

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

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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 ¹³C 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 I > Br > 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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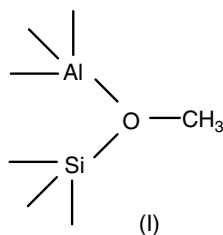
Keywords: Nucleophilic; Zeolite; Faujasite; NaX; Alkyl Halide; Substitution; Elimination; Adsorption; Alkoxide; Olefin; Dehalogenation; Dehydrohalogenation

1. Introduction

Zeolites are microporous aluminosilicate materials made up of [SiO₄]⁴⁻ and [AlO₄]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 ¹³C NMR [10] and later by neutron diffraction [11,12] and infrared techniques [13].

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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], Mota and co-workers [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 [8,25]. 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) 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

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