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ZEOLITE
MOLECULAR
SIEVES



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ZEOLITE MOLECULAR SIEVES

STRUCTURE, CHEMISTRY, AND USE

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PREFACE

Long winded writers I abhor,
And glib, prolific chatters:
Give me the ones who tear and gnaw
their hair and pens to tatters:
who find their writing such a chore
they write what only matters.

— From "Crooks" by Piet Hein

Several years ago, I undertook the preparation of the manuscript for this book confident that zeolite science had attained a reasonable level of maturity and that the time had come for publication of an appropriate monograph. Today, with file boxes filled with obsolete manuscripts, I am much wiser. Each chapter has been subjected to several revisions and the manuscript size has increased to the point of becoming unwieldy. However, I believe that most of the important developments published and available by the end of 1972 are included. As author, I have had to use my judgment, hopefully objectively, as to the subject matter.

In order to be comprehensive, much of the detailed information on structure, synthesis, ion exchange, and adsorption has been summarized in tables. Appropriate illustrations and photographs are used. Chapter 2 includes a collection of stereophotographs of all of the basic zeolite framework structures. Most readers will find a stereoviewer desirable. A considerable amount of previously unpublished information obtained by my associates at Union Carbide Corporation during the last 25 years is included in the book.

The reader will quickly observe by a perusal of the Table of Contents that the important subject of zeolite catalysis has been deliberately omitted. This was a decision we had to make due to size and time limitations. We hope to prepare a second volume which will be concerned with zeolite catalysis and certain other areas of interest to the user of zeolites.

In the preparation of this volume, I have relied very heavily on friends and colleagues. I especially want to thank Professor J. V. Smith for his comments and review of Chapters 1, 2, and 3. He also supplied many of the models illustrated in Chapter 2. I wish to thank Ms. E. M. Flanigen and Mr. R. L. Mays for their critical review of the manuscript.

I especially want to thank my editor, Ms. N. L. Marcus, for her perseverance. The work would have been impossible without her help. I want to thank Dr. W. H. Flank for proofreading the entire manuscript and for his constructive comments. Finally, I wish to thank Union Carbide Corporation for their support and encouragement.

D. W. Breck
July, 1973

of silica for making zeolite Y.

In one process metakaolin is seeded with a small amount of an amorphous zeolite precursor slurry with a particle size of less than 0.1 micron. The amorphous aluminosilicate "seeds" were first prepared by aging a sodium silicate-sodium aluminate mixture at ambient temperature for 16 hours. The metakaolin-sodium silicate slurry was added to another sodium hydroxide-sodium silicate solution which was seeded with the amorphous zeolite seeding mixture. Typically, crystallization is completed at 100°C in 18 to 36 hours. The formation of zeolite Y with a ratio of 4.9 to 5.9 is reported. However, what happens in the absence of the amorphous seeding mixture is not disclosed (62).

Diatomite silica may be used to make zeolite Y. The diatomite is first washed with hydrochloric acid and calcined at 430°C for 2 hours. This is used together with the usual sodium hydroxide-sodium aluminate combination. A typical reactant composition which results in the formation of zeolite Y is reported to be about $3.6 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot 97\text{H}_2\text{O}$ (61).

The manufacture of the mordenite-type zeolite from amorphous aluminosilicate precursors may be preferred. The precursor is prepared from sodium silicate solution ($\text{SiO}_2/\text{Na}_2\text{O} = 3.2$) and aluminum sulfate. Although the precursor precipitate is washed to remove the sodium sulfate which is formed, it is reported that such washing is unnecessary. Crystallization of the mixture to mordenite is accomplished hydrothermally at 300°C (87 bars) in 15 hours. The ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the initial reaction mixture varied from 9 to 13. The direct preparation of agglomerated, that is, pelletized mordenite, is also reported; this was accomplished by extruding the amorphous aluminosilicate precursor in a paste followed by drying and calcining at 600°C. Subsequently, the extruded particles were hydrothermally treated at 300°C for 15 hours (27).

The Processing of Zeolite Minerals into Commercial Products

The most extensive application of zeolite minerals in commercial products seems to have been made in Japan. The two zeolite minerals occurring in usable deposits in Japan are mordenite and clinoptilolite. Zeolite production in Japan is reported to be 5,000 to 6,000 tons per month (68). Zeolite minerals are used in Japan in the following appli-

cations: (a) in papermaking; (b) in air separation adsorption processes, (c) as desiccants; (d) in fertilizers; (e) as soil conditioners—this application is based upon the ability of the zeolite to ion exchange with soil nutrients; (f) in agricultural applications—these include the use as deodorants in the raising of pigs and chickens; (g) in the treatment of radioactive wastes; (h) as carriers for toxic materials; and (i) as adsorbents for toxic gases.

The distribution of zeolite deposits in Japan was discussed in Chap. 3. The Zieglite Chemical Company operates a plant at Itagaya. The main material mined is a potassium-rich clinoptilolite which exists in a thick white tuff approximately 250 meters thick (Fig. 9.5). This is one of the larger deposits and is estimated to contain about 500,000 tons. Most of the material is mined from shafts and is taken to a plant where it is crushed, dried, powdered, and then meshed into three grades based on particle size (Figs. 9.6, 9.7)

Figure 9.5 View of zeolite deposit and processing plant at Itagaya, Japan. (Photograph courtesy of Professor H. Minato.)

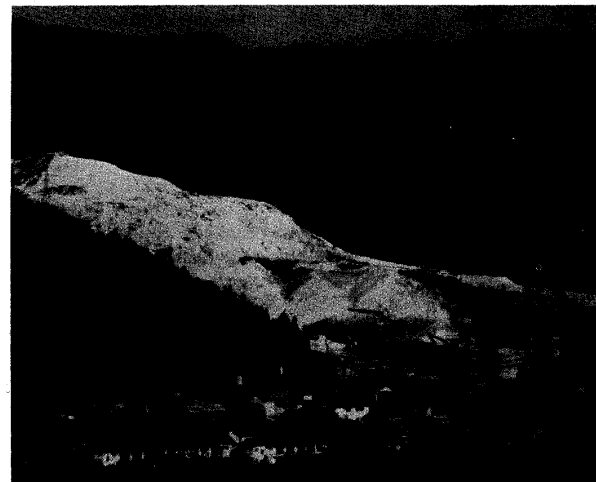




Figure 9.6 Zeolite plant at Itagaya, Japan. (Photograph courtesy of Professor H. Minato.)

B. THE PELLETIZATION OF SYNTHETIC ZEOLITE POWDERS

High purity zeolite crystals to be used in adsorption processing, must be formed into agglomerates having high physical strength and attrition resistance. Methods for forming the crystalline powders into agglomerates include the addition of an inorganic binder, generally a clay, to the high purity zeolite powder in wet mixture (77). The blended clay zeolite mixture is extruded into cylindrical type pellets or formed into beads which are subsequently calcined in order to convert the clay to an amorphous binder of considerable mechanical strength (Fig. 9.8). As binders, clays of the kaolin type are generally used. In some instances, the use of metal powders has been reported (69).

The zeolite may be formed into binderless particles by hot pressing techniques. When subjected to high pressures at an elevated temperature, a mass of the zeolite crystals may self-bond into a 100% zeolite pellet. This method, although utilized for various laboratory applications, has not achieved extensive industrial use.

A third method might be to form the zeolite in single crystal form in particle size ranges suitable for actual use. Although single crystals up to 100 microns in size have been reported, these processes have not yet achieved commercial significance. Single 100-micron crystals of zeolite may be suitable for fluidized-bed adsorption processes.

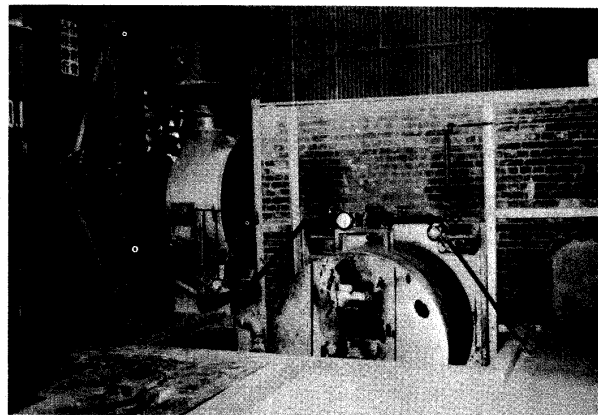
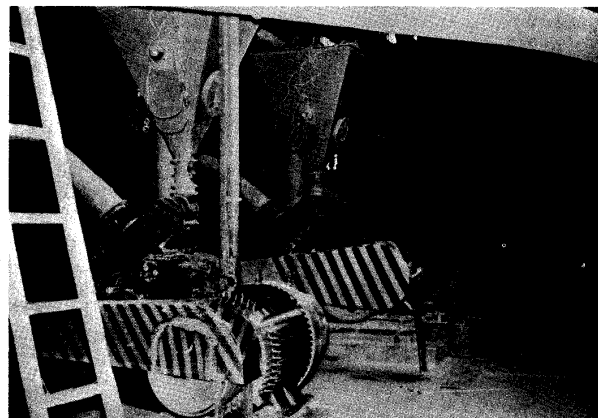
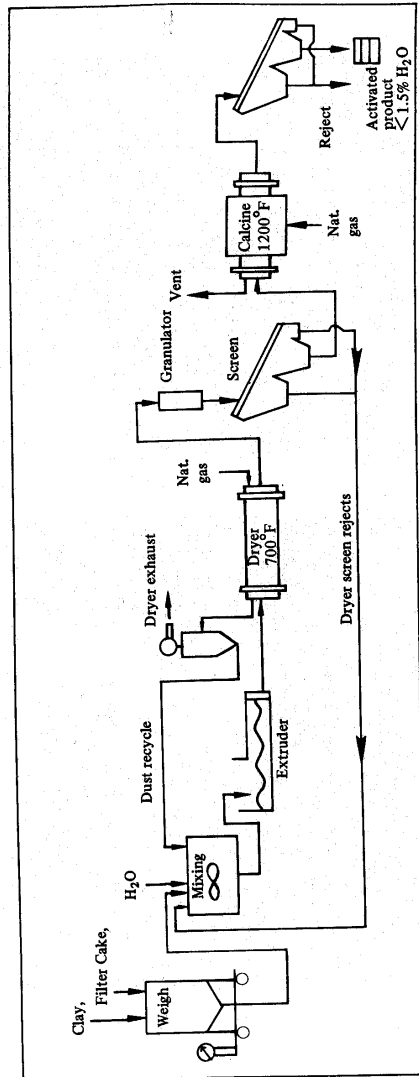


Figure 9.7 (a) Roller mill for crushing zeolite minerals; (b) Rotary kiln for drying zeolite. (Photographs courtesy of Professor H. Minato.)

Figure 9.8 Pelletization Process



In many applications using pelleted molecular sieves, the physical resistance of the pellets to mechanical attrition is important since it will determine the economic life of the material in typical adsorption processes.

The preparation of zeolite-binder agglomerates as spheres or cylindrical pellets which have high mechanical attrition resistance would not be difficult. However, in order to utilize the zeolite in a process of adsorption or catalysis, the diffusion characteristics must not be unduly interfered with. Consequently, the binder component in the pellet must be such that a macroporosity is maintained which does not increase the diffusion resistance. The problem, therefore, is one of optimizing the binder-zeolite combination so as to achieve a pellet of maximum density (to produce a high adsorption capacity) with maximum mechanical attrition resistance and minimum diffusion resistance. Some applications are based upon using the equilibrium adsorption capacity of the zeolite component with essentially infinite time being allowed for adsorption (for example, as a cartridge in a refrigeration system for removing trace amounts of water). In adsorption processes involving the use of fixed-beds of molecular sieves, suitable macroporosity must be maintained in the pelleted conglomerate.

Binderless pellets of zeolite A are manufactured by first preparing a zeolite A-silicic acid granule composite which contains 15% silica on a dry basis followed by treating these granules by cold aging in sodium aluminate solution for about one day. This is followed by a digestion treatment at 80°C in aqueous NaOH for several hours (70).

In another method, the zeolite is first synthesized from an aqueous gel system prepared from caustic, alumina trihydrate and colloidal silica (71). The zeolite crystals are recovered by filtration, washed with water and converted to the ammonium form by ion exchange and then mixed with kaolin clay which is activated in steam at 700 - 750°C for several hours. These final activated pellets contain 10% zeolite. In this case, steam activation probably produces a stabilized form of zeolite Y. (See Chap. 6.)

A slurry of zeolite contained in the mother liquor from which it was crystallized is dispersed in an acidified sodium silicate solution so that the final pH is about 4-4.5 (73). This produces a silicate gel which after aging for 30 minutes is added to a mixture of aluminum sulfate and ammonium hydroxide. A silica-alumina matrix is formed surrounding the zeolite crystals. The final zeolite content in this com-

posite is about 10% by weight, in an amorphous silica matrix comprising 92.5% silica and 7.5% alumina. Additional ion exchange treatment of the zeolite can be performed within this matrix.

Zeolite Y has been formed into a composite containing 10 wt% zeolite in an amorphous silica matrix. This is accomplished by spray drying a slurry of the zeolite in a silica hydrogel which is prepared by acidifying sodium silicate to a pH of 4.3. Prior to the spray drying the pH is adjusted to 3.7 and aged for 6 hours (74).

One process results in a composite primarily designed for use as a catalyst containing zeolite Y in an amorphous silica matrix. After crystallization the zeolite in the mother liquor is slurried directly with an acidified sodium silicate solution so that the final pH of the mix is 4.0-4.5. After spray drying the composite particles are converted to an ammonium form by ion exchange for catalytic use (75).

Zeolite-clay composites may be prepared as spheres (76). The spherical agglomerates are formed by dry blending the clay and the zeolite powder and then adding controlled amounts of water in a rotating drum. The spheroidal bodies form during tumbling. The surface of these spheres may be further hardened by soaking in a soluble silicate solution and drying the coating on the surface. After impregnation, the coated spherical pellet is calcined to harden the surface silicate coating.

C. PROPERTIES OF COMMERCIAL MOLECULAR SIEVES

Commercially available molecular sieve products and related materials are listed in Table 9.6. These products are listed according to the basic zeolite structure types which were discussed in Chap. 2. The major cation species, the pore size, the particle sizes, typical bulk density values, the crushing strength of the pellet, and the water adsorption capacity are shown. In most cases the water content is less than 1.5 to 2.5 wt%; certain products, however, are sold as fully hydrated crystalline powders. The water capacity given in the last column is the total water adsorption capacity on an activated basis. In those products where the binder is present to the extent of about 20 wt% of the activated composite, the water capacity is equal to about 80% of the water adsorption capacity of the pure crystalline zeolite powder.

Adsorption properties and other properties of commercial products are affected by the binder. Generally, however, the binder acts as a

Table 9.6 Commercial Molecular Sieves

Product	Structure Type	Major Cation	Pore Size (Å)	Particle Size	Bulk Density (lb/cu ft)	Crush Strength (lb)	Water Content (wt %)	Water Capacity (wt %)	Ref.
Type 3A Linde	A	K ⁺	3	1/16" pellet	40	6.4	<1.5	20	F21A (80)
Type 4A Linde	A	Na ⁺	4	1/8" pellet Powder < 10 µm 1/16" pellet 0.0575 - 0.0775 in 1/8" pellet 0.115 - 0.135 in 14 x 30 mesh 0.0232 - 0.0555 in 8 x 12 beads 0.0661 - 0.0937 in 4 x 8 beads 0.0937 - 0.187 in Powder < 10 µm 1/16" pellet 0.0575 - 0.0775 in	40 40 41 41 40 42 40 50	14.5 10.4 21 6.9 18 20	<1.5 <2.5 <1.5 <1.5 <1.5 <2.5	20 23 22 22 22 25	F22 (80) F3206 (80) F2209 (80) F2184B (80)
Type 4A -30 Linde	A	Na ⁺	4	8 x 12 mesh bead	0.082 g/cc	10			
Type 4A -XH-2 Linde	A	Na ⁺	4	4 x 8 mesh bead	0.77 g/cc	19			
Type 5A Linde	A	Ca ²⁺	5	1/16" pellet 0.0575 - 0.0775 in 1/8" pellet 0.115 - 0.135 in Powder < 10 µm	45 45	5.8 12.6	<1.5 <1.5 <2.5	21.5 21.5 28	

Table 9.6 Commercial Molecular Sieves (continued)

Product	Structure Type	Major Cation	Pore Size (Å)	Particle Size	Bulk Density (lb/cu ft)	Crush Strength (lb)	Water Content (wt %)	Water Capacity (wt %)	Ref.
Type 10X Linde	X	Ca	8	1/16" pellet 0.0575 - 0.0775 in 1/8" pellet 0.115 - 0.135 in Powder < 10 µm	40 ^c	9	<1.5	31.6 ^b	3097 (80)
Type 13X Linde	X	Na	10	1/16" pellet 0.0575 - 0.0775 in 1/8" pellet Powder < 10 µm	38	12	<2.5	35 ^b 28.5 ^a	F23 (80)
Type AW-300, Linde	mordenite	Na	4	1/8, 1/16" pellet	55.4	25	<1.5	28.5	F2308 (80)
Type AW-500, Linde	chabazite	Na, Ca	5	1/8, 1/16" pellet	45.4	30	<2.5	34	
SK40 Linde	Y	Na		Powder 1 - 2 µm Extrudate 1/8" x 1/4"	38				F-10 (80)
SK41 Linde	Y	NH ₄ ⁺		Powder 1 - 2 µm					F-4 (80)
SK45 Linde	L	K ⁺		Powder 5 - 10 µm		33			F2988 (80)
SK120 Linde	Y	Rare earth, 0.5% Pd		1/8" extrudate	38 - 45	15			F12 (80)
SK500 Linde	Y	Rare earth		1/8 - 1/4" extrudate	38 - 45	15			F-15 (80)
Zeolon-100, Norton	mordenite	Na	7	Powder 5 - 12 µm	40			14	Z-50 (81)
		H	8 - 9	Powder 5 - 12 µm	42			15	

Table 9.6 Commercial Molecular Sieves (continued)

Product	Structure Type	Major Cation	Pore Size (Å)	Particle Size	Bulk Density (lb/cu ft)	Crush Strength (lb)	Water Content (wt %)	Water Capacity (wt %)	Ref.
Zeolon-200, Norton	mordenite	H	8 - 9	1/8" extrudate	38			12	Z-50 (81)
Zeolon-300, Norton	mordenite	mixed cations	3 - 4	1/8" extrudate	48			5.5	Z-50 (81)
Zeolon-500, Norton	chabazite	mixed cations	4 - 5	1/8" extrudate	47			13.5	Z-50 (81)
Zeolon-900, Norton	erionite	Na	7	1/8" extrudate	40			10	Z-50 (81)
	mordenite	H	8 - 9	1/16" extrudate self-bonded 20 - 50 mesh 1/8" extrudate	45			11	Z-50 (81)
Type 3A Davison	A	K	3	8 - 12 mesh, spheres 4 - 9 mesh, spheres Powder, 3 - 5 µm	46 46 32	7 11 —	1.5 1.5 1.5	21.0 21.0 23.0	82 82 82
Type 4A Davison	A	Na	4	8 - 12 mesh, spheres 4 - 8 mesh, spheres 14 - 30 mesh, granules 10 - 16 mesh, spheres Powder, 3 - 5 µm	44 44 — — 30	7 11 — — —	1.5 1.5 1.5 1.5 1.5	23.0 23.0 23.0 28.5 21.7	82 82 82 82 82
Type 5A Davison	A	Ca	5	8 - 12 mesh, spheres 4 - 8 mesh, spheres 20 - 50 mesh, spheres Powder, 3 - 5 µm	44 44 40 30	7 11 — —	1.5 1.5 1.5 1.5	21.7 21.7 28.0 29.5	82 82 82 82
Type 13X Davison	X	Na	10	8 - 12 mesh, spheres 4 - 8 mesh, spheres Powder, 3 - 5 µm	43 43 30	6 10 —	1.5 1.5 1.5	29.5 29.5 36.0	82 82 82

^a lbs H₂O/100 lbs activated adsorbent at 25°C, 17.5 torr.^b lbs H₂O/100 lbs activated adsorbent at 25°C, 25 torr.^c Settled.

diluent. The binder affects adsorption by contributing secondary porosity in the form of macropores.

Although detailed information on the distribution of voids in composite pellets of molecular sieves is not available in every case, some typical data are shown in Tables 9.7 and 9.8. In Table 9.7 the distribution of voids in a single, typical molecular sieve pellet is given in terms of two components, the void volume present in the crystals themselves and the void volume present between the crystals. This, together with the volume fraction occupied by the zeolite crystal framework and the solid binder total 100%.

When these pellets are packed in a bed, the distribution of voids as typically found is shown in Table 9.8. Again, the breakdown is in terms of the two types of voids present, those in the individual pellet together with the voids present between the pellets in the packed bed. For example, in the case of the 1/16-inch pellets, the voids total nearly 74 vol% of the packed bed.

Typical physical properties of the molecular sieve type 5A in two sizes of pellets, 1/16 and 1/8 inch, are shown in Table 9.9. Typical distribution curves of a lot of molecular sieve type 5A pellets are shown in Fig. 9.9 for two sizes of pellets. The distributions are shown in terms of the length of the pellets. In either case, the average length to diameter ratio is about 1.6 to 1.7. The heat capacity of the molecular sieve pellets is important in considering adsorption processes and a typical curve showing the heat capacity of 5A pellets versus temperature is given in Fig. 9.10. The heat capacities were calculated from enthalpy values obtained over a temperature range of 32 to 572°F (79). The sample was first activated for 12 hours at 662°F at a pressure of 0 to 1 torr.

Table 9.7 Volume Distribution in Single Molecular Sieve Pellets

	1/16-inch Pellet (%)	1/8-inch Pellet (%)
Intracrystal voids	28.1	28.8
Intercrystal voids	33.4	31.5
Solid portion of crystals	29.2	30.1
Solid portion of binder	9.3	9.6
	100.0	100.0

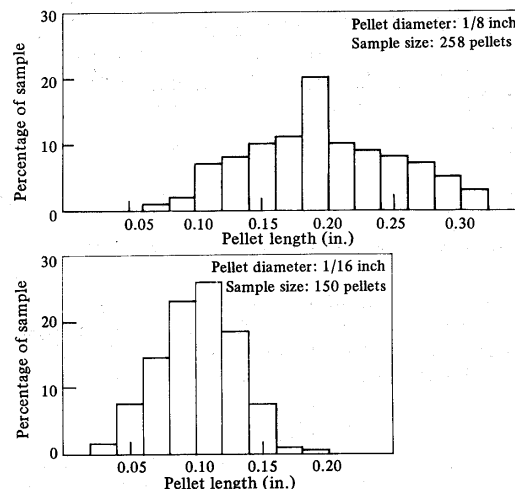


Figure 9.9 Typical length distribution of molecular sieve type 5A pellets.

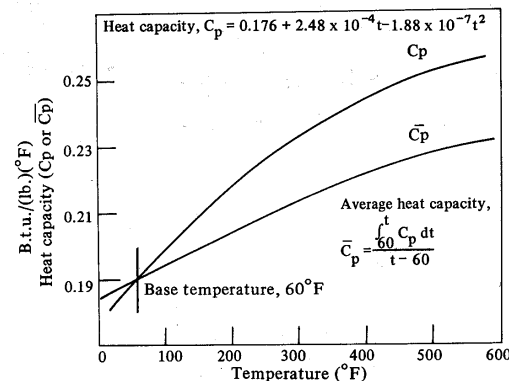


Figure 9.10 Heat capacity of molecular sieve type 5A pellets.

Table 9.8 Volume Distribution in Beds Packed with Molecular Sieve Pellets ^a

	<i>Bed Packed with 1/16-inch Pellets (%)</i>	<i>Bed Packed with 1/8-inch Pellets (%)</i>
Intracrystal voids	19.1	19.6
Intercrystal voids	22.7	21.4
Interpellet voids	32.0	32.0
Solid portion of crystals	19.9	20.5
Solid portion of binder	6.3	6.5
	100.0	100.0

^a Based on a bed packed with an external void fraction, ϵ , equal to 0.32 (interpellet voids).

Pellet densities of activated molecular sieve pellets were determined using a mercury displacement technique. The external void fraction in a packed bed is determined directly from the bulk density and particle density. The external void fraction, ϵ , is given by:

$$\epsilon = 1 - \frac{\text{Bulk density}}{\text{Particle density}}$$

The external void portion, determined by packing the pellets in columns of up to 8 inches in diameter and 5 feet in length, is generally in the range of 0.32 to 0.36. Initial packing is not as dense as that obtained after the bed has settled or been in operation for some time. Therefore, the void fraction in a settled bed will be less. The initial value for the void fraction in a large packed bed is probably about 0.38 but, after settling, generally falls to a value of 0.32.

Table 9.9 Typical Physical Properties of Molecular Sieve Type 5A Pellets

<i>Physical Property</i>	<i>Units</i>	<i>Pellets</i>	
		<i>1/16-inch</i>	<i>1/8-inch</i>
Pellet density	lb/cu ft	70.0	72.0
Bulk density, newly packed	lb/cu ft	43.4	44.6
Bulk density, settled bed	lb/ cu ft	47.5	48.8
External void fraction, newly packed	—	0.38	0.38
External void fraction, settled bed	—	0.32	0.32
Average pellet length	ft	0.00900	0.0173
Pellet length distribution	—	See Fig. 9.9.	
Average pellet diameter	ft	0.00522	0.0107
Average ratio of length to diameter	—	1.72	1.63
External surface area of pellets	sq ft/ cu ft	655	370
Effective particle diameter (based on Ergun's expression)	ft	0.00606	0.0122
Effective particle diameter (based on sphere with equal external surface area)	ft	0.00777	0.0155
Heat capacity	Btu/(lb)(°F)	See Fig. 9.10.	