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# Chemical and Physical Properties of the ZSM-5 Substitutional Series

D. H. OLSON, W. O. HAAG, AND R. M. LAGO

*Central Research Division, Mobil Research and Development Corporation, Princeton, New Jersey 08540*

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ZSM-5 is a new silica-rich zeolite that has been synthesized with greatly differing $SiO_2/Al_2O_3$ ratios; the aluminum content, while always small, can be varied by several orders of magnitude. ZSM-5 thus constitutes a substitutional series whose physical, chemical, and catalytic properties are reported and discussed in terms of their structural and compositional dependance. Ion exchange capacity, catalytic activity, and water sorption (at $P/P_0 = 0.006$) are shown to vary linearly with aluminum content and extrapolate smoothly to the end member of the series, a pure silica ZSM-5. Other properties such as X-ray diffraction pattern, pore size and volume, framework density, and refractive index are primarily a result of the structural features and are largely composition independent. From a comparison of their properties, the recently reported "silicalite" appears to be a member of the ZSM-5 substitutional series.

## INTRODUCTION

Although natural zeolites of the "molecular sieve" type were known to mineralogists for many years, the art of synthesizing such minerals is of recent origin, and the synthetic materials remained laboratory curiosities until about 1954 when commercial production of Linde "A" zeolite began. The early work by R. M. Barrer, who pioneered in synthesizing zeolites systematically, utilized completely inorganic reaction mixtures which on hydrothermal treatment produced one or more crystalline zeolites, some of these having no natural counterpart. In a few instances, organic nitrogenous cations were also used in zeolite syntheses (*1*, *2*). All the synthetic crystals had $SiO_2/Al_2O_3$ molar ratios in the range of 2 : 1 to 10 : 1, as did the natural zeolites. Synthetic mordenite, with its $SiO_2/Al_2O_2$ ratio of 10 : 1 was the most siliceous synthetic zeolite. To this day the most siliceous *natural* zeolites are ferrierite, clinoptilolite, and mordenite, all with a 10 : 1 $SiO_2/Al_2O_3$ ratio.

The natural and *early* synthetic zeolites had certain other properties in common that were characteristic of this class of materials. If not containing salt occlusions, they all had a metal cation complement equivalent to the content of tetrahedrally bonded aluminum. This cation complement was ion exchangeable, at least to the extent that it was not trapped in the cavities of a particular zeolite. These zeolites all were highly hydrophilic, the available pore space becoming completely filled even at a very low partial pressure of water vapor. This hydrophilic character, however, is not an inherent property of the porous zeolite structure itself but is related directly to the high aluminum content of the natural and early synthetic zeolites. Chen has shown for a series of dealuminized mordenites that the amount of water sorbed decreases linearly with decreasing alumina content, which he attributed to the increase in the number of the nearly homopolar (hydrophobic) $\equiv Si—O—Si \equiv$ bonds and concomitant decrease in the number of hydrophilic aluminum tetrahedra and associated cation centers (*3*).

About 18 years ago G. T. Kerr and coworkers in the laboratories of Mobil Research and Development Corporation began an extensive study of the synthesis of zeolites from reaction mixtures that con-

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tained organic nitrogenous cations. One of the new zeolites obtained early in the investigations was zeolite beta (*4*), of interest because its $SiO_2/Al_2O_3$ ratio was about three times that of mordenite. This was followed by other new highly siliceous zeolites, including ZSM-5 and similar substances (*5*). This new class of high silica zeolites is of considerable significance as catalyst material. Examples of its uses include the conversion of methanol to gasoline, the dewaxing of distillates, and the interconversion of aromatic compounds (*6*). ZSM-5 has been shown to possess unusual hydrophobicity, leading to potential applications in the separation of hydrocarbons from polar compounds, such as water and alcohols (*7*).

In view of the unusual properties of the high $SiO_2/Al_2O_3$ ratio materials that can be synthesized with organic nitrogenous cations, they are of scientific interest as well as of commercial importance.

This paper presents detailed data on many physical and some catalytic properties of ZSM-5, a member of this new class of highly siliceous zeolites. It was chosen since more information was available about it than about the other members of this class.

## STRUCTURE AND COMPOSITION OF ZSM-5

The crystal structure of ZSM-5 was described in March 1978 (*9*). This zeolite is formed by including nitrogenous organic molecules such as tetrapropylammonium bromide in the reaction mixtures (*5, 10*); for very high $SiO_2/Al_2O_2$ preparations, no source of aluminum need be deliberately included in the solution (*10*). The organic molecules are incorporated into the zeolite structure as it is formed, and such as-synthesized materials have been aptly called "nitrogenous zeolites" (*1, 11*) and less specifically "organosilicates" (*10*). ZSM-5 may be freed of the organic guest molecule by high temperature treatment without change of its framework topology as had been found earlier for other quarternary ammonium-containing zeolites (*2b*).

The nitrogenous structure and organic-free ZSM-5 material have no natural counterpart, and possess other features which set the crystals apart from more common zeolite types. The ZSM-5 structure has been synthesized with $SiO_2/Al_2O_3$ molar ratios from about 20 to greater that 8000 (*5, 10*). Thus, this zeolite in its least siliceous form has about twice the silica/alumina mole ratio of the most siliceous common zeolite, mordenite. Although it is known that isotypic zeolite structures can be synthesized or found in nature which contain different concentrations of aluminum, such as in the series of zeolites X, Y, and faujasite, the relative percentage change of aluminum content is relatively limited. On the other hand, for ZSM-5 the aluminum content can be changed by several orders of magnitude with silicon contents approaching and including that of substantially pure silica.

Many properties of ZSM-5 vary with composition, i.e., with its $SiO_2/Al_2O_3$ ratio. In different applications of ZSM-5, certain ranges of composition are therefore frequently favored or required. Examples of composition-dependent properties are ion exchange capacity, catalytic activity, and hydrophobicity. As will be shown below, these properties vary linearly with aluminum content and extrapolate smoothly to the end member of the substitutional series, an aluminum-free, pure silica ZSM-5.

Many other properties of ZSM-5 are essentially invariant with composition, i.e., they are little or not at all affected by $SiO_2/Al_2O_3$ ratio, but depend primarily on its framework structure. These include the X-ray diffraction pattern (shown in Fig. 5), pore size and volume, framework density, and refractive index; values of these properties are shown in Table 1.

A report from another laboratory has recently appeared which describes the preparation and physical properties of a synthetic material which was referred to as

TABLE 1

Comparison of Physical Properties

| | ZSM-5 | "Silicalite"[a] |
|---|---|---|
| Refractive index (25°C) | | |
| As synthesized | 1.48[b] | 1.48 |
| Air calcined at 600°C | 1.40[b] | 1.39 |
| X-Ray pattern | (Identical—see Fig. 5) | |
| Structure type | ZSM-5 | ZSM-5 |
| Channel Size[c] (Å) | | |
| Straight [010] | 5.4 × 5.6 | 5.0 × 5.6 |
| Sinusoidal [100] | 5.1 × 5.5 | 5.3 |
| Framework density (T atoms/1000 Å$^3$) | 17.9 | 18.1 |
| Density (g/cm$^3$) | | |
| Observed | 1.77[b] | 1.76 |
| Calculated | 1.79 | 1.80 |
| Micropore volume (cm$^3$/g) | 0.18[d] | 0.19 |
| Adsorption volumes (at 25°C, cm$^3$/g) | | |
| *n*-Hexane | 0.18[d] | 0.199 |
| Benzene | 0.13[d] | 0.134 |
| Isosteric heat of absorption | | |
| *n*-Hexane (kcal/mol) | 18–20[e] | 16–18 |

[a] From Ref. (*8b*).
[b] For $SiO_2/Al_2O_3$ molar ratio of 6400.
[c] Based on an oxygen radius of 1.35 Å.
[d] For HZSM-5 with a $SiO_2/Al_2O_3$ molar ratio of 75.
[e] For HZSM-5 with a $SiO_2/Al_2O_3$ ratio of 8660.

"silicalite." Like ZSM-5, it is prepared from a reaction mixture that contains organic, nitrogenous cations; it is described as hydrophobic and devoid of ion-exchange properties (*8a, b*). Reported values of its physical properties have also been included in Table 1. A comparison of these data strongly suggests that the two materials are the same. This is not surprising since the framework structure reported for "silicalite" (*8b*) is identical to that defined by the structural features reported for ZSM-5 (*6a, 6c, 9*). The framework of ZSM-5 zeolite contains a novel configuration of linked tetrahedra consisting of eight five-membered rings. The channel system, which is three-dimensional and defined by somewhat elliptical ten-membered rings of tetrahedra, consists of intersecting straight [010] and sinusoidal [100] channels. The X-ray powder diffraction pattern of ZSM-5 ($SiO_2/Al_2O_3$ = 75) and the pattern simulated for "silicalite" from the data given in Flanigan *et al.* (*8b*) are compared in Fig. 5. The two patterns are essentially identical.

## COMPOSITION-DEPENDENT PROPERTIES OF ZSM-5

### *Ion Exchange*

It is well established that the ion-exchange capacity of the classical zeolites is equivalent to the tetrahedral aluminum content of the zeolite structure, and that non-framework or impurity aluminum results in a cation/aluminum equivalence ratio smaller than 1. Siliceous zeolites of very low aluminum content strain or may even exceed the capability of the available analytical methods, however, and require particular care both in analysis and in the conclusions derived from the results.

Cesium was ion exchanged into a series of hydrogen form ZSM-5 samples with silica/alumina ratios ranging from 89 to 8660 (349 to 4 μmol Al/g of cesium zeolite, respectively). Aluminum and cesium contents were determined by atomic absorption and neutron activation methods, respectively. The compositional data of the resulting CsZSM-5 samples are shown in Fig. 1. A very good stoichiometric correlation is observed indicating that the relation of framework aluminum to ion-exchange capacity observed for the classical zeolites holds also for the siliceous zeolites, even at very low aluminum levels, although if

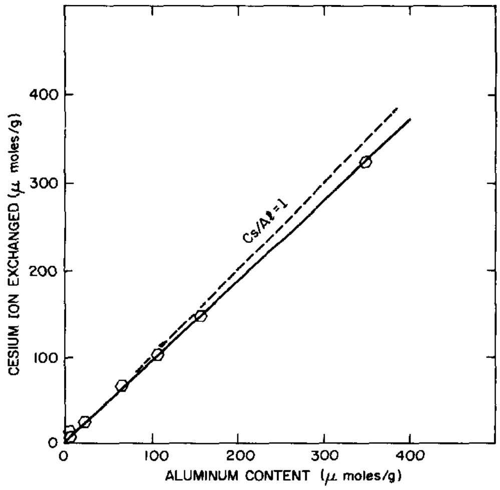

FIG. 1. Effect of aluminum content of ZSM-5 materials on ion-exchange capacity.

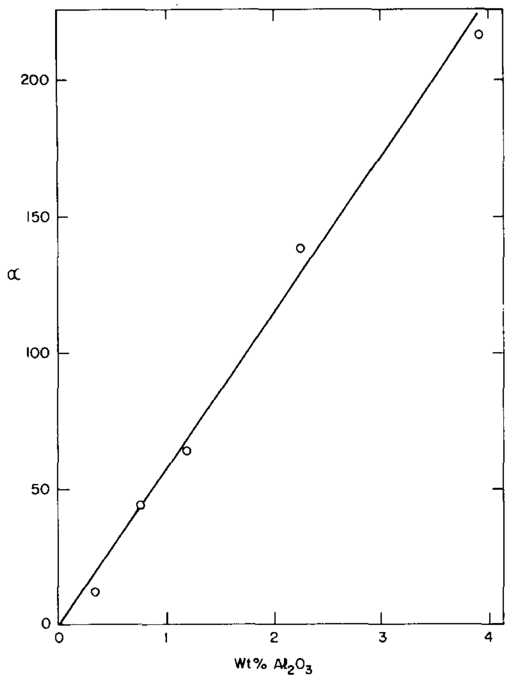

FIG. 2. Dependence of hexane cracking activity ($\alpha$) on HZSM-5 alumina content.

sufficiently small it may escape direct detection.

*Catalytic Properties*

It is well known that hydrogen zeolites promote acid-catalyzed reactions and that the acid activity generally originates with protons associated with the negatively charged aluminum (framework) tetrahedra. The acid activity of a series of HZSM-5's has been determined for the cracking of *n*-hexane at 100°F. The data are presented in Fig. 2. They show that the catalytic activity is a linear function of aluminum content, that is, the activity per aluminum is constant, even over a 400-fold change in aluminum content. This correlation holds down to alumina levels as low as 100 ppm. Separate experiments showed that nonframework aluminum is inactive for hexane cracking under the test conditions; therefore, the activity cannot be due to extracrystalline, impurity alumina. In addition, other catalytic experiments measuring the shape selective cracking of normal and branched $C_6$ paraffins confirm that the catalytic sites are indeed intracrystalline. The findings of the activity test are in excellent agreement with the ion-exchange properties. They establish that all of the samples of ZSM-5 with different $SiO_2/Al_2O_3$ ratios are members of the same substitutional series.

*Hydrophobicity*

Chen demonstrated the hydrophobicity of HZSM-5, beta, and dealuminized mordenite (*3*, *7*). For the latter, he showed further that the degree of hydrophobicity is dependent on the $SiO_2/Al_2O_3$ ratio.

For HZSM-5, Fig. 3 shows the amount of water sorbed for samples with different $SiO_2/Al_2O_3$ ratios, as measured at 100°C and $p_{H_2O} = 4.6$ Torr. While all samples are hydrophobic, as evidenced by the low sorption values, there is a linear dependence of the amount of sorbed water on alumina content. The relationship is followed for alumina contents as low as 0.02 wt%, corresponding to a framework structure in which 99.98% of the tetrahedra are based on silica. The very small amount of sorption (~0.3 mg/g) indicated in Fig. 3 for zero $Al_2O_3$ content may be due to sorption by surface hydroxyls.

Figure 4 shows the water adsorption iso-

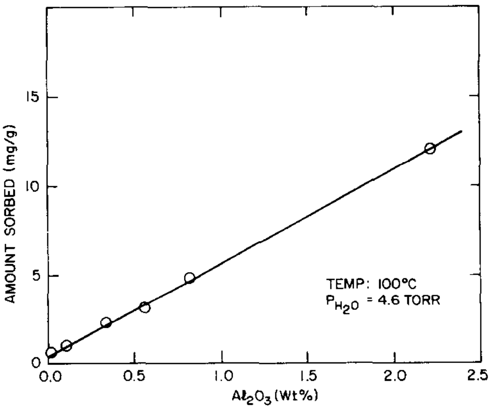

FIG. 3. Effect of alumina content on water sorption of HZSM-5 zeolites at $P/P_0 = 0.006$.

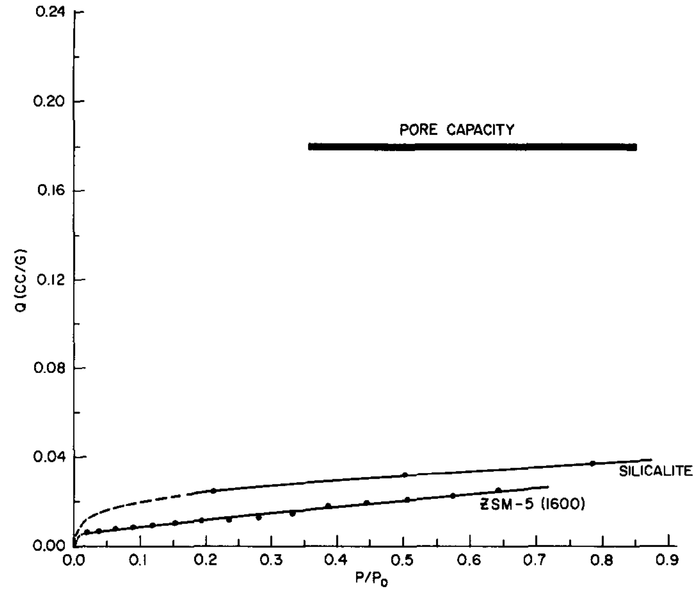

FIG. 4. Water adsorption isotherms for HZSM-5 ($SiO_2/Al_2O_3$ = 1600) and "silicalite" (data taken from Ref. *8b*). For comparison a line showing pore capacity is shown.

therm for "silicalite," as reported by Flanigen *et al.* (*8b*) and of an HZSM-5 with a $SiO_2/Al_2O_3$ ratio of 1600. In both instances the low water sorptions relative to the pore capacity indicate the marked hydrophobic nature of these high silica materials.

## SUMMARY AND CONCLUSION

We have shown that the ZSM-5 structure can exist over a very wide span of compositions, with silica contents approaching 100%. Its least siliceous form has a higher $SiO_2/Al_2O_3$ ratio than naturally occurring and earlier synthetic zeolites. ZSM-5 type materials thus are members of a new class of high silica zeolites. Many of its physical properties are dependent predominantly on the structure and are, therefore, essentially invariant over the entire compositional range, while others change with composition in a linear fashion that extrapolates smoothly to the end member of the substititional series, a pure silica ZSM-5. The ZSM-5 series exhibits classical composition-related ion-exchange behavior. However, relative to the traditional zeolites, its ion-exchange capacity is always small; with the most siliceous members it may become vanishingly small and ultimately nonexistent. In contrast to the classical zeolites, these new materials are all hydrophobic with the degree of hydrophobicity increasing as the aluminum content decreases.

In view of these facts, it is possible to regard the ZSM-5 class of high silica zeolites as synthetic porous tectosilicates that may have varying amounts of aluminum in the lattice. What has been shown for the ZSM-5 zeolite substitutional series demonstrates that this new material has properties which span the range from conventional synthetic and natural zeolites to the pure silica isotype. "Silicalite" appears to be a member of the ZSM-5 substitutional series.

## APPENDIX–EXPERIMENTAL

The hydrogen form of the ZSM-5 samples was prepared in each case from the parent as-synthesized zeolite by drying at 125°C, calcining at 538° in a nitrogen atmosphere and exchanging with $NH_4Cl$ solution; the $NH_4$ form was then converted to the H form by an air calcination in which the temperature was raised at a rate of

2°C/min from 25 to 538°C and held at 538°C for 10 hr.

In order to obtain the cesium form, the zeolite in the H form was contacted three times at 25°C, with agitation, in a polyethylene bottle, with 45 ml of 0.1 *N* CsCl solution/g of zeolite. The first exchange was for 1 hr and for this treatment the solution contained, in addition to the CsCl, 110% of the CsOH required to neutralize the zeolitic acid. The two subsequent exchanges were for 2 hr each. The silicon and aluminum contents of the zeolites were measured by atomic absorption. The cesium analysis was by neutron activation and conducted at the Institute for Environmental Studies, University of Illinois, Urbana, Illinois.

Catalytic activities were evaluated by determining the first-order rate constant of cracking *n*-hexane. This acid-catalyzed reaction has been developed into a standard test, called the $\alpha$ test (*12, 13*); the $\alpha$ activity is the value of the cracking rate constant for a given catalyst relative to that of equal volume of a standard amorphous silica–alumina catalyst. For greater accuracy, the bulk volume of the ZSM-5 catalysts being evaluated was determined from their mass and a bulk density of 0.55 g/cm$^3$. The measurements were all made at 538°C, instead of varying the temperature as previously described (*13*). Suitable conversions were obtained by varying reactant flow rate and amount of catalyst to give contact times ranging from 10 to $10^{-3}$ sec; this allows us to determine rate constants with a range of greater than four orders of magnitude. In order to avoid particle diffusion effects, particles smaller than 30 mesh were used for the most active samples ($\alpha > 100$), while 14–30 mesh particles were satisfactory for less active materials.

The sorption data were obtained on a computer-controlled Du Pont 951 TGA. Adsorption volumes were computed from these data assuming normal liquid densities for the sorbates. The isosteric heats were computed in conventional manner from sorption isotherm data and the Clausius–Clapeyron relationship.

The density was measured at 25°C by mercury displacement using an Aminco 60,000 psig motor-driven porosimeter.

The refractive indices were measured at 25°C using the Becke line method.

The X-ray pattern of ZSM-5 shown in Fig. 5 was obtained with Siemens powder

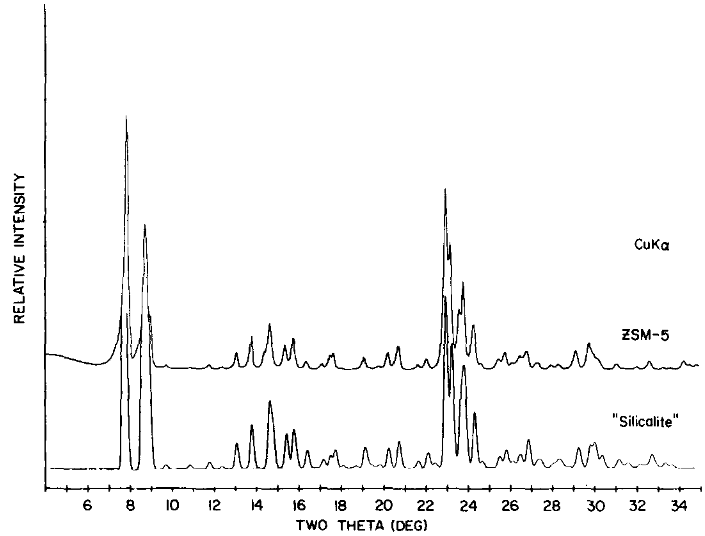

FIG. 5. X-Ray powder diffraction pattern of ZSM-5 ($SiO_2/Al_2O_3$ = 75) and of "silicalite" calculated from parameters of Ref. (*8b*).

diffraction equipment using monochromated CuK$\alpha$ radiation and step scanning with 0.05° steps.

## ACKNOWLEDGMENTS

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