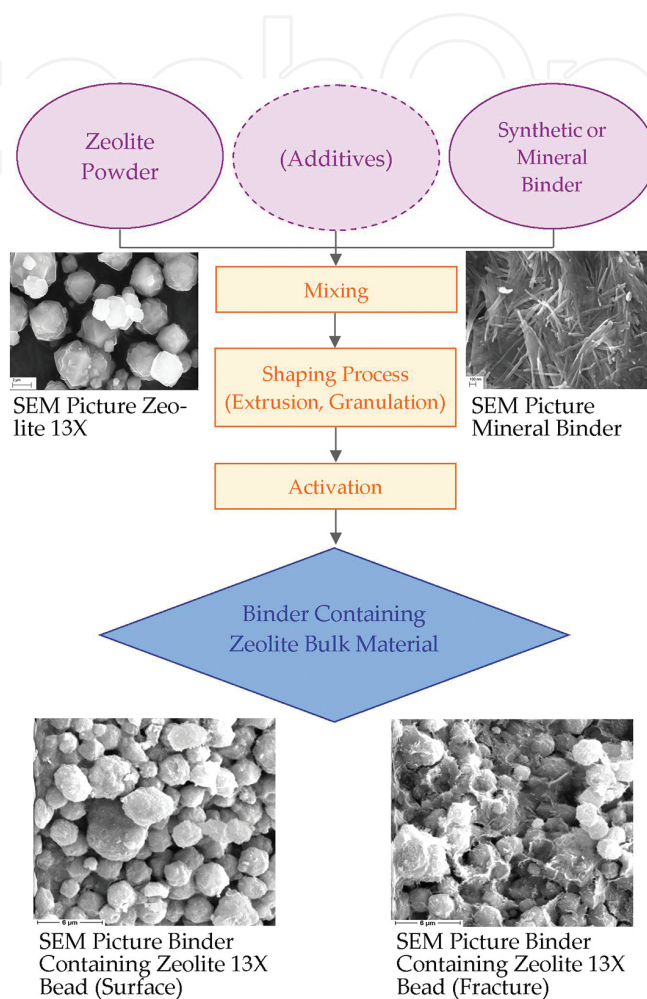


Figure 2. Scheme of the principle manufacturing procedures for binder-containing zeolite molecular sieve shapes (bulk material).

After the (mainly dry) mixing of all aforementioned materials in the pre-mixture usually a certain amount of water is added in order to adjust the viscosity and plasticity of the mixture for the related shaping process that can be agglomeration granulation [59], spray granulation [61], or extrusion [62]. After the shaping process, the molecular sieve has to be dried and activated in a thermal step, for example, in a rotary kiln [63] or belt calciner [64] to remove the water and other adsorbed compounds. The applied temperature is often higher than required for the zeolite activation, since the binder system needs such higher temperatures for setting. The zeolite component in zeolite NaX beads with attapulgite as binder materials, for example, needs not more than 350–400°C for a complete activation (residual water content <1 wt% measured by Karl-Fischer titration) [65]. But the attapulgite binder needs approximately 500

°C for getting converted into a mechanically stable structure [53, 59]—a temperature which can already be critical for the structural stability of the zeolite [66, 95]. Due to the limited hydrothermal stability [67–69, 95] of hydrophilic zeolites, the activation step has to be carried out carefully. To avoid (partial) zeolite destruction during the activation step, the released water needs to be removed from the shape as fast as possible in order to avoid the appearance of hydrothermal conditions. The higher the temperature and higher the moisture concentration directly at the zeolite centers the higher the probability for (partial) zeolite destruction [70]. By applying a controlled temperature increase, a low height of the granules bed and/or a dry purge gas can be met these conditions. Depending on the particular conditions, a residual water content of less than one percent can be reached. During the cooling step as well as during the storage of the activated material, the presence of humidity or other adsorptive components should be avoided to prevent undesired adsorption on the material. Therefore, activated zeolite molecular sieves are usually packed in hermetically sealed packaging units, as, for example, sealed steel drums or big bags equipped with sealed inliners.

The mentioned use of a binder system opens a large variety of zeolite molecular sieves with different properties. Depending on the final application, the properties of the single shapes or the bulk material have to be optimized. For instance, with regard to the particle size, two limits should be considered: The bigger the single shape, the higher the probability for a possible limitation of the mass transfer within the shape. That means the diffusion within the single shape might be so slow that the active adsorptive matter is not completely used if the full adsorption/desorption cycle is very fast (e.g., in (vacuum) pressure swing processes [71]) [72]. But the smaller the single shapes, the larger the pressure drop over the fixed bed and the higher the risk of fluidization. Therefore, the adjustment of the size of the shapes is a critical parameter in the design of an adsorption process. Besides the size also other characteristics of the bulk material are to be adjusted such as mechanical properties such as dust formation caused by attrition/abrasion between shapes or the shapes and the wall of the adsorber vessel. Because dust may cause problems in a running adsorption process (e.g., blocking of valves), the dust formation has to be avoided by applying an optimal type and amount of binder as well as by generating single shapes with as smooth as possible surfaces. To receive smooth surfaces on single shapes of bulk material, the shaping process has to be run accurately. So, for example, in the case of extruded material an optimal plasticity of the extrusion mixture (pre-mixture), and in the case of agglomeration granulation, a post-granulation surface polishing step may help avoid/lower attrition/dust formation. Besides dusting, the mechanical stability (crush resistance) of the shapes has to be considered. The higher the bulk bed in the adsorber the bigger the weight and force that affects the lowest single shapes in the bed, which could finally result in a destruction of the shapes, and hence, generation of fines and an increased pressure drop. The binding mechanism of activated binder-containing zeolite molecular sieves is based on the generation of a network of binder material, wherein the zeolite crystals are embedded. **Figure 2** shows SEM pictures of the raw materials. The zeolite crystal agglomerates (top left) and the binder (top right) form a physically strong bound shape, which is demonstrated in **Figure 2** downright. As mentioned earlier, the use of (adsorption inert) binder material reduces the adsorption capacity zeolite molecular sieves by approximately the percentage of binder in the shape (see **Table 1**).

	Zeolite NaX powder	Binder-containing zeolite NaX beads
Water adsorption capacity at 55% relative humidity, 25°C/wt%	31.5	26.5
N ₂ adsorption capacity at 1000 mbar, 25°C/cc(STP)/g	10.7	8.0
CO ₂ adsorption capacity at 333 mbar, 25°C/cc(STP)/g	120.7	95.4

Table 1. Adsorption capacities for zeolite NaX (pure zeolite NaX powder and binder-containing bulk material with 82.5 wt% zeolite NaX and 17.5 wt% attapulgite).

In addition to the mechanical properties, the type and amount of binder (and the shaping process applied) have an essential influence on the structure of the secondary pore system of the shape—the part of the shape through which the transport of the molecules to and from the zeolites crystals within the shape is realized [66, 73]. Said secondary (or transport) pore system strongly influences the kinetics of the adsorbent, and hence, the adsorption process. So the zeolite NaX beads mentioned in **Table 1** show an attrition of <0.1 wt% (determined using Chemiewerk Bad Köstritz GmbH method) but relatively tight transport pores, which can lead to a slower diffusion within the zeolite beads. Using a lower amount of binder material, the adsorption capacity increases and the transport pores become slightly wider; see **Figure 3**. A faster diffusion is possible. But using a lower amount of binder material leads to an increased attrition value (0.2 wt%, determined using Chemiewerk Bad Köstritz GmbH method); for some applications that might be a high risk for an operating plant.

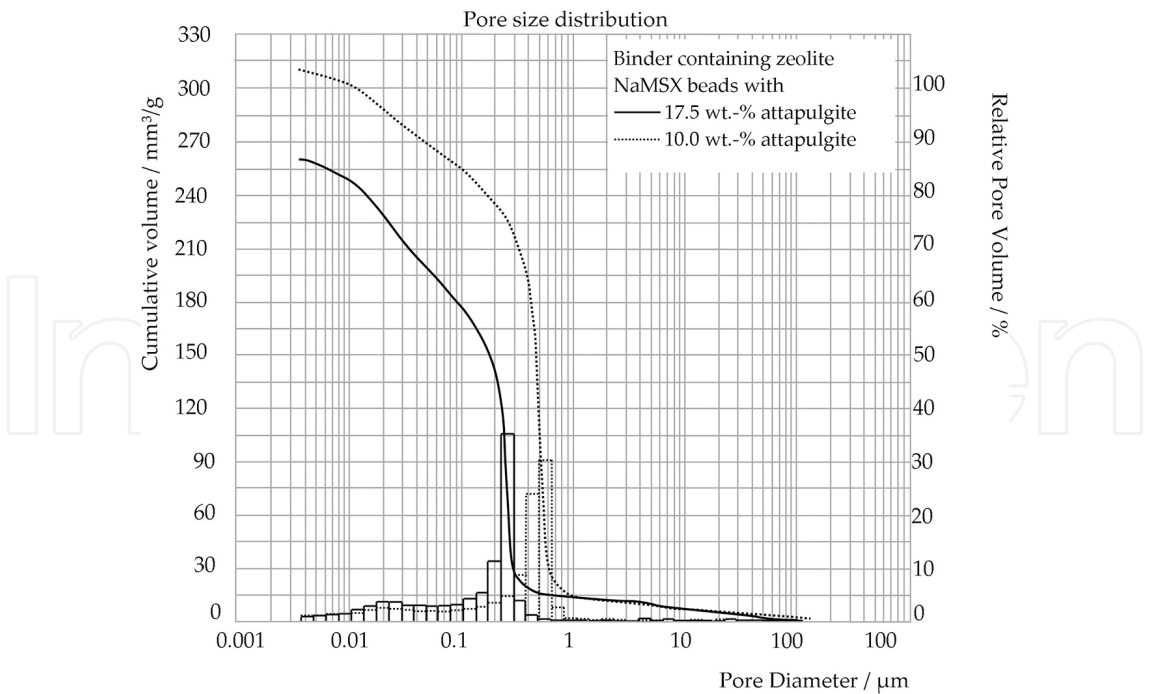


Figure 3. Hg intrusion curves of binder-containing zeolite NaX bulk material with 17.5 and 10.0 wt% of attapulgite binder.

4. Binderless zeolite molecular sieves

To avoid the above-mentioned disadvantages of binder-containing zeolite molecular sieve bulk materials such as adsorption capacity reduction by adsorption inert binders or influence of the secondary pore structure by the binder material, the so-called binderless zeolite molecular sieves were developed. There are different manufacturing procedures for binderless molecular sieves described in the open or patent literature. In most of those processes, the same shaping principles as mentioned earlier for the manufacturing of binder-containing zeolite molecular sieve are applied. They differ in the raw materials, respectively, the composition—especially the type and amount of the so-called temporary binder—of the starting pre-mixture, or the conditions for the conversion of the temporary binder into zeolite matter. Important for the generation of binderless zeolite molecular sieve is that the temporary binder contains only those elements, which are present in the target zeolite matter; that means in most of the cases silicon, aluminum, and sodium, for example, for binderless molecular sieves of A, NaX, and NaY type (or mixtures thereof). Only for the preparation of binderless zeolite LSX-type molecular sieves, potassium-containing systems are used [74].

Thus, it is possible to generate binderless zeolite shapes using temporary binder material such as kaolin as starting material [75]. A mixture of temporary binder material such as kaolin, metakaolin or silica, and zeolite powder or zeolite filter cake is also mentioned [76–83]. The conversion step can be a wet chemical [75, 79] or an at least partially autogenic thermal reaction [84].

Figure 4 shows the principle manufacturing procedure starting with shaping a pre-mixture using the above-mentioned technologies agglomeration granulation, spray granulation, or extrusion. Taggart [75] reported about shaping a mixture of kaolin and sodium hydroxide followed by drying of the shapes. It should be considered that kaolin has good binding properties but nearly no chemical reactivity. Due to that fact, the kaolin needs to be converted thermally (about 600 °C) into the chemically more reactive metakaolin. Depending on the target zeolite type, a suitable reaction solution comprising of sodium, aluminum, and/or silicon components is prepared. Usually, the shapes are aged and further processed in that reaction solution to convert the temporary binder into the desired zeolite matter. Finally, the shapes are washed, dried, and activated. Taggart mentioned that, due to the limited accessibility of the interior of the shapes by the mentioned reaction solution (blocked or too tight secondary pore system), the degree of the conversion of the temporary binder into zeolite matter, and hence, the adsorption capacity of the resulting material is limited, and can be enhanced if zeolite powder is used in the starting mixture. However, the mechanical stability of the resulting shapes is lower. Therefore, Howell et al. [85] propose the utilization of pore-forming agents (spacers), which are burned out in the following thermal treatment, thereby leaving space for the better accessibility of the interior of the shapes. Goytisoló et al. [76], Barrer et al. [77], Nozemack et al. [78], Brandt et al. [79], and Schumann et al. [80] described the manufacturing of binderless zeolite molecular sieves using a mixture of metakaolin, zeolite powder of such zeolite type, in which the metakaolin should be converted into, and additional sodium and silicon compounds such as sodium hydroxide, silicic acid or sodium silicate as feed for

the shaping process. The zeolite powder in the mixture has obviously crystallization triggering properties and supports the generation of an open, for the reaction solution accessible pore system. It has to be considered that metakaolin has practically no binding properties. Thus, one has to make sure, that the process is carried out in a way, that the shapes, which are coming out of the shaping process, are mechanically stable enough until the conversion of the non-

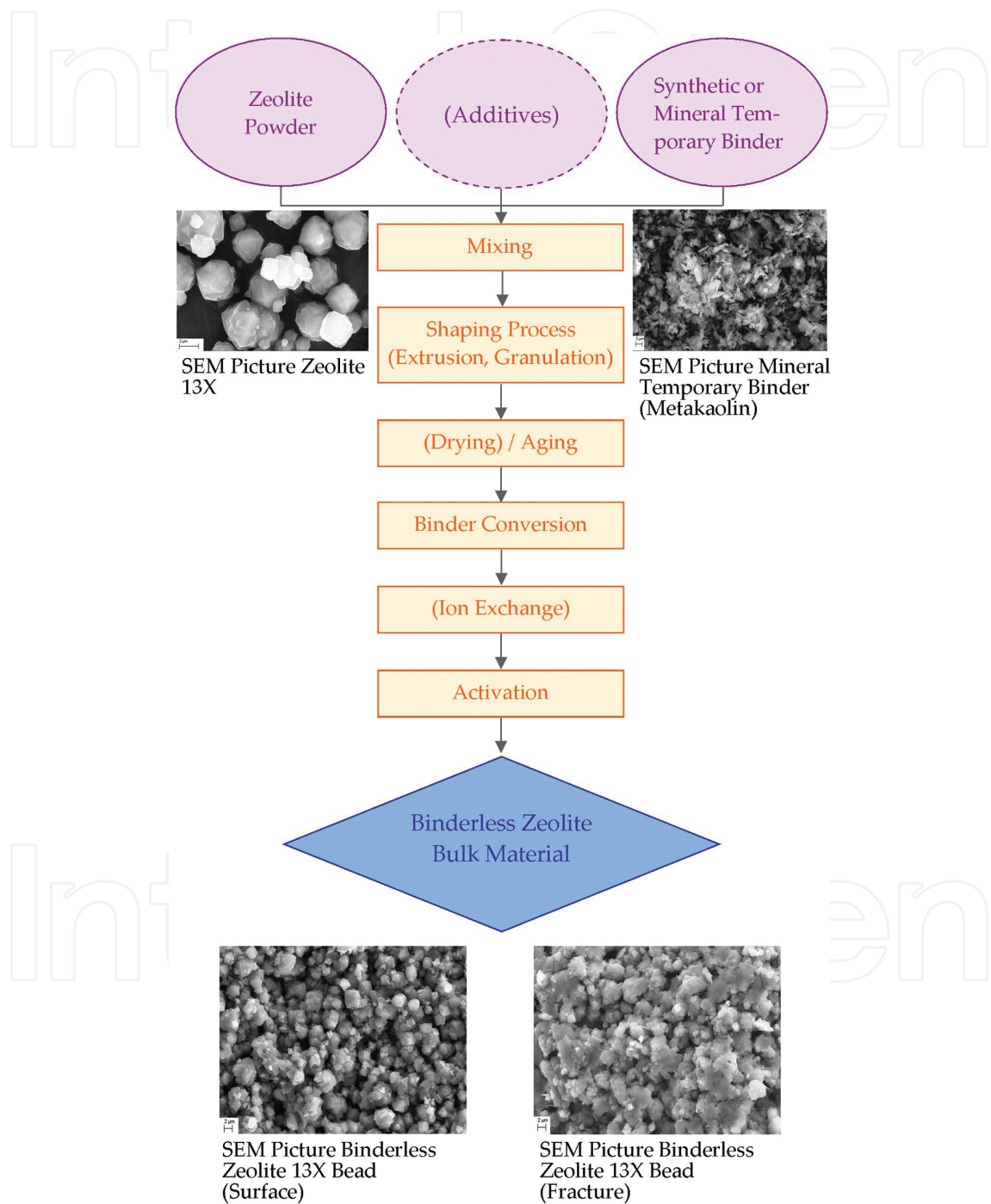


Figure 4. Scheme of the principle manufacturing procedure of binderless zeolite molecular sieve shapes (bulk material).

zeolitic compounds into zeolite matter in the reaction solution is completed. Said conversion is the basis for the mechanical stability of binderless molecular sieve shapes (see below). If it is possible to put all necessary compounds into the starting mixture for the shaping the reaction solution can be water [77, 78], otherwise all missing components for the desired zeolite formation have to be present in the reaction solution [75, 79, 80]. Another way to manufacture binderless zeolite molecular sieves is the use of silica as synthetic temporary binder. The shapes obtained are aged to achieve a certain water stability [81] followed by the conversion of the temporary binder in a solution consisting of aluminum and sodium components [82, 83].

The wet chemical reaction for the conversion of the temporary binder is preferably carried out by recirculating the reaction solution over the bulk material at suitable temperatures without moving the single shapes in order to avoid attrition between the still relatively soft shapes.

In the course of the chemical conversion of the non-zeolitic components into zeolite matter, the binding mechanism changes. In the case of kaolin/metakaolin-based systems, the mechanical stability of the shapes is now based on intergrowths between zeolite crystals in the single shape (see **Figure 4** bottom). Said intergrowths are formed during the conversion of the metakaolin into a polycrystalline zeolite matter [86]. Such unusual crystallization behavior can be explained by considering the available space for crystallization in a shape. On the outer surface of a single shape, there is enough space for a conventional and epitaxial crystal growth (see **Figure 4** down left for zeolite NaX), whereas in the interior, the space is obviously limited in a way that typical zeolite crystals such as octahedrons or cubes with rounded corners cannot be formed, but polycrystalline structures consisting of zeolite in untypical shape only (see **Figure 4** bottom right for zeolite NaX) [86]. After the chemical conversion, the bulk material is separated from the mother liquor (which can be reused for further reactions) and washed until a desired pH or conductivity of the effluent is achieved. Optionally, an ion exchange (applying a suitable ion exchange solution) can be affiliated. Finally, the material is dried and thermally activated in a suitable device (e.g., rotary kiln or belt calciner). As the mechanical stability of binderless molecular sieve shapes is already achieved during the temporary binder conversion step said thermal treatment is just needed to activate the zeolite, and not anymore to set a binder component. Thus, usually lower temperatures can be applied, which saves costs and is more gentle to the thermally sensitive zeolite structure. Despite the different manufacturing procedures of binder-containing and binderless zeolite bulk material, the mechanical stability of the resulting shapes is similar. In the case products produced according to [79] and [80], a higher mechanical strength for bigger binderless zeolite spheres in comparison with binder-containing zeolite spheres of the same size and zeolite type is observed. Using comparable analytical methods for both kinds of zeolite bulk material, the attrition/dust formation is also similar.

As can be shown exemplary in **Table 2**, the static adsorption capacity of binderless zeolite NaX bulk material is similar to that of pure zeolite NaX powder. That indicates that the binderless zeolite bulk material consists of nearly 100% of zeolite matter.

	Zeolite NaX powder	Binder-containing zeolite NaX beads	Binderless zeolite NaX beads
Water adsorption capacity at 55% relative humidity, 25°C/wt%	31.5	26.5	31.2
N ₂ adsorption capacity at 1000 mbar, 25°C/cc(STP)/g	10.7	8.0	10.5
CO ₂ adsorption capacity at 333 mbar, 25°C/cc(STP)/g	120.7	95.4	119.4

Table 2. Adsorption capacities for zeolite NaX (pure zeolite NaX powder, binder-containing bulk material with 82.5 wt% zeolite NaX and 17.5 wt% attapulgite and binderless zeolite NaX bulk material).

A further interesting observance is, that in the above-described special manufacturing process for binderless molecular sieves, a very open secondary pore system is generated, which allows faster kinetics as compared to conventional binder-containing zeolite molecular sieves with the (usual) binder content of around 20% [86], **Figure 5** proves the presence of a larger amount of macro pores. While the ratio of meso-pore to the sum of meso- and macro-pores is 30% for conventional binder-containing zeolite molecular sieves (pre-mixture consisting only of zeolite and attapulgite) the same ratio is only 5% for binder-less zeolite molecular sieves (produced according to [80]) [66].

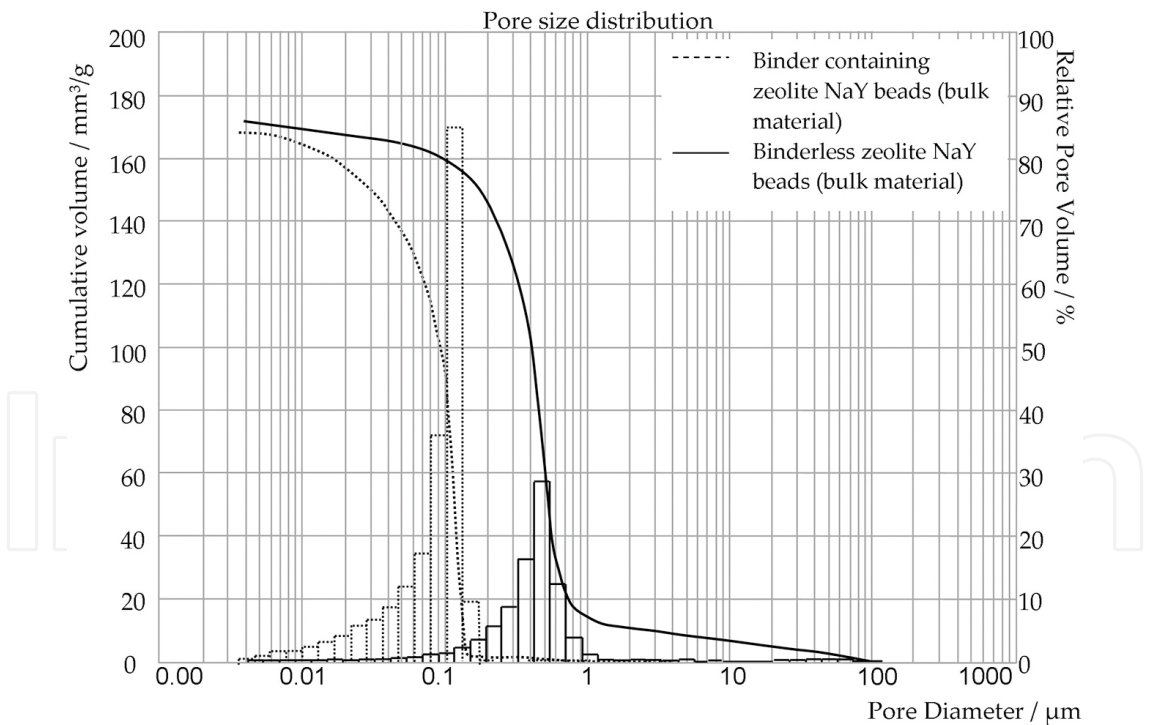


Figure 5. Hg intrusion curves of binder-containing and binderless zeolite NaY bulk material.

Due to the mentioned open secondary pore system, the above-mentioned problems concerning the inner shape transport limitations in binder-containing shapes depending on the size are eased in the case of binderless shapes.

It should, however, besides all obvious advantages of binderless over binder-containing molecular sieves mentioned earlier, noted, that, at least in the case of the kaolin/metakaolin-based systems, the structure of the binderless shapes is more rigid (less flexible) than the one of related binder-containing shapes. This can easily be explained by the different binding mechanisms: intergrowths in the case of the binderless structures, embedment in the case of binder-containing structures. This is a fact which must not be underestimated and needs to be taken into consideration especially in applications, which are connected with structural compressions/expansions (e.g., as a result of fast heat release and/or lattice changes by adsorption/desorption).

5. Compact zeolite bodies

In order to improve the overall effectivity of a given adsorption process, the increase of the volume-related adsorption capacity of the adsorbent used is often desirable. Said volume-related adsorption capacity is depending on the (bulk) density of the bulk material and on the amount of adsorption active matter within the shape (binder-containing or binderless zeolite bulk material). The bulk density itself depends on the density of the single shape(s) and on the void space between the shapes. It is known, that, for example, the packing density of a close-packing of spheres of equal diameter is ca. 74%; thus, the void space is about 26%. Theoretically, an increase of the packing density (and thus, of the bulk density) can be achieved by mixing spheres of optimal adjusted sizes, but it is certainly very difficult and expensive to produce and arrange such bed consisting of spheres of optimal sizes, the more, as the influence of the packing density on the pressure drop has always to be considered. An alternative to dense packed bulk beds can be compact zeolite bodies such as multi-channel tubes or honeycombs. By choosing appropriate geometries of such compact zeolite bodies with optimal channel dimensions a space filling (packing density) of much more, the mentioned 74% (theoretically up to 100% in the case of a void free compact body) is possible. In addition, such compact bodies can be modified in many ways to meet the requirements of the related adsorption process. Thus, a gas flow can be guided straight through the parallel arranged channels of a honeycomb-like structure, but through alternately blocking of the channels, a compulsorily perfusion is also possible [35].

Most of the manufacturing procedures of such compact zeolite bodies described in the literature are based on the use of (adsorption inert) binder material. As in the above-mentioned cases of binder-containing zeolite bulk material, synthetic binder [87] and mineral binder materials [88] are applied in the case of compact shapes as well. Consequently, the same disadvantageously impacts on the properties of the related adsorbents need to be considered: The introduction of the mentioned binder material causes a dilution of the adsorptive active matter and consequentially a reduction of adsorption capacities, and the binder material could affect the desired adsorption and desorption processes by forming a disadvantageous secondary pore system [66], an effect which at least partly can be cured by applying thermally removable pore-forming substances [89], and the fact, that impurities present in mineral binders may support undesired chemical side reactions.

At that point, it seems to be worth to remember, what was discussed above in this regard—to overcome the disadvantages of binder-containing molecular sieves bulk material. The solution (at least to a certain extent) was the application of binderless systems. And recently it could clearly be demonstrated that the same principle concept works in the case of zeolite-containing compact bodies as well: A high volume-related adsorption capacity can be reached [35]. The related honeycombs, multi-channel tubes, cylinder, etc. exhibit a remarkable adjustable high space filling (up to 100%), but at the same time a similar open secondary pore system such as mentioned earlier for binderless zeolite bulk material [90, 35].

For both types of compact zeolite bodies (binder-containing and binderless structures), the production process starts with mixing the ingredients zeolite powder, (temporary) binder, water and if needed shaping aids (such as e.g., glycerol or cellulose derivates) or in case of binder-containing compact bodies pore-forming substances if necessary (see **Figure 1**). Shaping technologies can be extrusion, pressing, or molding—depending on the desired geometry of the compact zeolite body. It should be noted that in the case of the binderless systems, the application of kaolin instead of metakaolin as main non-zeolitic component has been shown as being advantageous. In case of the binder-containing compact zeolite bodies, the following and final manufacturing step is the thermal treatment for drying and activation, where the organic compounds are burned out as well as the all water and other adsorbed compounds present in the system is removed and the binder is set. In case of binderless compact zeolite bodies, a first thermal treatment is needed for removing the organic shaping aids and converting kaolin into metakaolin [35, 91]. The generated metakaolin is converted into zeolite during a following wet chemical reaction. The related reaction solution consists of all ingredients necessary for the conversion of the metakaolin into the desired zeolite type (A, X or NaY) similar to the manufacturing of binderless zeolite bulk material. The conversion can be followed by further modification processes, for example, ion exchange. The completeness of the conversion of the non-zeolitic into zeolite matter can be demonstrated, for example, by adsorption measurements (in combination with XRD [35]). The static water adsorption capacity for zeolite 4A honeycombs in comparison with the fully crystalline zeolite 4A powder is shown in **Table 3** proving that the honeycomb consists of nearly 100% zeolite 4A matter.

	Zeolite 4A powder	Binderless zeolite 4A honeycomb
Water adsorption capacity at 55% relative humidity, 25°C/wt%	24.8	24.7

Table 3. Adsorption capacities for zeolite 4A (pure zeolite 4A powder and binderless zeolite 4A honeycomb).

Just for completion it should be noted that compact zeolite-containing bodies can also be manufactured by washcoating [92, 93], where mainly for catalytic applications, the catalytically active zeolite component is deposited onto monolithic support structures, as, for example, ceramic (in most cases cordierite) honeycombs by washcoating. The result is a compact body with a thin zeolite layer. Furthermore, the crystallization of zeolite matter directly on

aluminum foams is published [94]. Such structures exhibit interesting flow characteristics, but due to the rather large void fraction and a relatively thin zeolite layer onto the aluminum support, a low volume-related zeolite amount, and hence, a low volume-related adsorption capacity is observed.

6. Conclusion

Zeolite molecular sieves play an important role as highly effective adsorbents in major industrial adsorption processes. The properties of such molecular sieves can be tailored according to the requirements of the related applications. Besides the common binder-containing molecular sieves, binderless grades are applied. Due to the particular binding mechanism and the related special secondary pore system, binderless molecular sieves are mainly applied where fast kinetics is required, thus, especially in (vacuum) pressure swing adsorption processes. Furthermore, the principle concept for the manufacturing of binderless zeolite bulk material can be applied to the manufacturing of compact zeolite bodies, too. This opens ways for a further improvement of the related adsorption processes.

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