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Room temperature reactions of alkyl halides in zeolite NaX: Dehalogenation versus dehydrohalogenation

Charles W. Kanyi, David C. Doetschman *, Szu-Wei Yang, Jürgen Schulte, Barry R. Jones

Department of Chemistry, Binghamton University, Binghamton, NY 13902-6000, USA

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Abstract

Alkyl halides were shown to undergo room temperature, nucleophilic substitution reactions in NaX Faujasite zeolite with some evidence of elimination chemistry [Kanyi et al., *Mesopor. Micropor. Mater.* 92 (2006) 292–299]. Presented here is a study of the dependence of these two types of chemistry on (1) halogen, (2) order of halogenated C atom, and (3) chain length. Primary, secondary and tertiary alkyl halides (Cl, Br, and I) were adsorbed into zeolite NaX at room temperature. Products were analyzed using ^{13}C and ^1H nuclear magnetic resonance (NMR) and infrared spectroscopy (IR).

Primary chloro and bromoalkanes underwent dehalogenation and dehydrohalogenation, forming framework alkoxy species and olefins, respectively, while their secondary counterparts formed predominantly olefins. Primary iodoalkanes formed only framework alkoxy, while secondary iodoalkanes formed both. Tertiary alkyl chloride, bromide, and iodide were unreactive. Haloethanes formed no olefin, but longer haloalkanes did.

Balance between substitution and elimination can be understood in terms of factors: (1) Relative rates of C–X (X = Cl, Br, I) and C–H cleavage, whereupon substitution is predominant when the C–X cleavage rate is greater than the C–H cleavage rate. C–X cleavage rates decrease in the order $\text{I} > \text{Br} > \text{Cl}$. (2) Relative stability of the framework alkoxy species, as a result of steric hindrance in the zeolite. This stability decreases, primary > secondary > tertiary.

Reasons for haloethanes undergoing exclusively substitution are not clear, but the fact suggests that framework ethoxy is more stable than all of the larger framework alkoxy species.

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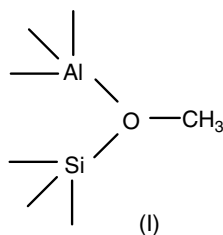
Keywords: Nucleophilic; Zeolite; Faujasite; NaX; Alkyl Halide; Substitution; Elimination; Adsorption; Alkoxide; Olefin; Dehalogenation; Dehydrohalogenation

1. Introduction

Zeolites are microporous aluminosilicate materials made up of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra. Every aluminum tetrahedron present in the framework carries a negative charge that is balanced with an exchangeable cation [1]. The tetrahedra give zeolites an open framework structure, consisting of cavities and pores that readily accommodate organic compounds. Zeolites have been widely used as catalysts, particularly in the petroleum industry [2,3]. Recent

research has shown that in addition to catalysis, zeolites can be regarded as reagents [4–7]. They oxidize alkenes to radical cations [4,5] and cleave alkyl halides to form carbocations [6,7]. However, the carbocations are seldom observed in a free state on the zeolite surface [8]. The oxygen atoms of the zeolite framework act as nucleophilic centers that interact with the positively charged carbon to form a covalent bond. The covalently bonded species is referred to as an alkoxy or alkoxide intermediate [9], such as the one shown in Scheme 1 for framework methoxy. Framework alkoxy were first characterized using solid state ^{13}C NMR [10] and later by neutron diffraction [11,12] and infrared techniques [13].

* Corresponding author. Tel.: +1 607 777 2298; fax: +1 607 777 4478.
E-mail address: ddoetsch@binghamton.edu (D.C. Doetschman).



Scheme 1. Framework methoxy structure.

Most framework alkoxy in zeolites are obtained from the protonation of olefins [14] and the dehydration of alcohols [15]. Framework alkoxy are also generated from the reaction of alkyl halides in zeolites [11,12,16–18]. Using solid-state ^{13}C NMR, Haw et al. [16,17] reported the formation of framework methoxy (58 ppm at the framework bound ^{13}C) and ethoxy (69 ppm at the framework bound ^{13}C) for reactions of methyl iodide and ethyl iodide, respectively, with CsX and CsY zeolites. Bosacek et al. [11,12] reported similar observations for methyl iodide in NaX. Dichloromethane and chloroform, adsorbed into zinc exchanged zeolites [18], form framework chloromethoxy and dichloromethoxy.

Alkyl halides in zeolites form olefins [8,19,21] in addition to framework alkoxy. At temperatures of 150–400 °C, 1- and 2-chlorobutanes in NaX form butene isomers (1-butene, 2-butene, and isobutenes) [19]. Dehydrochlorination of 2-chloropropane on silica and alumina and in ZSM5 commences at 400 K to form propene and HCl [20]. In this reaction an E1 process was proposed, occurring through nucleophilic substitution to give rise to 2-propoxy and followed by proton elimination to give propene.

Using density functional theory (DFT), Rosenbach and Mota [21] proposed a different mechanism from that of Kladnig [19] and of Pistarino [20], where alkoxide and olefin formation can occur in parallel. According to Rosenbach, the formation of alkoxy or olefin depends on two factors. One factor is the structure of the alkyl halide. Primary and secondary alkyl halides prefer alkoxy formation, with tertiary alkyl halides undergoing elimination only [21]. However, their experiment with tertiary butyl chloride in Na^+ , Ag^+ , Cu^{2+} , Fe^{3+} exchanged Y zeolite did not agree with their DFT results. The tertiary butyl chloride formed either alkoxy or olefins, depending on the particular exchangeable cation [8]. The second factor is the Cl^- , Br^- or I^- leaving group. DFT results show that the difference between the energy barriers for alkoxy and olefin formation are lower for bromides (8.2 kcal/mol) and iodides (9 kcal/mol) than for chlorides (12.4 kcal/mol) [21].

Unlike unimolecular or bimolecular elimination reactions proposed by Kladnig and Noller [19], Rosenbach and Rodrigo [8,21] proposed a bimolecular reaction for both dehalogenation and dehydrohalogenation.

Despite the numerous theoretical predictions, only butyl chloride has been studied in order to understand the type of reaction, where butoxy was shown to be stable, using the

IR technique at room temperature [22,25]. However, unlike the solid-state NMR technique used in this study, the infrared technique (IR) is not very sensitive to the position of the olefin double bond and the class of alkoxy (methyl, 1°, 2° or 3°) formed. IR is therefore a less appropriate technique for distinguishing between the classes of olefin or alkoxy, in cases where both species are present.

The dehydrohalogenation process and the dehydrochlorination process, in particular, permit dechlorination and recovery of chlorine, as chloride, from chlorine containing organic wastes, possibly obviating the need for their incineration. Incineration of chlorine compounds, including poly (vinyl chloride) (PVC) is environmentally dangerous because of the risk of producing poly (chlorodibenzodioxins) (PCDDs) and furans (PCDFs) [22]. The conversion of chlorine containing compounds into alkoxy species and olefins is not only environmentally benign, but is also of possible economic interest, as the two products find wide application in Friedal Crafts alkylation and as intermediates in the production of alkylbenzenesulfonate surfactants [23,24]. Therefore, an understanding of alkoxy formation in the present context is important.

In our earlier work [26], we reported the presence of both propoxy and propene in the reaction of 1-chloropropane in NaX at room temperature. Continuing this work, we explore other classes of alkyl halides, primarily using ^{13}C solid-state NMR, along with other characterization techniques, because of its ability to resolve the olefins and its ability to identify and distinguish framework alkoxy species. The influence of the nature of the halogen and its position in the alkyl halide will be considered, in addition to the effects of carbon chain length and branching (α - and β -methyl substituents).

2. Experimental

All of the alkyl halides, pyridine, and the zeolite (Si/Al = 1.23) br00367@binghamton.edu used in this study were obtained from Sigma Aldrich in the highest grade available and were used, as received, except for the dehydration of the zeolite. The zeolites were dried by evacuation at 450 °C for 24 h, achieving a pressure of about 1.2×10^{-5} Torr. The adsorbates were taken through three freeze-pump-thaw cycles before adsorption into the zeolites by evaporative transfer. Adsorbates were loaded at 3 molecules per supercage, unless otherwise stated. After adsorption, samples were left overnight for equilibration at room temperature.

The adsorbates and products were extracted from the zeolite after reaction using deuterated chloroform (CDCl_3) and the extracts were analyzed with ^{13}C and ^1H NMR, using a Bruker AM 360 NMR spectrometer. A total of eight scans were performed for each solution, proton NMR experiment. Solid powdered samples were measured with a Bruker AC 300 spectrometer, equipped with a Doty 7 mm CP MAS probe. The cross-polarization, magic angle spinning (CP MAS) technique was used as follows: After a 6.0 μs , $\pi/2$, high power, proton excitation pulse, cross-

151 polarization was achieved via a 2 ms contact time. The
 152 recycle delay was 3 s and the spinning rate was 4 kHz. A
 153 total of 2048 scans were collected with chemical shifts
 154 adjusted to TMS for most solid-state MAS NMR runs.
 155 A Bruker Equinox 55 infrared (IR) spectrometer was used
 156 for IR analyses. The pellets used in transmission IR exper-
 157 iments were prepared by thoroughly mixing 1% of the zeo-
 158 lite-product mixture with KBr and then pressing the
 159 mixture to form a pellet weighing approximately 0.1 g. A
 160 total of 128 scans were collected.

161 3. Experimental results

162 In connection with the observations in this section,
 163 groups of spectra are also gathered together in a support-
 164 ing information document available at [http://www.science-](http://www.science-direct.com/science)
 165 [direct.com/science](http://www.science-direct.com/science), in order to illustrate specific trends,
 166 which cut across and duplicate spectra presented here in
 167 conventional chemical series order. Also presented in the
 168 [supporting information](#) document are experimental spectra
 169 for NaX reactions with compounds that were not commer-
 170 cially available for the complete series of halogens, X = Cl,
 171 Br, I. Finally the [supporting information](#) includes a quali-
 172 tative summary table in which we indicate the presence or
 173 absence of framework alkoxy and olefin products from the
 174 reaction of zeolite with the alkyl halides examined.

175 3.1. Studies of the factors influencing dehalogenation and 176 dehydrohalogenation

177 3.1.1. Results with different halogens

178 Fig. 1 shows the ^{13}C NMR spectra arising from (a) ethyl
 179 chloride, (b) ethyl bromide, and (c) ethyl iodide adsorption
 180 over NaX. All of these adsorbates form framework ethoxy,
 181 characterized by the broad peak at 69 ppm and the smaller
 182 one at 18 ppm. The peaks at 15 and 31 ppm are associated
 183 with residual adsorbates [17]. The presence of residual
 184 adsorbate was further confirmed in the ^1H NMR of the
 185 CDCl_3 extracts (see attached [supporting information](#)).

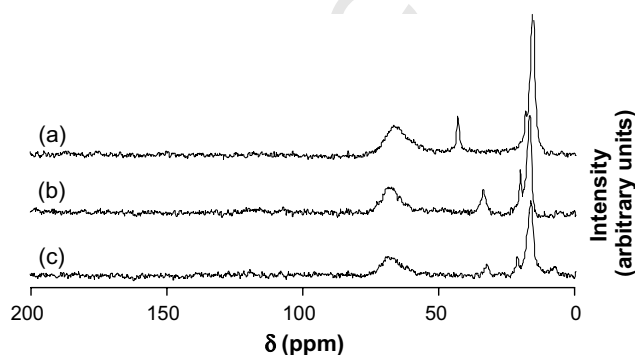


Fig. 1. Solid-state 75.4 MHz ^{13}C CPMAS NMR spectra of (a) ethyl chloride, (b) ethyl bromide, and (c) ethyl iodide adsorbed on NaX. Spectra are offset for clarity. Chemical shift is indicated by δ . No attempt has been made to keep peaks on scale or to avoid overlap in the methyl and methylene region in order to emphasize the other product peaks.

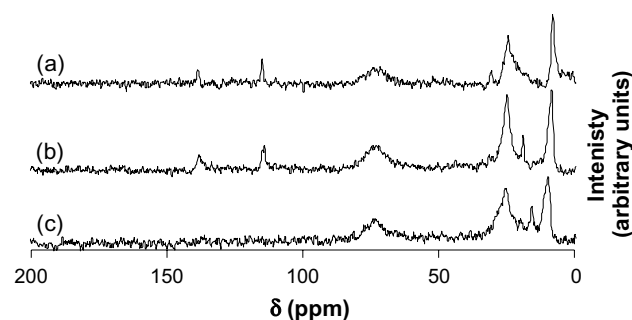


Fig. 2. Solid-state 75.4 MHz ^{13}C CPMAS NMR spectra of (a) 1-chloropropane, (b) 1-bromopropane and (c) 1-iodopropane exposed to NaX. Spectra are offset for clarity. Chemical shift is indicated by δ .

186 There was no evidence of ethene formation in ^1H liquid
 187 NMR, solid ^{13}C NMR (specifically at 122 ppm), or ethene
 188 IR formation in the gas phase over the zeolite, as reported
 189 elsewhere at high temperatures (see [Supporting informa-](#)
 190 [tion](#)) [16].

191 Products obtained from adsorption of primary chloro,
 192 bromo and iodopropanes in NaX are shown in Fig. 2.
 193 The peaks at 113 and 135 ppm are associated with propene
 194 and the peak at 71 ppm is associated with the primary,
 195 framework propoxy species. Both primary chloropropane
 196 and bromopropane form mixtures of propene and primary
 197 framework propoxy, as shown in Fig. 2a and b. Only pri-
 198 mary framework propoxy (71 ppm) is observed from the
 199 reaction of the zeolite with primary iodopropane (see
 200 Fig. 2c).

201 The influence of the nature of the halogen group on selec-
 202 tivity was further extended to primary halobutanes. Fig. 3
 203 shows the ^{13}C solid-state NMR spectra of primary halo-
 204 butanes after adsorption into NaX zeolite. Peaks at 140, 113,
 205 27.4 and 13.4 ppm (see spectra (a) and (b) in Fig. 3) are
 206 assigned to 1-butene [27]. In addition to 1-butene, the pri-
 207 mary bromobutane also formed primary framework butoxy
 208 (72 ppm). The reaction of 1-iodobutane was analogous to
 209 that of 1-iodopropane (see Fig. 2) with formation of pri-
 210 mary framework butoxy (72 ppm) as the only product.

211 The results from the reaction with primary halopentanes
 212 are presented in Fig. 4. Peaks at 114 and 143 ppm in Fig. 4a

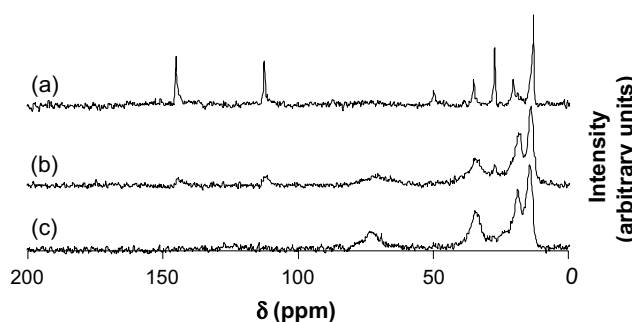


Fig. 3. Solid-state 75.4 MHz ^{13}C CPMAS NMR spectra of (a) 1-chlorobutane, (b) 1-bromobutane and (c) 1-iodobutane exposed to NaX. Spectra are offset for clarity. Chemical shift is indicated by δ .

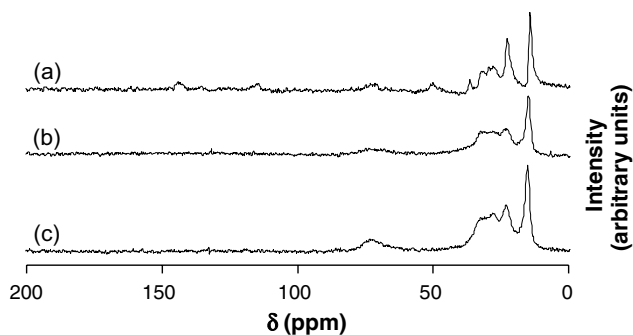


Fig. 4. Solid-state 75.4 MHz ^{13}C CPMAS NMR spectra of (a) 1-chloropentane, (b) 1-bromopentane and (c) 1-iodopentane exposed to NaX. Spectra are offset for clarity. Chemical shift is indicated by δ .

213 are assigned to 1-pentene, with the lower frequency peaks
 214 assigned to residual primary halopentane and primary
 215 framework pentoxy (73 ppm). The behavior of primary
 216 iodopentane was consistent with that of primary iodobu-
 217 tane and iodopropane in that primary framework pentoxy
 218 (73 ppm) is the only product of reaction with the zeolite.
 219 The behavior of 1-bromopentane, however, contrasts with
 220 that of 1-bromopropane and 1-bromobutane, in that no 1-
 221 alkene is formed. A significant decrease in reactivity was
 222 observed as one progressed from primary halobutane to
 223 halopentane. This is evidenced by the large amounts of
 224 residual halopentane found in the CDCl_3 extracts, as ana-
 225 lyzed by ^1H and ^{13}C NMR (see supporting information).
 226 Due to 1-iodohexane not being available, only 1-chloro-
 227 and 1-bromohexane were studied. Upon exposure of
 228 NaX, 1-chlorohexane gave a mixture of primary frame-
 229 work hexoxy and 1-hexene, while 1-bromohexane gave
 230 the hexoxy exclusively. See supporting information Fig. 1S.

3.1.2. Results according to halogen position and order of the adjacent carbon

231 The position of the halogen and substitution at the hal-
 232 ogenated carbon has a profound influence on product
 233 selectivity, as can be seen by comparison of the spectra of
 234 (a) 2-chloro- 2-methylpropane and (b) 2-chloropropane in
 235 Fig. 5 with the spectrum of 1-chloropropane in Fig. 2a.
 236 Figs. 2a and 5b show that propene (114, 138 ppm from
 237 2-chloropropane in Fig. 5b) is obtained from both the pri-
 238 mary and secondary chloropropanes. The secondary pro-
 239 pane (see Fig. 5b) did not yield detectable framework
 240 propoxy (71 ppm). However, no reaction takes place when
 241 one of the α -protons of 2-chloropropane (2-chloro-2-meth-
 242 ylpropane) is replaced with an alkyl (methyl) group, as
 243 shown in Fig. 5a. The spectra compared here are also gath-
 244 ered in a single figure, Fig. 2S, in the Supporting informa-
 245 tion for the readers' convenience.

246 Further evidence concerning the detailed dependence of
 247 propene formation by secondary alkyl halides on halogen
 248 position and order of adjacent carbon is shown for the
 249 products from the bromopropanes in Figs. 2b and 6. Simi-
 250 lar to the chloropropanes, no reaction takes place when
 251 the α -proton of 2-bromopropane or the β -proton of

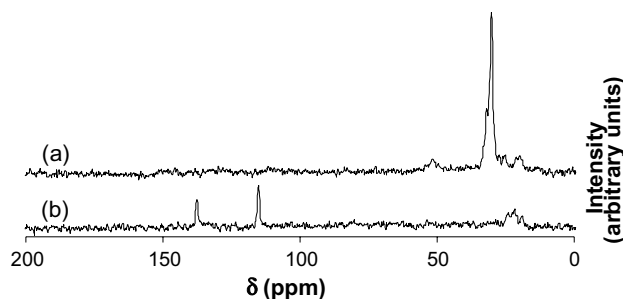


Fig. 5. Solid-state 75.4 MHz ^{13}C CPMAS NMR spectra of (a) 2-chloro-2-methylpropane and (b) 2-chloropropane exposed to NaX. Spectra are offset for clarity. Chemical shift is indicated by δ .

254 1-bromopropane is substituted with a methyl group
 255 (Fig. 6a and b). Mainly propene, but only trace amounts
 256 of secondary framework 2-propoxy (80 ppm), were
 257 detected in the reaction of 2-bromopropane with zeolite,
 258 as shown in Fig. 6c. A mixture of propene and substantial
 259 framework 1-propoxy were formed in the reaction of 1-
 260 bromopropane (see Fig. 2b). The spectra compared here
 261 are also gathered in a single figure, Fig. 3S, in the sup-
 262 porting information for the readers' convenience.

263 A comparison of the chemical shifts (72 and 82 ppm,
 264 respectively) of the products from 1- and 2-bromopropane
 265 in Figs. 2b and 6c, respectively, shows that they form differ-
 266 ent framework propoxy species. The two chemical shifts
 267 are attributed to framework 1-propoxy and 2-propoxy,
 268 respectively [28]. This is an indication that the primary
 269 framework propoxy does not rearrange to secondary
 270 framework propoxy, or vice versa. The spectra compared
 271 here are also gathered in a single figure, Fig. 4S, in the sup-
 272 porting information for the readers' convenience.

273 Spectra in Figs. 2c and 7 show the switchover between
 274 primary and secondary iodo compounds from the forma-
 275 tion of framework alkoxy alone to mixtures of framework
 276 alkoxy and olefins upon exposure of NaX. The latter
 277 behavior is akin to that obtained with primary chloro
 278 and bromo compounds presented earlier. The chemical
 279 shifts of the framework alkoxy species in Fig. 2c and 7b
 280 are similar to those of primary and secondary bromopro-
 281 pane, respectively (see Figs. 2 and 6), a further indication

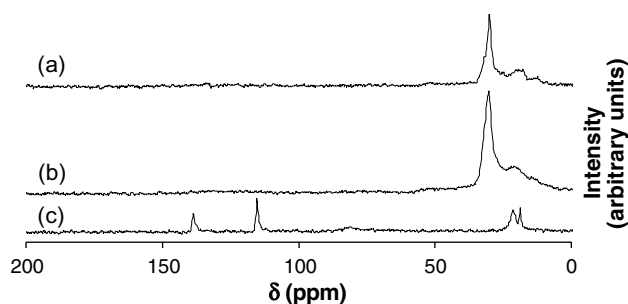


Fig. 6. Solid-state 75.4 MHz ^{13}C CPMAS NMR spectra of (a) 1-bromo-2-methylpropane, (b) 2-bromo-2-methylpropane and (c) 2-bromopropane exposed to NaX. Spectra are offset for clarity. Chemical shift is indicated by δ .

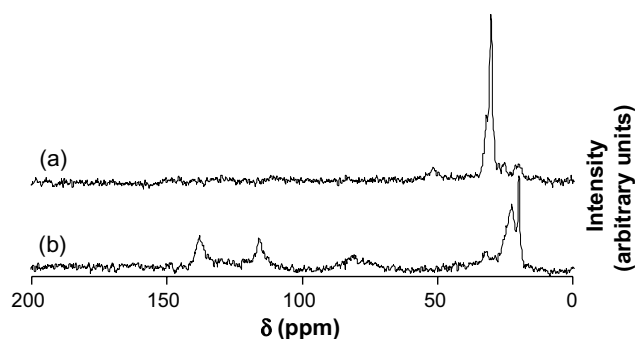


Fig. 7. Solid-state 75.4 MHz ^{13}C CPMAS NMR spectra of (a) 2-iodo-2-methylpropane and (b) 2-iodopropane exposed to NaX. Spectra are offset for clarity. Chemical shift is indicated by δ .

282 that rearrangement does not take place. Again, the tertiary
283 iodo compound shows no reactivity (see Fig. 7a). The spec-
284 tra compared here are also gathered in a single figure,
285 Fig. 5S, in the supporting information for the readers'
286 convenience.

287 Trends in the preferential formation of olefins by sec-
288 ondary halolakanes are illustrated by the reactions of 1-
289 and 2-chlorobutane and 1- and 2-chloropentane, as shown
290 in the ^{13}C NMR spectra of products shown in Figs. 3, 4
291 and 8. In Fig. 3b, peaks at 112, and 145 ppm are attributed
292 to 1-butene formation from 1-chlorobutane, while
293 the 127 ppm peak in Fig. 8a is assigned to 2-butene [27]
294 formation from 2-chlorobutane. In Fig. 4b, the 114 and
295 143 ppm peaks are attributed to 1-pentene formation from
296 1-chloropentane, while the isomer 2-pentene formed from
297 2-chloropentane is associated with peaks at 125 and
298 135 ppm (see Fig. 8b). In addition to 1-pentene, 1-chloro-
299 pentane formed primary framework pentoxy with a chemi-
300 cal shift of 73 ppm (see Fig. 4a). The spectra compared
301 here are also gathered in a single figure, Fig. 6S, in the sup-
302 porting information for the readers' convenience.

303 Similar results were obtained with the bromo com-
304 pounds, as shown in Figs. 3b, 4b and 8c and d. These spec-
305 tra are gathered in a single figure, Fig. 7S, in the supporting
306 information for the readers' convenience. Consistent with

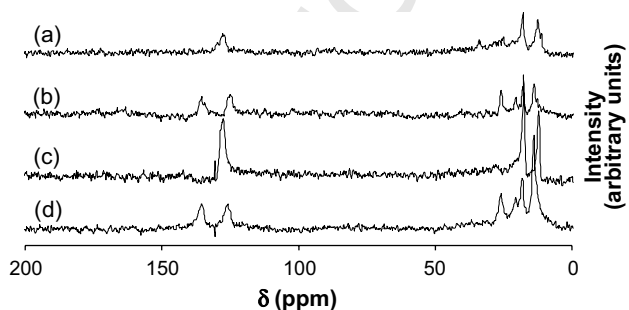


Fig. 8. Solid-state 75.4 MHz ^{13}C CP MAS NMR spectra of (a) 2-chlorobutane, (b) 2-chloropentane, (c) 2-bromobutane and (d) 2-bromopentane exposed to NaX. Spectra are offset for clarity. Chemical shift is indicated by δ . No attempt has been made to avoid overlap in the methyl and methylene region in order to emphasize the other product peaks.

the 2-iodopropane results, 2-iodobutane formed predomi- 307
nantly 2-butene. No framework butoxy was detected. The 308
1-iodopentane forms the 1-pentoxy exclusively. See sup- 309
porting information Fig. 8S. 310

3.2. Study of the regioselectivity and stereoselectivity of 311 dehydrohalogenation 312

trans-Olefinic products were obtained in higher amounts 313
than the *cis* products. An example is shown in Fig. 9 for 2- 314
butene extracted from 2-halobutanes. The intensity of the 315
17 ppm peak associated with the *trans* isomer is stronger 316
than that of the *cis*-isomer (13 ppm). The results may have 317
to do with thermodynamic stability. 318

In addition to stereoselectivity, a higher regioselectivity 319
was achieved with exposure of NaX to secondary alkyl 320
halides (Table 1). The internal olefins yields in NaX were 321
higher than those obtained with liquid bases. An example 322
is shown in Fig. 10 in the ^1H NMR spectrum of the CDCl_3 323
extract of 2-chlorohexane exposed NaX zeolite. The 5.80 324
and 4.96 ppm peaks (marked with arrows) represent termi- 325
nal olefin (1-hexene) while the strong 5.44 ppm peaks rep- 326
resent the internal olefin (2-hexene). 327

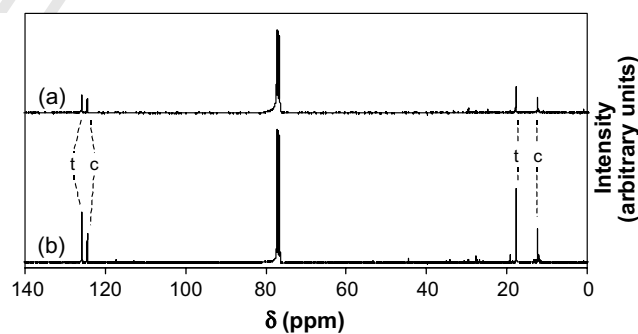


Fig. 9. Solution 90.5 MHz ^{13}C NMR of the CDCl_3 extract of NaX exposed to (a) 2-chlorobutane and (b) 2-bromobutane. Letters c and t denotes *cis* and *trans* respectively. Spectra are offset for clarity. Chemical shift is indicated by δ . The peak at 77 ppm is from the CDCl_3 solvent.

Table 1

Percentage yields of terminal and internal olefin in NaX as obtained by the integration of ^1H peaks, in comparison with available yields in solution [40]

Substrate	Percent composition of alkene			
	1-Alkene		2-Alkene	
	In NaX	In solution	In NaX	In solution
2-Chlorobutane	4	33	96	67
2-Bromobutane	1	19	99	81
2-Iodobutane	3	–	97	–
2-Chloropentane	7	13	93	87
2-Bromopentane	6	–	94	–
2-Chlorohexane	4	–	96	–
2-Bromohexane	4	–	96	–

Uncertainties are estimated to be of the order of 1%.

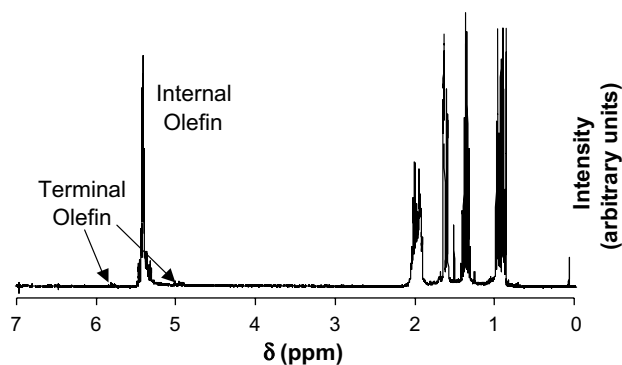


Fig. 10. Solution 360 MHz ^1H NMR spectrum of the CDCl_3 extract of NaX exposed to 2-chlorohexane. Chemical shift is indicated by δ . The ^1H NMR peaks of the terminal and internal olefin products are indicated. In order to emphasize the other product peaks, no attempt has been made to keep the methyl and methylene region on scale.

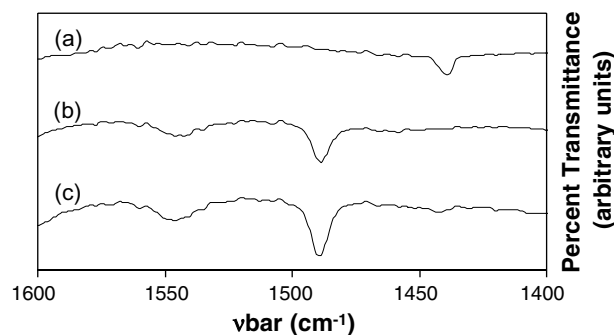


Fig. 11. IR spectra of (a) NaX (b) NaX exposed to 1-chlorobutane and (c) HX, all subsequently exposed to pyridine. Spectra (offset for clarity) are shown versus energy in wavenumber units (ν bar).

3.2.1. Difference in the capacity of NaX for reaction with 1°, 2°, and 3° RX in zeolite

In order to determine the different capacities of NaX to reaction with various orders of substitution at the halogen bearing carbon atom, we have studied the amount of residual, unreacted alkyl halide of each order, as a function of the number of adsorbed alkyl halide molecules per supercage of NaX. The results show a significant dependence on the order of substitution at the halide bearing C atom of the alkyl halide. Determination of residuals in chloroform (CDCl_3) extracts from primary and secondary haloalkanes in the zeolite indicates a higher reactivity with the secondary compared to the primary. For example, incomplete consumption of reactant sets in between 2 and 3 molecules of primary chlorohexane, whereas incomplete consumption of reactant does not set in until between 8 and 9 molecules of secondary chlorohexane. No reactivity was found for any tertiary alkyl halide (see supporting information).

3.3. Study of dehydrohalogenation in zeolite

In the dehydrohalogenation of alkyl halides in zeolites at high temperatures, HCl gas is formed [30]. In our study, HCl gas was not detected at room temperature in the resulting zeolite or surrounding gas phase IR. This absence prompted us to examine the reaction involved in NaX at room temperature further. We hypothesized a slightly different reaction, where the abstracted β -proton takes up the Na^+ role in the framework, and did experiments to confirm this idea. The exchange of Na^+ with H^+ would result in converting the basic NaX zeolite to acidic HX. To confirm this reaction, pyridine was loaded at 3 molecules per supercage to the NaX previously loaded with alkyl halide after evacuating the resulting zeolite of its volatile contents at room temperature. For comparison, unloaded NaX was also treated with pyridine at the same loading. Spectra are shown in Fig. 11 that illustrate the changes that occur when pyridine is added to NaX reacted with 1-chlorobutane in

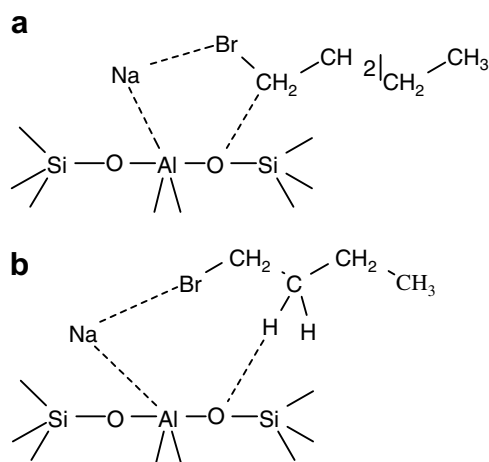
comparison with plain NaX and with authentic HX to which pyridine was added. The band at 1436 cm^{-1} in Fig. 11a of unloaded NaX with pyridine is associated with Lewis acid site (PyNa^+) [31,32]. It denotes the presence of Na^+ counterions in the zeolite. This band is absent in the NaX loaded with 1-chlorobutane shown in Fig. 11b. Instead, two new bands appear at 1548 and 1492 cm^{-1} . The two are attributed to a Bronsted acid site and to a site combining both Bronsted and Lewis acid character, respectively [31,32]. In an effort to confirm that the two bands (1492 , 1548 cm^{-1}) are representative of authentic HX, NaX was exchanged with H^+ using ammonium nitrate followed by heating. The prepared HX was then loaded with pyridine at the same loading of 3 per supercage. The two new bands (1548 , 1492 cm^{-1}) reported in Fig. 11b were present in the prepared HX (Fig. 11c), confirming the conversion of NaX to HX through reaction by exposure to 1-chlorobutane.

4. Discussion

For a general reference to the types of products that were or were not formed in the experiments for the purposes of this discussion, a summary of whether framework alkoxy, olefin, both, or neither is formed is given in tabular form in the supporting information for all alkyl halides examined.

4.1. Influence of particular halogen on the reaction

In presence of alkyl halides, zeolites behave either as a nucleophile, a base, or both, as shown in Scheme 2. In Scheme 2a, the zeolitic oxygen acts as a nucleophile by attacking the electron deficient α -carbon on one end of the alkyl halide, while the framework cation interacts with the halogen. As the halogen leaves, the carbocation is stabilized by the zeolitic oxygen to form the framework alkoxy. In Scheme 2b the zeolitic oxygen acts as a base by abstracting the β -proton, while the framework cation stabilizes the halogen. The end result is olefin formation. The preference for substitution versus elimination depends on the relative strength of nucleophilicity versus basicity.



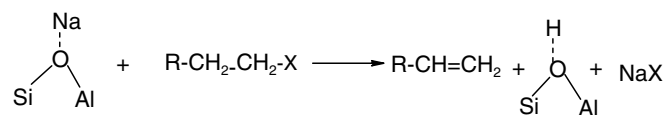
Scheme 2. Interactions in (a) alkoxy formation and (b) olefin formation for the example of 1-bromobutane. After reference [33].

403 For the primary alkyl halides, the choice of reaction is
 404 dependent on the halogen leaving ability. A better leaving
 405 group (X) attached to the alkyl chain allows C–X rupture
 406 to occur more rapidly than C–H cleavage [34]. Relative
 407 rates of halides reaction with liquid bases are about
 408 30,000, 10,000, and 200 for iodides, bromides and chlorides,
 409 respectively [29]. In iodoalkanes the iodide ion, being a
 410 good leaving group, the C–X cleaves before the C–H
 411 cleaves, favoring substitution over elimination. The
 412 advancement of the C–X cleavage over the C–H cleavage
 413 is facilitated by the fact that Faujasite zeolites are consid-
 414 ered weak bases with their basicity equivalent to 70% meth-
 415 anol solution [35]. For bromo compounds, with the
 416 moderate leaving group bromide, a mixed behavior of sub-
 417 stitution and elimination. Under certain circumstances only
 418 substitution is observed. In case of the much slower chloride
 419 leaving group, elimination and substitution also occur
 420 simultaneously but with a lesser preference for substitution
 421 in secondary chloroalkanes than in primary chloroalkanes.
 422 Only substitution is observed in the ethyl halides, where ste-
 423 reochemistry may play a role in their unique behavior.

424 4.2. Influence of halogen position on the reaction

425 A comparison of the products obtained from primary
 426 and secondary alkyl halides for all the three halides studied
 427 shows a preference for dehydrohalogenation by the second-
 428 ary alkyl halides relative to the primary. Trace amounts of
 429 alkoxy in secondary alkyl halides were only observed with
 430 2-bromopropane (see Fig. 6) and 2-iodopropane (see
 431 Fig. 10). We explain this switchover in two ways.

432 Firstly, as shown in Scheme 3, the substitution reaction
 433 involves the zeolite acting as a nucleophile. Nucleophilicity
 434 involves backside attack and suffers greatly from steric hin-
 435 drances both by the nucleophile and the alkyl halide [29].
 436 The zeolitic oxygen (nucleophile) is already sterically hin-
 437 dered by the tetrahedral arrangements of Si, Al and O in
 438 the wall of the zeolite supercage and possibly by the pres-
 439 ence of the charge balancing cation. In primary halolalk-



Scheme 3. Proposed dehydrohalogenation scheme for the example of the primary alkyl halides.

440 anes the α -protons offer very little hindrance to backside
 441 attack, favoring alkoxy formation. In secondary haloalk-
 442 anes, one of the protons is substituted with a more bulky
 443 group, usually the methyl group in our studies, which ste-
 444 rically hinders the zeolitic oxygen from attacking the α -car-
 445 bon. This slows down the nucleophilic substitution to form
 446 framework alkoxy in favor of elimination to form olefins.
 447 The hindrance is even more pronounced in tertiary alkyl
 448 halides, where both α -protons have been substituted with
 449 alkyl groups. These molecules are hindered at the halide
 450 bearing C atom, so that the cations cannot approach the
 451 halide close enough to facilitate cleavage. Our results con-
 452 tradict those of Rodrigo et al. [22], in which they report
 453 higher reactivity with tertiary butyl chloride in NaY zeolite
 454 than with their primary and secondary counterparts. A the-
 455 oretical and experimental (IR) study in our laboratory on
 456 tertiary butyl halides in NaX zeolite showed no chemical
 457 reactivity of the *t*-butyl halides with NaX [38]. Our previ-
 458 ous paper [26] and another paper [17] show that there is
 459 very little activity with NaY zeolite of any kind, including
 460 the tertiary butyl halides [39] due to the scarcity of site III
 461 cations in the supercage in NaY [36,37].

462 Secondly, the relative stabilities of the olefin and alkoxy
 463 play a role in determining the type of reaction. Primary
 464 framework alkoxy species (obtained from primary haloalk-
 465 anes) are more stable than secondary or tertiary ones [40].
 466 The methyl groups in secondary or tertiary alkoxide pre-
 467 vent the positively charged carbon from approaching the
 468 zeolitic oxygen, leading to a destabilization of the frame-
 469 work alkoxy. Density functional theory predicts that C–
 470 O bond distance decreases in the order $2^\circ > 1^\circ$, giving the
 471 framework alkoxy stability the order, $1^\circ > 2^\circ$ [21,25]. On
 472 the other hand, internal olefins obtained from 2° RX are
 473 more stable than terminal olefins (Sayzeff rule), favoring
 474 olefins over secondary framework alkoxy. Although it is
 475 difficult to quantify the relative amounts of framework al-
 476 koxy formed with solid-state ^{13}C NMR, there seems to be a
 477 higher selectivity for elimination than substitution in NaX
 478 compared with the preference in liquid bases. For example,
 479 using ethoxide ion as a base, 2-chloropropane yields 2-eth-
 480 oxypropane and propene in ratios of 0.25:0.75 [29], while in
 481 NaX, secondary framework propoxy was below the detec-
 482 tion limit (see Fig. 5).

483 4.2.1. Regioselectivity

484 Although bimolecular elimination (E2) is considered to
 485 be a concerted mechanism, the transition state can either
 486 have an advanced C–X (E1-like), C–H (E1cb-like), or syn-
 487 chronous transition state [41]. Advanced C–H leads to a

488 carbanion like transition state to form terminal olefins, as a
 489 major product (e.g. with a strong base and/or a poor leaving
 490 group, such as an alkyl fluoride). In the case of advanced C–
 491 X, a carbocation like intermediate results in the formation
 492 of internal olefins as the major products. The Na cation
 493 present in Faujasite-X interacts with the halogen, assisting
 494 with the C–X cleavage. As a result, the transition state
 495 develops a carbocation character that favors formation of
 496 internal olefin. Such interactions, not present in liquid
 497 bases, contribute to the observed enhanced regioselectivity
 498 from 67% in ethanol solvent [40] to 96% in the NaX zeolite.
 499 A lower regioselectivity of 87%, 81% and 67% is for with I,
 500 Br and Cl respectively with liquid bases [42].

501 4.2.2. Absence of rearrangement

502 The results of Figs. 6 and 7 clearly illustrate that pri-
 503 mary and secondary halolakanes form alkoxy (72 and
 504 80 ppm) framework stabilized at different C atoms in the
 505 chain. This definitely indicates that the framework alkoxy
 506 does not undergo rearrangement chemistry that is common
 507 with unimolecular substitution [29]. In the case of unimo-
 508 lecular substitution, the primary carbocation would rear-
 509 range to form the more stable secondary carbocation, as
 510 is seen for reactions in solution. The results are in agree-
 511 ment with theoretical predictions (DFT) by ~~Correa and~~
 512 ~~Rosenbach~~ [21,25] that substitution is bimolecular (S_N2).
 513 Another piece of evidence supporting bimolecular substitu-
 514 tion is the relative reactivity rate of the alkyl halides. Our
 515 observed order of preference for alkoxy formation,
 516 1° > 2°, is in agreement with the relative reactivity rate
 517 observed for bimolecular substitution in solution in the
 518 order, 1° > 2° > 3°. Unimolecular substitution (S_N1) has
 519 the reverse order, 3° > 2° > 1° [29].

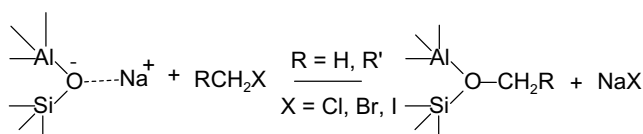
520 4.3. Proposed reaction schemes

521 In dehydrohalogenation, the cation pulls the halogen to
 522 form the sodium salt. The eliminated β-proton takes up the
 523 place of cation, as shown in Scheme 3 for NaX zeolite.

524 With this reaction, the originally basic NaX zeolite
 525 transforms to acidic HX. This transformation was con-
 526 firmed using IR with the band at 1548 cm⁻¹, shown in
 527 Fig. 11 and associated with pyridinium ion (PyH⁺). This
 528 is an indication that the original Lewis acid sites of NaX
 529 have been converted to Bronsted acid sites [31,32].

530 Substitution of the halogen occurs with the formation of
 531 salt and a carbocation stabilized by the zeolite, the frame-
 532 work alkoxy. This reaction is shown in Scheme 4.

533 ~~The presence of NaCl in the methyl iodide chemistry in~~
 534 NaX was confirmed in our previous report [26].



Scheme 4. Proposed halogen substitution reaction scheme.

5. Conclusions

536 Alkyl halides containing alkyl chains with more than
 537 two carbon atoms in zeolite NaX form framework alkoxy
 538 species, olefins or mixtures of the two, except for those with
 539 the halide at a tertiary C atom. The particular reaction that
 540 takes place depends on the specific halogen and the posi-
 541 tion of the halogen in the alkyl halide chain in ways that
 542 are characteristic of the relative rates of C–H and C–X
 543 bond cleavage and stereochemical accessibility of the halo-
 544 gen bearing C atom. Primary chloro and bromo alkanes
 545 form mixtures of framework alkoxy species and olefins,
 546 while the primary iodo alkanes form framework alkoxy
 547 species only. Predominantly, the formation of olefins takes
 548 place with secondary bromo and chloro alkanes. Second-
 549 ary iodo alkanes also give framework alkoxy in the product
 550 mixture. In general, a shift towards elimination is observed,
 551 as one progresses from primary to secondary alkyl halides.
 552 Halo ethanes undergo exclusively substitution reactions.
 553 Elimination reactions yield sodium halide salt and Bron-
 554 sted acid zeolite sites, distinct from the hydrogen halide
 555 gas formation found in solution chemistry. Double bond
 556 migration is inhibited in the zeolite chemistry relative to
 557 that found in solution.

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 564

Appendix A. Supporting information available

565 The supporting information available at <http://www.sciencedirect.com/science> includes two types of mate-
 566 rial. Experimental spectra are given for NaX reactions with
 567 compounds that were not commercially available for the
 568 complete series of halogens, X = Cl, Br, I. Groups of
 569 spectra are gathered together, in order to illustrate specific
 570 points discussed in this paper, which cut across and dupli-
 571 cate spectra presented in this paper in conventional chem-
 572 ical series order. A summary of whether framework alkoxy,
 573 olefin, both, or neither is given in tabular form.
 574 Supplementary data associated with this article can be
 575 found, in the online version, at [doi:10.1016/j.micromeso.2007.03.032](https://doi.org/10.1016/j.micromeso.2007.03.032).
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