Similarly, $[W_2(OCMe_3)_6]$ reacts with $EtC\equiv C-C\equiv CEt$ to give $[(Me_3CO)_3W\equiv C-C\equiv W(OCMe_3)_3]$ which resembles a μ_2-bicarbide complex.[9]

In summary, we have prepared the first fully characterized heterodinuclear μ_2-carbide complex. We are investigating the reaction chemistry of this complex, which we hope will provide insights into the reactivity of carbides on catalyst surfaces.

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Supplementary Material Available: Tables of positional and thermal parameters, bond distances, bond angles, and least-squares planes for the structure of **1** (5 pages); tables of observed and calculated structure factors for the structure of **1** (18 pages). Ordering information is given on any current masthead page.

High-Symmetry, High-Temperature Zeolite Lattice Structures

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Considerable progress has been made in recent years in the investigation of the structures of zeolite catalysts by solid-state high-resolution ^{29}Si MAS NMR techniques.[1] For low Si/Al ratio materials, the spectra give a description of the distribution of Si and Al throughout the lattice, while for completely siliceous analogues the spectra may be related directly to the lattice structures.[2] The effect of removing all of the aluminum from the lattice is to give very narrow resonances in the ^{29}Si MAS NMR spectrum which are all due to Si[4Si] environments and which reflect the number and populations of the crystallographically inequivalent lattice sites in the unit cell. These latter spectra have been used to probe various subtle effects on the lattice structures via the short-range ordering[2] and are a very useful complement in structural investigations to the more conventional powder XRD technique. In the present communication, we describe how these spectra combined with variable-temperature operation can be used to detect the existence of high-symmetry phases for various zeolites at elevated temperatures. It is only with materials of sufficiently high quality such as those investigated that the spectral resolution is good enough to detect and characterize these phases.

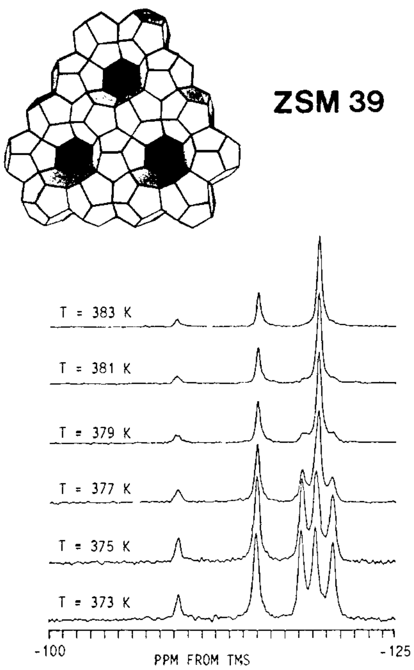

Figure 1. ^{29}Si MAS NMR spectra of zeolite ZSM-39 (79.5 MHz, 500 scans, 7-s delay, and 0-Hz line broadening) at the temperatures indicated. The cubic structure for ZSM-39 is shown also.[3]

ZSM-39 is a highly siliceous zeolite previously shown to be cubic by powder XRD measurements (Figure 1, inset).[3] However, the authors of the diffraction study pointed out that the existence of a number of very low intensity reflections indicated a deviation from cubic symmetry and termed it "pseudocubic". This was confirmed by ^{29}Si MAS NMR measurements[4] which showed five resonances of relative intensities 1:4:4:4:4 rather than three of 1:4:12 expected for a perfect cubic lattice and indicated that the deviation involved the loss of the 3-fold [1,1,1] axis of symmetry.[4]

Figure 1 shows variable-temperature ^{29}Si MAS NMR spectra for a perfectly crystalline, completely siliceous sample of this material over the temperature range of the phase transition. As the temperature is raised, the resonances all remain narrow but there is a clear change over a very small temperature range to a new spectrum of three peaks whose relative intensities of 1:4:12 clearly indicate cubic symmetry at least on a local basis and on the NMR time scale. The changes are completely reversible and are also shown by less crystalline materials with correspondingly reduced resolution.

Similar increases in lattice symmetry are also shown by ZSM-5[5] and ZSM-11. In the case of ZSM-5, the spectrum changes from a 24-line pattern at room temperature to a pattern of 12 lines (Figure 2A) consistent with a change in symmetry from monoclinic to orthorhombic. In the material studied, all 12 resonances can be detected at different temperatures. Figure 2B shows the limiting high-temperature spectrum (373 K) for a very highly siliceous sample of zeolite ZSM-11 and its resolution into seven Lorentzian peaks of relative intensities, 1:(2 + 2):2:1:2:2, exactly consistent with the postulated lattice structure.[6] The room-temperature spectrum shows more than seven resonances, again consistent with a lower symmetry,[7] and line broadening indicating a distorted lattice.

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(1) (a) Lippmaa, E.; Magi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 4889. (b) Fyfe, C. A.; Thomas, J. M.; Klinowski, J.; Gobbi, G. C. *Angew. Chem.* **1983**, *95*, 257; *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 259.

(2) (a) Fyfe, C. A.; Kokotailo, G. T.; Kennedy, G. J.; Gobbi, G. C.; DeSchutter, C. T.; Ozubko, R. S.; Murphy, W. J. In *New Directions in Chemical Analysis*, Shapiro, B. L., Ed.; Texas A & M University: College Station, 1986. (b) Kokotailo, G. T.; Fyfe, C. A.; Kennedy, G. J.; Gobi, G. C.; Strobl, H.; Pasztor, C. T.; Barlow, G. E.; Bradley, S.; Murphy, W. J.; Ozubko, R. S. *Pure Appl. Chem.* **1986**, *58*, 1367.

(3) Schlenker, J. L.; Dwyer, F. G.; Jenkins, E. E.; Rohrbaugh, W. J.; Kokotailo, G. T.; Meier, W. M. *Nature (London)* **1981**, *294*, 340.

(4) Kokotailo, G. T.; Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J.; DeSchutter, C. T. *J. Chem. Soc., Chem. Commun.* **1984**, 1208.

(5) (a) Fyfe, C. A.; Kennedy, G. J.; Kokotailo, G. T.; Lyerla, J. R.; Fleming, W. W. *J. Chem. Soc., Chem. Commun.* **1985**, 740. (b) Hay, D. G.; Jaeger, H.; West, G. W. *J. Phys. Chem.* **1985**, *89*, 1070.

(6) Kokotailo, G. T.; Chu, P.; Lawton, L.; Meier, W. M. *Nature (London)* **1978**, *275*, 119.

(7) Fyfe, C. A.; Kokotailo, G. T.; Kennedy, G. J.; DeSchutter, C. T. *J. Chem. Soc., Chem. Commun.* **1985**, 306.

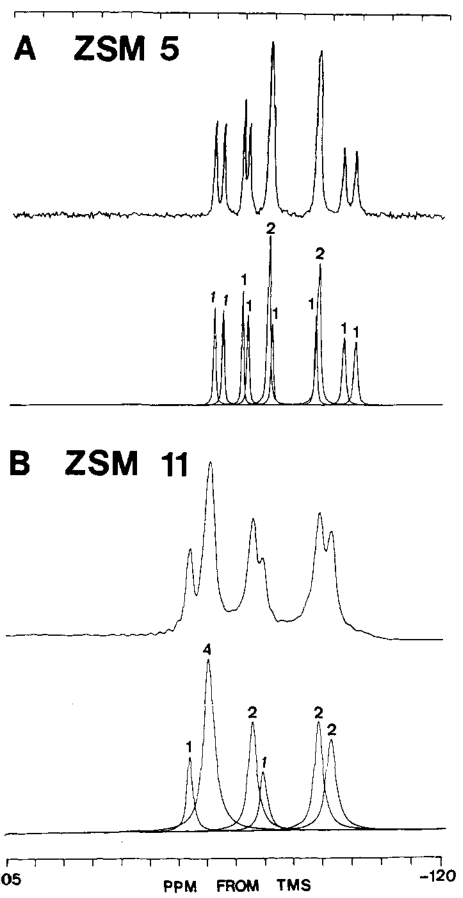

Figure 2. (A) Observed (79.5 MHz, 3914 scans, 7-s delay, and 0-Hz line broadening) and calculated ^{29}Si MAS NMR spectra of zeolite ZSM-5 at 393 K; (B) Observed (79.5 MHz, 3500 scans, 7-s delay and 0-Hz line broadening) and calculated ^{29}Si MAS NMR spectra of zeolite ZSM-11 at 373 K. The numbers in the theoretical spectra reflect the relative peak intensities.

The nature of these high-temperature phases is somewhat ambiguous at the present time. The NMR spectra may reflect a change to genuine (static) structures of different and higher symmetries. This could occur if the Si–O bond lengths were too short to exactly accommodate the lattice structure, resulting in strain and subsequent distortion from the ideal symmetry which is removed at elevated temperatures by lattice expansion. However, the spectra are also compatible with dynamic structures whose (average) structures are of higher symmetry. Thus, by their sensitivity to those cases where mobility induces apparent phase changes with the *number* of lines reflecting an associated change in the symmetry, the spectra may be reflecting more mobile lattices for zeolites in general than hitherto anticipated. The case of ZSM-39 is important in this regard as it is very dense (and hence relatively rigid) structure.

We are further investigating these systems to resolve this point, complementing the NMR data with synchrotron-based X-ray investigations at both ambient and elevated temperatures[8] which will provide greatly improved diffraction structures although it is recognized that the lattice changes detected by the NMR data may be too small to be resolved, even using synchrotron radiation. The NMR data can also be augmented by measurement of the spectra and also relaxation times of the ^{27}Al and most importantly the ^{17}O nuclei in the lattice, as their relaxation mechanisms will be via quadrupolar interactions and should directly reflect any lattice motions.

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(8) Cox, D.; Kokotailo, G. T.; Fyfe, C. A., et al., unpublished results.

Flavocyclodextrin as a Promising Flavoprotein Model. Efficient Electron Transfer Catalysis by Flavocyclodextrin

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Flavoproteins play key roles in electron transport,[1] respiration, photosynthesis, bioluminescence, and other oxidation–reduction systems,[2] catalyzing the electron transfer[3] from NADH (or NADPH) to the flavin and further to the electron acceptor.

The function of flavoproteins may be "reconstructed" artificially by providing an appropriate self-organizing system for flavin and dihydronicotinamide to associate reversibly.

There are only two unnatural "artificial flavoprotein families" known, flavopapains[4] and flavoporphyrins,[5,6] but the latter has small association constants with the nicotinamideimidazole. Cyclodextrins (CD) are well known to associate with guests strongly and rapidly.[7] These characteristics should make it possible to prepare an artificial flavoenzyme if flavin is implanted in CD.

We wish to report the synthesis of flavo-α-cyclodextrin, **1**,[8] and its very efficient electron transport.

Compound **1** was prepared from 6-tosyl-α-cyclodextrin and 8α-bromoriboflavin according to Scheme I. Separation and purification of **1** was performed by silica gel thick-layer chromatography and Sephadex G-10 column chromatography. The structure determination was based on the following spectra and analysis [UV–vis 270 (2.5×10^4), 350 (7.3×10^3), 450 nm (1.0×10^4), IR 3380, 2940, 1708, 1585, 1548, 1155, 1080 cm^{-1}; FAB-MS 1363 $(M + H)^+$; ^{1}H NMR δ from Me$_4$Si 2.58, 2.85, 3.21, 3.5–4.0, 4.07–4.10, 4.48, 5.06, 8.01, 8.07 ppm; ^{13}C NMR δ from Me$_4$Si 18.16, 33.79, 35.57, 47.40, 60.01, 63.29, 68.74, 71.57–73.68, 82.12, 85.13, 101.98, 117.88, 131.78, 132.12, 134.50, 135.41, 137.41, 145.20, 150.96, 155.42, 159.80 ppm. Elemental anal. Calcd for $C_{53}H_{78}N_4O_{35}S\cdot H_2O$: C, 46.09; H, 5.84; N, 4.06. Found: C, 45.81; H, 5.67; N, 4.57.] The ^{13}C and ^{1}H NMR spectra showed the ordinary absorptions ascribed to 8α-S-Me riboflavin and C$_6$SH-α-cyclodextrin (shifted less than 1.0 ppm for ^{13}C and 0.2 ppm for ^{1}H) except for the following shifted absorptions: ^{13}C; Fl 8α, at 33.79; C$_6$ A-ring at 35.57; C$_4$ A-ring at 85.13. All of the observed ^{1}H absorption intensity ratios indicate an exactly 1:1 combination of both moieties.

The electron-transfer activities of **1** for *N*-alkyldihydronicotinamides (RNAH, **2a–c**) were studied in water, pH 7.4 at

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(1) Walsh, C. *Enzymatic Reaction Mechanisms*; W. H. Freeman and Co.: San Francisco, 1979. Walsh, C. *Acc. Chem. Res.* **1980**, *13*, 148.

(2) Bruice, T. C. *Acc. Chem. Res.* **1980**, *13*, 256. Iyanagi, T.; Mason, H. S. *Biochemistry* **1973**, *12*, 2297.

(3) Simondsen, R. P.; Weber, P. C.; Salemme, F. R.; Tollin, G. *Biochemistry* **1982**, *21*, 6366. Tabushi, I.; Kodera, M. *J. Am. Chem. Soc.* **1986**, *108*, 1101.

(4) (a) Levine, H. L.; Nakagawa, Y.; Kaiser, E. T. *Biochem. Biophys. Res. Commun.* **1977**, *76*, 64. (b) Otuski, T.; Nakagawa, Y.; Kaiser, E. T. *J. Chem. Soc., Chem. Commun.* **1978**, 457. (c) Levine, H. L.; Kaiser, E. T. *J. Am. Chem. Soc.* **1980**, *102*, 343. (d) Slama, J. T.; Radziejewski, C.; Oruganti, S.; Kaiser, E. T. *J. Am. Chem. Soc.* **1984**, *106*, 6778. (e) Hilvert, D.; Kaiser, E. T. *J. Am. Chem. Soc.* **1985**, *107*, 5805. (f) Stewart, K. D.; Radziejewski, C.; Kaiser, E. T. *J. Am. Chem. Soc.* **1986**, *108*, 3480. (g) Rokita, S. E.; Kaiser, E. T. *J. Am. Chem. Soc.* **1986**, *108*, 4984. (h) Kokubo, T.; Sassa, S.; Kaiser, E. T. *J. Am. Chem. Soc.* **1987**, *109*, 606.

(5) Tabushi, I.; Kodera, M.; Yamauchi, T. *Symposium on Biofunctional Chemistry*; Japan, June 1986; Abstract p 205.

(6) See, also, preparation of flavoporphyrin Takeda, J.; Ohta, S.; Hirobe, M. *Tetrahedron Lett.* **1985**, *26*, 4509.

(7) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1978.

(8) The use of the cyclodextrins as models, however, is not without difficulty.[9c]

0002-7863/87/1509-4734$01.50/0