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Linear, primary monohaloalkane chemistry in NaX and NaY faujasite zeolites with and without Na^0-treatment
Zeolites as nucleophilic reagents II

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Abstract

This work undertakes, we believe for the first time, a study of the chemistry of alkyl halides in Na^0 treated zeolites. It concludes that untreated zeolites do nucleophilic chemistry to the degree that the host is electron donating. It concludes that Na^0 treated zeolites do a mixture of nucleophilic, electron-transfer, and free radical chemistry.

Zeolites NaX and NaY and their Na^0 treated forms (Na^0/NaX and Na^0/NaY) were exposed to linear1-haloalkanes (Cl, Br, I). NaY is inert in all cases. Framework alkoxy and halide ion are formed in NaX from the Br- and I-alkanes in an electrophilic attack of framework oxygen on the alkyl halide, while the leaving of the halide ion is assisted by the electrostatic attraction of the NaX site III or III′ Na ions.

In Na^0NaX and Na^0/NaY direct reaction of Na^0 with the alkyl bromide or iodide yields a larger alkane and halide ion, probably via a free radical mechanism involving two Na^0 and two alkyl halides.

The NaX–alkyl chloride chemistry includes exclusively or partly dehydrohalogenation, yielding 1-alkenes and chloride ion. Na^0/NaX or Na^0/NaY–alkyl chloride dehydrohalogenation chemistry yields chloride with 2-alkenes in low yield and alkanes in higher yields. 1-Chloropropane yields the framework propoxy and propene from NaX and yields these products plus other olefins from Na^0/NaX.

Overall the yields and reactivity fall into a pattern of Lewis basicity increasing in the order NaY < NaX < Na^0/NaY < Na^0/NaX.

Keywords: Zeolite; Nucleophilic; Alkylhalide; Substitution; Dehydrohalogenation

1. Introduction

This work undertakes, we believe for the first time, a study of the chemistry of alkyl halides in Na^0 treated zeolites. It concludes that untreated zeolites do nucleophilic chemistry to the degree that the host is electron donating and that Na^0 treated zeolites do a mixture of nucleophilic, electron-transfer, and free radical chemistry.

The characteristics of the reactions of zero-valent alkali metals with halogens and organohalogens are sufficiently violent so as to render them subjects of textbooks and safety documents. Consequently, little is known in detail of their mechanisms. Evidence exists from gas-phase studies of the reaction of K with I_2 for a through space electron transfer to form a highly coulombically attractive $K^+–I_2^-$ ion pair in the textbook "harpoon" reaction [1]. In zeolites alkali metals exist in special environments or give rise to powerful alkali electron-donor species [2–9], These forms of Na^0 in porous zeolites constitute interesting, unusual, and potentially useful reagents for reactions with adsorbed halogen and alkyl halide molecules. Zeolites in the absence of Na^0 also have electron donor characteristics [10].

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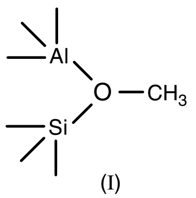
In this study we have examined the chemistry of the Na^0-treated faujasite zeolites, NaX and NaY (abbreviated Na^0/NaX and Na^0/NaY), with the alkyl halides, methyl iodide, ethyl bromide, ethyl iodide, 1-chloropropane, 1-chlorobutane, and 1-iodobutane. The *tert*-butylhalides were examined in a recent infrared (IR) spectroscopic study and exhibited no reactivity in untreated NaX [11]. The present study does not otherwise attempt to explore the differences between primary, secondary, and tertiary monohaloalkanes in the reactivity with Na^0/NaX or Na^0/NaY and untreated NaX and NaY. In order to allow us to distinguish these results from results due to the interactions of the alkyl halide molecules with the faujasite framework alone, we also examined the untreated faujasite zeolites upon adsorption of these molecules. The results point to a different mechanism for the alkyl chlorides than the bromo- and iodoalkanes. Thus this work focuses on the mechanism of the primary monobromo- and monoiodoalkanes. The behavior of the primary alkyl chlorides, the comparative behavior of the primary, secondary, and tertiary monohaloalkanes, and the behavior of the polyhaloalkanes will be explored in future works.

The results of these studies point to the importance of several unexpected factors.

In the work of Choi [12] the shifts of the near-ultraviolet bands of adsorbed halogen molecules indicate an enhancement of the Lewis basicities of the framework oxygen atoms by zeolite type, with greater basicity in NaX than in NaY [12]. This oxygen atom Lewis basicity was seen to be further increased with the degree of Na^0-treatment in the experiments on Br_2 adsorbed in Na^0/NaX and Na^0/NaY. Br_2 does not undergo reaction in Na^0NaX or Na^0/NaY. This order of relative basicities in the zeolite types and treatments will be seen to characterize the chemistry between alkyl halide and zeolite.

The zeolite will prove to play an unexpected and very active role in the chemistry, a significant amount of which occurs even without Na^0 treatment. The zeolite plays the role of electron donor, as well as a leaving group facilitator in the case of NaX, in nucleophilic displacement reactions. We have recently completed a study of this kind on the chemistry of dimethyl methylphosphonate (DMMP) [13]. In this study DMMP products were identified, consistent with the nucleophilic displacement of methyl methylphosphonate and methylphosphonate ions by zeolite oxygen. The presence of a framework methoxy species (I) was implicated and possibly observed.



(I)

The formation of framework methoxy species (I) has been reported by several workers [14–16] upon exposure of the zeolites to alkyl halides. The corresponding ethoxy species has also been observed upon the exposure of the zeolites to ethyl halide [17]. A tertiary framework butoxy species has also been observed upon adsorbing 2-methyl-2-propanol into acid H-ZSM-5 [18].

2. Experimental details

All adsorbates were obtained from Sigma–Aldrich in the highest grade available and were used as received. Zeolites X and Y were also obtained from Sigma–Aldrich. The Si/Al ratios of NaX and NaY were 1.23 and 2.63, respectively. The zeolites were heat-treated under vacuum, on a system capable of achieving 1.2×10^{-8} Torr, at 450 °C for 24 h. Complete dehydration of zeolites is imperative, because even trace amounts of water can affect cluster formation during Na^0 treatment. There was no measurable residual water content in the NaX and NaY used in these experiment according to thermogravimetric analysis (TGA).

For the preparation of the Na^0 treated zeolite, previously dehydrated zeolite was thoroughly mixed with NaN_3 in the glove box under an argon atmosphere. (Caution: mixing should not be done with abrasive tools and containers, nor should the mixture be ground. NaN_3 is explosive.) The sample container was then attached to the vacuum line. The argon gas was pumped out, and the sample was re-heated cautiously through the NaN_3 decomposition temperature (675 K). Upon treatment in this manner, zeolites NaX and NaY turned blue and pink respectively. The blue and pink colors of the Na^0/NaX and Na^0/NaY are lost upon exposure to water, due to the gettering action of Na^0 on water, and the presence of these colors precludes significant residual water content in these samples.

The adsorbates were taken through three freeze–pump–thaw cycles before adsorption into the zeolites by evaporation or sublimation. After adsorption, samples were left overnight for equilibration.

Electron paramagnetic resonance (EPR) measurements of the Na^0 treated zeolites were characterized before and after exposure to the adsorbate. UV–visible diffuse reflectance measurements were made on the adsorbate-exposed, Na^0/treated zeolite samples and on the untreated, exposed zeolite samples.

Three hundred and sixty mega hertz of ^1H NMR measurements were performed on a Bruker AM 360 spectrometer, using $CDCl_3$ extracts of adsorbate exposed, sodium treated zeolite samples or extracts of exposed untreated samples. A total of 8 scans were recorded for each sample. A Bruker AC 300 spectrometer with modifications for solid state NMR experiments was used for the solid zeolite samples. The samples of adsorbate exposed zeolite or sodium treated zeolite samples were transferred to spinners in the Ar atmosphere of a glovebox. The solids after extraction were transferred to the spinners in air. 75.4 MHz ^{13}C CP/MAS spectra were recorded, employing a 6.0 μs, π/2, high power, proton excitation pulse. The contact time was 2 ms with a recycle delay of 3 s and a magic-angle spinning rate of 4 kHz. A total of 512 transients were collected with proton decoupling and the FID was treated with an apodization function (line broadening: 15 Hz) prior to Fourier transform. Proton and carbon spectra are referenced to an external (tetramethylsilane) TMS sample.

Infrared (IR) measurements were made of the adsorbate-exposed zeolite, the exposed, treated zeolite and of the gaseous products evolved upon exposure. Characterization of residual product and of structural changes in the zeolite was investigated using the KBr pellet technique. The weights of the zeolite including adsorbate were chosen to be approximately 0.8% of the total pellet weight (≈0.1 g). A Bruker Equinox 55 IR spectrometer with a resolution of 2 cm^{-1} was employed to obtain the spectra. A total of 128 and 32 scans were recorded for each sample of zeolite and adsorbate and for the gaseous products, respectively, over the spectral range 4000–400 cm^{-1}. An IR gas cell (100 cm^3) was used to analyze the gaseous products from the reaction of the sodium treated zeolite with the adsorbate. The gas cell was first evacuated to a pressure of about 2.5×10^{-8} Torr before collecting the gas. A Canulla technique was used to collect the gas from the zeolite tube. Argon gas was used to back fill the cell to atmospheric pressure.

All of the above measurements were done at room temperature.

3. Experimental results

Solid state ^{13}C CP/MAS NMR spectra of NaX, NaY, with Na^0 treatment at 3 atoms per supercage and without treatment were obtained after exposure to ^{13}C enriched CH_3I in amounts of 3 molecules per supercage of zeolite. The spectra are shown in Fig. 1. A peak at $\delta = 56$ ppm is observed in NaX exposed to $^{13}CH_3I$ that lies in the region typical for the methoxy group ^{13}C and has been attributed to the framework methoxy species (I) [14–16]. It is noteworthy that much (I) is formed from Na^0/NaX, a comparable amount from untreated NaX (58 ppm), a very small amount, if any, from Na^0/NaY, and none from NaY. The intensity of the peak at $\delta = -17.5$ ppm is from unreacted $^{13}CH_3I$. The unreacted $^{13}CH_3I$ peaks are weak in Na^0/NaX but relatively strong in NaX (−17.5), NaY (−22 ppm), and Na^0/NaY (−20 ppm). A small peak at 50 ppm in $^{13}CH_3I$ exposed, Na^0/NaY, by comparison with an authentically $^{13}CH_3OH$ loaded NaY, is attributable to $^{13}CH_3OH$. A very, very small peak from (I) is found at 60 ppm in $^{13}CH_3I$-exposed, Na^0/NaY. Similar relative amounts of a framework ethoxy species (appearing at 69 ppm) and residual, unreacted ethyl bromide or iodide are observed in similar experiments with ethyl bromide or iodide exposed, NaX, NaY, Na^0/NaX, and Na^0/NaY. Similar results were found with 1-iodobutane but not with 1-chlorobutane. The different result with 1-chlorobutane will be discussed separately. 1-Chloropropane yields the framework propoxy and propene from NaX and Na^0/NaX, with the latter also yielding additional olefins, yet to be identified.

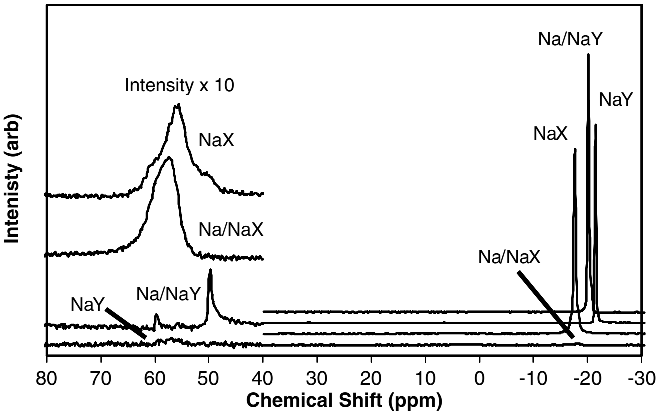


Fig. 1. Solid state 75.4 MHz ^{13}C CPMAS NMR spectra of $^{13}CH_3I$ exposed Na^0/NaX and Na^0/NaY zeolite (denoted Na/NaX, Na/NaY, respectively) and untreated NaX and NaY (denoted NaX, NaY, respectively). The levels of activation were 3 Na^0 per supercage and the exposure level was also 3 molecules per supercage. The 40–80 ppm region is magnified by a factor of 10 for comparison of the small peaks in this region.

The relative amounts of CH_3I extracted with $CDCl_3$ from samples, in which CH_3I at several different levels of loading was brought into contact with NaX, NaY, Na^0/NaX, and Na^0/NaY at several Na^0 levels, was examined with ^1H NMR. The strong CH_3I peak at 2.2 ppm found in CH_3I exposed NaX and NaY, was significantly reduced in CH_3I-exposed Na^0/NaX and Na^0/NaY. The CH_3I was generally more greatly reduced in the CH_3I-exposed, Na^0/NaX than the CH_3I-exposed, Na^0/NaY. Similar results were found for the $CDCl_3$ extracts of the ethyl bromide and iodide, 1-chloropropane, 1-chlorobutane, and 1-iodobutane exposed zeolites. A minor deuterium exchange of ($\leqslant 1.6$ times the original $CHCl_3$ content of the solvent of the order of 1%) was observed as $CHCl_3$ in the $CDCl_3$, upon performing the extraction after the alkyl halide treatments of Na^0/NaX, Na^0/NaY, NaX, and NaY. Methanol is not found in any of the $CDCl_3$ extracts.

Reactions of the longer-chain alkyl chlorides, that exist as easily handled liquids, show a related but distinct pattern of behavior upon exposing the alkyl halides to the Na^0-treated and untreated zeolites. Examination of 1-chlorobutane exposure of Na^0-treated and untreated NaX leaves a small amount of residual 1-chlorobutane in the $CDCl_3$ extracts from NaX but none in the extracts from Na^0/NaX. However, in an examination of the ^{13}C solid state NMR spectrum of the exposed NaX zeolites, no characteristic, immobilized framework alkoxy species is observed in the vicinity of 75 ppm, as was found in the iodobutane exposure. Instead, ^{13}C peaks with characteristic alkene ^{13}C chemical shifts in the range 110–140 ppm were found. See Fig. 2. The product from untreated NaX, found in the zeolite, along with a small amount of unreacted 1-chlorobutane, appears to be 1-butene

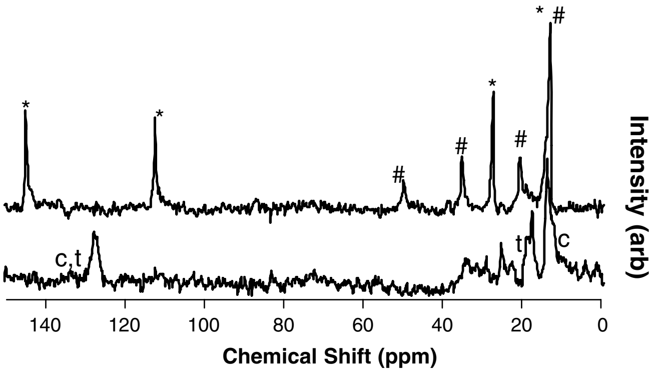


Fig. 2. Solid state 75.4 MHz ^{13}C CP/MAS NMR spectrum of NaX (top) and Na^0/NaX (bottom) exposed to 1-chlorobutane at a level of 3 molecules per supercage. The level of Na^0 treatment was also 3 Na^0 per supercage. Assignments are (*)1-butene, (#) residual 1-chlorobutane, (c) *cis*-2-butene, and (t) *trans*-2-butene.

($\delta = 140$, 113, 27.4, 13.4 ppm) [19]. (A trace of unreacted 1-chlorobutane also appears in the ^{1}H NMR spectrum of the $CDCl_3$ solvent in which untreated NaX is exposed to the adsorbate.) However, the semi-quantitative nature of the ^{13}C solid state NMR measurements does not rule out the presence of a small amount of 2-methyl propene ($\delta = 141.8$, 111.3, 24.2 ppm [19]) in the zeolite. The product from Na^0/NaX, also found with little if any unreacted 1-chlorobutane in the zeolite, appears to be *cis*- ($\delta = 124.2$, 11.4 ppm [10]) and/or *trans*-butene ($\delta = 125.4$, 16.8 ppm [19]).

The visual blue and brick-red colorations of the Na^0/NaX and Na^0/NaY, respectively, both fade or disappear gradually upon exposure of the samples to the alkyl halides. The observations are corroborated by the reduction or disappearance of both the 490 nm band and 646 nm shoulder of Na^0/NaX and the 496 nm band of Na^0/NaY upon exposure to CH_3I and the reduction of the EPR spectra of the Na^0 treated zeolites [2].

The FTIR spectra of the gaseous products from the reactions of Na^0/NaX and Na^0/NaY treated at a level of 3 Na^0 per supercage exposed to 3 molecules of CH_3I per supercage of zeolite are given in Fig. 3. The spectra were compared to authentic spectra of CH_4 published by the Chemistry Website at Widener University [20] and C_2H_6 published by NIST [21]. The spectra exhibit primarily the bands of C_2H_6 in the C–H stretching and CH_2 bending regions. In the reaction of CH_3I with Na^0/NaX about 1.5 times more C_2H_6 was formed than CH_4. In the reaction with Na^0/NaY almost exclusively C_2H_6 was formed. No detectable gaseous products were found upon exposure of untreated NaX and NaY. Exposure of Na^0/NaX to ethyl bromide and iodide gave gaseous products, whose IR spectra resembled that of ethane, but with relatively less rotational structure. However, there were subtle differences that suggest the presence of a longer alkane, such as butane in the experiments with ethyl bromide and iodide. The IR spectra of the gases evolved from the exposure of Na^0 treated and untreated NaX and NaY to 1-chlorobutane were examined. Substantial amounts of alkane products of greater size than ethane were evolved upon exposure of Na^0/NaX and Na^0/NaY to 1-chlorobutane. There was also evidence for the presence of olefin. There was also evidence of a trace of olefin in the IR spectra of gases evolved from Na^0/NaX and Na^0/NaY exposed to ethyl bromide and 1-iodobutane. No evidence was found for the presence of HCl gas. No gaseous products were evolved from the untreated NaX and NaY.

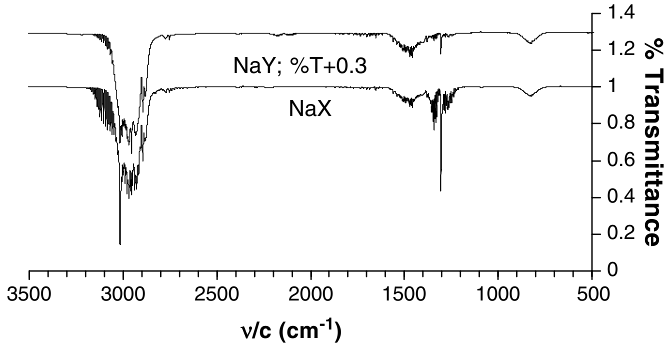


Fig. 3. IR spectra of the gaseous products recovered from the exposure of Na^0/NaX and Na^0/NaY to CH_3I. The level of treatment was 3 Na^0 per supercage and the exposure level was also 3 molecules of CH_3I per supercage.

The gaseous products obtained by CH_3I exposure of Na^0/NaX and Na^0/NaY were also examined with gas chromatographic mass spectrometry (GC/MS). Difficulties with the detection of the fast methane elution peak resulted in the ability to detect only higher molecular weight species. The results confirm the presence of ethane with no higher molecular weight species (except for possible traces of oxygen) in both CH_3I exposed, Na^0/NaX and Na^0/NaY.

Experiments were performed in order to determine the amount of iodide ion generated upon exposure of Na^0/NaX, Na^0/NaY, NaX, and NaY to methyl iodide. The zeolites were treated at the level of 3 atoms per supercage and loaded with CH_3I at 3 per supercage. The exposed zeolite was washed free of CH_3I, a potential source of I^- in the presence of certain precipitation agents, e.g. Ag^+. The washed, exposed zeolite was then agitated in water and filtered from the filtrate with $Pb(NO_3)_2$. The PbI_2 precipitate was dried and weighed. The percentages of I^- precipitated as PbI_2 per mole of CH_3I are given in Table 1.

Generally similar results were found for the ethyl halides and 1-chlorobutane, although somewhat higher halide ion

Table 1
Yields of iodide ion per mole of CH_3I (at 3 per supercage) in Na^0/NaX and Na^0/NaY (at 3 Na^0 per supercage) and untreated NaX and NaY

Zeolite	Yield (%)	Uncertainty
NaX	49.8	0.2
NaY	3.22	0.11
Na^0/NaX	64.8	4.0
Na^0/NaY	45.8	9.1

yields were observed in untreated NaY than for methyl iodide.

4. Discussion

The formation of the framework alkoxy species from methyl, ethyl, and butyl iodide, from ethyl bromide, and from 1-chloropropane, like products formed in our study of phosphonates in Part II of this series [13] suggests that the zeolite framework can act as a nucleophile. The framework oxygen serves to displace the negatively charged, halogen, leaving group in this nucleophilic attack on the alkyl halide carbon that bears the halogen. The yields suggest that the nucleophilicity of the zeolite is in the order $Na^0/NaX > NaX > Na^0/NaY > NaY$. This order is the same as we have found for the zeolite framework oxygen basicity, as determined by the shifts in the visible absorption band of Br_2 and I_2 in our work and as was found for I_2 in the work of Choi [12]. The slightly differing framework methoxy, solid state, ^{13}C NMR chemical shifts observed in NaX and NaY may also be due to differences in the electron donating character of the framework oxygen atom [12]. 1-Chlorobutane, in contrast with 1-iodobutane, does not give a detectable framework butoxy species, but instead undergoes a zeolite assisted dehydrohalogenation. 1-Chloropropane in NaX, on the other hand, gives both framework propoxy and propene. We plan a separate paper on the dehydrohalogenation, showing that it still appears to take advantage of the electron denoting character of the framework oxygen atom and leaving group assistance from the zeolite Na^+.

We make reference to several reports of the solid state ^{13}C MAS CP NMR spectra of alkoxy species in the literature [22,23]. The most relevant of these is by Bosácek et al. [22] who observe the spectrum of the methoxy species from CH_3I in evacuated samples of NaX. The chemical shift is in excellent agreement with the 55 ppm observed in our work. The presence or absence in these studies of spinning sidebands evidently relates to the absence or presence of other species in the zeolite that induce averaging of the anisotropy of the spectrum. Our samples have been exposed to an atmosphere of Ar, which evidently induces averaging.

The amounts of unreacted, adsorbed, residual CH_3I and CH_3I that are extracted from the system generally mirror the amount of framework methoxy formation. A noteworthy exception is the significant reduction in CH_3I extracted from Na^0/NaY, while only a very small amount of framework methoxy is observed. Also noteworthy is the formation of methanol. The very small amounts of residual CH_3I in Na^0/NaX and Na^0/NaY are not always observed in the extract. We attribute this to CH_3I that may exist in the zeolites at sites too distant to the Na^0 or appropriate framework oxygen sites to react. Mobilization by the solvent enables reaction of the adsorbate to occur before being extracted.

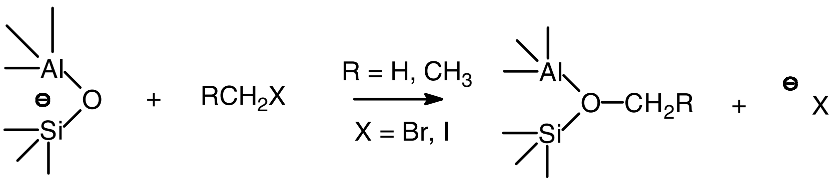
Therefore, we propose the mechanism in Scheme 1 to explain these observations.

One of the consequences of Scheme 1 is the formation of halide ion. The iodide analysis of the experiments on CH_3I in Table 1 semi-quantitatively supports this mechanism. Large iodide yield is seen in Na^0/NaX, where large framework methoxy (I) formation is observed. Significant iodide formation is also observed in untreated NaX and in Na^0/NaY. However, the iodide yields are large in the latter cases, where small, very small, and unobservable framework methoxy (I) formation is observed in Na^0/NaY and untreated NaY, respectively.

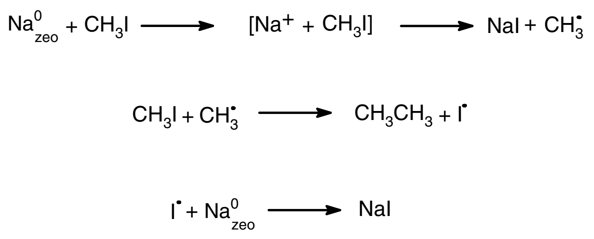
The complete absence of framework alkoxy formation in NaY and the very small amount observed in Na^0/NaY suggests a fundamental difference between the X and Y zeolites. As proposed for phosphonates [13], the presence of Na^+ in supercage sites III or III′ in X type zeolite stabilizes the transition state of the nucleophilic substitution reaction. The supercage Na^+ serves to stabilize, electrostatically, the incipient halide leaving group, X^-, in the mechanism of Scheme 1. The comparative paucity of site III or III′ Na^+ in Y type faujasite zeolite [24–29] does not provide this kind of stabilization for the formation of the framework alkoxy species in NaY.

The formation of methane and ethane from CH_3I is not predicted in Scheme 1, nor does it take into account the reducing power of the Na^0 treatment of the zeolite. It is clear that ethane is only produced when the zeolite is Na^0 treated. It appears to be significant that only ethane, with no methane, is formed in Na^0/NaY, in which essentially no framework methoxy is formed. We conclude that the framework methoxy is not needed to form ethane, consistent with the mechanism in Scheme 2. This would explain the sizeable iodide yield in Na^0/NaY, in spite of the very small amount of framework methoxy (I) formed. The appreciable, residual CH_3I in Na^0/NaY and in the extract from it, is consistent with the 40–50% iodide yield.

Conversely, it appears to be reasonable that in untreated NaX, in which framework methoxy (I) is formed, no ethane is formed. The fact that framework methoxy (I) in the absence of Na^0 treatment does not lead to ethane



Scheme 1. Proposed mechanism for the formation of framework alkoxy and halide ion from zeolite and alkyl halide.

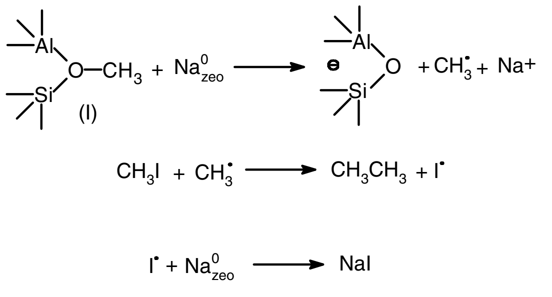


Scheme 2. Proposed mechanism for the formation of ethane and sodium iodide from methyl iodide and Na^0 treated zeolite.

appears to make sense from the redox standpoint. The methoxy to ethane transformation is a reduction process, requiring a reducing agent, and no Na^0 has been introduced. The ability of untreated NaX to consume CH_3I appears to be limited, in view of substantial residual CH_3I observed in the zeolite and in the extract and in view of the ca. 50% iodide yield.

In Na^0/NaX the evident consumption of CH_3I, through the apparently combined processes of Schemes 1 and 2, seems to be capable of achieving the somewhat higher iodide yield of 60–70% observed and the lower residual amount of CH_3I observed in the zeolite and in the extract. However, the evidence does not rule out the possibility of a hybrid mechanism involving the framework methoxy (I), shown in Scheme 3.

Substantial formation of methane occurred in the Na^0/NaX but was formed in small amounts in untreated NaX. Thus the circumstantial evidence appears to associate the greater or lesser methane formation with the greater or lesser presence of the framework methoxy (I) in Na^0/NaX or NaX. The source of the hydrogen to convert the framework methoxy to methane is problematical. However, the zeolite is known from its characteristic IR band to contain substantial amounts of siloxy species, which could be the source of hydrogen for methane formation from the framework methoxy species. This would be a two-electron reduction that is feasible in the Na^0 treated NaX, with Na^0_{zeo} being the reducing agent. However, this would be hard to explain in the untreated NaX, where the methane yield is indeed correspondingly small. Alternatively, more complex chemistry with other organic species may be taking place the product of which is methane. Additional work beyond the scope of this project will be required sort out the potentially complex mix of nucleophilic, electron-transfer, and free radical chemistry that is probably involved in this system.



Scheme 3. Proposed alternative mechanism for the formation of ethane and sodium iodide from methyl iodide and Na^0 treated zeolite in the presence of framework methoxy.

Rather than forming a framework alkoxy species, 1-chlorobutane exposed, untreated NaX yields 1-butene. This is clearly a dehydrohalogenation type product, but no evidence of HCl (or other products) is found in an IR investigation of potential gaseous products of the chemistry. Dehydrohalogenation product (propene) is also found along with framework propoxy from 1-chloropropane exposed NaX.

The formation of small amounts of methanol from CH_3I is observed in Na^0/NaY, but not in NaY. None is found in Na^0/NaX or untreated NaX. A source of oxygen for this process is difficult to identify without turning to trace amounts of water or oxygen present in the zeolite, perhaps from the brief and limited air exposure during the insertion of the non-air-tight NMR rotor cell into the NMR instrument. We speculate that water is the oxygen source and that the phenomenon is restricted to NaY, in which water mobility is expected to be greater than in NaX because of the lower sodium ion content. This is owing to the larger Na^+ content in NaX than in NaY, particularly in the supercage, which is able coordinatively to tie down the water molecules. This restriction is less severe in NaY. Results discussed above point to the exclusive operation of the mechanism of Scheme 2 in Na^0/NaY. Presumably traces of methanol are formed by the reaction of methyl radical with traces of water. We have little evidence about the fate of the small amounts of hydrogen atoms that would be formed in such a reaction, which may simply combine with other methyl radicals or iodine atoms.

The very nature of the chemistry being observed for the alkyl halides clearly suggests the likelihood of chemistry occurring to $CDCl_3$, the extraction and NMR solvent. However, the advantages of $CDCl_3$ for these purposes were found to outweigh the small, carefully monitored amount of hydrogen–deuterium exchange. The observation of the exchange in both Na^0/NaX and Na^0/NaY, but not in NaX and NaY, suggests that the mechanism does not involve a framework alkoxy species from nucleophilic attach on $CDCl_3$. This work does not otherwise appear to generate any evidence relevant to the specific hydrogen–deuterium exchange mechanism.

It is known that Na^0 exists in NaX and NaY as a color center, ionic complex, Na_4^{3+} in Na^0/NaY or Na_6^{5+} in Na^0/NaX; it is also known that in the same preparations Na^0 may also exist as neutral sodium clusters, Na_n^0 [2–10]. The proportions of these two types of Na^0 depend both on the degree of Na^0 activation and on the zeolite type, X or Y. The results observed here upon exposure of Na^0/NaX or Na^0/NaY to the adsorbates does not appear to depend in any obvious way upon the form in which Na^0 exists in the zeolite.

5. Conclusions and summary

Experiments, in which zeolites NaX, NaY, Na^0/NaX, and Na^0/NaY were exposed to representative primary, linear, monohaloalkanes, were characterized by NMR, IR, MS, gravimetric, and other methods. No alkyl fluoride chemistry was explored in this work. Whereas the untreated NaX is reactive to the bromides and iodides, NaY is not, a fact that we ascribe to the halide ion leaving group assistance provided by the site III or III′ Na^+ found in NaX but not in NaY. Framework alkoxy species are found in NaX upon exposure to the bromides and iodides and to 1-chloropropane, which we attribute to nucleophilic displacement of halide ion by the framework oxygen atoms of the zeolite that point into the supercages. Halide ion X^- is found in high yield by gravimetric analysis of PbX_2 formation.

We propose that in the Na^0/NaX and Na^0/NaY, Na^0 reacts directly with the alkyl bromide and alkyl iodide or with framework alkoxy from them, releasing alkyl radical and forming sodium halide. The alkyl radical is proposed to attack another alkyl halide molecule, leading to a larger alkane plus halogen atom, which reacts with another Na^0 to form sodium halide. Evidence for the larger alkanes is found from the IR and MS experiments and the halide ion is observed gravimetrically as PbX_2. Product yields are generally higher in NaX than in NaY.

Preliminary work on untreated NaX exposed to the alkyl chlorides, available as room-temperature liquids, form 1-alkene and halide ion products, with the exception of the additional formation of framework propoxy from 1-chloropropane. Little chemistry occurs upon exposure of NaY to these alkyl chlorides. The chemistry upon exposure of Na^0/NaX to 1-chlorobutane yields small amounts of 2-butenes and larger amounts of an alkane or alkanes. With 1-chloropropane, propoxy, propene, and other olefins are formed. Experiments beyond the original scope of this work will be needed to fully understand the alkyl halide-zeolite chemistry. For example, no alkyl fluoride chemistry was explored in this work and future work of this kind might further illuminate the trends appearing in the chloride series. Alternatively extension of the 1-haloalkane series beyond the four carbons of the 1-halobutanes might indicate what determines the switchover from halide displacement to dehydrohalogenation.

The trends of this work as a whole imply that the zeolites have nucleophilic character that increases in the order NaY < NaX < Na^0/NaY < Na^0/NaX.

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Appendix A. Supporting information available

Experimental details and supporting spectroscopic data are available free of charge via the Internet at http://www.sciencedirect.com. The colored Na^0 treated zeolite samples are shown and the electron paramagnetic resonance (EPR) characterization of the samples at various loading levels is presented. The apparatus with which weighed or volumetric amounts of adsorbate in one container are transferred by evaporation into the evacuated NaX, NaY, Na^0/NaX, or Na^0/NaY sample in another container is shown. ^{13}C CP/MAS spectra of untreated NaX exposed to (a) methyl iodide, (b) ethyl bromide, (c) ethyl iodide, (d) 1-chloropropane, (e) 1-iodobutane are presented. ^{13}C CP/MAS spectra of (a) Na^0/NaX and (b) NaX exposed to 1-chloropropane are given. ^1H NMR spectra of the $CDCl_3$ washings of NaX, NaY, Na^0/NaX, and Na^0/NaY exposed to CH_3I are shown, as an example illustrating the amounts of residual adsorbate that were not decomposed by the zeolites. The IR spectra of the gaseous products of ethyl iodide-exposed, (a) Na^0/NaY and (b) Na^0/NaX and the IR spectra of the gaseous products of 1-chlorobutane-exposed, Na^0/NaX and Na^0/NaY are presented. GC/MS trace of the gases evolved from the exposure of Na^0/NaX to CH_3I are shown. Iodide and chloride ion yields for the reactions of other alkyl halides than CH_3I with the treated and untreated zeolites are given. A table giving the wavelengths of visible absorption maxima ($\sigma^* < -\pi^*$) of Br_2 in solution and in Na^0/NaX, Na^0/NaY, NaX, and NaY is presented as an indication of the relative basicities or electron donating power of the zeolites. The dehydrohalogenation is discussed further, showing it to take advantage of the electron denoting character of the framework oxygen atom and leaving group assistance from the zeolite Na^+. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2006.01.017.

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