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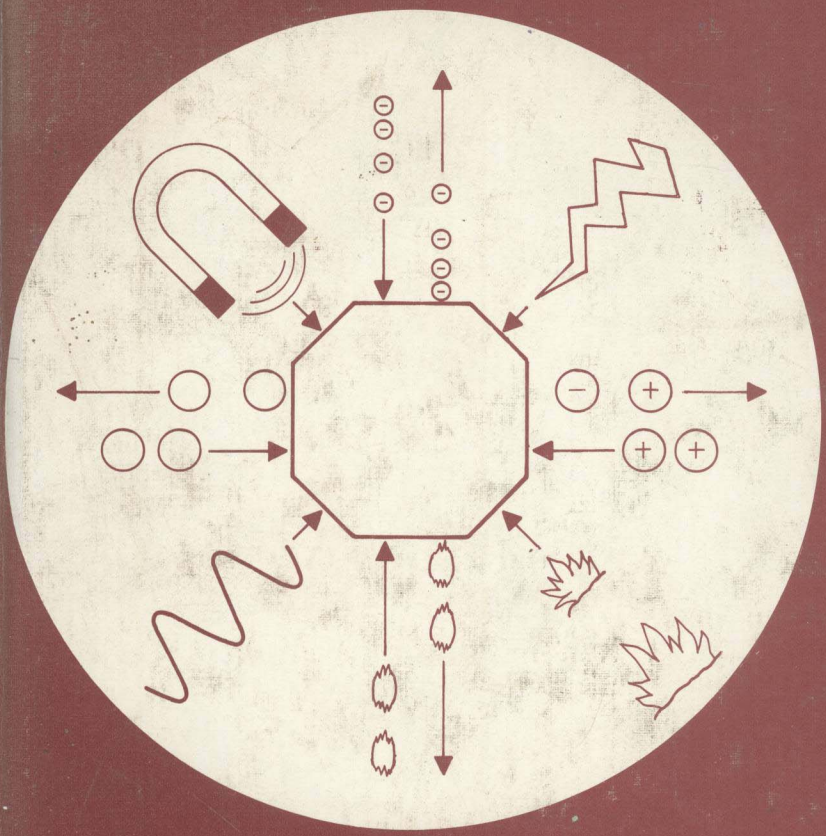

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STRUCTURE AND REACTIVITY OF MODIFIED ZEOLITES

P.A. Jacobs, N.I. Jaeger, P. Jírů, V.B. Kazansky
and
G. Schulz-Ekloff
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STRUCTURE AND REACTIVITY OF MODIFIED ZEOLITES

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PREFACE

Progress in the practical application of zeolites in catalysis will largely depend on a better understanding of their structural stability, the nature and strength of acid sites, and their bifunctional action. The papers contributed to the Conference on Structure and Reactivity of Modified Zeolites in Prague, which are collected in this volume, reflect the current ideas on these problems and present many new results.

The descriptions of the methodology, used in the investigation of structures, interactions and intermediates, include frequency response diffusion, Mössbauer spectroscopy, Szilard-Chalmers type recoils, ^{129}Xe NMR, ^{29}Si NMR, ^{27}Al NMR, XPS ESR, UV-VIS, IR and quantum chemical calculations. The reports on synthesis and modification procedures focus on Y, mordenite, offretite, ZSM-5, (Be, B, Al, Ga)-ZSM type and on GaSi and AlGe analogues of X. Metal complexes, cations and particles of Pt, Pd, Rh, Ru, Cu, Ni, Co, Fe and Cr are studied with respect to their structure and function, e.g. in hydrogenation reactions. The aromatization of ethane on metal loaded high-silica zeolites that is described is an important example of bifunctional action. The shape selectivity in acid catalyzed reactions is mainly investigated for the conversions of methanol, olefins and methylbenzenes.

The Organizing Committee felt obliged to carry out editorial changes in the papers where obvious typing errors or vagueness affected the clarity and understanding, and we apologize for not being able in each case to obtain an authorization in time. Our alternative was not to publish these papers, which would not have been justified in view of the quality of the published data.

The Organizing Committee are very grateful to all authors and hope that lively discussions will ensue from the publication of these papers.

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MODERN METHODS OF ZEOLITE RESEARCH

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ABSTRACT

In this paper two frequency response methods will be described for determining the diffusion coefficients of sorbates which are in sorption equilibrium with the zeolite phase. Mossbauer spectroscopy, which involves the emission of recoilless, soft gamma photons, will be shown to provide useful information on cation/framework oxygen coordinations and interactions. The interaction of sorbate molecules with these Mossbauer active cations can also be determined. Finally the Szilard-Chalmers type recoils which cations are subjected to on emission of hard gamma photons following capture of a neutron by the cation nucleus is used to assess the site preferences of cations in zeolite framework as a function of calcination temperature.

FREQUENCY RESPONSE DIFFUSION COEFFICIENTS.

A new method of determining the diffusion coefficients of sorbates in the micropores of zeolites has recently been developed [1]. In this method the volume of a chamber, containing the permeating gas in equilibrium with the sorbent, is varied sinusoidally with an amplitude of only a few percent. The phase angle and amplitude of the pressure change of the gas phase induced by the volume variation are measured as a function of the frequency of the driving oscillations. Characteristic functions, representing in-phase and out-of-phase components of the pressure variations, can be calculated on the basis of Fick's law of diffusion in (i) a plane sheet and (ii) an isotropic sphere as models for one- and three- dimensional channels in zeolites respectively.

The sinusoidal volume change may be described by

$$V = V_e\ (1-ve^{i\omega t}) \qquad (1)$$

where V_e denotes the volume at equilibrium, v is the relative amplitude of the volume variation and ω is the angular velocity of the sinusoidal generator. The perturbed gas pressure, P, and the concentration, C, of the diffusing sorbate in the zeolite are expressed in general, in a periodic steady state, by

$$P = P_e\left\{1 + pe^{i(\omega t + \phi)}\right\} \qquad (2)$$

and

$$C = C_e\left\{1 + \gamma e^{i(\omega t + \phi - \chi)}\right\} \qquad (3)$$

Both the relative amplitudes p and γ and the phase lags ϕ and χ depend on ω.

Assuming that the diffusion coefficient, D, is constant, since the perturbation to the system is small, Fick's second law can be solved for the above boundary conditions. For diffusion down channels of length L the solution for the one-dimensional case leads to the following two equations

$$(v/p)\cos\ \phi - 1 = K\delta_c \qquad (4)$$

$$(v/p)\sin\ \phi = K\delta_s \qquad (5)$$

where δ_c and δ_s are defined by

$$\delta_c = \frac{1}{\eta}\left\{\frac{\sinh\eta + \sin\eta}{\cosh\eta + \cos\eta}\right\} \qquad (6)$$

and

$$\delta_s = \frac{1}{\eta}\left\{\frac{\sinh\eta - \sin\eta}{\cosh\eta + \cos\eta}\right\} \qquad (7)$$

and $\eta = (\omega L^2/2D)^{\frac{1}{2}}$. The coefficient K is related to the gradient of the sorption isotherm at $P = P_e$.

For diffusion in isotropic spheres of radius, a, we once again obtain Eqn. 4 and 5 but δ_c and δ_s are now defined by

$$\delta_c = \frac{3}{\eta}\left\{\frac{\sinh\eta - \sin\eta}{\cosh\eta\quad\cos\eta}\right\} \qquad (8)$$

and

$$\delta_s = \frac{6}{\eta}\left[\frac{1}{2}\left\{\frac{\sinh\eta + \sin\eta}{\cosh\eta - \cos\eta}\right\} - \frac{1}{\eta}\right] \qquad (9)$$

and $\eta = (2\omega a^2/D)^{\frac{1}{2}}$

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By determining the phase lag, ϕ as a function of ω the in-phase and out-of-phase components $(v/p) \cos \phi - 1$ and $(v/p) \sin \phi$ can be plotted against ω. From Eqn. 4 and 5 the best fit to the experimental data is obtained. From Eqn. 6 and 7 or 8 and 9 η is derived and hence D . By carrying out similar measurements at different equilibrium pressures, P_e, the sorption isotherm may also be obtained.

Yasuda [1] used the frequency response technique to measure the sorption and diffusion of krypton in sodium mordenite at $-20^{o}C$ over angular velocities ranging from 1 to 100 rad/min. Using Eqn. 6 and 7 for one-dimensional diffusion Yasuda found that $(D/L^2) = 5.3 \times 10^{-3} s^{-1}$ at equilibrium pressures around 300 Pa. but he did not attempt to estimate the length of the diffusion channels, L , and so did not obtain D. However, the order of magnitude of D/L^2 was comparable to that determined by more standard methods [2].

Yasuda [1] found that the in-phase and out-of-phase components were not asymptotic at high frequencies as predicted by theory. He interpreted this difference as resulting from a very fast intercrystalline, three-dimensional diffusion. However, the apparatus he used could not operate at high enough angular velocities to determine the magnitude of this fast, intercrystalline diffusion coefficient.

Betemps [3] has also recently determined diffusion coefficients of sorbates in zeolites using a method similar in nature to the frequency response technique described above. Betemps obtained an impulse response function of the equilibrium gas/sieve pair through the cross-correlation between a pseudo random binary variation of the gas phase volume and the resulting pressure variations. Using this technique the diffusion coefficient of argon in zeolite 5A at 298 K was found to be $1.66 \times 10^{-14} m^2 s^{-1}$ which agrees reasonably well with the corresponding coefficient obtained by Ruthven and Derrah [4] from sorption uptake rates.

MOSSBAUER SPECTROSCOPY

Mossbauer spectroscopy is concerned with the recoil-free emission and re-absorption of soft gamma photons by nuclei which belong to atoms or ions which are firmly bound in crystalline lattices [5]. In solids the lattice binding energies ($\sim$10eV) are much higher than the recoil energies of $\sim 10^{-2}$eV associated with the emission or absorption of soft gamma photons. Momentum is conserved during a Mossbauer gamma transition. However, in a fraction of these events, (f), the whole crystal recoils and in a fraction of events,

(1-f), the energy is taken up by the phonon vibrational levels of the lattice. When the whole crystal recoils the recoil energy is small compared with the natural line width and hence transitions will be at the full gamma energy with a line width given by the Heisenberg principle.

Many elements have Mossbauer active isotopes e.g. ^{57}Fe, ^{119}Sn, ^{40}K, ^{73}Ge, ^{83}Kr, ^{121}Sb, ^{125}Te, ^{127}I, ^{129}Xe, ^{133}Cs, ^{133}Ba, several transition-metal, rare-earth and actinide elements. Apart from ^{57}Fe and ^{119}Sn it is usually necessary to cool both the source of the recoilless gamma photons and the absorber to liquid N_2 temperatures and, in many cases, to liquid He temperature before f becomes large enough to give useful spectra. Of all the Mossbauer spectra published in the literature the great majority are concerned with ^{57}Fe. The 14.414 keV gamma photon emitted by ^{57}Fe is ideal for Mossbauer spectroscopy. It has low energy and hence significant recoil free fractions, f, even above room temperature. The decay time of the first excited level of the ^{57}Fe nucleus of $t_{\frac{1}{2}} = 99.3$ ns leads to line widths of 4.594×10^{-9} eV. The 14.414 keV level is efficiently populated via the electron capture decay of ^{57}Co. The source of the recoilless gamma radiation is usually ^{57}Co diffused into a cubic lattice e.g. metallic Pt. Since the half-life of ^{57}Co is 270 days sources have useful lives of at least three years.

The great energy resolving power available using the Mossbauer effect (eg. ^{57}Fe it is 1 part in 3×10^{12}) allows an investigation of the interaction of the surrounding electrons with the nucleus and hence of the chemical environment to be made. The parameters obtained are the chemical isomer shift (IS), the quadrupole splitting (QS) and the magnetic hyperfine interaction. The isomer shift is given by

$$IS = \text{constant} \left\{ |\psi_s(0)_A|^2 - |\psi_s(0)_s|^2 \right\} \qquad (10)$$

where $|\psi_s(0)|^2$ is the s-electron density at the centre of the nucleus of the absorber, A , and source, S , respectively. The constant is negative in the case of ^{57}Fe and, hence, the isomer shift decreases in an absorber as the s-electron density at the absorber nucleus increases. The isomer shift is useful in the case of iron in assessing the valence and spin state of the absorber atom, as shown in Table 1.

TABLE 1

Typical isomer shift values for ^{57}Fe. (IS quoted in mm s^{-1} w.r.t. natural iron foil)

Valence State	Electronic Configuration	High Spin	Low spin
Fe(I)	[Ar] $3s^2 3d^7$	1.9 - 2.1	0.2 - 0.4
Fe(II)	[Ar] $3s^2 3d^6$	0.8 - 1.5	-0.2 - 0.4
Fe(III)	[Ar] $3s^2 3d^5$	0.2 - 0.6	-0.2 - 0.3
Fe(IV)	[Ar] $3s^2 3d^4$	-0.1 - 0.1	0.1 - 0.2
Fe(O)	[Ar] $3s^2 3d^6 4s^2$	0	

Generally iron in tetrahedral sites have lower isomer shifts than in octahedral sites due to increased covalency effects.

Nuclei with spin states greater than I = 1/2 are non-spherical and interact with non-cubic electric fields to remove some of the degeneracy of the nuclear spin states. This gives rise to multiple peak spectra and results in experimentally accessible quadrupole splittings. For ^{57}Fe the ground state has spin I = 1/2 and is unsplit in an electric field gradient (efg) but the excited state has spin I = 3/2 and is split in non-cubic electric fields into two energy levels. These energy levels are given by

$$E_{\pm} = \pm \frac{e^2qQ}{4} [1 + \eta^2/3]^{\frac{1}{2}} \qquad (11)$$

where the efg is expressed in terms of two parameters $V_{zz} = eq$ and $\eta = [V_{xx} - V_{yy}]/V_{zz}$ is an asymmetry parameter. Q is the quadrupole moment of the nucleus in the excited state. If the Mossbauer atom is in a site of axial symmetry (ie $V_{xx} = V_{yy}$) then $QS = e^2q\,Q/2$. For ^{57}Fe, the interaction of the quadrupole moment with the efg leads in most cases to symmetric doublets. Only the magnitude of the QS can normally be measured but it is possible by applying external magnetic fields to measure the sign of V_{zz}.

If there is a net magnetic field at the nucleus during the Mossbauer event then the nuclear spin degeneracy of both the ground and excited states are completely removed and multi-peak spectra result. The eigenvalues are given by

$$Em = -g_N \beta_N Hm_I \qquad (12)$$

where m_I is the z-component of the nuclear spin, g_N is the nuclear g-factor, β_N is the nuclear magneton and H is the effective magnetic field at the nucleus. In the case of ^{57}Fe the resulting spectra contain 6 equally spaced lines (selection rate only allows $\Delta m_I = 0, 1$) with relative intensities for powdered samples of 3:2:1:1:2:3. The magnetic field at the nucleus may arise from a) an externally applied magnetic field, b) within the atom itself or c) from exchange interactions within the crystal. The internal magnetic field results from (i) the Fermi contact term and (ii) terms due to the interaction of the nucleus with the spin moment and orbital magnetic moment of the atom.

We have studied the Mossbauer spectroscopy of ^{57}Fe zeolites in depth and obtained much information on the location, chemical state and effect of sorbate molecule interaction on the iron cations present in the zeolites. When ferrous cations are ion exchanged into zeolite Y at room temperature Mossbauer spectroscopy at room temperature shows that the cations are very loosly associated with the framework oxygens when the zeolite is fully hydrated [6]. The very low f factor obtained indicated a strong preference of the ferrous ions for the zeolitic water molecules and a rapid diffusion of these hydrated ions in the channels of the zeolite. On dehydration at 360°C for 24 h under vacuum a strong Mossbauer signal was obtained at room temperature which comprised of two quadrupole split doublets. One doublet was ascribed to Fe^{2+} ions sited in the hexagonal prism sites (site A, [7]) of zeolite Y. The other doublet had parameters which are very unusual for Fe^{2+} species. We proposed that these ferrous ions were sited in the puckered six-ring separating the sodalite cage from the supercage i.e. site G, [7]. We tested this hypothesis by next studying the Mossbauer spectra of ferrous ions exchanged into zeolite A where the puckered six-ring was expected to be the only site occupied by the ferrous ions. The first interesting feature of these spectra [8] was the very large f factor obtained at room temperature from the fully hydrated zeolite indicating that ferrous ions were coordinated to framework oxygens rather than zeolitic water molecules. The much higher negative charge density on the framework oxygens of zeolite A compared with zeolite Y must be the explanation of these findings. On dehydration of zeolite A the Mossbauer signal actually was degraded by 20% indicating the presence of a new loose mode of vibration for the ferrous ions perpendicular to the plane of the six-ring and the parameters obtained (IS = 0.835 mms^{-1}, QS = 0.469 mms^{-1}) were very similar to those found for ferrous ions in site G of dehydrated zeolite Y. The very small QS observed results from a near cancellation of the large,

positive efg from the valence component (i.e. the 6th 3d electron) with the large, negative efg from the negatively charged oxygen framework ligands. Because of the puckered nature of the six-ring only the three nearest-neighbour, oxygens in a planar, trigonal configuration dominate the lattice component. Normally ferrous ions are in tetrahedral or octahedral coordination with ligands and the lattice term is then much smaller than the valence term.

When adsorbate molecules are now sorbed onto these ferrous ions located in site A [7] of dehydrated zeolite A the coordination becomes more symmetrical, i.e. tetrahedral-like at low loadings or octahedral-like at high sorbate loadings, and the QS increases to the more normal values for these coordinations. Mossbauer spectroscopy of ferrous zeolite A loaded with various sorbates is a very sensitive method of studying sorbate-cation interactions. We have shown, for example, that in partially hydrated (Na^+, Fe^{2+})-A zeolite the following equilibrium exists

$$(Z - O)_3Fe^{2+} - H_2O \rightleftharpoons (Z - O)_3Fe^{2+} - OH^- + H^+$$

with proton hopping between framework oxygens and the hydroxyl group on the ferrous cation occuring with a half-life greater than 10^{-7}s (the Mossbauer event time) at room temperature. On cooling to liquid N_2 temperatures the equilibrium is shifted strongly to the left. In the fully hydrated zeolite the proton hopping is too fast to observe in the 10^{-7}s time scale but on cooling, the spectra indicate the two different ferrous environments represented in the above equilibrium. Exchange of the Na^+ ions by Ca^{2+} and NH^{4+} to produce (Ca^{2+}, Fe^{2+})-A and (NH_4^+, Fe^{2+})-A was found to slow down the proton hopping and the above two different Fe^{2+} species were observed in the spectra of even the fully hydrated materials at room temperature [9, 10].

Adsorption of ethylene in (Na^+, Fe^{2+})-A at ethylene: Fe^{2+} loadings well below one gave spectra which showed only one doublet at room temperature but on cooling below 200 K two doublets began to be resolved, one doublet with the parameters of the bare ferrous in site A and the other with parameters consistent with the distorted tetrahedron resulting from sorption of an ethylene molecule on the ferrous cation [11]. Once again these results demonstated that at room temperature the ethylene molecules were hopping from one ferrous ion to the next with residence times much shorter than 10^{-7} s. On cooling to ~200K the residence time was 10^{-7}s. Analysis of the spectra as a function of temperature gave approximate energies of activation for the

ethylene jump of 23 k J mol^{-1}.

The Mossbauer spectra of ferrous exchanged Na- and Ca-A zeolites showed that the ferrous ions could be oxidised to ferric by dry oxygen at 360°C or wet air at ambient temperatures [12]. On dehydration under vacuum of the fully hydrated ferric forms some 20% of the ferric ions were reduced to ferrous. The ferric ions could also be reduced to ferrous by treatment with hydrogen at 360°C for 4 h. No metallic iron was observed after these treatments with hydrogen. The co-cation present in the zeolite was found to have a profound influence on these reactions.

The Mossbauer spectrscopy of ferrous exchanged zeolite L has also been studied [13]. The ferrous ions were found to be coordinated only to the zeolitic water molecules after exchange of the ferrous ions into the zeolite at room temperature. On dehydration at temperatures of 360°C and above the ferrous ions were found to be located in both the hexagonal prism sites (site A) and in site E. In this latter site the ferrous ions are coordinated to four framework oxygens in a square-planar complex. As found in dehydrated zeolite A the lattice contribution to the efg is large and a partial cancellation of the efg produced by the valence electron results in low IS and QS values (IS = 0.95 mms^{-1}, QS = 0.66 mms^{-1}).

The spectra of dehydrated, ferrous zeolite L were taken after additions of various sorbates (e.g. water, ethanol, propan-2-ol, 2-methyl propan-2-ol, methyl cyanide and triethylamine) had been made [14]. The low QS doublet due to ferrous ions in site E was found to be progressively reduced in intensity when most of the above sorbates were titrated into the zeolite with the formation of a wide QS doublet due to ferrous ions now sited in site D coordinated to framework oxygens and one sorbate molecule. The loading of sorbate corresponding to complete removal of ferrous ions from site E could, therefore, be determined.

The Mossbauer spectra of zeolites containing $Fe(CO)_5$, $(C_5H_5)_2$ Fe, ferrocene, ferrocyanides and nitroprussides sorbed in or on the zeolites have been recorded [15]. The effect of photochemical and thermal activation of these sorbed species was also followed. The sorbates were, also, reduced in hydrogen between 300 and 500° C. Ferrocene, on reduction, gave a weak six-line spectrum due to α-iron metal along with a strong central doublet. Reduction of the iron carbonyl systems led to complete reduction to α-iron with quite large particles of 7.5 - 12.5 nm diameter. Reduction of the ferrocyanides and nitroprussides also produced large particles of metallic iron.

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