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Chloromethoxyl and dichloromethoxyl formation on zeolite ZnY, an in situ NMR and flow reactor study

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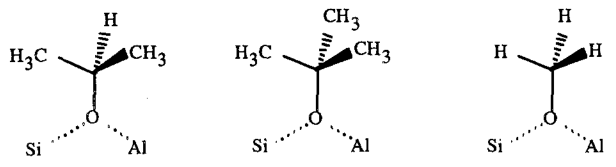
In situ ^{13}C and ^{27}Al MAS NMR and flow reactor studies were used to study the decomposition of dichloromethane and chloroform on zeolite ZnY. The initially formed products were framework-bound chloromethoxyl (from dichloromethane) and dichloromethoxyl (from chloroform) species, analogous to the non-halogenated alkoxyls observed in previous investigations. The principal components of the ^{13}C chemical shift tensors were: chloromethoxyl, $\delta_{11} = 116$ ppm, $\delta_{22} = 79$ ppm and $\delta_{33} = 37$ ppm; dichloromethoxyl, $\delta_{11} = 128$ ppm, $\delta_{22} = 91$ ppm and $\delta_{33} = 65$ ppm. Formation of both species occurred at 298 K, and each decomposed at 423 K. This decomposition formed HCl which dealuminated the zeolite (as monitored by ^{27}Al MAS NMR) causing deactivation (flow reactor studies). Further evidence for the destruction of the zeolite was the NMR observation of CO formation, implying incorporation of oxygen from zinc hydroxyl or framework sites. Although ZnY is shown to be unsuitable for catalytic chlorocarbon destruction, the observation of chloromethoxyl and dichloromethoxyl species is significant, and the formation of halogenated alkoxyl species should be considered in future investigations of halocarbon chemistry on oxides and molecular sieves.

Keywords: dichloromethane; chloroform; zeolite; alkoxyl; ^{13}C MAS NMR

1. Introduction

A number of previous NMR studies have identified various framework-bound alkoxyl species formed by the reactions of selected olefins or alcohols on acidic zeolites or alkyl monohalides on metal-exchanged (basic) zeolites. Haw identified the isopropoxyl species **1** (scheme 1) which formed during the low temperature oligomerization of propene on zeolite HY [1,2]. The observation of the *t*-butoxyl species **2**, formed by dehydration of 2-methyl-2-propanol-^{13}C in zeolite HZSM-5, was first reported by Aronson and later by Stepanov [3,4]. Murray [5,6] formed the methoxyl species **3** from methyl chloride, methyl bromide and methyl iodide on a variety of alkali-, alkaline earth- and transition metal-exchanged zeolites and characterized an ethoxyl species formed from ethyl iodide on CsX. Bosáček [7] reported similar observations for the reactions of methyl iodide on basic zeolites. Other NMR studies of halocarbons in zeolites include Maciel's study of trityl cation formation from carbon tetrachloride and benzene [8], and the reactions of HFC-134, reported by Grey [9].



(1) (2) (3)

Scheme 1.

Kazansky has described theoretical work that supports the intermediacy of alkoxyl species in zeolite acid catalysis [10]. More recently, van Santen has suggested that alkoxyl species need not form in some zeolite catalyzed reactions [11] and Chang has presented mechanistic evidence that toluene disproportionation does not proceed through a methoxyl route [12]. Regardless of the generality of this proposal, many electrophilic species can bond to the zeolite framework, and when formed these must be considered in detailed descriptions of the reaction chemistry.

In this letter we report the ^{13}C NMR characterization of the chloromethoxyl species **4** and dichloromethoxyl species **5** (scheme 2). These formed from the reactions of methylene chloride-^{13}C and chloroform-^{13}C, respectively, on zeolite ZnY. **4** and **5** were indefinitely stable at 298 K, but decomposed at 423 K with dealumination

(4) (5)

Scheme 2.

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of the zeolite, as shown by ^{27}Al MAS NMR. Dealumination also occurred upon direct reaction of anhydrous HCl under similar conditions. Other NMR evidence for involvement of the zeolite framework in chlorocarbon decomposition included formation of ^{13}CO as the major carbon-containing product. Flow reactor studies of dichloromethane on ZnY also showed rapid deactivation, verifying the limitations of ZnY for halocarbon destruction.

2. Experimental

Zeolite NaY was obtained from Strem Corp. The exchange process to prepare the ZnY zeolite used a solution of the nitrate and was identical to that employed previously [5]. ^{29}Si and ^{27}Al MAS NMR as well as neutron activation analysis determine that the elemental composition of the zeolite is as follows: Si/Al = 2.6; 10.9 mmol Si/g; 4.2 mmol Al/g; and 1.7 mmol Zn/g. All materials were activated prior to use with a multistep procedure over 13 h to 673 K [1].

Chloromethane-^{13}C, dichloromethane-^{13}C, and chloroform-^{13}C were obtained from Cambridge Isotopes. Gaseous chloromethane-^{13}C was transferred from a cylinder to a gas bulb attached to a vacuum line. Liquid dichloromethane-^{13}C and chloroform-^{13}C were transferred prior to use into adsorption vessels under an anhydrous nitrogen atmosphere. The reagents were then degassed by three freeze–pump–thaw cycles. Anhydrous hydrogen chloride was prepared from the reaction of phosphorous pentachloride and ammonium chloride at 413 K under vacuum [13]. The gas was collected in a bulb immersed in liquid nitrogen. All NMR samples were prepared by adsorption at 298 K using an improved shallow bed CAVERN apparatus similar to that described elsewhere [14].

^{13}C MAS NMR spectra were acquired on either a CMX-360 spectrometer at 90.5 MHz or on a home built instrument operating at 50.0 MHz. Several dozen spectra were collected in each study utilizing experiments such as Bloch decay, cross polarization and dipolar dephasing [15]. All reported ^{13}C MAS Bloch decay spectra were obtained with quantitative conditions. ^{27}Al MAS spectra were acquired at 93.8 MHz using a 10° flip angle [16]. Active spin speed control was used in all cases.

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. The bed was composed of 0.5 g powdered ZnY mixed with 2 g of glass beads (60–80 mesh) to allow for free flow of reactant gases through the fine mesh zeolite powder. Glass beads (60–80 mesh, 3 g) were also used as a precolumn to heat the reactant gases. ZnY was activated for 16 h utilizing a temperature ramp program with a maximum temperature of 723 K and flowing nitrogen. Mass flow controllers and a liquid bubbler were used to saturate a stream of nitrogen with dichloromethane (weight hourly space velocity = 1.26 h^{-1}, or 0.46 equivalents h^{-1}) diluted with a pure nitrogen flow (5 : 1 molar ratio nitrogen : dichloromethane) into the reactor. HCl was trapped prior to GC detection by means of a NaOH column placed before the sampling loop. The products were analyzed on-line utilizing a HP 5890 GC with a thermal conductivity detector. The column was a 30 m long capillary with a 0.53 mm internal diameter and a 7 μm dimethyl polysiloxane coating (Restek).

3. Results and discussion

Fig. 1 shows ^{13}C MAS NMR spectra from a representative study of chloromethane-^{13}C on zeolite ZnY at 398 K. Two isotropic peaks were observed at 56 and 29 ppm, and these were assigned to the framework bound methoxyl 3 and unreacted chloromethane, respectively. The spectroscopic and chemical behavior of the methoxyl was consistent with prior work [5,6]. For example, the resonance at 56 ppm is enhanced with cross polarization, survives dipolar dephasing and displays sidebands due to chemical shift anisotropy at lower spin-

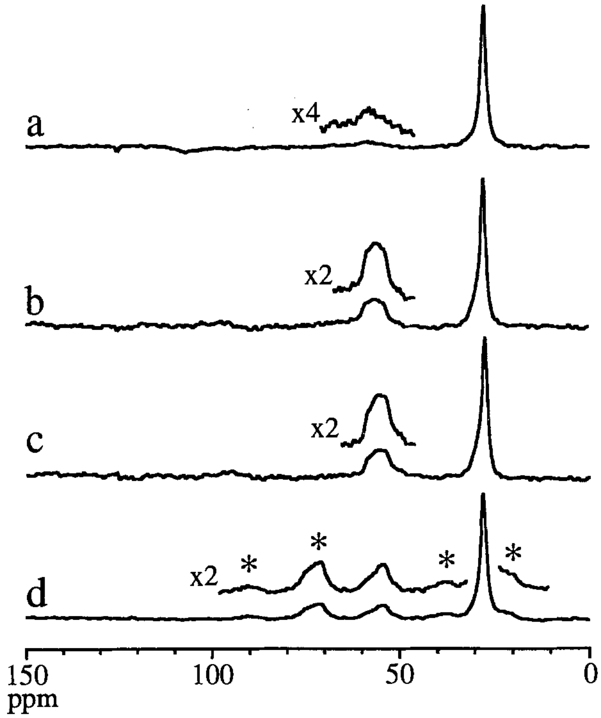

Fig. 1. 90.5 MHz ^{13}C MAS NMR spectra of 0.1 equiv. chloromethane-^{13}C on zeolite ZnY. Chloromethane-^{13}C reacted at 398 K to generate a framework bound methoxyl (56 ppm). Spectra shown are: (a) quantitative Bloch decay, (b) cross polarization, (c) dipolar dephasing, (d) slow MAS cross polarization. The spinning speed was 3500 Hz in (a)–(c) and 1500 Hz in (d). Spectra (a)–(c) are averages of 256 transients, while (d) is a result of 1024 transients. Asterisks denote spinning sidebands.

Table 1
Summary of ^{13}C relaxation rates, principal components of the chemical shift tensor and line widths for methoxyl, chloromethoxyl and dichloromethoxyl species on ZnY at 298 K. All measurements were performed at 4.7 T and 8.45 T. ^{13}C T_1 was measured via inversion recovery at 90.5 MHz

Species	^{13}C T_1 (s)	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	$\Delta\delta^{a}$ 4.7 T (ppm)	$\Delta\delta$ 8.45 T (ppm)
methoxyl^{b}	0.6	56	82	81	9	5.2	5.3
chloromethoxyl	2.1	78	116	79	37	8.3	6.3
dichloromethoxyl	2.9	95	128	91	65	14.8	10.6

[a] Full width at half maximum based upon a pure Lorentzian line shape.
[b] Ref. [4].

ning speeds. The principal components of the ^{13}C chemical shift tensor for **3** were calculated by the method of Herzfeld and Berger [17] and are summarized in table 1. The value 0.02 for the asymmetry parameter (η) reflects the local three-fold symmetry of the methyl group. The ^{13}C T_1 of **3** was relatively short, 0.6 s. The methoxyl study provides a basis for comparison of the well established species **3** with the novel species **4** and **5**.

Fig. 2 shows that dichloromethane-^{13}C (55 ppm) reacts on ZnY at 298 K to form a significant amount of a species with a ^{13}C isotropic shift of 78 ppm. This resonance was enhanced by cross polarization, eliminated by dipolar dephasing and displayed significant sidebands at lower spinning speeds. These results are fully consistent with the assignment of the peak at 78 ppm to the framework-bound chloromethoxyl species **4**. Note that the resonance due to the methoxyl species **3** survives dipolar dephasing as a result of rapid rotation about the O–C bond; such rotation would be greatly reduced, if not precluded, for species **4**, and this explains the difference in dipolar dephasing behavior. The lack of reorientation of the framework bound chloromethoxyl is also reflected in the chemical shift anisotropy observed with slow MAS (table 1). Most significantly, the asymmetry parameter for the ^{13}C tensor of **4** was 0.90, consistent with an appreciable reduction in time-averaged symmetry. Furthermore, the ^{13}C T_1 of **4**, 2.1 s, was significantly longer than that of the methoxyl. In addition to this evidence, the ^{13}C isotropic chemical shift of 78 ppm for the framework-bound chloromethoxyl species compares favorably with a structurally similar model compound, bis(chloromethyl) ether, previously reported at 76.9 ppm [18].

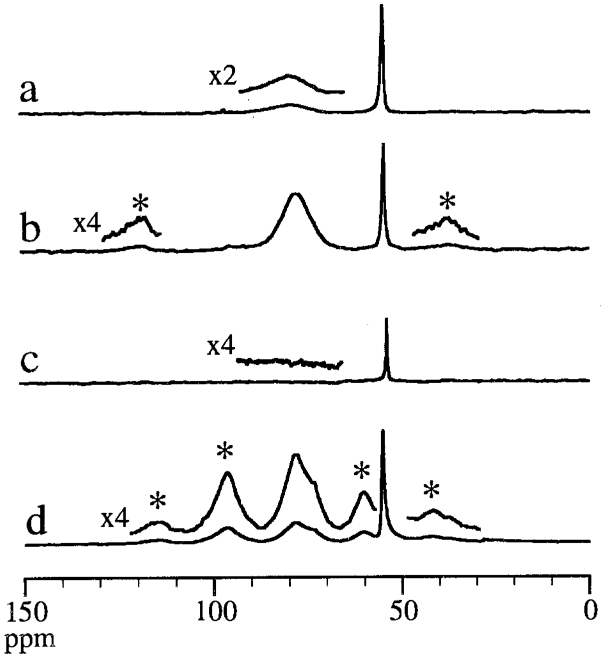

Fig. 2. 90.5 MHz ^{13}C MAS NMR spectra of 0.5 equiv. dichloromethane-^{13}C on zeolite ZnY. Chloromethoxyl (78 ppm) was formed upon adsorption of dichloromethane (55 ppm) at 298 K. Spectra shown are: (a) quantitative Bloch decay, (b) cross polarization, (c) dipolar dephasing, (d) slow MAS cross polarization. The spinning speed was 3700 Hz in (a)–(c) and 1600 Hz in (d). Spectra (a)–(c) are averages of 512 transients, while (d) is a result of 4660 transients. Asterisks denote spinning sidebands.

Fig. 3 reports selected ^{13}C MAS spectra from a similar study of chloroform-^{13}C on ZnY. Two isotropic peaks were observed in the Bloch decay spectrum at 78 ppm and 95 ppm; the former was assigned to unreacted chloroform, while the latter was enhanced by cross polarization, did not survive 50 μs of dipolar dephasing and had a relatively long T_1, 2.9 s. The 95 ppm peak was, therefore, assigned to the dichloromethoxyl species **5**. The principal components of the ^{13}C chemical shift tensor (table 1) were again consistent with restricted dynamics and absence of local three-fold symmetry, having an asymmetry parameter of 0.78.

Table 1 reports the ^{13}C MAS line widths (in ppm) of **3**, **4** and **5** at two dissimilar magnetic field strengths. For the methoxyl **3**, the line width (in ppm) is essentially field independent, as is typical for hydrocarbons in the solid state. However, it is very well established that dipolar coupling to nearby quadrupolar nuclei (the archetypal example is ^{14}N) can broaden or even split ^{13}C MAS peaks. This results from the fact that the field of the quadrupolar nucleus is not quantized along the Zeeman direction, but rather the axis of the effective field. For sufficiently large values of B_0, the quadrupolar term in the Hamiltonian can be neglected, and one then predicts that MAS will be effective in removing the dipolar cou-

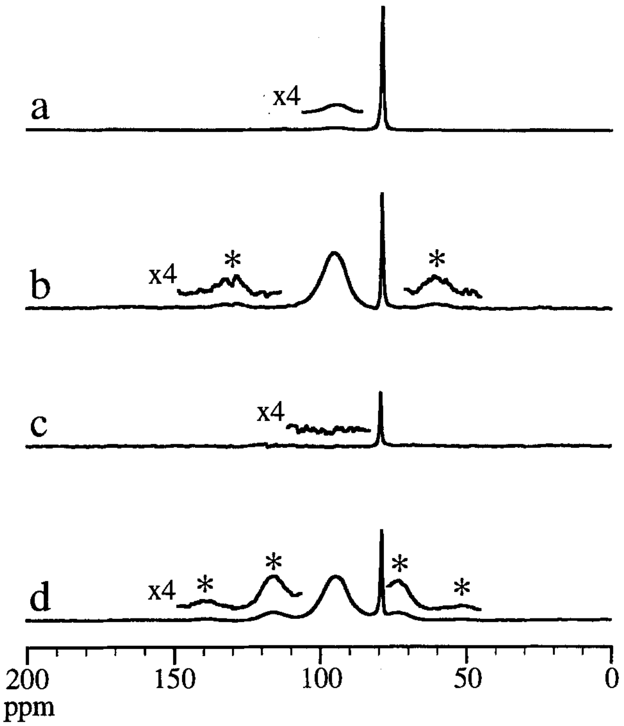

Fig. 3. 90.5 MHz ^{13}C MAS NMR spectra of 0.5 equiv. chloroform-^{13}C on zeolite ZnY. Dichloromethoxyl (95 ppm) was formed upon adsorption of chloroform (78 ppm) at 298 K. Spectra shown are: (a) quantitative Bloch decay, (b) cross polarization, (c) dipolar dephasing, (d) slow MAS cross polarization. The spinning speed was 3000 Hz in (a)–(c) and 2000 Hz in (d). Spectra (a)–(c) are averages of 512 transients, while (d) is a result of 4096 transients. Asterisks denote spinning sidebands.

pling between the quadrupolar nucleus and the observed nucleus (e.g., ^{13}C). However, at lower field strengths the quadrupolar term is important, and MAS may be only partially effective for averaging dipolar couplings [19,20].

Both ^{35}Cl and ^{37}Cl are NMR active ($I = 3/2$) and each has an appreciable magnetogyric ratio. Thus, the observation in the solid state of ^{13}C resonances from carbons bound to chlorine can be challenging; this particular problem has been studied by Harris [21]. Our results in table 1 show that the ^{13}C MAS lines of **4** and **5** broaden at lower fields, and this is very strong evidence that these species are immobilized and have one or more chlorine nuclei at or near bonding distance.

Our original hope in studying the chemistry of dichloromethane and chloroform on ZnY was that we might gain some insight into catalytic reactions of environmental significance; it may be that haloalkoxyl species will be involved in future catalytic processes for the destruction of halocarbons, unfortunately ZnY is rapidly deactivated by dichloromethane or chloroform. Indeed, heating samples of these adsorbates in the MAS rotors to 423 K or higher resulted in the appearance of carbon monoxide in the ^{13}C spectrum, and the likely sources of oxygen were the consumption of zinc hydroxyl species [6] or destruction of the framework.

Another major product of the decomposition reactions was HCl, and we established that this product rapidly dealuminated ZnY. This was investigated by acquiring ^{27}Al MAS spectra of ZnY samples subjected to various treatments; and these studies are summarized in fig. 4. Activated ZnY with adsorbed chloroform showed a single (broad) resonance at 54 ppm. This result is similar to that obtained for dehydrated ZnY with no adsorbates. Upon rehydration of this sample, the resonance sharpened and moved slightly downfield to 59 ppm. Water "relaxes" the zeolite framework and significantly lowers the quadrupole coupling constant of ^{27}Al – a well known result. Figs. 4a and 4b clearly demonstrate that neither activation, chloroform adsorption or rehydration result in any detectable amount of octahedral aluminum. Samples in which dichloromethane or chloroform was converted to carbon monoxide (as observed by ^{13}C MAS NMR) showed evidence of extensive dealumination; approximately 30% of the observable ^{27}Al intensity was located in a resonance near −3 ppm upon rehydration (fig. 4c). Indeed, when ^{13}C and ^{27}Al MAS spectra were acquired nearly simulta-

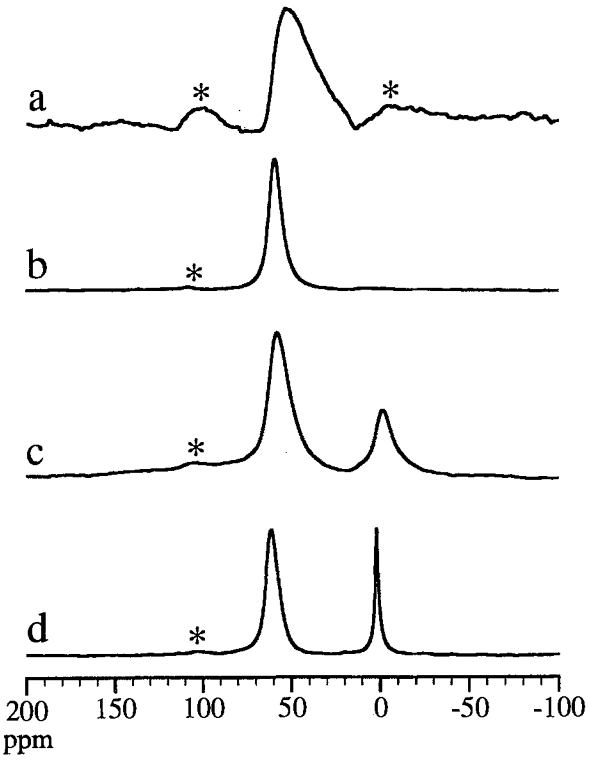

Fig. 4. 93.8 MHz ^{27}Al MAS NMR spectra of ZnY. (a) Activated ZnY with 0.5 equiv. chloroform-^{13}C per Zn showed only tetrahedral aluminum (ca. 54 ppm). (b) Activated ZnY followed by rehydration had no detectable dealumination due to thermal treatment or water treatment. (c) ZnY following conversion of dichloromethoxyl to CO showed a large amount of dealumination (−3 ppm) following rehydration of the zeolite. (d) Following activation and room temperature adsorption of 2.03 mol HCl per mol of Zn. The spinning speed was 5500 Hz for all ^{27}Al spectra. All spectra were a result of 1024 transients. Asterisks denote spinning sidebands.

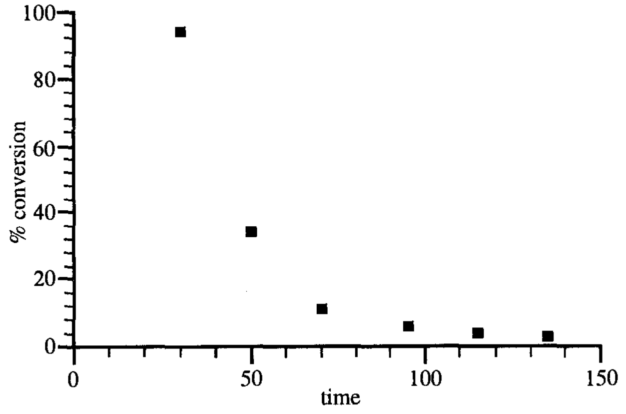

Fig. 5. Representative flow reactor study of dichloromethane on ZnY at 423 K: (■) the conversion 0.46 equiv. per hour of CH_2Cl_2 to CO. Due to reactor and trap design, quantitation of CO production commenced following 30 min of reactant flow.

neously during the course of a variable temperature experiment, it was obvious that decomposition of the halocarbon and dealumination of the lattice proceeded at similar rates. Finally, fig. 4d shows the result of treating ZnY with 2.03 mol of HCl per mol of Zn, heating to 448 K, followed by cooling and rehydration. The results in fig. 4 strongly implicate HCl as the cause of dealumination. The small differences in the isotropic shifts for the octahedral aluminums in figs. 4c and 4d reflect ligand effects and small contributions from the quadrupole shift.

Flow reactor studies using low space velocities suggested that the reaction of dichloromethane with the zeolite was approximately stoichiometric, and this process was closely correlated with deactivation. Fig. 5 shows a representative result, where the molar percent conversion is defined as moles of carbon monoxide produced over the moles of dichloromethane and carbon monoxide. After ca. 0.5 mol of CH_2Cl_2 per mol Zn had flowed over the zeolite, the conversion was reduced to ca. 40%. The conversion had dropped to nearly zero by the time a full equivalent of CH_2Cl_2 had been introduced.

4. Conclusions

CH_2Cl_2 and $CHCl_3$ are converted to CO and HCl on zeolite ZnY. The HCl destroys the activity of the zeolite by dealumination and other means that provide oxygen for the formation of CO. *Thus, this reaction is stoichiometric rather than catalytic.* In the course of this study, we formed the first two reported haloalkoxyl species bound to a zeolite framework, and these were characterized by ^{13}C MAS NMR.

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