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FLEXIBILITY IN ZEOLITES: ^{29}Si NMR STUDIES OF ZSM-5 FRAME TRANSITIONS

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Zeolites are most often perceived as rigid solids. Recent evidence has demonstrated that the temperature or the adsorption of molecules whose dimensions approach the pore dimensions induce changes in the solid structure, i.e., a flexing of the solid lattice. For pentacil zeolites, as ZSM-5, a transition between monoclinic and orthorhombic forms of the crystalline structure is found with a change in temperature or the adsorption of ring containing molecules. We find that the temperature at which this transition occurs depends on the Si/Al ratio within ZSM-5 and the discrete, reversible transition can be measured by ^{29}Si NMR, confirming prior X-ray studies. A similar dependence is found for ZSM-11. Phosphorous modification of the ZSM-5 does not change the transition temperature; however, steam treating of the zeolite does. The implications of these measurements to the flexibility and to the potential for transport is discussed. An analogy between transport and flexibility in one-dimensional polymers and that in the three-dimensional, open, solid network of zeolites is suggested.

1. Background

Zeolitic materials are most often crystalline alumina-silicates with microporosity (less than 15 Å) created by interconnected ring-like structures. These channels give sorbing molecules access to the intraparticle surface where chemisorption and reactions occur. Since the channels within the lattice are similar in size to sorbing molecules, the term "configurational diffusion" has been used to describe intraparticle transport [1]. The limited size of the products for the reactions of hydrocarbons, selective sorption, and selectivity in isomerization and trans-alkylation reactions have been ascribed to this "shape selectivity."

Until recently the inorganic lattice has been considered as an inflexible network structure. They are, however, effectively three dimensional, inorganic polymers. Within in the last few years, several studies of zeolites have demonstrated that the framework structure of zeolitic materials is flexible. This flexibility was seen during sorption of organic molecules.

High silica zeolites are crystalline solids primarily consisting of three dimensional linked silica tetrahedra. For inorganic solids the term crystalline connotes a rigid framework structure. One readily envisions dense solid particles or powders. For zeolites the term crystalline denotes a regular geometric arrangement of the atoms which can involve void fractions well in excess of 50%. The atomic coordination is explicitly four for the silicon and two for the oxygen within most zeolites, this contrasts with atomic coordination for closed packed crystalline solids of up to twelve. This "looser", but still regular, arrangement can have profound consequences. Fewer bonds or bond angles need to change for long range fundamental changes in the framework to occur. In 1984 Hay and Jaeger [2] used powder X-ray diffraction to demonstrate that a transformation between the orthorhombic and monoclinic symmetric arrangement of the lattice occurs with heating ZSM-5 zeolites to modest temperatures (< 350 K). The transformation was affected by the Si/Al ratio or the adsorption of hydrocarbons within the zeolite. They found that the transition occurred at 317–325 K and for the high silica ZSM-5 (as silicalite), at 295 K for an intermediate Si/Al ratio of 198/1 and at < 272 K for ratios $< 110/1$. The facile transformation between crystal symmetries due to different pretreatments of ZSM-5 has been known for the last several years [3].

Early in 1984, Fyfe et al. [4] used ^{29}Si MAS-NMR to demonstrate that the adsorption of xylene, benzene and pyridine induced a change in the Si environment in the zeolitic framework of ZSM-5. In other words, the lattice flexed on adsorption. Concurrently West used ^{29}Si MAS-NMR to document that water, which can enter the channels, and trimethylbenzene, which cannot, do not change the silicon spectra; however, other hydrocarbons, particularly benzene, induce significant shifts to higher field values for up to two-thirds of the lattice silicons [5]. Parise et al. [6] used neutron diffraction to demonstrate a change in the "degree of ellipticity" of zeolite RHO with temperature (from 11 to 573 K). These studies document both the flexibility and the sensitivity of the lattice force constants to modest temperatures. Adsorption gives rise to channel shape changes [7]. Mägi et al. [8] showed, again by ^{29}Si MAS-NMR, that the nature of the silica tetrahedra, specifically the Si-O-Si bond angles, change with the nature and concentration of both anions and cations in silicate lattices.

It is well known that the selectivity of acid catalyzed reactions in the zeolite framework is enhanced with the addition of promoters (metals, oxides or phosphates). The reasons for these selectivity increases are not fully understood, however, pore blockage [9] and pore-mouth constriction [10] have been suggested. In the case of pore blockage, it is argued that the diffusive pathway into the zeolite becomes increasingly tortuous thus the effective pore length increases. As in chromatography, the separation of molecules, based on molecular size, is enhanced with an increase in the effective length... *to a point*. In the proposed pore mouth constriction model, the openings of the pores are decreased and the selectivity for access to the internal surface based on molecular dimensions increases. Between these extremes, the internal pores are partially blocked and only the smaller molecules are permitted to pass. Others have argued that certain acidic sites are selectively poisoned [11]. As examples, the selective production of aromatics smaller than durene (1,2,4,5 tetramethylbenzene) during the condensation of methanol (or other organics), and the selective transmethylation of toluene to produce para-xylene (and benzene) over ZSM-5 zeolite have been cited.

None of these explanations are totally satisfactory. In terms of the partial pore blockage or pore mouth constriction models, all estimates of the molecular sizes compared to ring size with any additional atom(s) suggest that if each is rigid there will be no passage past the obstructing atom(s). In terms of the pore blockage and site poisoning models, there should be a concomitant dramatic decrease in overall activity. The argument is that the reaction becomes extremely diffusion controlled. The specific activity for the production of the desired product is not always decreased dramatically; furthermore, a decrease in the reaction activation energies, as would be expected for a transformation to diffusion control, is not found [12].

As mentioned above, one of the fundamental assumptions inherent in each of these explanations is that both the zeolitic framework and the sorbing, diffusing, molecules are rigid. In the recent International Zeolite conference, this was one of the "basic assumptions" made by Nowak and Cheetham in their simulation of adsorption and diffusion in zeolites [13]. As has recently been documented, zeolites are flexible and change with the inclusion of sorbing organic molecules within the framework structure. It has also been suggested that the Si-O bonds may break-and-reform during adsorption at elevated temperatures (> 300 ° C) [14].

Cyclohexane adsorption on ZSM-5 (and other ZSM-like zeolites) was recently studied by Chester et al. [15]. They concluded that, "the effective pore dimensions are larger than the crystallographically calculated pore sizes... thus siliceous zeolites appear to behave as if the pores are elliptical under hydrocarbon adsorption..." Zeolite flexibility was not envisioned. The amount and rate of cyclohexane adsorption was half that for n-hexane adsorption. Wu et al. [16] have shown that the diffusion coefficients do not change as ZSM-5 approaches saturation with cyclohexane but it increases as benzene or xylene adsorb. They also note that steaming and the addition of K or P increases the diffusion coefficient for each of the species while it decreases the pre-exponential and activation energies for diffusion. The calculated "activation energy" for diffusion of cyclohexane was 53 kJ/mole, much larger than found for fluid phase diffusion. In general the diffusion coefficient decreased an order of magnitude with phosphorus or magnesium impregnation, and they attributed the change to pore blockage. They did conclude, however, that geometric factors play "an important role in the diffusion process."

The use of MAS-NMR, and XRD on a variety of high silica zeolites was recently studied by Kokotailo et al. [17]. For ZSM-5 they found a *reversible discrete transition* from monoclinic to orthorhombic symmetry between 343 and 362 K. The change was evident in both the NMR and XRD spectra. More recently, a similar transition was found at 318–323 K for ZSM-11, a closely related pentasil zeolite [18]. Our studies, described below, confirm the differences by NMR-MAS analyses. Does the temperature of this transition also change with modifications by promoters known to increase the selectivity?

2. Experimental

A series of zeolite catalysts were studied. The approach was to employ ^{29}Si NMR spectrometry to discern differences in the flexibility of the zeolite as reflected in the transitions between monoclinic and orthorhombic space groups. As discussed above, these transitions reflect a change in the shape of the "pores" within the crystalline zeolite. The inter-crystalline Si/Al ratios for several of the samples were determined by measurements of the tetrahedral aluminum by ^{27}Al-NMR. This technique was employed as it directly measures the tetrahedral aluminum (i.e., that which is substituted within the silica framework) and is the most quantitative for high silica structures (as contrasted with Atomic Adsorption for aluminum or Si NMR). The focus of these studies was to study if the transition temperatures change with changes in the Si/Al ratio of the zeolites, by the removal of aluminum by steaming or by the addition of phosphate promoters.

The ^{29}silicon NMR signals at a signal frequency of 79.5 MHz of the ZSM-5 zeolites were studied using a Bruker Fourier Transform NMR Spectrometer, a MSL-400. The samples were spun at a rate of at least 3000 Hz. The chemical shifts are referenced to that of TMS. The number of scans was generally 400. The zeolites were used directly from the container without treatment. The temperature of the NMR experiment was varied between 253 and 390 K. Four types of H-ZSM-5 samples were used: Silicalite from Union Carbide which contains essentially no aluminum; H-ZSM-5 samples from Mobil and Peter Jacobs; H-ZSM-5 samples provided by J. Lercher treated with varying amounts of phosphorus; two ZSM-5 zeolites before and after steaming (which dealuminates the sample) provided by Haldor Topsøe Co. Two samples of ZSM-11 were provided by Mobil and by Prof. Mark Davis of Virginia Polytechnic Institute.

3. Results and discussion

At room temperature all ZSM-5 samples showed one peak at approximately 112 ppm upfield from TMS. At higher temperatures; however, the signal devel-

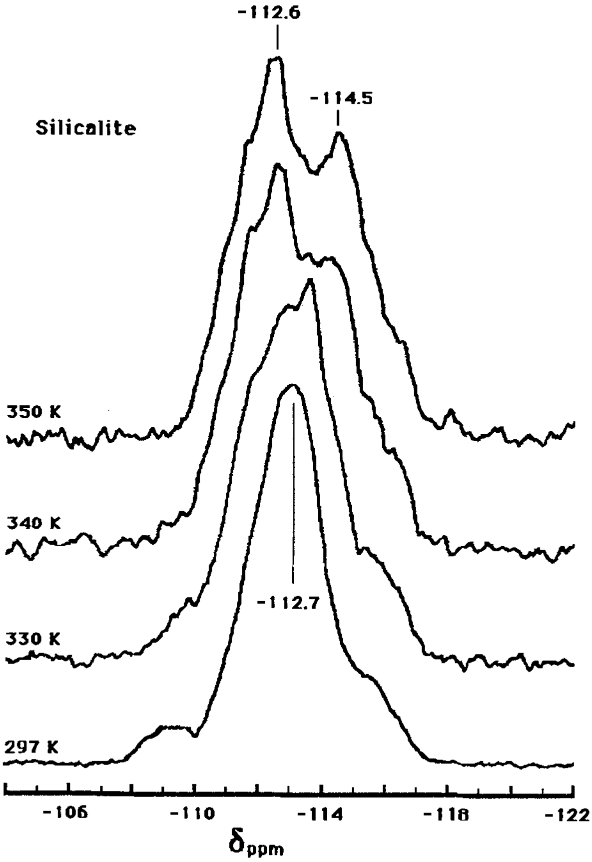

Fig. 1. ^{29}Si NMR as a function of temperature for silicalite.

oped a shoulder which became an easily recognizable peak at 114 ppm. The spectra for a sample of silicalite are shown in fig. 1, where it is apparent that a change in the nature of the spectra occurs at around 340 K. This change corresponds to the transition from the orthorhombic to monoclinic symmetries. Surprisingly the transition occurred within 5 K and was completely reversible without any noticeable hysteresis. Figure 2 shows the spectra as a function of temperature for H-ZSM-5 provided by J. Lercher with a Si/Al ratio of 86.5/1 measured by the integration of the Al NMR signal. The formation of the specific signal at ~ 114 ppm is seen to occur between 326 and 330 K. There was a substantial difference in the fairly precise transition in the NMR spectra for the different samples. These representative data are tabulated in table 1.

Several trends are evident from the data. Within each set of data represented above the transition temperature decreases as the aluminum content increases. This trend is evident for both ZSM-5 and ZSM-11 samples studied. Note that this trend confirms the prior indications from XRD studies [2]. However, several differences are apparent. Whereas we find the transitions at temperatures close to

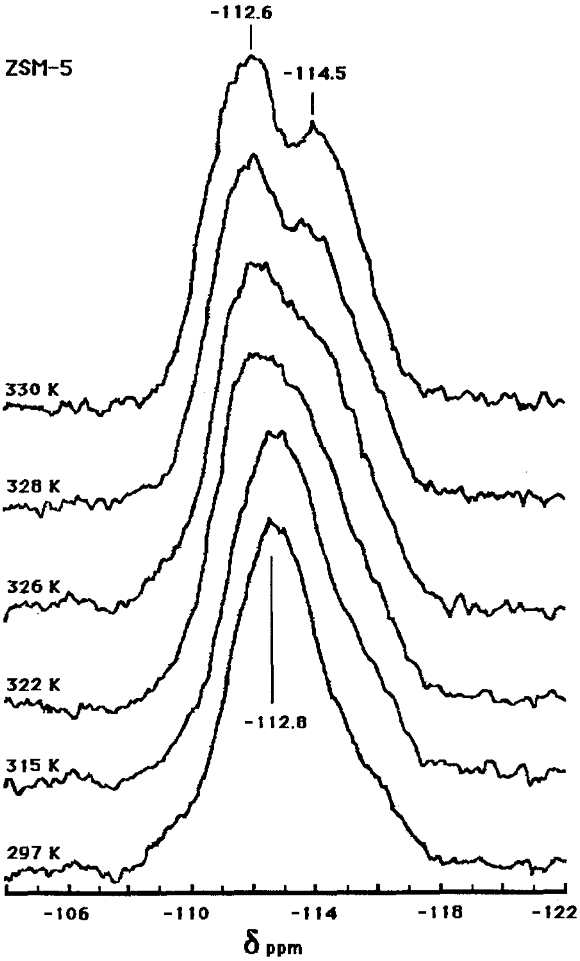

Fig. 2. ^{29}Si NMR as a function of temperature for ZSM-5 (Si/Al = 86.5).

those found in the XRD studies, we did not find a transition for the highest aluminum content samples. Further, we found that, although the groupings employed in the table showed the trend of an increasing transition temperature with a decreasing Al content, the trend did not hold up in a comparison between groupings. Neither the steamed sample from Haldor Topsøe nor the samples from Lercher's laboratories gave a monotonic change in transition temperature with Si/Al ratio, although, they confirmed the general trends found between the extremes. As we did not study other aspects of the samples such as particle size, shape or distribution of aluminum within the particles and these might have an effect of the ability of the samples to transform between the two forms, it is apparent that Si/Al ratio alone is not the only factor controlling this transition.

Steaming of the zeolites which is employed to form an "ultra-stabilized" zeolite (and also lowers the aluminum content) results in a change in the

Table 1
Transition temperature of zeolites from ^{29}silicon MAS NMR

Zeolite	Si/Al(Al-NMR*)	Additives	Transition temperature (K)
From Union Carbide, Mobil & P. Jacobs			
Silicalite	>1000 est.		340
H-ZSM-5	263 *		322
H-ZSM-5	24.6 *		313
ZSM-5	11.6 *		no transition
From Haldor Topsøe			
ZSM-5	500 est.		343
ZSM-5	43 est.	Steamed	332
From J. Lercher			
H-ZSM-5	82 *		327
H-ZSM-5	86.5 *	1% P	328
H-ZSM-5	86.5 *	5% P	326
ZSM-11 from Mobil & M. Davis			
ZSM-11 Davis	>1000 est.		320
ZSM-11 Mobil	160 est.		313

est. = estimated by those providing the samples but not independently measured.

transition temperature and thereby the flexibility. However, the addition of phosphorus which is known to increase the shape selectivity for certain catalytic hydrocarbon rearrangements does not change the temperature of the transition.

In summary, we find that the transition temperature is influenced by the Si/Al ratio in the lattice. However, this is not the only factor governing the temperature of the transition as particle (crystalline domain) dimension, the distribution of the aluminum or the presence of adsorbing molecules, as well as other factors, might influence the ability of the solid to transform.

In the vast majority of the samples (confirming the prior XRD studies) it is evident that an increase in aluminum in the zeolitic lattice decreases transition temperature from monoclinic to orthorhombic configurations, i.e., as Si/Al decreases so does the transition temperature. As the aluminum within the lattice is increased, the nature of the bonding changes. It is accepted that the substitution of aluminum within a tetrahedral silica lattice results in a local charge imbalance and the creation of Brønsted acidity. Microscopically, the result is perceived as creating a positive charge associated with each aluminum substituted within the lattice. The three-dimensional crystalline lattice is able to transfer and share any local charge throughout the lattice network. As a consequence, an increase in the aluminum content of the structure results in a gradual transformation from *more covalent* to *more ionic* bonding throughout the lattice. As covalent bonding is inherently more flexible than ionic bonding, it might be concluded that an increase in the aluminum content would result in a stabilization of the lower temperature form, i.e., the monoclinic crystalline configuration. With increasing aluminum content, the transition decreases and does not increase as would be inferred from this stability/bond-type argument.

Another explanation for the general trends found in these NMR studies and those found from XRD studies [2] is that the monoclinic form (i.e., the lower symmetry form since the monoclinic form is a disordered orthorhombic form) is more favored in an ionic as opposed to a covalent solid three-dimensional bond network.

The specific transition between orthorhombic and monoclinic symmetries has not been discussed in terms of the potential influence on the intraporous transport. However, there will certainly be an influence. In the transition between spatial forms, the primary change is a corresponding decrease and increase in two angles on one face of the unit cell forming a parallelogram. The other axes are still at right angles. The result is a change in the ellipticity of the pores as found for Rho zeolite on adsorption [7]. Molecules which could not pass through the more circular pores might now enter the pores. Alternately, the rotation of planar adsorbing molecules around their axes collinear with the pore axes could favor a more circular pore topology, i.e., the orthorhombic configuration. The initial experimental observations seem to favor this second explanation.

It should, however, be noted that the change in the unit cell for the transition between orthorhombic and monoclinic symmetries for the pentacil zeolites is not large, i.e., representing a change of less than one degree in the solid angles. This would seem to suggest that the change is inconsequential. However, it is a significant enough of a change to be induced by the adsorption of large ring containing molecules into the zeolites. Changes in the transition temperature would reflect differences in the ability of the solid lattice to rearrange, as does the glass transition for polymeric solids where changes in the glass transition temperature are found to correlate with the rate of diffusion of large solute molecules within the polymer [19]. The specific transition temperature would be an indication of lattice flexibility rather than representing the complex dynamic transitions that may directly control the transport through the porous network.

The fundamental question posed by these explanations is how the flexibility of the lattice and the vibrational/rotational modes of the adsorbing molecules interact. Gorring suggested a "window effect" relating the rates of diffusion for n-paraffins of different length to the spatial periodicity of the zeolite lattice [20]. Are there longer range breathing modes of the lattice that are induced by the inclusion of sorbed molecules?

This research has not provided definitive answers to these fundamental questions as to the influence of the lattice flexibility on adsorption. However, it underscores the necessity of understanding the dynamic nature of adsorption within zeolites as controlled by the nature of the lattice, pretreatment, promoters and adsorbing species.

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