

Novel Synthesis of Ionic Clusters (Na_4^{3+}) in Zeolites

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The ionic cluster Na_4^{3+} in zeolite matrix is synthesized selectively and in high yields by the liquid phase treatment of NaX with organolithium reducing agents at room temperature.

Formation of the interesting ionic clusters from alkali metals such as Na_4^{3+} , (refs. 1—10) K_4^{3+} , (refs. 5—7) and Cs_4^{3+} (ref. 11) in zeolite matrices has received increased attention owing to their potential as heterogeneous catalysts for hydrocarbons. However extensive investigations of their utility have been hampered by the limited number of reproducible methods (especially on a large preparative scale), heretofore involving such high temperature and high vacuum techniques as vapour phase deposition of the sodium metal^{1—7} or pyrolysis of impregnated sodium azide.^{8—10} Furthermore, the Na_4^{3+}

cluster is thermally unstable,^{1,2} and the requisite elevated temperatures of the extant procedures inevitably lead to the simultaneous formation of sodium aggregates (Na_x).⁶

Stemming from our interest in liquid phase catalysis by zeolites, we now report a novel and general method for the selective and convenient synthesis of ionic clusters in high yields at ambient temperatures, as typified here by Na_4^{3+} . For example, the addition of an hexane solution of n-butyl-lithium to NaX zeolite in an inert atmosphere at room temperature immediately led to a colour change and ultimately produced a

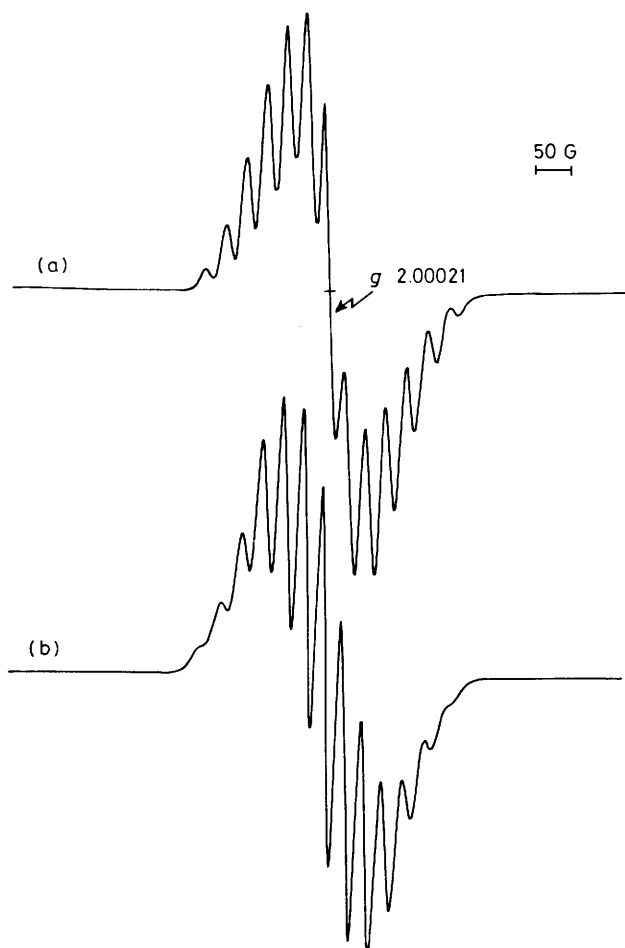


Figure 1. (a) E.s.r. spectrum of Na_4^{3+} from the reduction of NaX zeolite by butyl-lithium in hexane at room temperature. (b) Simulated spectrum using Lorentzian rather than Gaussian linewidths.

purple solid.[†] The brilliant purple zeolite was obtained by filtration followed by washing with additional hexane and drying *in vacuo*. The resolved e.s.r. spectrum ($\langle g \rangle = 2.0031$) showed negligible contamination by sodium atom clusters [see Figure 1(a)]. The computer simulated e.s.r. spectrum in Figure 1(b) verified the 13-line hyperfine splitting due to Na_4^{3+} with $a_{\text{Na}} = 29$ G.[‡] The Na_4^{3+} clusters prepared by this method were thermally unstable. Thus, the purple sample was bleached when heated overnight at 120 °C under an argon atmosphere; its e.s.r. spectrum was then dominated by the sharp singlet of Na_x at $\langle g \rangle = 2.0024$. Exposure of the Na_4^{3+} clusters to oxygen immediately produced a colourless zeolite, the e.s.r. spectrum of which was assigned to superoxide by comparison with that obtained earlier.^{2,3} The purple zeolite also reacted readily with water to afford a diamagnetic, colourless solid.

[†] Optimum preparative results were obtained by treating NaX zeolite doped with ~1% Co^{II} with butyl-lithium for two days. Alternatively, a diethyl ether solution of phenyl-lithium can be employed as the reductant.

[‡] $G = 10^{-4}$ T. For the simulation, $a_{\text{Na}} = 28.7$, $\Delta H_{\text{pp}} = 26$ G, Lorentzian lineshape. The conversion of NaX by conventional methods leads to blue Na_6^{5+} . (refs. 2, 8)

A bright red zeolite was obtained when the same method was applied to NaY. The associated e.s.r. spectrum consisted of a 13-line splitting due to Na_4^{3+} ($\langle g \rangle = 2.0010$, $a_{\text{Na}} = 35$ G), together with a strong central component ($\langle g \rangle = 2.0024$) due to Na_x . The latter dominated the e.s.r. spectrum of the black zeolite obtained from NaA zeolite. The characteristic 13-line hyperfine splitting of Na_4^{3+} was not observed when the sodium ions in NaX were completely exchanged with either Li^+ , K^+ , Mg^{2+} , or Co^{2+} .

Ionic clusters of Na_4^{3+} in zeolites were reproducibly prepared by this simple method, as judged by the resolved e.s.r. spectra (similar to that shown in Figure 1) which were routinely obtained. Furthermore, the method is readily amenable to large scale preparations since 10 g quantities of NaX zeolite can be conveniently converted with 15 ml of 1–2 M butyl-lithium in hexane. The concentration of Na_4^{3+} in the purple NaX was estimated to be eight per unit cell based on the quenching with either water, tetranitromethane, or $\text{Mn}(\text{CO})_5(\text{NCMe})^+$.¹³ This result supports the previous proposal of the existence of Na_4^{3+} clusters in the sodalite unit.⁶

NaX zeolite can also be converted directly into Na_4^{3+} clusters, by the actinic irradiation of the stirred ethereal slurry containing phenyl-lithium. Thus a dramatic colour change from white to intense purple occurred when NaX suspended in an ethereal solution of PhLi was irradiated at $\lambda > 350$ nm. The e.s.r. spectrum of the purple zeolite showed the 13-line hyperfine splitting (Figure 1), together with varying intensities of the central resonance that depended on the amount of phenyl-lithium added. No change was observed when NaX was irradiated in the absence of organolithium compounds.

Ionic clusters of Na_4^{3+} prepared by these mild and selective procedures show unique behaviour as reducing agents for carbon monoxide,⁷ aromatic hydrocarbons, organometallic complexes, *etc.* The unusual products will be reported at a later time.

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