Methyl Halide Reactions on Multifunctional Metal-Exchanged Zeolite Catalysts

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Abstract: Proximal sites consisting of a divalent metal cation as a hydroxide and/or oxide and an anion site in the zeolite framework are very active for the conversion of methyl halides to ethylene. These studies further support the effects of zeolite framework and halide leaving-group stability reported previously (*J. Am. Chem. Soc.* **1993**, *115*, 4732–4741) and demonstrate multiple roles for divalent metal sites. Whereas the basic zeolite CsX converted methyl iodide to hydrocarbons at temperatures as low as 498 K, this reaction commenced at 248 K on the multifunctional catalyst ZnX. The orders of activity $Zn^{2+} > Cd^{2+}$ and $Mg^{2+} > Ba^{2+}$ suggest that Lewis acidity is one of these roles. Zeolite CuY is very selective for ethylene formation. These reactions were studied by in situ ^{13}C solid-state NMR, by in situ FTIR spectroscopy with a flow cell, and with conventional flow reactors. The active sites of ZnZSM-5 were also probed with ^1H solid-state NMR. The first intermediate is a framework-bound methoxy group. The ^{13}C NMR and FTIR properties of this species have been correlated, and it is shown that this species is very similar or identical to that observed during methanol to gasoline chemistry. A detailed mechanism is proposed for the reaction of methyl halides on Zn and Mg zeolites that includes several explicit roles for the metal.

Introduction

The operative catalytic property of zeolites in most applications is Bronsted acidity.[1,2] Indeed, zeolites and Bronsted acidity are so closely associated that a bifunctional zeolite is tacitly assumed to be one in which active reduced metal particles are present in addition to Bronsted acid sites. As suggested in a number of recent accounts,[3–5] however, diverse roles for zeolites may be possible, and base catalysis is an emerging area of zeolite science. With suitable basic zeolites, methylation of toluene yields styrene and ethylbenzene,[6,7] and 2-propanol is converted to acetone;[8] the corresponding products in acidic zeolites are xylenes and propene.

The more basic zeolites have high aluminum contents in the lattice and are charge compensated by large univalent cations.[1] Thus X type zeolites with a Si/Al ratio slightly above unity are more basic than Y type zeolites (Si/Al > 1.5), which in turn are more basic than ZSM-5 zeolites, with Si/Al ratios of 10 or much greater. The archetypal basic zeolite is CsX, and base strength decreases in the order CsX > RbX > KX > NaX.

In a recent paper we reported that basic zeolites are very active for the conversion of methyl halides to ethylene and higher hydrocarbons.[9] The order of activity of the various zeolites studied was in good agreement with the expected order of basicity, with the exception that NaX was more active than CsX. We rationalized that anomaly in terms of a role for Lewis acidity of the cation in addition to the basicity of the framework. The present contribution demonstrates that the choice of metal cation has a dramatic effect on the activity for methyl halide conversion. Using the in situ NMR protocol, methyl iodide was partially converted to hydrocarbons after several minutes of reaction on zeolite ZnX below room temperature, and 50% conversion was achieved at 323 K. Comparable extents of reaction required temperatures 200 K higher on the more basic zeolite CsX, which lacked strong Lewis acid sites.

As in the previous study,[9] the activity of the methyl halides was in agreement with leaving-group stabilities ($I^- > Br^- > Cl^-$) and for a given metal the activity of the catalyst followed the trend in framework basicity (MX > MY > MZSM-5). Many of the materials prepared with divalent metals were sufficiently active that comparisons were most conveniently carried out using CH_3Cl on catalysts prepared with the less basic but more stable Y framework. The present studies provide strong evidence of explicit roles for the metal in catalyst activity. The activity of ZnY was much higher than that of CdY, and although MgY was very active for CH_3Cl conversion, BaY was nearly inactive.

Tanabe has described a variety of examples of reactions in solutions and on surfaces that proceed by "acid–base bifunctional catalysis" at rates greatly in excess of the sum of the rates estimated for acidic or basic rates alone.[10] Barthomeuf has introduced the term "conjugated acid–base pairs in zeolites" to explain the infrared spectroscopic properties of probe molecules adsorbed in alkali metal-exchanged faujasites.[11] The zeolite-catalyzed reactions reported in this contribution require both multifunctional metal activity and reasonable framework basicity for optimal activity. We propose a mechanism in which this activity results from the joint action of proximally located metal and framework sites. Although a full description of these sites remains to be discovered, the in situ ^{13}C and ^1H NMR and in situ FTIR studies reported here identified some aspects of their structure and function. As reported previously,[9] bound methoxy groups are implicated as precursors to hydrocarbon formation. Parallel in situ ^{13}C NMR and in situ FTIR studies of a system that forms this species in high yield permitted the correlation of these two forms of spectroscopy and demonstrate that the IR spectrum of the methoxy is identical to that described previously in a study

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Table 1. Cation Composition[a] of the Various Zeolites (%)[b]

zeolite	Na^+	Mg^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Cs^+	Ba^{2+}
NaY	91						
MgY	29	40					
CuY	23		51				
ZnX	5			48			
ZnY	23			40			
ZnZSM-5	<2			46			
CdY	21				41		
CsX	36					51	
BaY	25						40

[a] Obtained by neutron activation analysis. [b] Values are reported as percents of the total cation sites, taken as the aluminum content (6.7 mmol of Al/g of NaX, 4.2 mmol of Al/g of NaY, and 0.76 mmol of Al/g of NH_4ZSM-5).

of hydrocarbon synthesis from methanol.[12] These studies also show the partial conversion of M^{2+} to $M^{2+}OH^-$ and Bronsted acid sites during catalyst activation. We speculate that a related but uncharacterized metal oxide species assists in the deprotonation of the methoxy species and stabilizes the resulting carbenoid during the carbon–carbon bond-forming step.

The conversion of methyl halides has proven to be a test reaction which suggests that the chemistry of zeolites is richer than commonly believed. The synergistic action and low-temperature activities of the proximal multifunctional sites are reminiscent of enzymatic catalysis.

Experimental Section

Catalyst Preparation. Zeolites NaX (Si/Al = 1.2) and NaY (Si/Al = 2.5) were obtained from Strem, and HZSM-5 (Si/Al = 19) was obtained from UOP Corp. The exchange process to prepare the various metal zeolites using nitrate solutions was essentially identical to that employed in ref 9 with the exception that the HZSM-5 was first converted to NH_4-ZSM-5 while the sodium faujasites were directly exchanged. Neutron activation analysis, supplemented as necessary by ICP analysis, was used to determine elemental composition of all materials. Representative compositional data are reported in Table 1; when weighted by the charges of the cations, these numbers should sum to 100% of the framework aluminum sites. The elemental analysis data also indicate that copper is overexchanged in hydrated CuY, suggesting that some of the copper was present as Cu^+. All zeolites were activated within one day prior to use with a procedure described previously,[13] with the exception that the highest temperature for the X zeolites was only 623 K. Framework stability was ensured in the investigation by recording ^{29}Si MAS spectra that are sensitive to the framework aluminum content.

Sample Preparation. Methyl chloride-^{13}C, methyl bromide-^{13}C, methyl iodide-^{13}C, and ethylene-$^{13}C_2$ were obtained from Cambridge Isotopes. The details of sample preparation using the CAVERN apparatus were essentially identical to those used previously.[14] To facilitate comparison between different catalysts or reactants, the adsorbate loading was fixed at 0.5 molar equiv relative to the metal cation. The experiments reported here are representative of a large number of studies, most of which were reproduced at least once.

NMR Spectroscopy. The details of these procedures were very similar to those reported in ref 9. Briefly, ^{13}C MAS NMR spectra were obtained at 90.5 MHz using a Chemagnetics CMX-360 spectrometer. Several dozen spectra were collected in each study using experiments such as Bloch decay, cross polarization, and interrupted decoupling. For simplicity, all of the ^{13}C MAS spectra reported here were obtained using quantitative Bloch decay conditions. Typically 200–300 scans were obtained for the faujasites and 700 scans for ZnZSM-5. ^1H MAS spectra were acquired at 359.7 MHz.

FTIR Spectroscopy. In situ FTIR experiments were performed using a Nicolet 510P equipped with a diffuse reflectance cell and a Spectra-Tech catalytic reaction chamber. The reaction conditions were similar to those used in the NMR experiments. One thousand interferograms were acquired for each diffuse reflectance spectrum.

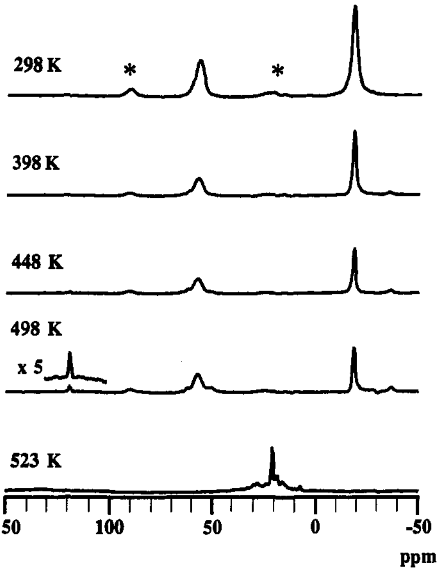

Figure 1. In situ ^{13}C MAS NMR study of the reactions of methyl iodide-^{13}C on zeolite CsX, reproduced from ref 9. Methyl iodide (–15 ppm) was partially converted to a methoxy (58 ppm) upon adsorption at 298 K. Ethylene (122 ppm) formed between 448 and 498 K and oligomerized to form a mixture of hydrocarbons at 523 K. Asterisks denote spinning sidebands.

Flow Reactor Studies. Catalytic flow reactions were carried out in a straight glass reactor with an internal diameter of 7.5 mm and a 2.5-mm wall thickness, giving an outer diameter of 12.5 mm. The catalyst bed was composed of 0.5 g of powdered zeolite mixed with 2 g of glass beads (60–80 mesh). Glass beads (60–80 mesh, 3 g) were also used as a precolumn to heat the reactant gases. ZnY was activated at 673 K for 16 h in flowing helium, while activation of ZnZSM-5 was achieved after 4 h at 873 K.

Reactions were carried out by utilizing mass flow controllers to introduce a stream of methyl chloride (weight hourly space velocity = 2.5 h^{-1}) diluted with helium (1:1 molar ratio) into the reactor. The product stream was passed through a solid sodium hydroxide bed to remove hydrogen chloride and then was analyzed on a $^1/_8$-in. o.d. by 6-ft stainless steel column packed with 100/120 mesh Porapak Q (Alltech Associates) using thermal conductivity detection.

Results

Thus far, in situ NMR studies of methyl halides have been carried out on over 20 different zeolites, and several of the more interesting systems have been investigated by in situ FTIR and/or a conventional flow reactor with on-line GC for product monitoring and lifetime studies. The results reported here were selected to include a survey of the very active zinc zeolites, two pairs of catalysts that demonstrate the effect of cation size on activity (ZnY, CdY and MgY, BaY), and a material with unique properties (CuY). All of the results reported in this contribution proceeded from experiments carried out with either the very reactive adsorbate methyl iodide or the less active but potentially more important starting material methyl chloride. In the cases in which methyl bromide was also studied, its reactivity was intermediate between that of the iodide and the chloride, as reported in the investigation of the alkali metal zeolites. This activity trend reflects the stability of the leaving groups: $I^- > Br^- > Cl^-$.

Many of the figures in this contribution are ^{13}C MAS NMR spectra obtained as an adsorbate reacted on a zeolite in a sealed rotor as it was heated in the NMR probe to the reported temperature. Figure 1 illustrates this in situ NMR protocol for methyl iodide-^{13}C on zeolite CsX. The spectral features in Figure 1 are as follows: The peak at –15 ppm is unreacted methyl iodide; the position of this resonance varies up to 6 ppm downfield relative to the neat liquid depending upon the specific metal cation in the other faujasite zeolites, and it moves ca. 2 ppm upfield in the ZSM-5 materials. The peak at 58 ppm in this study is the

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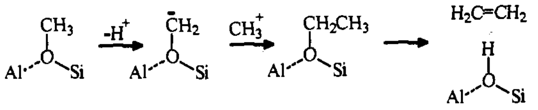
Scheme 1



framework-bound methoxy species that is believed to be an intermediate in the reactions of methanol and methyl halides on zeolites on the basis of previous studies using FTIR[12,15] and NMR.[16-18] This signal, which has small spinning sidebands in Figure 1, was extensively characterized in ref 9. More recently, Bosácek has also reported a detailed study of the formation of this species from methyl iodide and other adsorbates on a variety of zeolites.[16] The important features of his assignments and interpretations are identical to our conclusions. In the present study, the isotropic ^{13}C chemical shifts of the methoxy species were 56–58 ppm, with the exception of those for the species found in ZnZSM-5 and ZnX, which were 60 and 64 ppm, respectively. Referring again to Figure 1, hydrocarbon synthesis was first observed at 448–498 K with the formation of a small amount of ethylene (122 ppm). Complete conversion to hydrocarbons and secondary reactions such as oligomerization and cracking resulted in the mixture of branched aliphatics seen in the spectrum at 523 K; less intense, broad signals are also present from aromatics or coke.

Scheme 1 shows a reaction mechanism with features similar to those in some previous proposals[19,20] for methanol to gasoline (MTG) chemistry on zeolite HZSM-5 and invoked by us to explain the synthesis of ethylene from methyl halides in basic zeolites.[9] Framework ethoxy species were prepared directly from ethyl iodide in ref 9 and were shown to form ethylene at temperatures well below that required for the formation of ethylene from methyl iodide. Scheme 1 also satisfactorily accounts for the gross features of the reactions reported here. In the discussion section, a more detailed mechanism is introduced that includes explicit roles for the metal.

It should be noted that in this study catalyst activity is defined operationally as a comparative measure of the extent of reaction of an adsorbate sealed in a batch reactor, and thus kinetics and thermodynamics may be commingled to a certain degree. More accurate measurements of catalyst activity would require the determination of turnover frequency from flow reactor studies, but the large differences in apparent activity seen in the in situ experiments are expected to be suggestive of activity trends. The variable-temperature protocol was selected such that the reaction was proceeding relatively slowly during the course of spectral acquisition, and the spectral parameters used were such that the spectra were quantitative; thus, these spectra accurately reflect reactant concentrations throughout the course of the reaction.

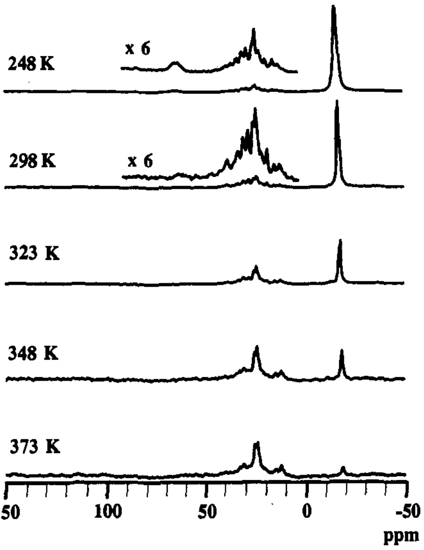


Figure 2. In situ ^{13}C MAS NMR study of the reactions of methyl iodide-^{13}C on zeolite ZnX. Aliphatic hydrocarbons and a methoxy species formed upon adsorption at 248 K. Conversion of methyl iodide to products was complete at 373 K.

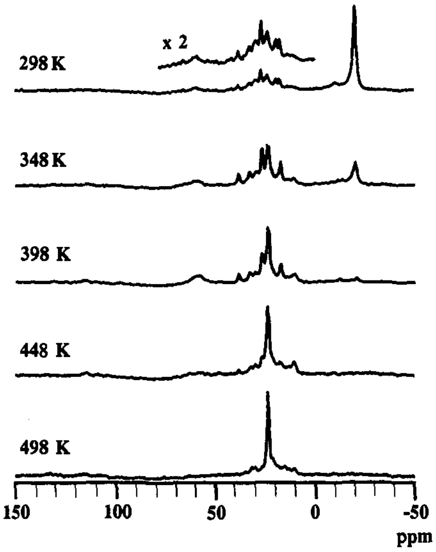


Figure 3. In situ ^{13}C MAS NMR study of the reactions of methyl iodide-^{13}C on zeolite ZnY. Aliphatic hydrocarbons and a methoxy species formed upon adsorption at 298 K, although to a lesser extent (cf. Figure 2). Conversion of methyl iodide was complete at 398 K.

Zinc Zeolites. Figure 1 gives a relative sense of the activity of a purely basic zeolite. Zeolite ZnX is expected to be less basic than CsX, but as Figure 2 shows, its activity for methyl iodide conversion is substantially higher. In this case the adsorption was performed at reduced temperature and the sample transferred to a cold NMR probe prior to spectral acquisition, yet hydrocarbon synthesis was already evident at 248 K. A small methoxy signal was also visible at 64 ppm. The intensity of the latter feature varied in a reproducible manner from catalyst to catalyst. We have not thoroughly investigated this variation, but its intensity probably reflects the steady-state competition between formation of the methoxy and its subsequent reaction to form a carbon–carbon bond. Methoxy formation was more extensive on basic zeolites like CsX, and its consumption was more rapid on very active catalysts such as ZnX. Conversion of methyl iodide to hydrocarbons was 50% complete after the sample temperature was raised to 323 K, and essentially 100% conversion was obtained at 373 K.

Despite the dramatic improvement in activity upon replacing the more basic CsX with the less basic zeolite ZnX, the catalyst framework was still essential to the chemistry, as demonstrated by Figure 3 (methyl iodide on ZnY) and Figure 4 (methyl iodide on ZnZSM-5). The activity order ZnX > ZnY > ZnZSM-5 clearly shows that framework properties contribute to activity. Although ZnX was the more active material in terms of initial conversion, it is expected to be less desirable for some applications than ZnY or ZnZSM-5, as a result of framework stability or coking reactions. Indeed, some dealumination of X type zeolites was seen after conversion of methyl halides at high temperature in the previous investigation,[9] so most of the experiments in the present investigation concern the more stable but still quite active metal Y zeolites.

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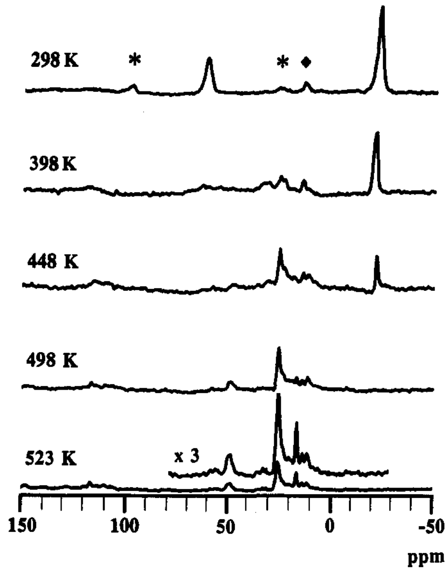

Figure 4. In situ ^{13}C MAS NMR study of the reactions of methyl iodide-^{13}C on zeolite ZnZSM-5. Methoxy formation occurred upon adsorption at 298 K. Production of aliphatic hydrocarbons began at 398 K and was essentially complete at 498 K. Asterisks denote spinning sidebands due to chemical shift anisotropy. The black diamond denotes a single downfield sideband of the methyl iodide resonance due to magnet inhomogeneity.

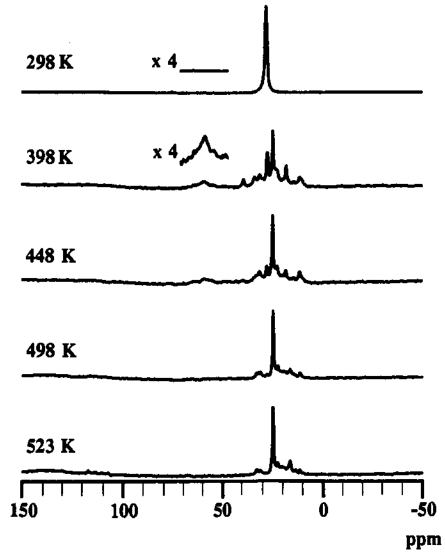

Figure 5. In situ ^{13}C MAS NMR study of the reactions of methyl chloride-^{13}C on zeolite ZnY. This adsorbate was significantly less reactive than methyl iodide. Conversion to aliphatic products began below 398 K and was complete below 498 K.

Effect of Cation Size. The simplest explanation for the activity order $Zn^{2+} > Na^{+} > Cs^{+}$ is Lewis acidity which increases with increasing charge and decreasing radius. Other possible roles of the metal are considered in the discussion section. Several metal Y zeolites were prepared in order to better establish the activity order based on cation size. To facilitate comparison, these experiments were carried out with methyl chloride as the reactant; these samples could be handled at room temperature without reacting, and alkyl chlorides might be more available starting materials in potential processes than alkyl iodides. Figure 5 shows results from an in situ ^{13}C MAS NMR experiment for methyl chloride-^{13}C on ZnY; 50% of the reactant (26 ppm) was converted to hydrocarbons at ca. 370 K, and reaction was essentially quantitative after the sample temperature was raised to 448 K.

Zeolite CdY was selected for comparison with ZnY because of the relative positions of these metals in the periodic table and because it was hoped that the NMR properties of cadmium would prove advantageous for this investigation.[21,22] The latter hope has not yet been realized, but as Figure 6 shows, the activity of CdY for methyl chloride conversion was much lower than that of ZnY—in agreement with the expected effect of cation size. Please see footnote 23 for a safety precaution associated with the preparation of Cd zeolites.

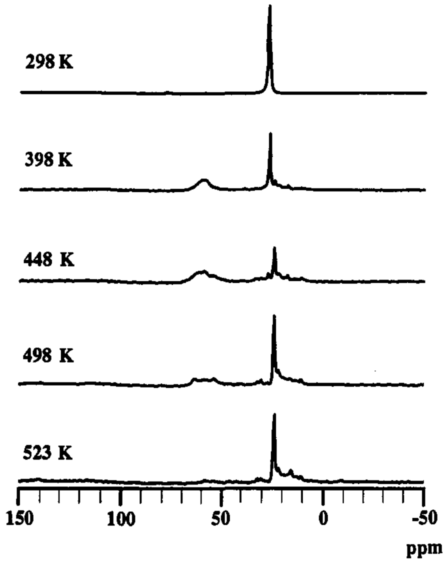

Figure 6. In situ ^{13}C MAS NMR study of the reactions of methyl chloride-^{13}C on zeolite CdY. This zeolite was less active than ZnY. Reaction of methyl chloride was complete at 448 K, although methoxy species persisted at 498 K.

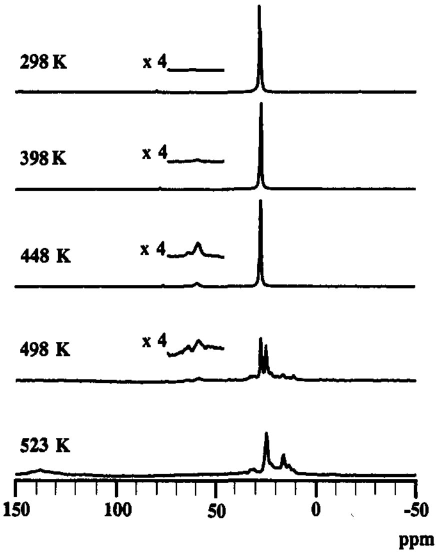

Figure 7. In situ ^{13}C MAS NMR study of the reactions of methyl chloride-^{13}C on zeolite MgY. Conversion to products was rapid at 498 K and complete at 523 K.

Figures 7 and 8 make an analogous comparison of zeolites MgY and BaY, respectively. Zeolite MgY was nearly as active as ZnY, but as expected, BaY with its much larger cation was nearly inactive.

Zeolite CuY. Copper zeolites are of current interest because of their redox properties in a number of reactions including the conversion of propylene to propylene oxide[24] and the reduction of nitrogen monoxide in automobile exhaust.[25] Most of the copper in freshly exchanged CuY was in the paramagnetic Cu^{2+} state,

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(21) Safety note: Activation of one sample of zeolite CdX resulted in the release of volatile Cd metal, as evidenced by the formation of a mirror on the glass vessel.

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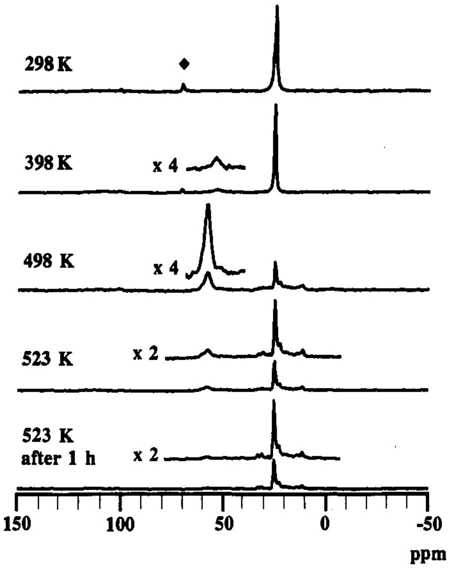

Figure 8. In situ ^{13}C MAS NMR study of the reactions of methyl chloride-^{13}C on zeolite BaY. This was the least active catalyst studied; hydrocarbons formed slowly with extended heating at 523 K. The black diamond denotes a single downfield sideband of the methyl chloride resonance due to magnet inhomogeneity.

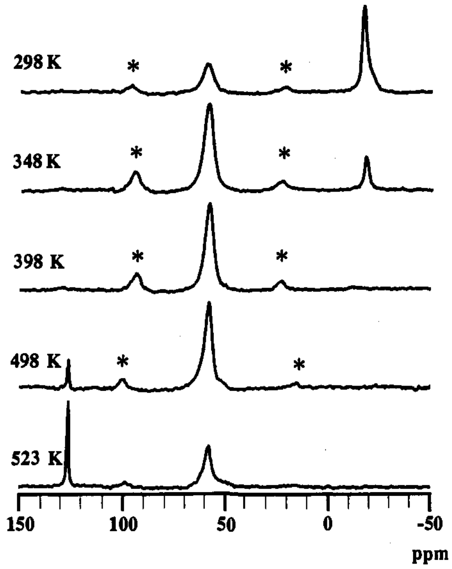

Figure 9. In situ ^{13}C MAS NMR study of the reactions of methyl iodide-^{13}C on zeolite CuY. Complete conversion to methoxy occurred at 398 K, and ethylene was generated selectively below 498 K. Asterisks denote spinning sidebands due to chemical shift anisotropy.

on the basis of the elemental composition data in Table 1. When ethylene-$^{13}C_2$ was adsorbed on freshly activated CuY, ^{13}C MAS spectra (not shown) showed large paramagnetic effects on both the observed shift and line width. Little or no such effects were seen in an in situ experiment for methyl iodide on CuY (Figure 9). This system was unique in that although a large methoxy signal formed at moderate temperatures, the temperature at which hydrocarbon synthesis commenced was more reminiscent of the univalent metal zeolites than of ZnY. Furthermore, the reaction was completely selective for ethylene, at least under the batch reactor conditions of the experiment in Figure 9. One plausible explanation for the unique activity and selectivity of this material and the absence of paramagnetic effects in the ^{13}C spectra obtained during methyl iodide conversion is reduction of the copper to the diamagnetic Cu^+ state by I^-, although good spectral resolution was also obtained in an analogous experiment with methyl chloride.

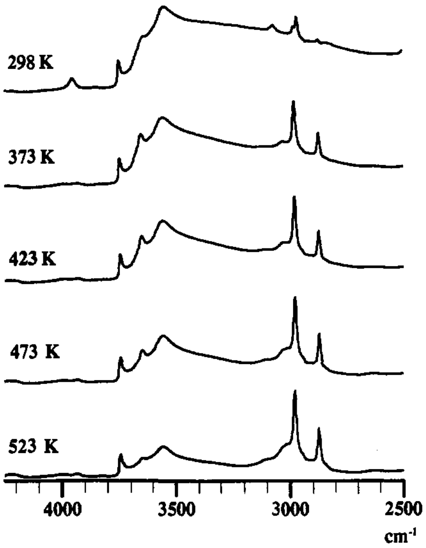

Figure 10. In situ FTIR study of methyl iodide on zeolite CuY under conditions similar to those used for the NMR study in the previous figure. See text for assignments and discussion.

The relative simplicity of the ^{13}C NMR spectra in Figure 9 suggested that methyl iodide on CuY would be a good system for a parallel in situ FTIR study. In particular, the robust NMR signal for the methoxy species and the large temperature range over which this species was stable provided an excellent opportunity to establish that this species was the same as that identified previously in infrared studies of other reactions in zeolites. Figure 10 reports diffuse reflectance FTIR spectra of ca. 0.5 equiv of methyl iodide (natural abundance) on CuY that were obtained as the reaction chamber was heated in a protocol as close as possible to that of the NMR study in Figure 9. All of the FTIR spectra show signals at 3647 and 3553 cm^{-1} due to the two Bronsted sites often seen in faujasites. Residual Bronsted sites have also been seen in the zinc zeolites; their origin and possible significance are discussed later. The peak at 3744 cm^{-1} is the familiar band due to silanols on the external faces of the zeolite crystallites. At 298 K, signals due to unreacted methyl iodide were apparent at 3949 and ~2965 cm^{-1} (several peaks), reasonably close to their positions in the neat solution. Complete conversion to a framework-bound methoxy was effected at 373 K. The two signals at 2976 and 2870 cm^{-1} are nearly identical to those observed by Forester and Howe in an in situ FTIR (flow cell) study of methanol to gasoline chemistry on HZSM-5.[12] Signals at 2980 and 2868 cm^{-1} were assigned by those authors to be the asymmetric and symmetric (CH_3) modes of a methoxy species bridging between a silicon and an aluminum in the zeolite lattice. A small amount of ethylene was also observed in the infrared spectra obtained at the higher temperatures (broad signals at ca. 3000 and 3100 cm^{-1}).

Characterization of the Active Sites. A number of experiments were performed on the zinc zeolites in an attempt to better characterize the active site; the spectra reported here were obtained on the simpler ZnZSM-5 system, but the essential features have also been observed in preliminary experiments on ZnY.

Figure 11 shows ^1H MAS NMR spectra of ZnZSM-5 before and after activation and, for comparison, a spectrum of activated HZSM-5. The unactivated material (Figure 11a) shows a broad signal due to physisorbed water. After activation (Figure 11b), the remaining proton signals include the familiar external silanol resonance at 2.0 ppm and a Bronsted site signal at 4.3 ppm,[26] which are also seen in the HZSM-5 sample (Figure 11c), but activated ZnZSM-5 also shows a ^1H resonance at 2.7 ppm. By analogy to well-characterized resonances due to OH groups on extraframework aluminum,[27] the resonance is assigned to

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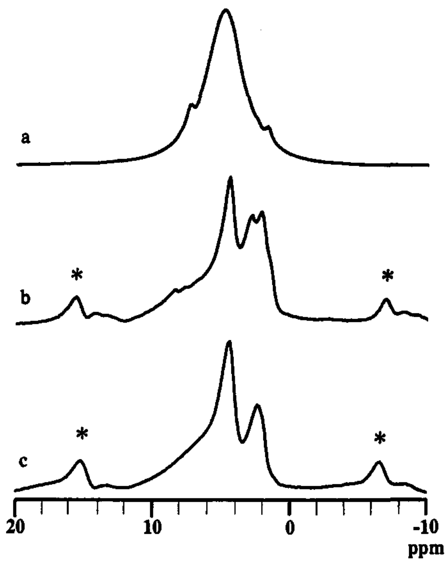

Figure 11. ^1H MAS NMR study of ZSM-5 zeolites: (a) ZnZSM-5 dried at 353 K and 760 Torr; (b) ZnZSM-5 activated at 673 K and 1 × 10^{-4} Torr; (c) HZSM-5 activated at 673 K and 1 × 10^{-4} Torr. Asterisks denote spinning sidebands due to chemical shift anisotropy.

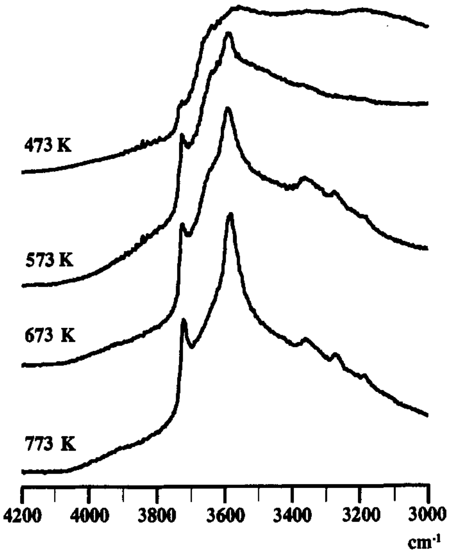

Figure 12. In situ FTIR study of ZnZSM-5 activation. Bronsted acid peaks were generated at 3610 cm^{-1} upon heating. The band due to the $ZnOH^+$ group is visible as a shoulder at 3660 cm^{-1}. The external silanol is at 3740 cm^{-1}.

$Zn^{2+}OH^-$ species in the zeolite channel. The formation and significance of this species and its accompanying Bronsted sites are discussed below.

Figure 12 shows an in situ FTIR study of the activation of ZnZSM-5. The desorption of water yielded well-resolved spectral features at 573 K and above; these spectra revealed a Bronsted site at 3610 cm^{-1}, an external silanol at 3740 cm^{-1}, and the broad, weak band at 3660 cm^{-1} previously assigned by Kazansky to $Zn^{2+}OH^-$ groups in zeolites.[28]

Flow Reactor Studies. Flow reactor studies were carried out in which methyl chloride was contacted for short times on ZnY at 623 K or ZnZSM-5 at 698 K. The product distributions support the general mechanism in Scheme 1. The major products were ethylene, hydrogen chloride, and C_4 and C_6 olefins; the latter are apparently oligomers of ethylene. The yields of propene and C_5 olefins were substantially lower. Lunsford and co-workers have reported that methyl chloride was converted to ethylene and propene on phosphorus-modified MgZSM-5.[29] Ethylene was reported as the initial product, but subsequent oligomerization and cracking resulted in propene formation at 773 K.

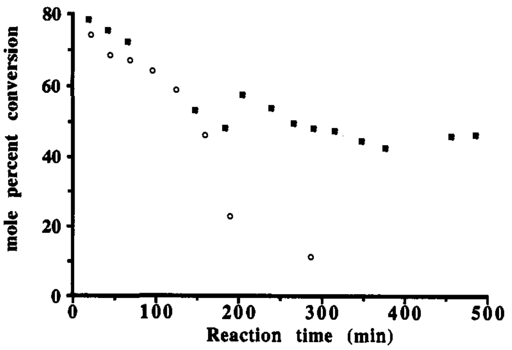

Figure 13. Flow reactor study of methyl chloride conversion to products vs time on stream: (○) methyl chloride on ZnY zeolite at 623 K; (■) methyl chloride on ZnZSM-5 at 698 K.

Scheme 2

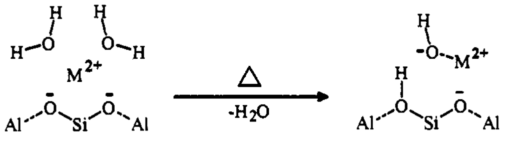

Figure 13 shows plots of conversion vs time on stream for ZnY and ZnZSM-5. Although the ZnY catalyst deactivated after 2 h, presumably due to coking, ZnZSM-5 maintained acceptable activity after longer reaction times.

Discussion

Nature of the Active Sites. The elemental analysis data show that the divalent metal cation compensates the negative charges of two framework sites in the as-prepared zeolites. In the hydrated zeolite, some degree of charge separation is possible, but upon activation the metal cation becomes closely associated with one framework site, and water is dissociated to provide charge compensation.[30] FTIR and ^1H MAS NMR indicate that activation of the Zn zeolite creates Bronsted sites and $Zn^{2+}OH^-$ metal hydroxide species. This process is depicted in Scheme 2, which for compactness shows the two framework sites in next-nearest-neighbor positions.

Metal hydroxide species such as $Zn^{2+}OH^-$ have been characterized previously by other workers,[28,31] as have been metal oxides or metal oxide clusters which have been proposed to form on a variety of zeolites including ZnZSM-5,[32] CuY,[33] and CsX.[34]

Proposed Reaction Mechanism. The flow reactor studies showed that ethylene and its oligomers are major products in the conversion of methyl chloride on ZnY and ZnZSM-5 at short contact times. HCl is the coproduct of these reactions. Secondary reactions on acid sites account for the thermodynamic mixture of hydrocarbons products seen in some of the in situ spectroscopic experiments.

Scheme 1 accounts for the gross features of the reaction of methyl halides on divalent metal zeolites, but since it does not describe an explicit role of the metal, it cannot explain the great difference in activity for the carbon–carbon bond-forming step

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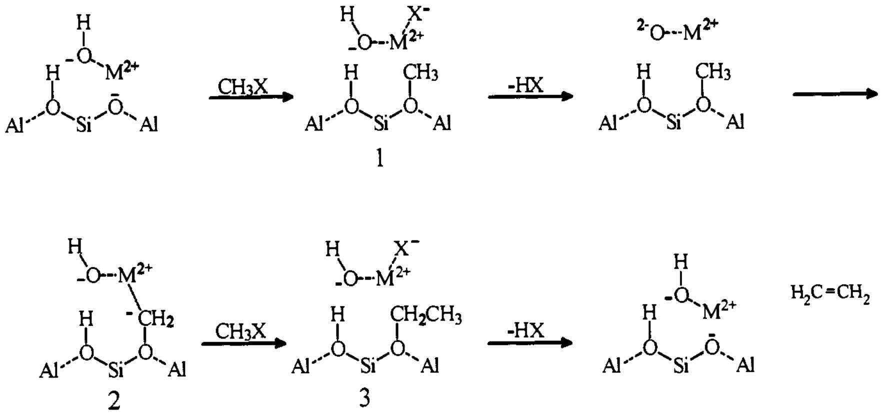
Scheme 3



between, for example, ZnX and CsX. Scheme 3 is an elaboration of the original mechanism that includes an explicit role for the metal in the key steps of hydrocarbon synthesis. This mechanism proposes three intermediate species containing carbon—all of them bound to the zeolite framework and one of them also stabilized by the metal. The methoxy species **1** was thoroughly characterized in the previous investigation.[9] In the present investigation, it forms at low temperatures in NMR-detectable quantities on all of the materials studied, and its relative extent of formation may reflect the relative basicity of the framework as well as the ease of the next step of the reaction. Formation of **1** occurred readily on CuY, but hydrocarbon synthesis did not occur until a much higher temperature on this catalyst. The correlation of the in situ NMR study of the methoxy intermediate with an in situ FTIR study carried out under very similar conditions is a significant result of this investigation. This correlation shows that NMR[9,16-18] and infrared[12,15] experiments are describing the same species and unifies the assignment arguments of both communities in favor of the framework-bound methoxy structure. This correlation also shows that the framework methoxy which forms from methyl halides in metal-exchanged zeolites is very similar if not identical to that observed by FTIR to form from methanol on acidic zeolites, and supports the view that a single mechanism accounts for the conversion of most methane derivatives to hydrocarbons in zeolites.

The second intermediate in Scheme 3, species **2**, is speculated to form during the key step of hydrocarbon synthesis. The framework-bound CH_2 species is variously described as a stabilized carbene or carbanion, depending on how one assigns formal charges.[19,20,29] For MTG chemistry in zeolite HZSM-5 it is unclear how deprotonation of the methoxy occurs, and no metal is available to stabilize the deprotonated species. Neither obstacle exists in Zn or Mg faujasites. The basic framework promotes the formation of methoxy, and the metal oxide or hydroxide species assists in its deprotonation. If the intermediate species **2** bears any analogy to organometallic species such as the relatively stable alkyl zinc compounds[35] or Grignards and other alkyl magnesium compounds,[36] interaction with the metal could provide considerable stability for the CH_2 species over and above interaction with the zeolite framework. A number of in situ NMR experiments have probed the conversion of methanol to hydrocarbons on zeolite HZSM-5 using a protocol very similar to that employed in the present investigation.[37-40] These studies showed that hydrocarbon formation did not commence until ca. 573 or 523 K after an induction period. If these two reactions proceed by similar mechanisms, the formation of hydrocarbons from alkyl halides on ZnX *at temperatures hundreds of degrees lower* is consistent with a dramatic stabilization of the transition state in the metal exchanged zeolite. Methanol is not particularly reactive in the metal-exchanged zeolites, because OH^- is a very poor leaving group. In acidic zeolites the leaving group is the much superior H_2O. In metal-exchanged zeolites the cation assists in the removal of halide leaving groups, and the basic framework "attacks" the methyl halide, forming intermediate **1**. In HZSM-5, methyl iodide is less reactive than methanol.[41] In fairness, it is not clear how far the analogy to MTG chemistry should be pushed; the zeolite environments are very different, and dimethyl ether can form from methanol.

The final intermediate, the framework-bound ethoxy species **3**, has been proposed in a number of studies of MTG and related zeolite reactions.[42] It has apparently never been observed spectroscopically in the conversion of methane derivatives to olefins but was easily synthesized in high yield by direct reaction of ethyl iodide on CsX.[9] This species was eliminated from the framework at temperatures lower than those needed to form ethylene from methyl iodide. Other evidence in support of this mechanism would include unambiguous spectroscopic evidence for the formation of a C_2 framework species during conversion of a C_1 derivative. Species **2** is sure to be close to the transition state, and its direct characterization would be an ambitious undertaking.

Scheme 3 describes a mechanism of carbon–carbon bond formation that involves catalysis by proximal metal and framework sites. Species derived from the metal function as a Lewis acid in the removal of the halide leaving group, as a base in deprotonation of the methoxy group, and possibly in a role reminiscent of organometallic chemistry in the stabilization of the transition state. The zeolite framework also contributes to activity.

Summary. The chemistry encountered with the methyl halide test reaction is somewhat reminiscent of the cooperative, multifunctional catalysis that occurs in enzymes. This study should reinforce the view that diverse chemistry is possible with zeolites. Scale up of alkyl halide conversions on zeolites will require learning to prevent catalyst deactivation, but studies such as this one are useful in that they call attention to primary reaction chemistry that could be exploited further if secondary reactions could be better controlled.

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