Novel Method To Generate Ionic Clusters within Zeolites

Y. S. Park, Y. S. Lee, and K. B. Yoon*

Department of Chemistry
Sogang University
Seoul 121-742, Korea

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Zeolite frameworks which consist of silicon and aluminum oxide have shown interesting properties as electron acceptors toward a variety of substrates in many important reactions.[1] Especially germane to this is the formation of ionic clusters of alkali metals such as Na_4^{3+}, Na_6^{5+}, K_4^{3+}, etc., which can be regarded as electrons shared by some alkali metal cations within the sodalite units of zeolites X, Y, A, and sodalite, when these zeolites are treated with strong reducing agents.[2-6]

The ionic clusters have received increased attention owing to their potential use as basic heterogeneous catalysts for hydrocarbons.[3] However, extensive investigations of their utility have been hampered since most of the techniques involved in the generation of the species have required high temperatures and high-vacuum techniques such as vapor-phase deposition of the alkali metal,[2] pyrolysis of impregnated alkali metal azides,[3] or irradiation of the zeolites with either γ- or X-rays *in vacuo*.[4] In this regard, we previously reported an efficient, large-scale alternative to generate sodium ionic clusters Na_4^{3+} within NaX and NaY by treating them with a hexane solution of *n*-butyllithium at ambient temperature.[5] Edwards et al.[6] also reported an ingenious method, which used solvated electrons formed *in situ* by dissolving lithium in primary amines. However, these methods involve the use of strong bases which are rather difficult to remove completely from zeolites. In this regard, we now report a new method to generate ionic clusters of sodium or potassium within zeolites X and Y at ambient temperatures.

When 1.0 g of NaY (Si/Al = 2.4), which previously had been dried at 250 °C *in vacuo* ($<10^{-5}$ Torr) for 10 h, was stirred with 0.02 g of sodium metal, Na, in tetrahydrofuran (THF) or diethyl ether with the aid of a magnetic stirrer in a glovebox charged with high-purity argon, the colorless zeolite slurry turned bright pink within 1–2 min. The pink hue intensified upon continued stirring, and after about 1 h it turned deep red while most of the Na (~8 atoms/unit cell) was consumed. The diffuse reflectance UV–vis spectrum of the colored, dried sample showed a broad band with a maximum (λ_{max}) at 495 nm (Figure 1A).

The ESR spectrum of the red zeolite, consisting of 13 equally spaced lines with hyperfine splitting constant $a = 36.3$ G and $g = 2.0042$ (Figure 2A), confirmed the presence of Na_4^{3+}. The
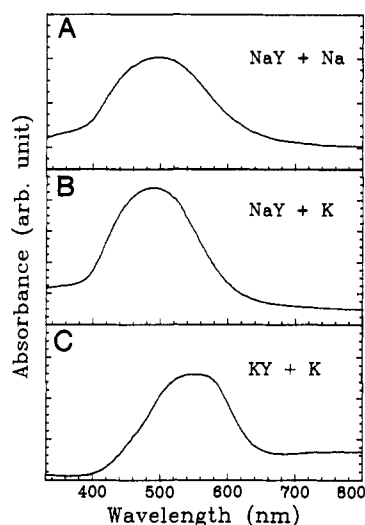

Figure 1. Diffuse reflectance UV–vis spectra of Na_4^{3+}(A, B) and K_4^{3+}-(C) within zeolite-Y obtained by stirring NaY with Na and K, respectively, and KY with K in THF (as indicated).
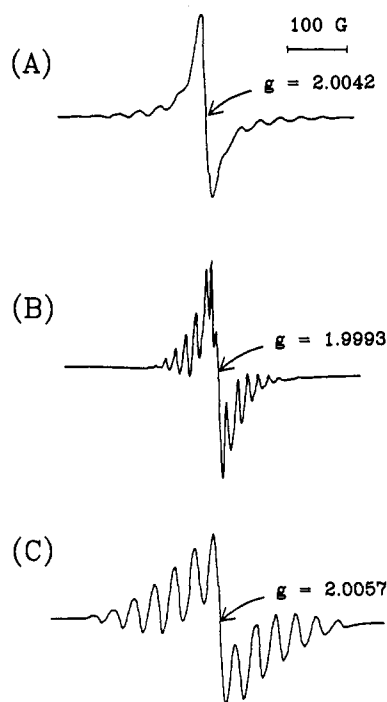

Figure 2. ESR spectra of (A) Na_4^{3+} and (B) K_4^{3+} within zeolite-Y obtained from NaY and KY, respectively, with K in THF, and (C) Na_4^{3+} obtained from NaY and Na in the presence of 18-crown-6 in THF.

broad singlet in the middle of the ESR spectrum along with the reflectance intensity in the UV–vis spectrum increased with an increase in the consumption of Na, in accordance with the results of Edwards et al.[2e] Interestingly, a significant increase in the rate of Na_4^{3+} formation in NaY was apparent when K was employed instead of Na (see Figure 1B).

When KY was treated with K in a similar manner, the mixture gradually turned dark purple upon stirring over a period of 1 h. The diffuse reflectance spectrum of the purple zeolite showed a broad envelope with $\lambda_{max} = 555$ nm along with a broad hump that extends to over 800 nm (Figure 1C). The ESR spectrum revealed the presence of 13 equally spaced lines with $a = 17$ G and $g = 1.9993$, characteristic of K_4^{3+}, overlapped by a sharp line at around the center (Figure 2B).

Interestingly, the above processes tended to be facilitated by the addition of small amounts of crown ethers such as 15-crown-5

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and 18-crown-6. The addition of a crown ether also affected the shape of ESR signals. Thus, when the THF slurry of NaY was stirred with K in the presence of a small amount of 18-crown-6, a clean ESR specrum of Na_4^{3+} ($a = 35$ G, $g = 2.0057$) resulted without the central broad singlet as shown in Figure 2C.

In NaX (Si/Al = 1.1), Na_4^{3+} was similarly generated by stirring the zeolite with K (but not with Na) in organic solvents.

In organic slurries, the amounts of alkali metals (Na and K) taken up by the faujasite-type zeolites varied, depending on the types of zeolites, exchanged cation, and alkali metal. In general, higher amounts of alkali metals were taken up by zeolite-Y than -X. The generation of ionic clusters was also much more facile within zeolite-Y and -X for a given alkali metal. We think this happens because NaY has higher oxidizing ability (acceptor strength) than NaX due to a higher silicon to aluminum ratio. The amounts of K taken up by Na^+-exchanged zeolites were usually higher than the amounts of Na taken up by K^+-exchanged zeolites, presumably due to the lower ionization potential of K than Na. Typically, the amounts of alkali metals incorporated into NaY ranged from 8 (Na) to 20 (K) atoms per unit cell (puc) in THF slurries. Most of the above processes were also highly effective with *n*-hexane as a convenient solvent.

Most surprisingly, direct stirring of zeolites with alkali metals *in the solid state* was even more efficient in terms of alkali metal uptake into zeolites. However, the efficacy in the formation of the ionic clusters in the solid state was very much dependent upon the stirring methods and the amounts of alkali metals initially added. Thus, when a small, powerful mechanical stirrer equipped with a glass blade was used for stirring, incorporation of more than 8 alkali metal atoms puc of zeolites could be easily achieved within 5–10 min from the mixture of zeolites and excess ($\sim$50 puc) amounts of alkali metals. In some cases (KX + Na, NaX + K), even the consumption of all the added alkali metals ($\sim$50 puc) was observed within 2 h. When smaller amounts of alkali metals ($<$8 puc) were added, the processes were somewhat slower.

However, a significant increase in the rates was noticed when alkali metals were squashed onto the inner wall of the reaction flasks, prior to stirring.

The solid-state method was also highly distinguished from the solution analog in terms of the variety of generated ionic clusters. Thus, while Na_4^{3+} was generated within NaY, Na_6^{5+} ($a = 27$ G, $g = 2.001$) was produced within NaX when stirred with Na or K. Interestingly, K_3^{2+} ($a = 16$ G, $g = 1.999$) was generated within KX, while a mixture of K_4^{3+} and an unidentified ionic cluster was formed within KY, when stirred with Na or K.

The zeolite colors (red, blue, or gray) darkened with an increase in the incorporated amounts of alkali metals, and they usually changed to black at higher loadings. The ESR spectra usually contained a central broad singlet even at low loadings ($\sim$1 puc). In the cases of NaY and KY, at low loadings ($\sim$1 puc), the ESR spectra showed the presence of some broad resonances with high g values (2.07–2.5), besides the ionic clusters.

The ionic clusters generated by our methods are indefinitely stable under the dioxygen- and moisture-free conditions. It is also important to note that the mere placement of NaY with a piece of freshly cut Na or K in the solid state or in organic slurries also results in the slow coloration of the surrounding zeolite powders near the alkali metal at ambient temperature.

The above methods are equally effective for larger-scale ($>$10 g) preparations of these ionic clusters within zeolites and may be applicable for the reduction of various chemical species encapsulated within zeolites. Our results also reveal the interesting property of zeolites that they react readily with bulk alkali metals (Na and K), even upon mere physical contact in the solid state, at ambient temperature.