and 69.6 kcal/mol. These typical values are those for ethyl chloride and bromide. In this way, the following estimates were made: $\Delta H_f(Cl(CH_2)_nBr(g)) = -28.9$ ($n = 3$), -35.9 ($n = 4$), and -39.9 kcal/mol ($n = 5$).

In a similar fashion, $\Delta H_f(HO(CH_2)_{3,4}Br(g))$ were estimated. The "typical" C–Br bond strength (above) and the "typical" C–OH bond strength (93.4 kcal/mol for ethanol) were used to conclude that $\Delta H = -23.8$ kcal/mol for the process

$$OH^{\bullet} + Br(CH_2)_{3,4}Br \rightarrow Br(CH_2)_{3,4}OH + Br^{\bullet}$$
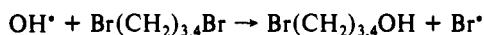
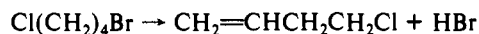Thus, we estimate that $\Delta H_f(Br(CH_2)_3OH(g)) = -58.2$ kcal/mol and $\Delta H_f(Br(CH_2)_4OH(g)) = -65.2$ kcal/mol.

In a similar way, $\Delta H_f(Cl(CH_2)_3OH) = -67.3$ kcal/mol was estimated from the heat of formation of the dichloride. For $Cl(CH_3)_{4,5}OH$, ΔH_f's had to be approximated from ΔH_f of the dibromides. Again, using the typical homolytic bond strengths cited above, it was assumed that $\Delta H_{rxn} = -38$ kcal/mol for the process

$$Br(CH_2)_{4,5}Br + OH^{\bullet} + Cl^{\bullet} \rightarrow Cl(CH_2)_{4,5}OH + 2Br^{\bullet}$$
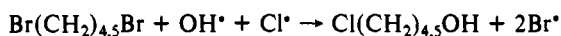
which results in the values $\Delta H_f(Cl(CH_2)_4OH(g)) = -77.1$ kcal/mol and $\Delta H_f(Cl(CH_2)_5OH(g)) = -81.1$ kcal/mol.

Heterolytic bond strengths involving $c\text{-}C_4H_8Cl^+$ and $c\text{-}C_5H_{10}Cl^+$ were computed by using the following estimates from MINDO/3 calculations:[25,27] $\Delta H_f(c\text{-}C_4H_8Cl^+) = 160.3$ kcal/mol; $\Delta H_f(c\text{-}C_5H_{10}Cl^+) = 151.7$ kcal/mol.

In the discussion of the reactions of Li$^+$ with the chloro and bromoalkanes, ΔH_f's were required for $CH_2{=}CHCH_2CH_2X$ (X = Cl, Br). They were estimated by assuming that, for

$$Cl(CH_2)_4Br \rightarrow CH_2{=}CHCH_2CH_2Cl + HBr$$

$$\Delta H_{rxn} = +16.5 \text{ kcal/mol, and for}$$

$$Cl(CH_2)_4Br \rightarrow CH_2{=}CHCH_2CH_2Br + HCl$$
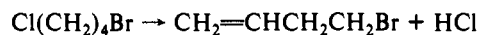
$\Delta H_{rxn} = +14.7$ kcal/mol. The reaction enthalpies reflect the energies required to dehydrohalogenate *n*-butyl chloride and *n*-butyl bromide, respectively. This yielded $\Delta H_f(C_4H_7Cl) = 10.4$ kcal/mol and $\Delta H_f(C_4H_7Br) = +14.7$ kcal/mol.

Proton affinities cited for organic molecules were taken from ref 20. The proton affinity of LiOH, 241 kcal/mol, is given in ref 35. Farrar et al.[15] cite $\Delta H_f(LiHCl^+) = 121$ kcal/mol; from this we determined that PA(LiCl) = 198 kcal/mol. Also, from the reported[15] binding energy of Li$^+$ to HBr of 19.1 kcal/mol, $\Delta H_f(LiHBr^+) = 134$ kcal/mol, thus PA(LiBr) = 195 kcal/mol.

Investigation of Methanol Adsorbed on Zeolite H–ZSM-5 by ¹³C NMR Spectrometry

Chihji Tsiao,[‡,§] David R. Corbin,[⊥] and Cecil Dybowski*,[‡]

Contribution from the Department of Chemistry and Biochemistry and Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19716, and Contribution No. 5211 from Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, P.O. Box 80262, Wilmington, Delaware 19880-0262. Received August 16, 1989

Abstract: ¹³C CPMAS NMR spectra of methanol adsorbed on H–ZSM-5 samples with different Si/Al ratios indicate that aluminum content affects the conversion of methanol to dimethyl ether. Spin–lattice relaxation experiments suggest the existence of at least three adsorbed methanol species. The reorientation activation energies (E_a) of these species are measured to be 10.0 (± 1.2), 1.5 (± 0.1), and 2.1 (± 0.2) kcal/mol, respectively.

Introduction

A novel process for the straightforward conversion of methanol to hydrocarbons over the synthetic pentasil zeolite H–ZSM-5 was developed over a decade ago.[1,2] The study of methanol adsorbed on zeolites is, thus, of practical and theoretical interest. Derouane et al.[3] investigated the conversion over a H–ZSM-5 catalyst with a single silicon to aluminum (Si/Al) ratio using ¹³C NMR spectroscopy and vapor-phase chromatography. The NMR spectra showed that a variety of species are formed on the surface of this catalyst. Recently, Anderson and Klinowski[4] have investigated the progress of this reaction to produce a mixture of organic products over a catalyst with Si/Al = 30. Aronson et al.[5] have used carbon NMR spectroscopy and TPD to determine coverages and exchange of chemisorbed ¹³CH₃OH with ¹²CH₃OH in H–ZSM-5 catalysts. They interpret the results in terms of complexes formed by proton transfer from the acid site to adsorbed alcohols and/or clusters of adsorbed molecules at or near the acid site. Salvador and Fripiat,[6] in work on a similar system, showed that

the adsorption of methanol on H–Y zeolite produces methoxysilane groups in the zeolite, which they identified by infrared spectrometry. This occurs by a reaction of the type
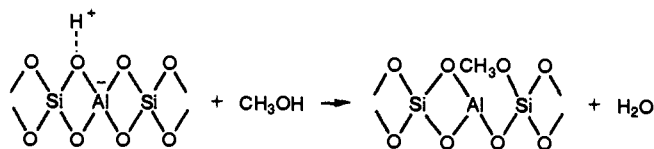
In another example of the use of ¹³C NMR to study organic materials at catalytic sites, Haw et al.[7] have detected long-lived

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*To whom correspondence should be addressed.
‡University of Delaware.
§Present address: Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.
⊥E. I. du Pont de Nemours and Co.

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(3) Derouane, E. G.; Nagy, J. G.; Dejaifve, P.; Van Hooff, J. H. C.; Spekman, B. P.; Vedrine, J. C.; Naccache, C. *J. Catal.* **1978**, *53*, 50.
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(7) Haw, J. F.; Richardson, B. R.; Ushiro, I. S.; Lago, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052.
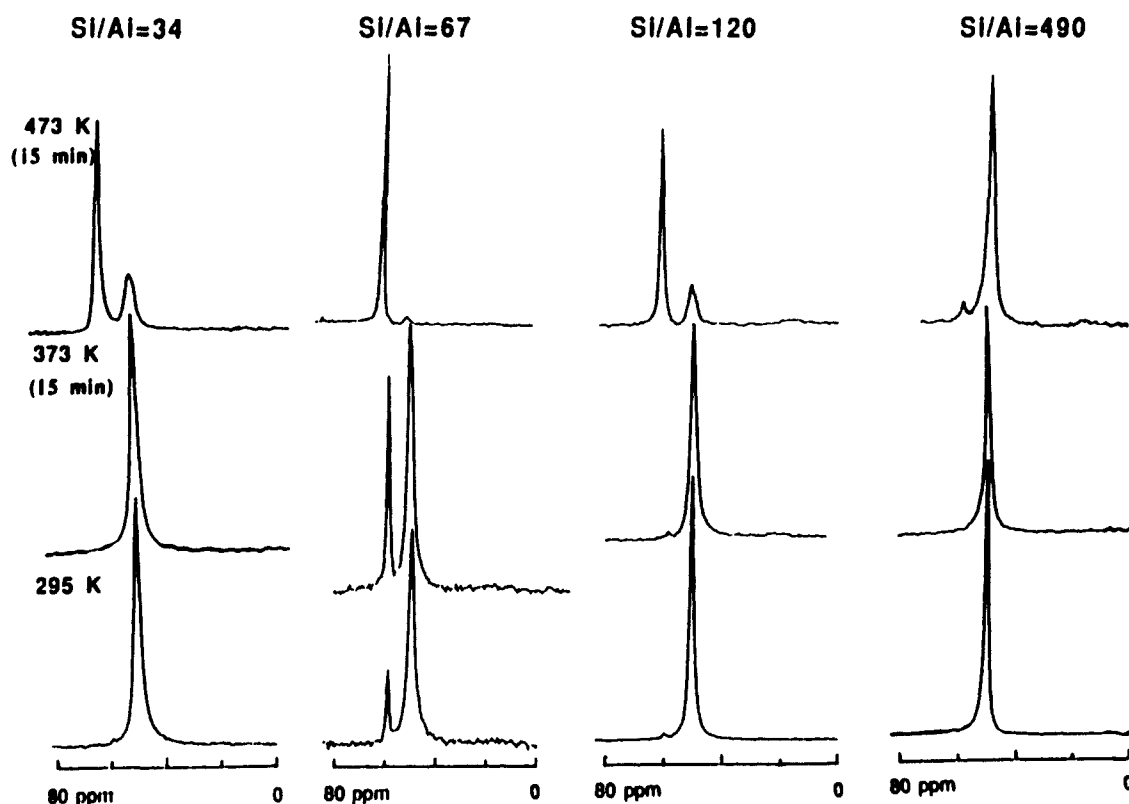
Figure 1. ^{13}C CPMAS NMR spectra of methanol adsorbed on various zeolite H-ZSM-5 samples. The numbers indicate pretreatment temperatures and durations. Si/Al ratios are indicated. Each spectrum results from the sum of 2000 transients.

intermediates, identified as alkyl silyl ethers, in the oligomerization reaction of propene on H-Y zeolite with ^{13}C CPMAS NMR spectrometry.

Aside from chemical identity based on shifts, NMR spectrometry gives information about molecular geometry and dynamics from spin-lattice relaxation. For example, dipolar couplings can give information on the bond distances in adsorbed molecules and between an adsorbed molecule and the substrate.[8] In an extensive investigation of the NMR relaxation of methanol adsorbed on a Y zeolite, Bronnimann and Maciel[9] measured the spin-lattice relaxation time (T_1) of ^{13}C in methanol. They found two resonances with solidlike characteristics corresponding to methoxysilane groups in the supercage (50.1 ppm; T_1 = 1.5 s) and β-cage (55.7 ppm; T_1 = 1.7 s) of H-Y zeolite and one resonance with liquidlike characteristics corresponding to more mobile "intracrystalline" methanol in the supercage (50.1 ppm; T_1 = 50 ms). They demonstrated that the ^{13}C-^{1}H dipolar interaction for the species observed at 50.1 ppm is inhomogeneous, indicating that the protons were isolated into small groups.

In the present work, we use ^{13}C CPMAS NMR spectrometry to investigate adsorption of methanol on samples of H-ZSM-5 having various Si/Al ratios. We identify species formed upon treatment at temperatures ≤473 K and report the ^{13}C spin-lattice relaxation times (T_1) and reorientation activation energies (E_a) extracted from the temperature dependence of the molecular correlation times (τ_c). We discuss the adsorption of methanol and the relation of spin-lattice relaxation parameters to the chemical and structural properties of the H-ZSM-5-methanol adsorption complexes in this methanol-conversion catalyst.

Experimental Section

Samples of Na-TPA-ZSM-5 with Si/Al = 34, 67, 120, and 490 (designated sample 34, sample 67, sample 120, and sample 490) were prepared by the method of Rollman and Volyocsik.[10] The crystallinity

of the samples was verified by X-ray powder diffraction using a Phillips APD 3600 diffractometer. Scanning electron micrographs showed that all samples have estimated crystallite sizes from 1 to 2.5 μm. The Si/Al ratios were determined by inductively coupled plasma spectrometry.[11] The Na-TPA-ZSM-5 samples were calcined in flowing air at 60 K/h to 823 K for 10 h to remove the TPA template. Sorption of xenon into the resulting Na-ZSM-5 forms showed the sample to be of comparable crystallinity to the materials before calcination, with sorption of approximately 1.4 × 10^{21} xenon atoms/g at saturation. Xenon-129 NMR spectra of the filled samples showed no resonances that would indicate large voids, nor did the xenon NMR line widths indicate a distribution of pore sizes.[12] The samples were exchanged three times with a 10% NH$_4$NO$_3$ solution at 363 K for 1 h, thoroughly washed and dried to give the ammonium forms, and stored for later use. H-ZSM-5 was obtained by calcination of NH$_4$-ZSM-5 while the temperature was increased at 100 K/h to 723 K for 20 h.

Prior to adsorption of methanol, H-ZSM-5 samples were treated by the following procedure: Approximately 0.25 g of zeolite was loaded into a glass NMR insert designed to fit into the rotor of a Chemagnetics m100S spectrometer. The sample was heated for 4 h to 673 K while attached to a glass manifold to maintain it under a vacuum of 1.0 × 10^{-5} Torr. It was maintained at these conditions for an additional 12 h. After being cooled to ambient temperature (295 K), the sample was exposed to 60% ^{13}C-enriched methanol vapor at 125 Torr (MSD Isotopes) for about 2 h. After equilibrium occurred, the zeolite was outgassed for 5 min and the insert sealed under flame. Care was always taken not to heat the sample region during this procedure.

^{13}C CPMAS spectra were recorded at 25.013 MHz with a Chemagnetics m100S spectrometer, with a Kel-F rotor specially drilled to accept the sealed inserts. These samples spun at speeds between 2.5 and 4 kHz in dry air. Each spectrum in Figure 1 derives from the accumulation of 2000 transients with a pulse delay of 2 s (sufficiently long compared to the proton T_1 to obtain a strong signal). The ^{13}C chemical shifts are reported with respect to external TMS. Spin-lattice relaxation measurements at different temperatures (253-323 K) were performed with cross-polarization and magic-angle spinning.[13,14] A variable-temperature

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Table I. [13]C T_1 of Methanol Sorbed on H–ZSM-5 at 293 K

Si/Al	T_1(A) (ms)	% A[a]	T_1(B) (s)	T_1(C) (ms)
34	13.2 ± 1.2	75.3 ± 1.8	1.75 ± 0.21	
67	13.5 ± 1.0	91.3 ± 1.2	1.70 ± 0.18	
120	13.8 ± 1.1	84.1 ± 1.4	1.88 ± 0.18	
490	13.0 ± 1.2	76.4 ± 1.3		55.8 ± 2.4

[a] The relative amount of magnetization is not necessarily representative of the relative amounts of the two different species, since there may be differences in cross-polarization efficiency for the two species.

accessory (Chemagnetics Inc.) kept the temperature constant within ±0.5 K. The amplitude of the signal following the ^{13}C sampling pulse was measured for at least 20 values of τ, the recovery interval, ranging from 1 ms to 8 s, and each ^{13}C NMR spectrum for T_1 measurements was the sum of 40 transients with a proton-repolarization delay of 2s. The error in T_1 is no greater than ±5%, at 95% confidence.

Results

Typical ^{13}C NMR spectra for methanol on H–ZSM-5, obtained after the sealed samples were subjected to various temperatures for 15 min, are shown in Figure 1. The spectra of materials before heating (labeled 295 K in Figure 1) show the characteristic resonance at 50.0 (±0.5) ppm of a methoxyl group, as reported previously.[3,4] The peak at 60.0 (±0.5) ppm can be attributed to the formation of dimethyl ether on sample 67, even at 295 K. Very weak resonances at 60.0 ppm can be detected for samples 34 and 120, but none is detected for sample 490.

After the sealed samples are held at 373 K for 15 min and quenched to 295 K, the dimethyl ether resonance increases in intensity relative to the methoxyl resonance, due to progressive conversion over sample 67. No change can be observed for the other three samples after treatment at this temperature.

After treatment at 473 K, it is observed that a higher proportion of methanol on samples 34 and 120 is converted to dimethyl ether and nearly all methanol is converted to dimethyl ether on sample 67. Only a trace of dimethyl ether is formed on sample 490 at this temperature, indicating that conversion of methanol to dimethyl ether is not efficient with this catalyst of low aluminum content. We observe no aromatic or aliphatic materials after these treatments, which are characteristic of the ultimate products of this methanol to hydrocarbon conversion catalyst.

We note that thermal treatment of sealed samples 34, 67, and 120 at 573 K produces rapid reaction and buildup of pressure, which resulted in explosive destruction of the samples in the heating block. Presumably, the reactions subsequent to dehydration of methanol occur rapidly in these samples, resulting in a rapid buildup of gas-phase products.

To clarify the state and influence of the local environment on the adsorbed methoxyl species, we measured the ^{13}C spin-lattice relaxation time (T_1) of the methoxyl groups on H–ZSM-5 samples using the pulse sequence described by Torchia.[14] The samples had been exposed to methanol at 295 K, with no treatment at higher temperature before the relaxation measurements were made. The magnetization does not decay exponentially, in agreement with results for methanol on Y zeolite.[8] The data were analyzed as a two-component decay with use of a Simplex non-linear-fitting program.[15] The spin-lattice relaxation time and the fractional magnetization of each component are listed in Table I for T = 293 K. Because cross-polarization may not be the same for the two species, the fractions do not necessarily represent the relative amounts of species.

The major magnetization component (with an average T_1(A) of 13.4 (±1.1) ms at 293 K) for all samples we assign to physisorbed methanol in the zeolite channels. It is a rather mobile material but is subject to cross-polarization. The minor component for samples 34, 67, and 120 (with an average T_1(B) of 1.77 (±0.15) s at 293 K) we refer to as a "chemisorbed species".[9] This chemisorbed species is probably bonded to a Brønstead acid site and moves anisotropically, as pictured in Figure 2. From Figure
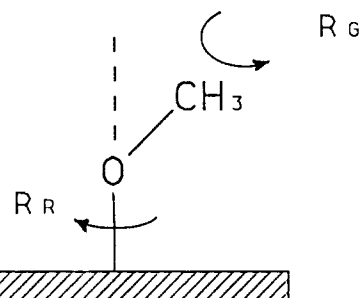
(14) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.
(15) Noggle, J. H. *Physical Chemistry on a Microcomputer*; Little, Brown: Boston, 1985.

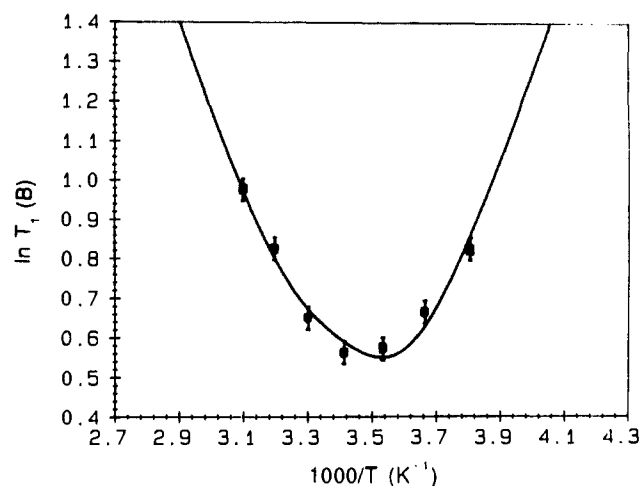**Figure 2.** Model of the chemisorbed methoxyl species on zeolite H–ZSM-5.

Figure 3. Plot of [13]C T_1(B) for sample 67. The solid curve is obtained from the best fit values with use of eqs 6 and 7.
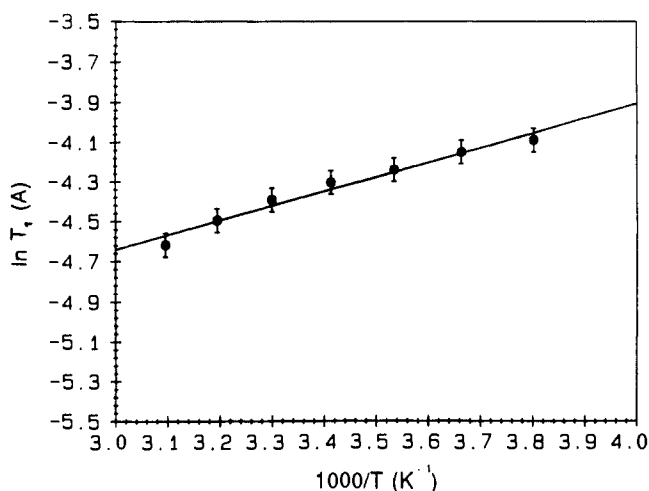
Figure 4. Plot of relaxation time T_1(A) for sample 67 as a function of 1000/T.

1, an obvious dimethyl ether resonance appears at 60.0 (±0.5) ppm for sample 67. We did not evaluate the dimethyl ether relaxation time for this sample.

The resonance at 50.0 ppm for sample 490 is also composed of two species, as distinguished by spin-lattice relaxation. Species A has T_1 = 13.0 (±1.2) ms, similar to that of samples with a lower Si/Al ratio. The second, which we call species C, has T_1(C) = 55.8 (±2.5) ms. From the temperature dependence of T_1 (vide infra), we infer that species C is different from species B seen in the other samples.

In Figure 3, ln T_1(B) for sample 67 is plotted as a function of reciprocal temperature. It passes through a minimum at 283 K. In Figures 4 and 5, ln T_1(A) for sample 67 and ln T_1(C) for sample 490 are plotted versus 1000/T. Dependences of relaxation time on temperature similar to those of Figures 3 and 4 were found for the other samples. The plots of Figures 4 and 5 are linear;
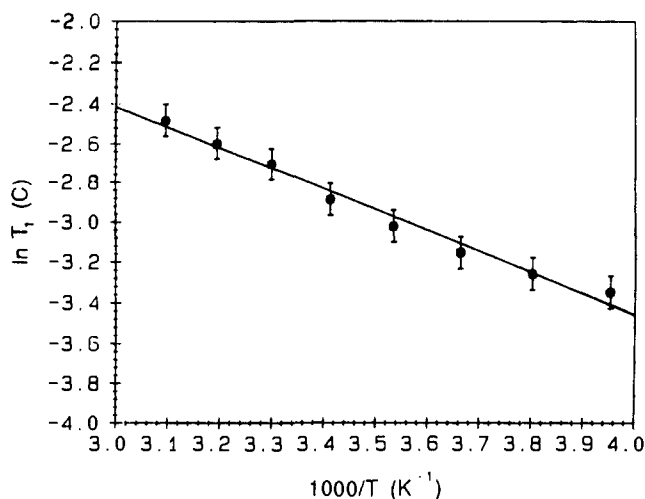
Figure 5. Plot of $T_1(C)$ for sample 490 as a function of $1000/T$.

however, ln $T_1(A)$ is inversely proportional to temperature, while ln $T_1(C)$ has the opposite dependence on temperature.

Discussion

In diamagnetic systems, one frequently finds the most important source of relaxation for spin $1/2$ nuclei is the fluctuating dipole–dipole interaction with other spins $1/2$. For nuclear spins I (in this case, ^{13}C) and S (in this case, ^1H) separated by a distance R_{IS}, the contribution to the relaxation time of nucleus I $(T_{1,DD})$ due to dipole–dipole coupling with a spin S is given by the expression[16]

$$\frac{1}{T_{1,DD}} = \frac{\gamma_1{}^2\gamma_S{}^2\hbar^2 S(S + 1)}{10 R_{IS}{}^6}\left[\frac{\tau_c}{1 + (\omega_1 - \omega_s)^2\tau_c{}^2} + \frac{3\tau_c}{1 + \omega_1{}^2\tau_c{}^2} + \frac{6\tau_c}{1 + (\omega_1 + \omega_S)^2\tau_c{}^2}\right] \quad (1)$$

where γ_1 and γ_S are magnetogyric ratios for ^{13}C and ^1H, respectively; S is the proton nuclear spin; τ_c is the molecular correlation time; and ω_1 and ω_S are the Larmor frequencies of nuclei I and S.

Equation 1 assumes a single correlation time (τ_c), the case for a rigid molecule undergoing *isotropic* motion. Molecules frequently tumble anisotropically. In particular, methanol *chemisorbed* on zeolite H–ZSM-5 (Figure 2) should move anisotropically, but even *physisorbed* molecules may have to be considered to more anisotropically. The modulation of ^{13}C–^1H dipolar couplings in an isolated methyl group is described by two independent rates, R_G and R_R, where R_G is the rate of rotation of the methyl group about its symmetry axis and R_R is the rate of movement of the axis. Equation 1 is valid in this case, provided the isotropic correlation time (τ_c) is replaced by an effective correlation time (τ_{eff}) calculated from Woessner's equation[17]

$$\tau_{eff} = A\tau_A + B\tau_B + C\tau_C \quad (2)$$

where A, B, and C are factors determined by the geometry of the motion. Using the geometry of methanol, one finds that eq 2 reduces to

$$\tau_{eff} = \tau_A/9 + 8\tau_B/27 + 16\tau_C/2 \quad (3)$$

where

$$\tau_A = \tau_R \quad (4a)$$

$$\tau_B{}^{-1} = \tau_R{}^{-1} + 1/6\tau_G \quad (4b)$$

$$\tau_C{}^{-1} = \tau_R{}^{-1} + 2/3\tau_G \quad (4c)$$

τ_G and τ_R are correlation times corresponding to R_G and R_R,

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Table II. Spin–Lattice Relaxation Parameters of Methanol Adsorbed on H-ZSM-5[a]

Si/Al	$E_a(A)$ (kcal/mol)	$\tau_R{}^0(B)$[b] (s)	$E_a(B)$ (kcal/mol)	$E_a(C)$ (kcal/mol)
34	1.58 ± 0.13	$(6.89 \pm 0.74) \times 10^{-15}$	8.82 ± 0.42	
67	1.46 ± 0.11	$(1.52 \pm 0.11) \times 10^{-16}$	11.00 ± 0.56	
120	1.53 ± 0.17	$(3.17 \pm 0.43) \times 10^{-15}$	9.28 ± 0.39	
490	1.39 ± 0.11			2.07 ± 0.15

[a]Errors are quoted with 95% confidence limits. [b]The preexponential factor for species B.

respectively. If the methyl internal rotation is fast, i.e., $\tau_R \gg \tau_G$, then eq 3 can be simplified[18]

$$\tau_{eff} = \tau_R/9 + 24\tau_G/9 \approx \tau_R/9 \quad (5)$$

Since three ^{13}C–^1H dipolar couplings contribute to relaxation of the methyl carbon, one must have a total relaxation rate that is 3 times the rate for a single dipolar coupling.

$$\frac{1}{T_{1,total}} = \frac{3}{T_{1,DD}} \quad (6)$$

We assume that τ_R is thermally activated according to eq 7. The

$$\tau_R = \tau_R{}^0 \exp(E_a/RT) \quad (7)$$

experimental data of $T_1(B)$ versus temperature for sample 67 shown in Figure 3 can be fit by such a mechanism. The solid line gives the best fit to eqs 6 and 7. The optimal parameters are given in Table II for all the samples. The optimal value of the parameter R_{IS} was found to be 1.21 (± 0.11) Å (in only fair agreement with the reference value of 1.09 Å). The calculated parameters for samples 34 and 120 are similar to those for sample 67 (Table II). Attempts to fit the data with other mechanisms give unreasonable values for parameters.

To explain relaxation of the methoxyl carbons of species A, we consider the spin–rotation mechanism. Generally, this mechanism is only important for small molecules with low barriers to internal rotation that interact weakly with one another due to steric effects, as might be expected for a physisorbed molecule in the narrow channels of the ZSM-5 structure. For molecules with near-tetrahedral or octahedral symmetry, the relaxation time derived from the spin–rotation mechanism for a nucleus at the center of symmetry is given by eq 8,[19] where I is the moment of inertia; k is

$$\frac{1}{T_{1,SR}} = \frac{2kTIC^2}{\hbar^2}\tau_j \quad (8)$$

Boltzmann's constant; C is the spin–rotation constant; and τ_j is the angular momentum correlation time. The reorientation correlation time (τ_c) is related to the angular momentum correlation time (τ_j) by Hubbard's relation:[20]

$$\tau_c\tau_j = \frac{I}{6kT} \quad (9)$$

One can rewrite eq 8 in combination with eqs 7 and 9 to give

$$\ln T_{1,SR} = \ln\left(\frac{3\hbar^2\tau_c{}^{0^2}}{I^2C^2}\right) + \frac{E_a}{RT} \quad (10)$$

Relaxation by the spin–rotation mechanism is characterized by a *decrease* in T_1 with increasing temperature in the fast-motion limit. This dependence may also appear for the dipole–dipole interaction in the slow-motion limit. We plot ln $T_1(A)$ as a function of $1000/T$ in Figure 4, from which one obtains a rather low activation energy, $(E_a(A))$ of 1.46 (± 0.11) kcal/mol for sample 67. Similar results are found for all samples (Table II). Given the low activation energy, we conclude that the motion is probably fast. Hence, the spin–rotation mechanism is probably dominant for this physisorbed species. These results (Table II)

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(19) Farrar, T. C.; Becker, E. D. *Pulse and Fourier Transform NMR*; Academic Press: New York, 1971.
(20) Hubbard, P. S. *Phys. Rev.* **1963**, *131*, 1155.

indicate that the motional states of species A and B do not depend appreciably on Si/Al, at least in the range 34 ≤ Si/Al ≤ 120.

The strength and number of acid sites in a zeolite depend on the concentration of tetrahedral aluminum atoms[21] and their locations in the pore structure.[22] For a highly dealuminated zeolite ZSM-5 such as sample 490, aluminum sites will generally be limited in number and methoxyl groups bound to silanol groups will have local structural and dynamic environments substantially different from that of a similar group adsorbed in H–ZSM-5 with a lower Si/Al ratio, in which case interactions with nearby aluminum centers is possible. The temperature dependence of the relaxation of species C (Figure 5) is like that of a spin relaxing through dipole–dipole coupling when $\omega_0\tau_c \ll 1$:

$$\ln T_{1,DD} = \ln K - \frac{E_a}{RT} \qquad (11)$$

The slope of the line in Figure 5 gives an activation energy of 2.07 (±0.15) kcal/mol, a very low activation energy compared to the activation energy of species B, which is also bound. Thus, species C must have more rotational freedom, because of (1) lack of direct interactions (e.g., with aluminum centers) that limit its rotational mobility at the site or (2) more facile exchange with the mobile physisorbed phase resulting in an average relaxation rate shorter than that of species B or (3) because both of these mechanisms are active. Clearly, species C is, in either case, more mobile than species B.

Conclusions

The ^{13}C NMR measurements of spin-dynamic parameters for the methanol/H–ZSM-5 system give information about molecular rotational mobility of three different sorbed species. Physisorbed methanol (A), most likely a mobile species in the channels of the ZSM-5 zeolite, has a rather short spin-lattice relaxation time, the temperature dependence of which can be ascribed to relaxation by spin–rotation coupling. Species B behaves as if it moves anisotropically, and it has the highest energy of activation—in the range 9–11 kcal/mol. We attribute this species to methanol *chemisorbed* at Brønsted sites in H–ZSM-5 with Si/Al < 120. The third species (C), existing only in sample 490, has a shorter relaxation time than species B under similar conditions. In this sample, the dominant characteristic is the much lower concen-

tration of aluminum in the framework. Methoxyl groups bound to silanols in this material have a much lower probability of interacting strongly with an aluminum center than do methoxyl groups in samples of lower Si/Al ratio. The reorientation activation energy and magnitude of the relaxation time of species C clearly show that this species has more rotational mobility than does species B. One can rationalize this result if species C is subject to fewer direct interactions with aluminum centers that restrict rotational mobility or if exchange causes more efficient relaxation.

In the cases where we observe species B (samples 34, 67, and 120), the reorientation activation energy of the motion that induces spin–lattice relaxation does not seem to depend strongly on the Si/Al ratio. Therefore, we conclude that the local environements of the bound methoxyl groups in these three materials are quite similar and allow less rotational mobility than in the highly siliceous material. Species A, which is present in all samples we investigated, has spin–lattice relaxation parameters that are independent of the Si/Al ratio, a fact consistent with the assignment of this species to physisorbed methanol.

Subjecting methanol-containing zeolites to temperatures between 295 and 473 K for short times results only in the conversion of methanol to dimethyl ether. The material with a Si/Al ratio of 490 is essentially inactive for this conversion, even at 473 K. Under the conditions of treatment in these experiments, we detect no subsequent products over any of the four catalysts.[3,4] Thus, the conversion to dimethyl ether is extremely facile over materials of sufficiently low Si/Al ratio, but the subsequent steps in the methanol to hydrocarbon conversion over H–ZSM-5 require a higher temperature to activate secondary reactions. Since this conversion only occurs for samples in which species B is present (samples 34, 67, and 120), we conclude that this species, which we have assigned as a methoxysilane group interacting with a Brønsted site, is the precursor that ultimately leads to production of hydrocarbons over this catalyst.

Registry No. CH$_3$OH, 67-56-1.

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Comparison of Free Energy Changes for Nitrogen Inversion and Electron Loss. 3. 9-Halo-9-azabicyclo[3.3.1]nonanes

Stephen F. Nelsen,* Peter A. Petillo, and Daniel T. Rumack

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received December 29, 1989

Abstract: The nitrogen inversion barrier for 1-Br was measured by dynamic ^{13}C NMR between −11 and +54 °C to be $\Delta G^\ddagger$(25°C) = 13.75 ± 0.09 kcal/mol, $E^{\circ\prime}$(CH$_3$CN/0.1 M Bu$_4$NClO$_4$, vs SCE) = +1.37 V, and vIP = 8.30 eV. For 1-I, the corresponding numbers are $\Delta G^\ddagger$(−93°C) estimated at 7.5 kcal/mole by the T_c method, $E^{\circ\prime}$ = +1.12 V, vIP = 8.07 eV. These numbers are compared with those for 1-Cl, 1-O*, 1-*t*-Bu, and 1-Me, as well as with semiempirical AM1 calculations. When separated from nitrogen pyramidalization effects, changes in ease of electron removal in solution for this series of 1-X compounds relative to 1-Cl are about 18 to 60% of those observed for vertical ionization in the gas phase.

Introduction

N-substituted cyclic and bicyclic dialkylamines of general formula R$_2$NX exhibit parallel behavior between their thermodynamics for cation radical formation and kinetics for nitrogen atom inversion.[1] Changes in alkyl group structure that cause

more difficult electron removal also raise the nitrogen inversion barrier for the neutral compound. The reason for this coupling

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