Conversion of Methyl Halides to Hydrocarbons on Basic Zeolites: A Discovery by in Situ NMR

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Received September 14, 1992

Abstract: It is shown that methyl halides (I, Br, Cl) react to form ethylene and other hydrocarbons on basic, alkali metal-exchanged zeolites at low temperatures. For example, methyl iodide is converted to ethylene on CsX zeolite at ca. 500 K. The order of reactivity of various catalyst/adsorbate combinations is consistent with the predictions of elementary chemical principles. The order of reactivity of the methyl halides follows the expected leaving-group trend. The activity of the catalyst framework correlates with its basicity (or nucleophilicity). All reactions were performed in a batch mode in sealed magic angle spinning (MAS) rotors while the contents were continuously monitored by in situ ^{13}C NMR. Methyl iodide reacts on CsX below room temperature to form a framework-bound methoxy species in high yield. An analogous ethoxy species readily formed from ethyl iodide. These species were characterized in detail. The ethoxy species was quantitatively converted to ethylene below 500 K. ^{133}Cs MAS NMR was used to characterize the interactions of methyl iodide and other adsorbates with the cation in zeolite CsZSM-5. Solvation of the alkali metal cation was reflected in large, loading-dependent chemical shifts for ^{133}Cs. Interactions between the cation and adsorbates were also reflected in the ^{13}C shifts of the alkyl halides and ethylene. The cumulative evidence suggests a mechanism for carbon–carbon bond formation analogous to one proposed by Chang and co-workers for methanol-to-gasoline chemistry on acidic zeolites (*J. Chem. Soc., Chem. Commun.* **1987**, 1320) that involves framework-bound methoxy and ethoxy species. The mechanism for methyl halide conversion is proposed to include roles for the basicity of the zeolite framework as well as the Lewis acidity of the cation.

Introduction

The efficient conversion of methane to higher hydrocarbons is an important scientific and technological goal.[1] Although a number of possible routes involving heterogeneous catalysis have been explored, the most successful processes to date require that methane first be steamed to syngas, a mixture of CO, CO_2, and H_2. Syngas can then be converted either directly to hydrocarbons using Fischer–Tropsch catalysts or first to methanol using Cu/ZnO/Al_2O_3 or related catalysts.[2,3] In the successful methanol-to-gasoline (MTG) process, methanol is converted to a mixture of hydrocarbons on the acidic zeolite catalyst HZSM-5 at a temperature of 623 K.[4,5] The present economics of the above processes are such that they have been commercialized only in regions that have abundant reserves of syngas precursors (natural gas or coal) and limited access to petroleum.

Alternative routes for converting methane to higher hydrocarbons can be imagined. In 1985, Olah and co-workers described the selective monohalogenation of methane over supported acid or platinum metal catalysts.[6] Those workers also described a second catalytic step for the hydrolysis of the methyl halide to methanol. Thus, methane could be converted to a hydrocarbon mixture by a three-step catalytic process: monohalogenation, hydrolysis, and then the MTG reaction on HZSM-5. In the present contribution, we describe a reaction that converts methyl halides directly into ethylene or (depending on reaction conditions) a mixture of higher hydrocarbons.

Acidic zeolites have proven to be excellent catalysts in a number of reactions. It has been realized, however, that base catalysis by zeolites is potentially an equally important area that is unduly neglected.[7,8] The most studied example of basic zeolite catalysis is the conversion of toluene and methanol to ethylbenzene on alkali metal-exchanged X zeolites.[9–12] This contrasts with acidic zeolite catalysts in which methanol alkylates the aromatic ring to form xylenes. Another model reaction is the dehydration of 2-propanol to acetone on basic zeolites such as CsX.[13,14]

The application of in situ spectroscopic techniques to the study of existing catalytic processes has been identified as a priority research area for the advancement of the science and technology of catalysis.[15] A second and perhaps more significant use of in situ spectroscopies could be a survey of the reactivity of rationally selected catalyst/adsorbate systems in a batch mode of operation in an attempt to discover new catalytic reactions. Promising candidates for such a survey could then be further investigated and optimized for continuous processes using flow reactors. We have been interested for several years in the development of in situ solid-state NMR and its application to important catalytic processes including olefin oligomerization,[16–18] cracking,[19] the

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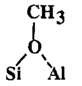
chemistry of acetylene,[20,21] methanol synthesis,[22] and the MTG process.[23,24] As an outgrowth of the latter work, we were motivated to survey the reactivity of other methane derivatives on zeolites, in particular the basic zeolites alluded to above.

This contribution reports in situ ^{13}C NMR studies that show that methyl halides (I, Br, and Cl) are readily converted to ethylene or other hydrocarbons on alkali metal-exchanged X zeolites at low temperatures. The most active catalyst studied was NaX, which converted methyl iodide to a mixture of hydrocarbons at a temperature of 450–500 K, whereas CsX was apparently selective for ethylene formation at ca. 500 K. RbX appeared to be selective for higher olefins and aromatics. The reactivities of the methyl halides followed the order expected on the basis of the stability of the leaving group, i.e., $I^- > Br^- > Cl^-$. The role of a basic zeolite framework was reflected in the activity trend for methyl iodide conversion: CsX > CsY > CsZSM-5 = HX > HZSM-5. CsX was slightly more active than RbX and KX, as expected from the order of basicity. The greater activity of NaX suggests that other factors such as cation size, distribution, or Lewis acidity[25] can affect activity. Except for the acidic zeolites, none of the catalysts studied were active for converting methanol, ethanol, or dimethyl ether to hydrocarbons, although these species were easily converted on alkali metal-exchanged X catalysts in the presence of methyl halides. The latter result probably reflects halogenation of the alcohol or ether by the acid halide eliminated in the conversion of the methyl halide to ethylene. Previous studies of the direct conversion of methyl halides to hydrocarbons appear to have been restricted to the reaction of methyl chloride on small pore zeolites either in the acidic form or exchanged with alkaline earth or transition-metal cations.[26-28]

The conversion of methyl halides to ethylene apparently proceeds through a framework-bound methoxy intermediate (I) which forms on up to ca. 20% of the exchange sites on CsX when CH_3I is adsorbed at or somewhat below 298 K. An analogous framework-bound ethoxy species (II) readily forms in similar yield upon adsorption of CH_3CH_2I, and this is quantitatively converted to ethylene below 500 K. A variety of NMR experiments was carried out to firmly establish the assignments of the alkoxy species and to characterize their properties.



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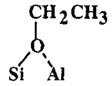

II

A number of ^{133}Cs NMR experiments are reported that suggest an interaction between methyl iodide or other electron-rich adsorbates and the alkali metal cation in the zeolite. This interaction is also reflected in the ^{13}C isotropic shifts of alkyl halides and ethylene.

Table I. Cation Composition of the Zeolite X Catalysts

zeolite	H$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
	cation composition[a] (%)[b]				
HX	79	21			
NaX	9	91			
KX	5	2	93		
RbX	20	15		65	
CsX	28	19			53

[a] Values for Na, K, Rb, Cs, and Al were obtained by neutron activation analysis. H was obtained by difference between the Al content and the sum of the alkali metal values. [b] Values are reported as percents of the total cation sites, taken as the aluminum content (6.4 mmol/g NaX)

The overall results of this study are interpreted in terms of a proposed mechanism that includes roles for a basic (or nucleophilic) zeolite framework and the Lewis acidity of the alkali metal cation. The straightforward reactivity trends observed in this study suggest that a predictive chemistry of zeolite-catalyzed reactions in a realistic goal.

Experimental Section

Catalyst Preparation. NaX zeolite (Si/Al = 1.2) and NaY zeolite (Si/Al = 2.3) were obtained from Strem Chemicals. Zeolite HZSM-5 (Si/Al = 19) was obtained from UOP Corp. CsCl, RbCl, KCl, NaCl, and NH_4Cl were obtained from Aldrich. These zeolites were exchanged to the ammonium cationic form to facilitate introduction of the larger alkali metal cations. The exchange procedure involved slurrying zeolite with 1 M NH_4Cl solution (30 mL per gram of zeolite) for 24 h at 298 K. After decanting, the procedure was repeated twice. Finally, the solids were filtered and dried under vacuum. Alkali metal-exchanged zeolites were prepared from the ammonium form by the same procedure using the appropriate salt. The catalyst activation procedure converted any residual ammonium ions to protons. Ion exchange in faujasites can be less than complete, especially when large cations are to be introduced. Neutron activation analysis was performed on all samples in order to determine the alkali metal cation distribution actually obtained. For the faujasites, the difference between the total of the alkali metals and the aluminum content was assumed to be due to protons. These elemental analysis results are reported in Table I. Elemental analysis suggested incomplete ion exchange for CsZSM-5 (73%). The lower exchange site concentration in CsZSM-5 made the neutron activation result for Cs suspect, so other experiments were performed to establish that the exchange was quantitative for this material. ^{1}H MAS NMR[29] revealed no signal for residual Bronsted sites. Furthermore, this sample showed no activity for the conversion of methanol to hydrocarbons. It was concluded that exchange was quantitative in the case of CsZSM-5.

All catalysts were activated within 1 day of use by a procedure described elsewhere.[16] Typically, the highest temperature used was 673 K. X zeolites are less thermally stable than corresponding materials with a lower framework aluminum content. X-ray structural investigations[30] have shown that CsX and KX were stable over a period of several hours at 673 K while RbX tended to decrystallize under these conditions. A preliminary investigation of the stability of CsX zeolite used in this investigation was performed using both X-ray powder diffraction and ^{29}Si MAS NMR. The latter technique permits a calculation of the silicon-to-aluminum ratio of the zeolite framework. These studies suggested that a modest loss of crystallinity occurred upon activation at 673 K and that a small amount of aluminum was removed from the framework by the extended reaction of methyl iodide at 523 K. Zeolite activation at 573 K was almost as effective as treatment at the higher temperature as measured by an in situ reaction of methyl iodide.

Sample Preparation. Methyl iodide-^{13}C, methyl bromide-^{13}C, methyl chloride-^{13}C, ethyl iodide-$1,2$-^{13}C, ethyl iodide-1-^{13}C, methanol-^{13}C, ethanol-1-^{13}C, and ethylene-$1,2$-^{13}C were obtained from Cambridge Isotopes. In a typical experiment, 0.25 g of activated catalyst was loaded in a drybox into a 7.5-mm (o.d.) zirconia rotor which was mounted in

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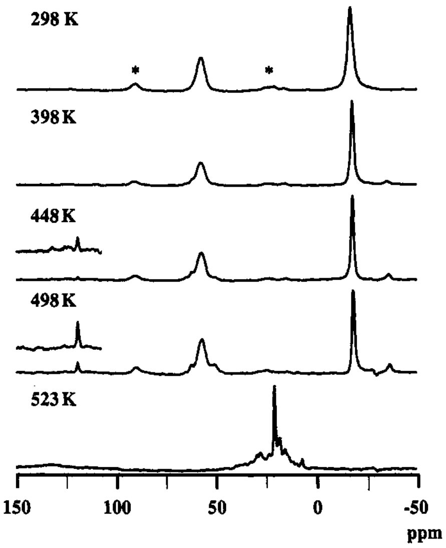

Figure 1. In situ ^{13}C MAS NMR study of the reactions of methyl iodide-^{13}C on zeolite CsX. Methyl iodide (−15 ppm) was partially converted to a framework-bound methoxy (58 ppm) upon adsorption at 298 K. Ethylene (120 ppm) formed between 448 and 498 K and oligomerized and cracked to a mixture of hydrocarbons at 523 K. * denotes spinning sideband.

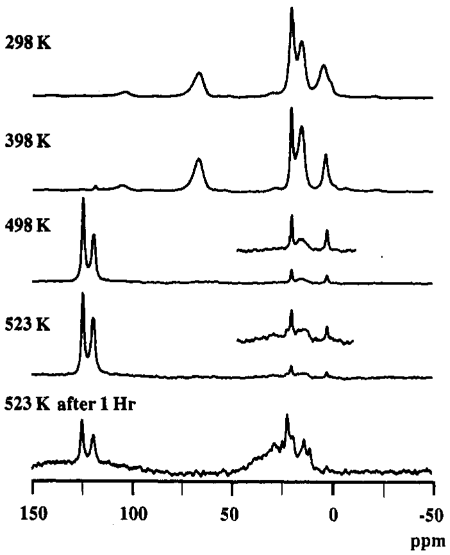

Figure 2. In situ ^{13}C MAS NMR study of the reactions of ethyl iodide-*1,2*-^{13}C on zeolite CsX. See Table II for chemical shift assignments. A framework-bound ethoxy formed upon adsorption at 298 K, and this was quantitatively converted to ethylene at 498 K. This product was partitioned between strong and weak adsorption sites (see text). Extended heating at 523 K led to further reactions.

a CAVERN apparatus.[31] The CAVERN was transferred from the glovebox to a vacuum line and evacuated. The adsorbate loading was quantified by manometry and was typically chosen to be 0.5 molar equiv of adsorbate per cesium or other principal alkali metal cation. After adsorption was complete, the rotor was sealed and transferred to the MAS NMR probe. Sample spinning and heating were performed using dry nitrogen gas.

NMR Spectroscopy. ^{13}C MAS NMR spectra were obtained at 90.5 MHz using a Chemagnetics CMX-360 Spectrometer with an Oxford wide bore 8.45-T magnet. Hexamethylbenzene was used as an external chemical shift reference. The accuracy of the ^{13}C shifts reported are 1 ppm or better as verified by the coadsorption of internal standards in select cases. Except where explicitly stated otherwise, all ^{13}C spectra shown in this contribution were obtained with direct excitation (90° pulse) and proton decoupling. ^{13}C T_1 measurements were performed on several samples at room temperature, and the longest value observed was 600 ms; therefore, 4-s pulse delays were used in all experiments to ensure quantitation. In several cases, spectra obtained with cross polarization[32] (4-ms contact time) or cross polarization with interrupted decoupling[33] (50 μs) are reported in order to aid in spectral assignments. All ^{13}C spectra are the result of 64 scans.

^{133}Cs MAS NMR spectra were obtained at 47.2 MHz and were externally referenced to 0.5 M CsCl aqueous solution. ^{133}Cs spectra were obtained using 5.6-μs 90° pulses and pulse delays of 1–20 s as necessary to avoid saturation. Typically, 24 scans were collected for CsX and 300 scans for the other catalysts. Careful measurements of the 180° flips on solution and catalyst samples confirmed that the excitation of the ^{133}Cs in the zeolite was nonselective, i.e., all seven transitions were excited uniformly.[34,35]

In situ experiments were performed by transferring the sealed rotor to the MAS probe and then monitoring the ^{13}C or ^{133}Cs spectrum as the sample temperature was stepped incrementally. Typically, several dozen spectra were obtained in an experiment, and most experiments were repeated at least once. The results reported are representative.

Results

Figures 1 and 2 introduce the reactions of CH_3I and CH_3CH_2I, respectively, on CsX zeolite—the most extensively studied catalyst in this investigation. The existence of adsorption complexes that may be best described as framework-bound alkoxy species is now widely accepted in the zeolite community. This is based on the evidence from a variety of techniques including spectroscopy,[16,36,37] temperature-programmed desorption measurements,[38,39] and theoretical investigations.[40,41] However, their NMR properties, and hence our evidence for their formation in this contribution, will be less familiar to some readers. Figures 3–6 are, therefore, devoted to summarizing some of the evidence for these assignments. Figures 7–14 report in situ ^{13}C studies analogous to Figure 1 which survey trends in reactivity as variations are made in the halogen on the adsorbate, the alkali metal exchanged in the zeolite, or the framework of the zeolite. Figures 15–18 summarize studies of the interactions of various adsorbates with the alkali metal cation.

Methyl Iodide on CsX. When $^{13}CH_3I$ was adsorbed on CsX zeolite at 298 K, two isotropic ^{13}C signals were seen in the MAS NMR spectrum (Figure 1). Unreacted methyl iodide adsorbed in the zeolite was observed at −15 ppm, 5 ppm downfield from its value in neat solution. For convenience, ^{13}C isotropic chemical shifts at 298 K for a number of the species observed in this investigation are summarized and compared to their corresponding values in solution[42] in Table II. The ^{13}C shifts of ethylene and the alkyl halides moved upfield 2–3 ppm at high temperatures; chemical shifts are compared at 298 K in this contribution whenever possible.

The second ^{13}C signal in Figure 1 is at a chemical shift of 58 ppm. This is due to the framework-bound methoxy species **I**. At the field strength of 8.45 T and the MAS spinning speeds of 3–4 kHz used in most of the ^{13}C spectra in this investigation, small first-order spinning sidebands due to the chemical shift anisotropy

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Table II. ^{13}C Isotropic Chemical Shifts Observed for Adsorbates on CsX at 298 K

species	carbon position	^{13}C chemical shift[a] obsd	soln[b]
methyl iodide (strong site)	C-1	−15	−20
methyl iodide (weak site)	C-1	−21	−20
methyl bromide	C-1	15	9
methyl chloride	C-1	29	24
methanol	C-1	51	49
dimethyl ether	C-1	61	60
framework-bound methoxy	C-1	58	
ethylene (strong site)	C-1	125	122
ethylene (weak site)	C-1	122	122
ethyl iodide (strong site)	C-1	6	0
	C-2	22	22
ethyl iodide (weak site)	C-1	3	0
	C-2	21	22
ethanol	C-1	58	56
	C-2	18	17
diethyl ether	C-1	66	65
	C-2		14
framework-bound ethoxy	C-1	68	
	C-2	17	

[a] Reported in ppm relative to TMS. [b] Reference 42.

of the methoxy group are also seen in Figure 1 and other spectra. These are indicated by asterisks for the spectrum at 298 K. When a similar experiment was performed but with the adsorption and spectroscopy carried out at 248 K using procedures designed to prevent sample warming during transfer, the ^{13}C spectrum (not shown) also showed a significant conversion of CH_3I to the methoxy species **I**. This species clearly forms very readily. Based on the measured loadings of CH_3I, the Si/Al ratio of the zeolite, and the relative integrated intensities from Figure 1, we estimate that ca. 20% of the exchange sites in CsX are methylated by CH_3I at 298 K. This measurement was reproducible for the several dozen samples of alkyl iodides on CsX prepared and studied in the course of this investigation.

When the temperature was raised to the range of 448–498 K (Figure 1), ethylene began to form as indicated by its single characteristic ^{13}C resonance. As will be shown later, when larger steady-state quantities of ethylene were generated, two ^{13}C signals due to ethylene were seen at 298 K, one at 125 (strong adsorption site) and the other at 122 ppm (weak adsorption site). These assignments were confirmed through an exhaustive investigation in which different loadings of ethylene were adsorbed directly on CsX and their NMR properties were determined as the sample temperature was cycled. Briefly, these studies showed that, whereas at room temperature all of the ethylene acted like an adsorbed species (e.g., cross polarized efficiently) and had a chemical shift of 125 ppm, a second peak, which cross polarized much less efficiently and showed a well-defined scalar multiplet without decoupling, grew in at 120 ppm when the temperature was raised. These effects were reversible. Evidence for two environments was also seen with high loadings of alkyl halides (vide infra). The nature of the two sites was not explored any further.

The MAS NMR probe temperature was raised to 523 K, and the final spectrum in Figure 1 was obtained. This spectrum shows that the methyl iodide and framework-bound methoxy were converted quantitatively to a mixture of light aliphatic hydrocarbons (12–37 ppm) and possibly a small amount of aromatics or coke (broad signal ca. 125–150 ppm). This hydrocarbon mixture did not contain detectable levels of methane. Interestingly, when ethylene was adsorbed directly on CsX, it was unreactive on this catalyst at 523 K. Apparently it was the HI eliminated from CH_3I that catalyzed the oligomerization and cracking reactions which converted ethylene, the first formed hydrocarbon, to other products.

Ethyl Iodide on CsX Zeolite. Figure 2 shows a typical in situ ^{13}C study of ethyl iodide-*1,2*-^{13}C on CsX. The overall results are entirely analogous to those of methyl iodide with the exception that the framework-bound ethoxy species (**II**) formed ethylene at a lower temperature than in the analogous experiment with methyl iodide. Identical experiments were also performed with ethyl iodide-*1*-^{13}C, and those studies support the following assignments. Two species were present in the vicinity of room temperature in nearly equal amounts. The methylene carbon of unreacted ethyl iodide (6.5 ppm) in the zeolite is about 7 ppm downfield from its value in solution, whereas the methyl resonance (22.4 ppm) was about 1 ppm upfield from the corresponding value in solution. These shifts suggest that the iodine on ethyl iodide was interacting with a Cs^+ cation in the zeolite. The second species was the framework-bound ethoxy species **II** with a methylene chemical shift of 68.5 ppm and a methyl shift of 17.5 ppm. The molar loading of ethyl iodide was nearly identical to the methyl iodide loading in the previous experiment, so twice as much ethylene was formed in the experiment in Figure 2 compared to the previous experiment. Not all of this ethylene could be accommodated at the strong adsorption site (125 ppm), so some of it was forced onto the weaker adsorption site (122 ppm). Essentially all of the adsorbate was converted to ethylene immediately after reaching 498 K. Prolonged heating at 523 K induced oligomerization and cracking chemistry.

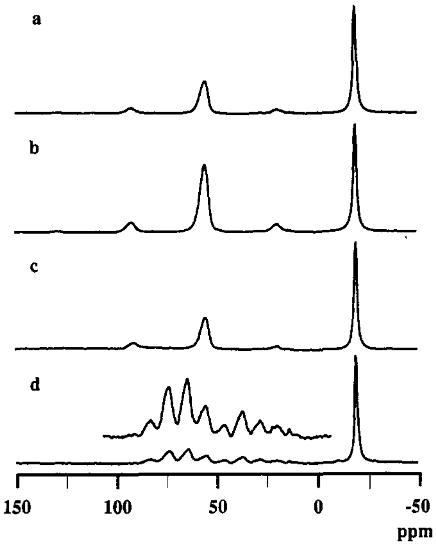

Figure 3. Selected ^{13}C MAS NMR results supporting the assignment of the methoxy resonance at 58 ppm (a) Bloch decay spectrum; (b) cross polarization spectrum; (c) spectrum with cross polarization and interrupted decoupling; (d) slow-speed spectrum obtained at 830 Hz. All spectra were acquired at 298 K.

Framework-Bound Alkoxy Species. Framework alkoxy groups have previously been observed to form from alcohols and olefins on zeolites HZSM-5 and HY using a variety of experimental techniques including in situ FT-IR[36] and NMR[16,37] experiments. Figures 1 and 2 indicate that framework alkoxys form on CsX from alkyl iodides at high levels, reflecting the high concentration of framework sites on this catalyst as well as the absence of other reaction pathways (e.g., elimination or oligomerization) for this catalyst/adsorbate combination at room temperature. Criteria previously proposed[16] for assigning ^{13}C signals to framework-bound alkoxy groups include the following: a chemical shift slightly downfield from the corresponding alcohol, the expected NMR behavior for a bound species including efficient cross polarization, the appropriate interrupted decoupling[33] response, the clear presence of spinning sidebands due to chemical shift anisotropy in slow-speed spectra, and the ready hydrolysis of the alkoxy to the corresponding alcohol upon exposure to moisture. These criteria were easily met for the alkoxy species in this contribution. Figure 3 shows selected results verifying the methoxy group assignment on CsX. Bloch decay (Figure 3a) and cross polarization (Figure 3b) spectra run under otherwise

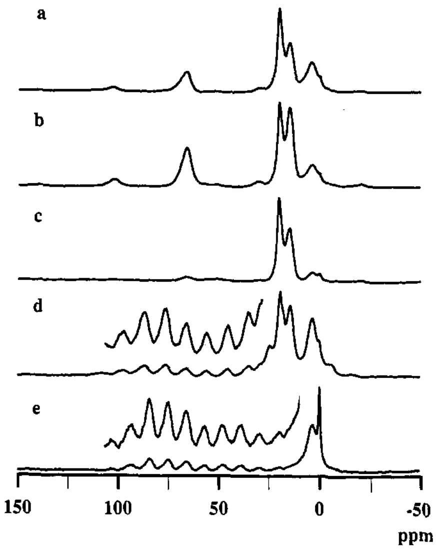

Figure 4. Selected ^{13}C MAS NMR results from ethyl iodide-*1,2*-^{13}C supporting the assignment of the ethoxy CH_2 resonance at 68 ppm and the CH_3 resonance at 17 ppm (a) Bloch decay spectrum; (b) cross polarization spectrum; (c) spectrum obtained with cross polarization and interrupted decoupling showing suppression of the methylene resonance of the ethoxy group; (d) slow-speed spectrum obtained at 930 Hz; (e) same as in d except that the ethoxy was prepared from ethyl iodide-*1*-^{13}C and the spinning speed was 820 Hz. All spectra were acquired at 298 K.

identical conditions confirmed that the alkoxy resonance was emphasized in a cross polarization spectrum. Its signal was reduced slightly, but not eliminated, in an interrupted decoupling spectrum (Figure 3c), as expected for a bound methoxy group. As shown in Figure 3d, at least three orders of spinning sidebands are associated with the methoxy resonance at a spinning speed of 830 Hz. Such a pattern is conclusive for a species incapable of isotropic reorientation on a millisecond time scale. The relative intensities of these peaks were analyzed by the method of Herzfeld and Berger,[43] and the following principal components of the ^{13}C chemical shift tensor were obtained: $\delta_{11} = 82$, $\delta_{22} = 81$, and $\delta_{33} = 9$. These values are in reasonable agreement with those for suitable model compounds[44] as well as methoxy species on other catalysts.[22] The chemical shift anisotropy (73 ppm) and asymmetry parameter (0.01) calculated from the principal components are consistent with a near-axially-symmetric methoxy group undergoing rapid rotation about the O–C bond but no other large amplitude motion.

Figure 4 shows selected results from an analogous study of the spectroscopic properties of ethoxy groups formed from ethyl iodide-*1,2*-^{13}C on CsX. The results are completely consistent with the proposed assignments. The ethoxy resonances are emphasized with cross polarization, and the methylene carbon of the ethoxy at 68 ppm is almost completely suppressed with interrupted decoupling while the methyl group of the ethoxy (17 ppm) is only slightly reduced. Both resonances due to the ethoxy showed several orders of spinning sidebands in a slow-speed spectrum (Figure 4d). The principal components of the methylene carbon ^{13}C chemical shift tensor were determined from a slow-speed spectrum of the ethoxy derived from ethyl iodide-*1*-^{13}C (Figure 4e). The values obtained were $\delta_{11} = 106$, $\delta_{22} = 81$, and $\delta_{33} = 16$. The large chemical shift anisotropy (90 ppm) and asymmetry parameter (0.56) suggest that the bulk of the methyl group precludes rapid motion about the O–C bond.

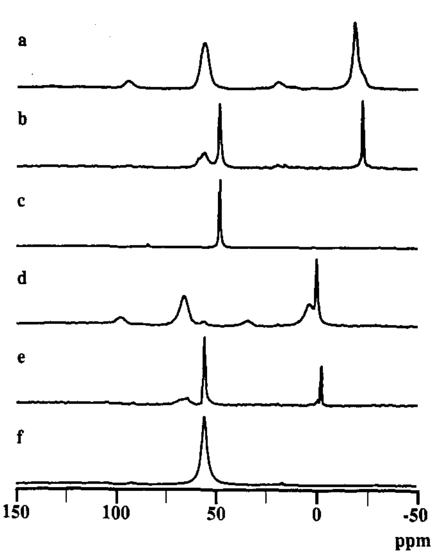

Figure 5. Selected ^{13}C MAS NMR results showing the hydrolysis of framework-bound alkoxy species to alcohols and ethers upon exposure to atmosphere. Methyl iodide-^{13}C on CsX: (a) before exposure, showing a methoxy signal at 58 ppm; (b) after exposure, showing methanol at 51 ppm and a trace of dimethyl ether at 61 ppm; (c) ^{13}C MAS spectrum of an authentic sample of methanol-^{13}C on CsX. Ethyl iodide-*1*-^{13}C on CsX: (d) before exposure; (e) after exposure, showing ethanol at 58 ppm; (f) ^{13}C MAS spectrum of an authentic sample of ethanol-*1*-^{13}C on CsX. All spectra were obtained at 298 K. Unreacted alkyl iodides partially diffused out of the catalysts during exposure.

The hydrolysis of framework-bound alkoxy species in zeolites upon exposure to moisture has been well documented in other studies[16,21] and is also consistent with the hydrolytic instability of analogous species on silica gel surfaces. Figure 5a and b compare ^{13}C MAS spectra of methyl iodide on CsX before and after exposure to humid atmosphere. Upon exposure, most of the methoxy was hydrolyzed to methanol (51 ppm) and dimethyl ether (shoulder at 61 ppm). In some in situ experiments described below, the zeolite retained traces of water after activation, and similar peaks formed immediately upon adsorption of a methyl halide. Adsorption of water also displaces the excess methyl iodide from the strong adsorption sites in the zeolite, resulting in a 5-ppm upfield shift to its solution-state value. The chemical shift of the methanol formed by hydrolysis is identical to that observed following direct adsorption of methanol-^{13}C (Figure 5c). Figures 5d–f present an analogous series of spectra showing the hydrolysis of the ethoxy species to ethanol-*1*-^{13}C upon exposure to atmospheric moisture. The chemical shift observed in Figure 5e is identical to that for a sample prepared by direct adsorption of ethanol-*1*-^{13}C onto CsX (Figure 5f). The assignment of the dimethyl ether resonance was verified by an analogous experiment. Neither methanol nor dimethyl ether reacted to form hydrocarbons on CsX at 523 K.

Magic angle spinning is usually thought to remove the homonuclear dipolar couplings between dilute pairs of ^{13}C. In a recent series of papers, Griffin and co-workers have characterized the phenomenon of rotational resonance, in which the dipolar coupling is selectively reintroduced by setting the spinning speed to be identical to (or a submultiple of) the frequency difference between the coupled nuclei.[45–47] Figure 6 shows the use of rotational resonance to further verify the assignment of the ethoxy species. As the spinning speed was set to match the rotational resonance condition (4646 Hz) for the two carbons in the ethoxy species, the line shapes of both resonances were split into doublet patterns. Observation of rotational resonance is unambiguous evidence that these resonances are due to an immobilized species with a single, short distance between the methylene and methyl

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(43) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021–6030.

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(45) Levitt, M. H.; Raleigh, D. P.; Creuzet, F.; Griffin, R. G. *J. Chem. Phys.* **1990**, *92*, 6347–6364.

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(47) McDermott, A. E.; Creuzet, F.; Griffin, R. G. *Biochemistry* **1990**, *29*, 5767–5776.

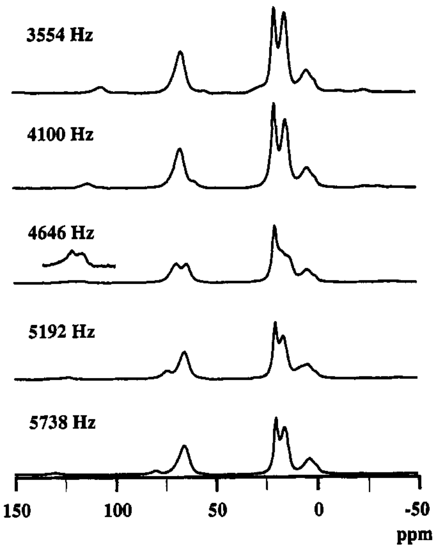

Figure 6. Demonstration of the rotational resonance effect for the framework-bound ethoxy species obtained on CsX from ethyl iodide-*1,2-*^{13}*C*. The rotational resonance condition is achieved when the spinning speed is set to match the frequency difference (4646 Hz) between the signals at 68 and 17 ppm. Rotational resonance reintroduced the ^{13}C-^{13}C dipolar coupling for the rigid ethoxy species, resulting in a splitting pattern that reflects the short internuclear distance.

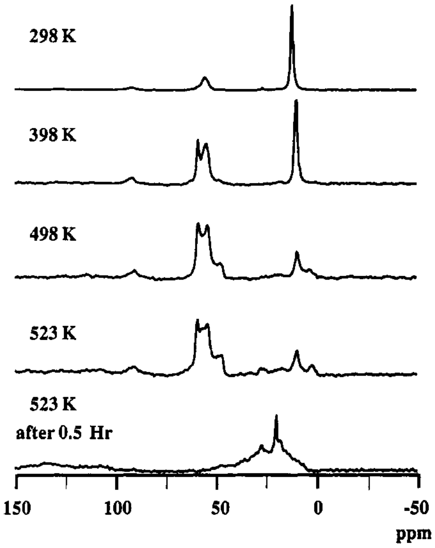

Figure 7. In situ ^{13}C MAS study of the reactions of methyl bromide-^{13}*C* on zeolite CsX. This adsorbate was slightly less reactive than methyl iodide (cf. Figure 1).

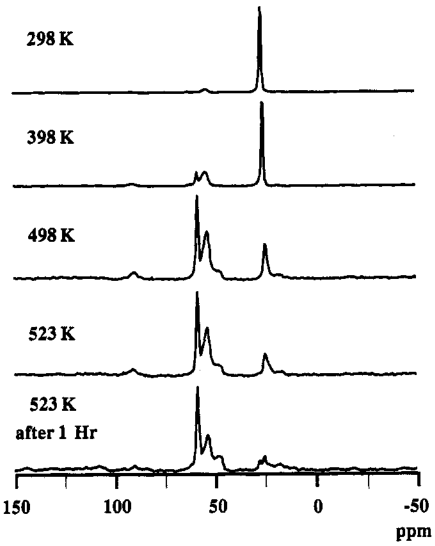

Figure 8. In situ ^{13}C MAS study of the reactions of methyl chloride-^{13}*C* on zeolite CsX. This adsorbate was significantly less reactive than methyl iodide or methyl bromide (cf. Figures 1 and 7).

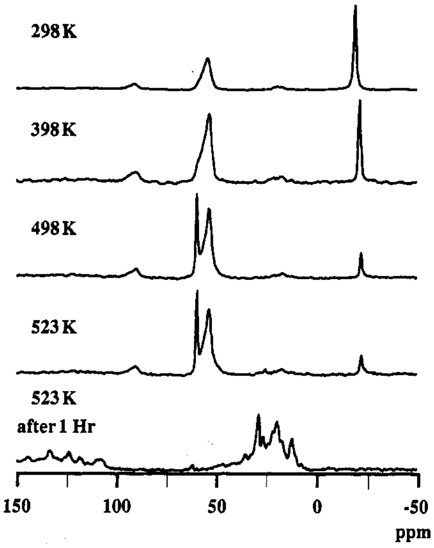

Figure 9. In situ ^{13}C MAS study of the reactions of methyl iodide-^{13}*C* on zeolite RbX. The zeolite was slightly less active than CsX and showed a selectivity for higher olefins and aromatics (cf. Figure 1).

carbons. The above evidence for the assignments to framework-bound alkoxy groups is, in our opinion, overwhelming.

Methyl Halides on CsX Zeolite. In situ ^{13}C MAS studies analogous to that for methyl iodide were carried out for methyl bromide (Figure 7) and methyl chloride (Figure 8) on CsX. These reactants showed the expected trend in reactivity. The concentration of methoxy groups formed followed the trend methyl iodide > methyl bromide > methyl chloride, as did the reactivity toward hydrocarbon synthesis. Methyl bromide was quantitatively converted to a mixture of hydrocarbons only after extended heating at 523 K, whereas methyl chloride formed only a trace of hydrocarbons at that temperature. Partial hydrolysis of the methyl halide due to residual water is apparent in both figures.

Effects of the Cation on Conversion of Methyl Iodide in Zeolite X. The conversion of methyl iodide was used as a test reaction to explore the effects of changing the monovalent cation in zeolite X. In situ experiments were performed using protocols similar to that in Figure 1 for methyl iodide on CsX. Figure 9 shows a ^{13}C in situ study of methyl iodide on RbX. The activity of this catalyst was slightly lower than that of CsX, but RbX differed in that it seemed to show a selectivity for higher olefins and aromatics. For example, the signals at 120 and 134 ppm are consistent with propene, but we have not attempted to firmly establish the identities of any of the products in Figure 9. The KX catalyst (Figure 10) was slightly more active than RbX, and the hydrocarbon products produced a broad signal between 115 and 145 ppm, but it is not possible to identify specific products from Figure 10. The NaX catalyst (Figure 11) was the most active catalyst for methyl iodide conversion found in this investigation. Essentially all of the adsorbate was converted to aliphatic and aromatic hydrocarbons below 500 K.

It is difficult to fully exchange all of the cation sites in an X zeolite, and these materials invariably contain residual protons. These protons are only weakly acidic in HX due to the very low Si/Al ratio, and they are further poisoned by partial exchange with alkali metal cations. Nevertheless, a control experiment was performed on zeolite HX to rule out the possibility that the catalyst activity seen in this study is due to residual Bronsted acidity. This experiment (Figure 12) showed that methyl iodide was nearly unreactive on HX. A small amount of framework-

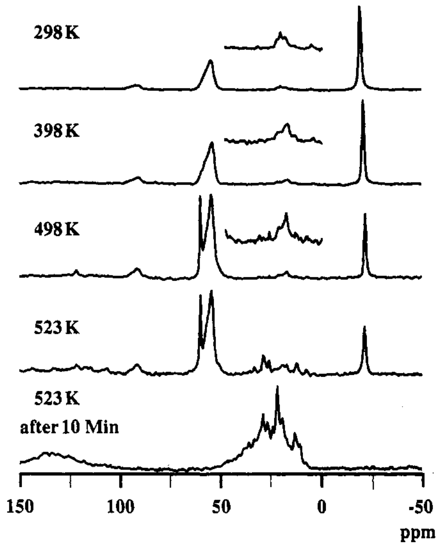

Figure 10. In situ ^{13}C MAS study of the reactions of methyl iodide-^{13}C on zeolite KX.

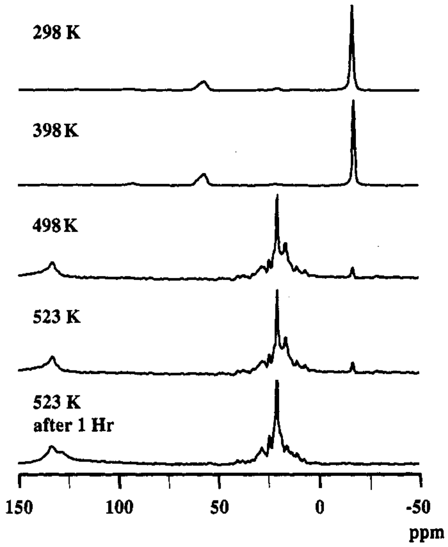

Figure 11. In situ ^{13}C MAS study of the reactions of methyl iodide-^{13}C on zeolite NaX. This was the most active catalyst studied.

bound methoxy formed above 348 K, and hydrocarbon formation occurred to a very limited extent at 523 K. This experiment clearly rules out Bronsted acid catalysis in the conversion of methyl iodide to hydrocarbons on zeolite X. The zeolite HX sample used in this investigation contained an appreciable amount of residual sodium cations (Table I), and it is plausible to associate the weak activity suggested by Figure 12 with those sites. Methyl iodide was unreactive on HZSM-5 at 523 K (not shown).

It is interesting to note that the ^{13}C isotropic shifts of methyl iodide on the X zeolites showed small but significant variations with the cation, and these variations correlated with the catalyst activity. For comparison, the shift of methyl iodide in solution is −20.3 ppm. The observed shifts in the zeolite were NaX, −14.7 ppm; CsX, −15.3 ppm; KX, −17.0 ppm; RbX, −17.2 ppm; and HX, −19.2 ppm.

Effects of Zeolite Framework on Methyl Iodide Conversion. In situ studies of methyl iodide on CsY (Figure 13) and CsZSM-5 (Figure 14) were also performed. From those studies, the order of activity appears to be CsX > CsY > CsZSM-5. Framework-bound methoxys did not form in a detectable amount in CsZSM-5.

^{133}Cs NMR Studies of Alkali Metal–Adsorbate Interactions. Some of the evidence presented thus far suggests an interaction

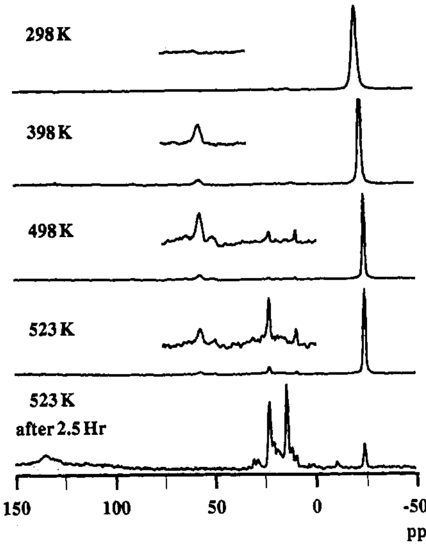

Figure 12. In situ ^{13}C MAS study of the reactions of methyl iodide-^{13}C on zeolite HX. This control experiment suggests that Bronsted acidity is not responsible for the observed activity of the alkali metal-exchanged zeolites. Note also the small extent of methoxy formation.

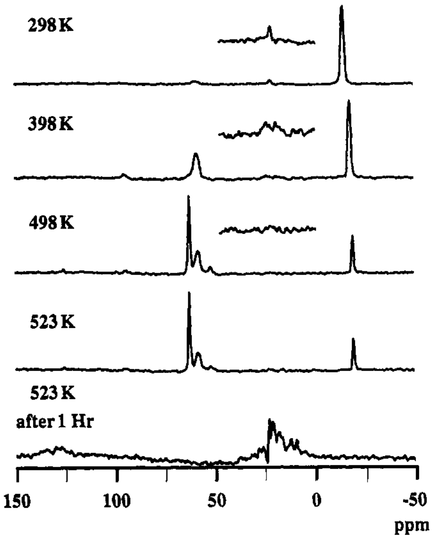

Figure 13. In situ ^{13}C MAS study of the reactions of methyl iodide-^{13}C on zeolite CsY.

between the methyl halide adsorbate and the alkali metal cation in the zeolite; in particular, the ^{13}C resonance of the carbon bearing the halogen is shifted downfield ca. 5 ppm upon adsorption and the alkali metal cation is essential for the highest catalytic activity. In order to better characterize this interaction and more firmly establish a role for the alkali metal carbon in the mechanism of carbon–carbon bond formation, a series of ^{133}Cs MAS NMR experiments was performed. The NMR properties of ^{133}Cs are fortuitous for this investigation.[48] It has a natural abundance of 100%, a large chemical shift range (ca. 400 ppm), and a quadrupole moment of $-3.0 \times 10^{-3} \times 10^{-28}$ m^2, a very small value. It also has a reasonable magnetogyric ratio (0.52 that of ^{13}C) that makes ^{133}Cs a convenient nucleus to study at 8.45 T. The combination of a small quadrupole moment and a large chemical shift range makes the ^{133}Cs isotropic shift very sensitive to chemical environment; indeed, the NMR properties of this nucleus are more reminiscent of a spin $^1/_2$ nucleus than a spin $^7/_2$ quadrupole. NMR studies of cations in zeolites have been reviewed.[49] Ahn, Iton, and co-workers have reported several ^{133}Cs studies of zeolite

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[48] Lindman, B.; Forsen, S. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; pp 129–183.

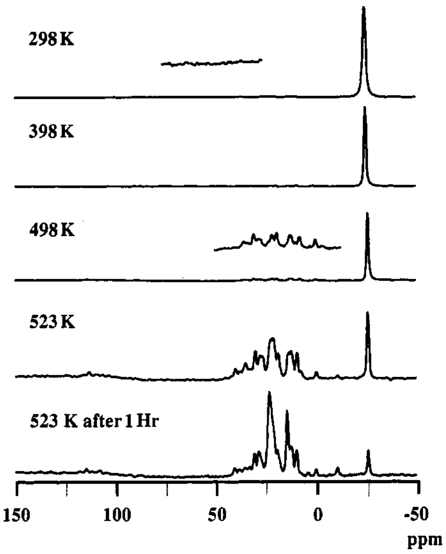

Figure 14. In situ ^{13}C MAS study of the reactions of methyl iodide-^{13}C on zeolite CsZSM-5.

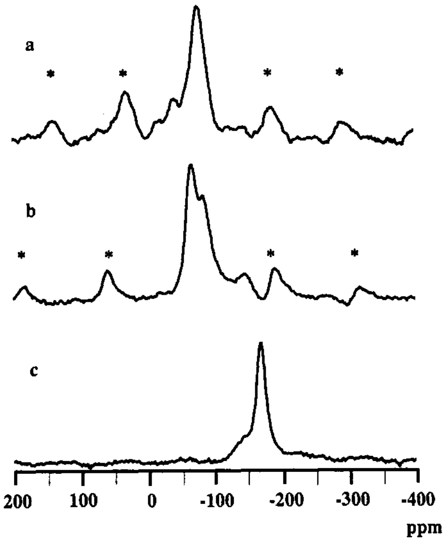

Figure 15. ^{133}Cs MAS NMR spectra of the zeolites studied in this contribution: (a) CsX; (b) CsY; (c) CsZSM-5. * denotes spinning sideband.

A,[50-52] and Gerstein and co-workers have examined Cs mordenite.[53] The observed chemical shift of ^{133}Cs in zeolites at high field apparently does not include a contribution from the quadrupole shift.

^{133}Cs observation was optimized using both solution samples and solid compounds whose spectra have been previously reported by other investigators. Solid-state NMR spectra of quadrupolar nuclei can either selectively excite the central transition only or nonselectively excite all transitions, depending on the relative values of the rf field and quadrupolar coupling constant.[34,35] Using an rf field of 45 kHz, we found that the rf pulses were nonselective for all of the zeolite samples studied. Figure 15 compares ^{133}Cs MAS spectra of CsX, CsY, and CsZSM-5. There are several different cation exchange sites in faujasites, and these are not expected to interact equally with adsorbates. In order to simplify interpretations, cesium–adsorbate interactions were probed on zeolite CsZSM-5. To a first approximation, there is only one type of cation in this material; this is reflected in the simple line shape obtained, especially in the presence of adsorbates.

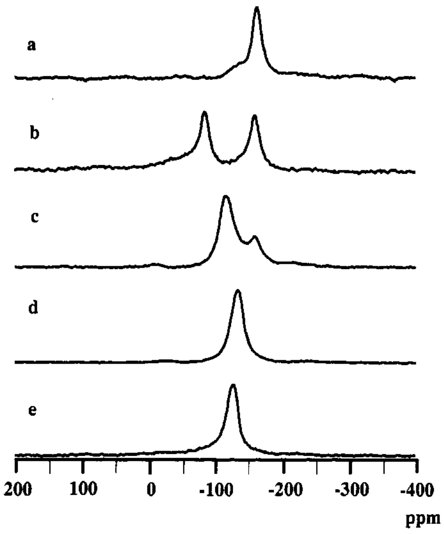

Figure 16. ^{133}Cs MAS NMR spectra showing the effects of the adsorption of 1 equiv of methanol on CsZSM-5. Deep bed adsorption led initially to two peaks, but a uniform distribution of methanol was achieved by heating the sample. Methanol on CsZSM-5: (a) at 298 K before adsorption; (b) at 298 K after adsorption; (c) immediately after stabilizing the temperature at 423 K; (d) at 423 K after 1.0 h; (e) at 298 K after heating.

Loading-dependent ^{133}Cs spectra were obtained for several adsorbates on CsZSM-5. Figure 16 illustrates an important aspect of sample preparation for these studies. Adsorptions on deep beds of catalysts can lead to nonuniform distributions of adsorbate. One equivalent of methanol (relative to Cs content, taken to be 0.6 mmol/g CsZSM-5) were adsorbed on a ca. 15-mm deep catalyst bed packed in an MAS rotor in a CAVERN apparatus, and the rotor was sealed. The ^{133}Cs MAS spectrum of this sample immediately after preparation (Figure 16b) shows two well-resolved peaks, one at the same chemical shift as adsorbate-free CsZSM-5 (−157 ppm) and a second resonance of nearly equal intensity at −82 ppm. Apparently, all of the methanol was adsorbed on the top half of the catalyst bed at 298 K. The sample was then heated to 423 K in the probe, and ^{133}Cs spectra monitored over the course of 1 h showed a gradual coalescence of the two peaks as a result of uniform diffusion of the methanol throughout the catalyst bed. The sample was returned to 298 K, and the ^{133}Cs chemical shift of −124 ppm was recorded as a measure of the effect of adsorbing 1 equiv of methanol. ^{13}C MAS spectra of the adsorbate confirmed that no reaction took place in this procedure.

All of the adsorbates studied induced loading-dependent downfield chemical shifts; the example of acetylene is shown in Figure 17. The ^{133}Cs shift was influenced by up to two or three acetylenes, at which point it leveled off with further increases in adsorbate. The changes in ^{133}Cs chemical shift ($\Delta\delta$) as a function of adsorbate loadings are plotted in Figure 18 for acetylene, methanol, ammonia, water, and methyl iodide. The largest induced shift was seen for a high loading of methyl iodide.

Discussion

Framework-Bound Alkoxy Species. Several previous investigations have described the formation of adsorption complexes consistent with framework-bound alkoxy species from alcohols or unsaturated hydrocarbons on acidic zeolites.[16,36-39] This is the first report of alkoxy formation on a zeolite from an alkyl halide or on a basic zeolite from any adsorbate. The species derived

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(49) Engelhardt, G. In *Introduction to Zeolite Science and Practice*; Van Bekkum, H., Flanigen, E. M., Jansen, J. C., Eds.; Elsevier: Amsterdam, 1988; pp 285–315.

(50) Ahn, M. K.; Iton, L. E. *J. Phys. Chem.* **1991**, *95*, 4496–4500.

(51) Ahn, M. K.; Iton, L. E. *J. Phys. Chem.* **1989**, *93*, 4924–4927.

(52) Tokuhiro, T.; Mattingly, M.; Iton, L. E.; Ahn, M. K. *J. Phys. Chem.* **1989**, *93*, 5584–5587.

(53) Chu, P. J.; Gerstein, B. C.; Nunan, J.; Klier, K. *J. Phys. Chem.* **1987**, *91*, 3588–3592.

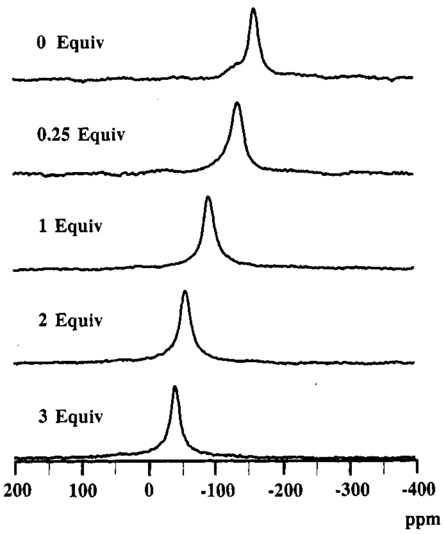

Figure 17. ^{133}Cs MAS NMR spectra of various loadings of acetylene on CsZSM-5.

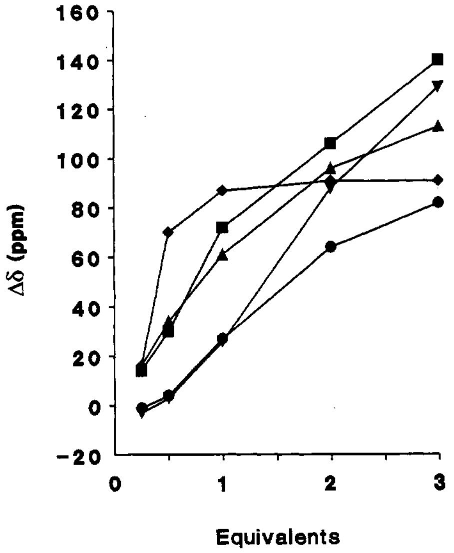

Figure 18. Summary of loading dependent ^{133}Cs shifts for various adsorbates on CsZSM-5: ■, methyl iodide; ▼, ammonia; ◆, water; ●, methanol; ▲, acetylene.

from alkyl iodides on CsX form to a greater extent and are considerably more stable than any alkoxy species previously characterized. This reflects, among other factors, the high concentration of framework sites in CsX as well as the absence of low-energy pathways for secondary reactions of the adsorbates. A systematic investigation of alkyl iodides on X zeolites would be a convenient approach to elaborate upon the chemistry and spectroscopy of framework-bound alkoxy species.

A Systematic View of Reactivity Trends. The reactivity order $CH_3I > CH_3Br > CH_3Cl > CH_3OH$ on CsX zeolite is exactly what one would expect on the basis of the leaving group trend for an S_N2 reaction in solution. The framework oxygen associated with the conjugate base site is, in our view, nucleophilic, and it "attacks" the heteroatom-substituted carbon, displacing the leaving group. A framework-bound alkoxy group is the product of this nucleophilic substitution reaction.

Basicity and nucleophilicity are distinct concepts, and the two need not go hand in hand. However, previous treatments of alkali metal-exchanged zeolites have focused on the former concept; so, for convenience we assume that the former is correlated with the latter. Barthomeuf and co-workers have reviewed basicity in zeolites.[7,8] Basic strength increases with higher Al content and the size of the alkali metal cation. The approximate order of basicity of faujasites is CsX > RbX > KX = CsY > NaX. Zeolites with very low Al contents such as ZSM-5 are predicted to be very weakly basic. With the exception of NaX and possibly KX, the above basicity order satisfactorily accounts for the observed order of methyl iodide activity described in this report. The reason for the anomalous activity of the NaX is unclear.

Interaction of the Adsorbates with the Cesium Cations. Lewis acidity in zeolites and its role in catalysis has recently been reviewed.[25] Previous IR[54] and NMR[18,55] studies have reported complexation shifts from the interactions of olefins with alkali metal cations. In the present study, the ^{13}C shift of ethylene is shifted 2–3 ppm downfield by interaction with strong adsorption sites in CsX, and the effect is larger for $^{13}CH_3I$ and correlates with the catalytic activity of the cation. These effects are mirrored in the response of the ^{133}Cs chemical shift in CsZSM-5 to the introduction of electron-rich adsorbates. Methyl iodide and other adsorbates solvate the Cs^+ cation and pull it away from its coordination environment on the zeolite framework. The framework oxygens induce a significant amount of magnetic shielding at the nucleus, so the net effect of introducing adsorbates is deshielding of the ^{133}Cs.

In summary, both the ^{133}Cs shifts in CsZSM-5 and the ^{13}C shifts in CsX indicate a strong interaction between the alkali metal cation and various adsorbates, alkyl iodides in particular. This observation is consistent with a role for the Lewis acidity of the cation in the reaction mechanism for the conversion of methyl iodide to ethylene.

Proposed Reaction Mechanism. The oxidative coupling of ZCH_2X to $ZCH{=}CHZ$, where X is a halogen and Z is an electron-withdrawing group like NO_2 or aryl, is a familiar reaction in solution.[56] This reaction requires base and is believed to proceed through carbanions and/or carbenes. This investigation has considered only Z = H, CH_3. These substituents are not effective for stabilizing carbanions, and heterogenous routes were therefore considered. The discussion of the mechanism of ethylene formation from methyl iodide on CsX is most conveniently introduced in the context of a debate regarding an analogous problem: the mechanism of the methanol conversion on HZSM-5.[4,5] Free-radical routes have been proposed for MTG chemistry,[57] but no solid evidence has been offered, and radical mechanisms have fallen into disfavor. The temperatures used in our study are low for radical processes, and we do not see the formation of CH_2I_2 from CH_3I, which might be expected with radical chemistry. Carbonium ion routes[58] require very strong acid sites that are not available on CsX. Oxonium–ylide routes have been proposed for MTG chemistry,[59,60] but the burden of evidence[36] is against them for that process on HZSM-5. An analogous chloronium–ylide route has been proposed for the conversion of methyl chloride to hydrocarbons on a bifunctional acidic–basic catalyst (Scheme I).[60] That mechanism is more attractive for reactions on CsX than for analogous processes on HZSM-5 because the existence of basic sites for the deprotonation of the

Scheme I

$$2\ CH_3X \longrightarrow CH_3X^+CH_3 \xrightarrow{-H^+} CH_3X^+CH_2^{\cdot} \xrightarrow{CH_3X} CH_3X^+CH_2CH_3$$

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[54] Liengme, B. V.; Hall, W. K. *Trans. Faraday Soc.* **1966**, *62*, 3229–3243.

[55] Pfeifer, H.; Meiler, W.; Deininger, D. *Annu. Rep. Nucl. Magn. Reson. Spectrosc.* **1983**, *15*, 291–356.

[56] March, J. *Advanced Organic Chemistry, Third Edition*; Wiley & Sons: New York, 1983; pp 1090–1091.

[57] Clarke, J. K.; Darcy, R.; Hegarty, B. F.; O'Donoghue, E.; Amir-Ebrahimi, V.; Rooney, J. R. *J. Chem. Soc., Chem. Commun.* **1986**, 425–426.

[58] Ono, Y.; Mori, T. J. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2209–2221.

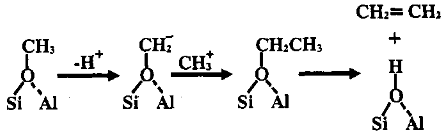
[59] van den Berg, J. P.; Wolthuizen, J. P.; van Hooff, J. H. C. In *Proceedings of the 5th International Conference on Zeolites*; Rees, L. V., Ed.; Heyden & Son Ltd.; London, 1980; pp 649–660.

[60] Olah, G. A.; Doggweiler, A.; Feldberg, J. D.; Feohlich, S.; Grdina, M. J.; Karpeles, R.; Keumi, T.; Inabe, S.; Ip, W. M.; Lammertsma, K.; Salem, G.; Tabor, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 2143–2149.

onium ion is not disputed for the former catalyst as it is for the latter. Unfortunately, we have not observed any spectroscopic signals that we can assign to the proposed intermediates in Scheme I. In some experiments (e.g., Figure 1) small but real signals were observed at ca. –22 and –34 ppm, but the assignments and possible significance of these small signals remain obscure.

Another previously proposed mechanism for MTG chemistry makes several predictions that are consistent with our observations of the chemistry of alkyl iodides on CsX. In 1987, Hellring, Schmitt, and Chang offered an alternative to the onium–ylide mechanism that included prominent roles for framework-bound alkoxy species;[61] we have summarized this mechanism in Scheme II. As originally formulated, the framework site would be methylated under MTG reaction conditions to form a methoxy group (I) which was assumed to be sufficiently acidic to deprotonation and form a sort of ylide stabilized by the zeolite framework. This species is then methylated by a second reactant molecule to form a framework-bound ethoxy species (II). The ethoxy was assumed to rapidly eliminate ethylene at reaction temperature.

Scheme II



The "alkoxy–ylide" mechanism proposed by Chang and coworkers[61] is consistent with many of the observations regarding the conversion of methyl iodide to ethylene. A framework methoxy forms readily from nucleophilic attack by the framework site, possibly with the assistance of a Cs^+ cation in the removal of the I^- leaving group. This species is assumed to be deprotonated by another basic framework site, of which many are available in CsX. This occurs as a second methyl iodide molecule is polarized by a Lewis acid–base interaction with an alkali metal cation and thus is activated for methylation of the alkoxy–ylide. The first species with a carbon–carbon bond is proposed to be the framework-bound ethoxy, which quickly eliminates ethylene at the temperature required for deprotonation of the methoxy. The framework-bound ethoxy readily forms from ethyl iodide, but we have not unambiguously observed it to form during methyl iodide conversion. Thus, although the above mechanism is attractive, it remains unproven.

Prospects for Scale-Up. The reaction of methyl iodide on CsX described in this contribution has much in common with a series of successful industrial processes for iodination of aromatics and related reactions.[62–66] These processes involve the reaction of the aromatic feedstock with I_2 on alkali metal-exchanged X zeolite at 523 K in the presence of molecular oxygen, which oxidizes the coproduct HI to I_2 and H_2O. Oxidation of the HI allows the recycle of the unused iodine and prevents catalyst deactivation by CsI formation. Indeed, without added oxygen, CsI is readily detected in X-ray powder data obtained for samples of CsX reacted with methyl iodide. The formation of H_2O is exothermic and contributes to the favorable thermodynamics of the process. The oxyiodination process shows similarities in both product distribution and kinetics for batch (sealed tube) and flow reactors, and in situ ^{13}C experiments probing oxyiodination of benzene using a protocol analogous to that in Figure 1 gave the expected results (experiments not shown). We carried out several in situ experiments in which methyl iodide was converted to ethylene in the presence of O_2 and saw no adverse effects on the reaction.

An overall scheme for the conversion of methane to ethylene would entail selective monohalogenation using one of the catalysts developed by Olah and co-workers[6] or an improved version thereof, followed by methyl halide coupling on an alkali metal-exchanged X zeolite. Oxidation of the acid coproduct would regenerate the elemental halogen needed for the first step. The low temperature needed for the conversion of methyl iodide to ethylene hints at a competitive process, but further speculation is unwarranted pending flow reactor studies.

Carbon–carbon bond-forming reactions are among the most important in heterogeneous catalysis as well as synthetic chemistry. It has been recognized that the synthesis of fine chemicals is an emerging application of zeolite catalysis.[67,68] Another possible use of the chemistry of alkyl halides on basic zeolites which should be explored is the synthesis of symmetrical functionalized C_4 olefins by the coupling of C_2 intermediates such as XCH_2CH_2OH or XCH_2COOH.

Acknowledgment. This work was supported by Eastman Chemical Company and the National Science Foundation (Grant No. CHE 89-18741). D.K.M. is a Robert A. Welch Foundation Fellow.

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