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IONIC CLUSTERS IN ZEOLITES FORMED BY INTERACTION WITH SODIUM SOLUTIONS IN LIQUID AMMONIA

S. BORDIGA, A. FERRERO, E. GIAMELLO, G. SPOTO and A. ZECCHINA *

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Torino, Italy

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An alternative route for the preparation of Na_4^{3+} paramagnetic clusters in Y zeolites is described involving contact of the solid with a solution of sodium in liquid ammonia. Besides the EPR signal of the cluster a second signal, likely due to be a solvated electron in the sodalitic cage, is also observed.

Keywords: Ionic clusters, zeolites, liquid ammonia, EPR spectroscopy

It is well known since the pioneering work of Kasai and coworkers [1–3] that exposing dehydrated, Na^+-exchanged Y zeolites to sodium vapours a paramagnetic cluster of formula Na_4^{3+} is formed in the zeolitic framework. Its formation (also observed after γ-irradiation of Na^+/Y) is basically due to the ionization of the sodium atom and subsequent trapping of the released electron by a cluster of four Na^+ ions. The EPR spectrum of the Na_4^{3+} cluster [1] is a well defined 13 lines signal typical of an electron shared among 4 equivalent sodium nuclei (nuclear spin $I = 3/2$).

Successively the subject has been revisited several times and it has been convincingly shown that the formation of the paramagnetic clusters Na_4^{3+} can also take place by evaporating alkali metals different from sodium: this means that the type of metal ion constituting the cluster is always that present in the parent zeolite and not that evaporated onto the solid [4,5]. Furthermore it is now accepted that the M_4^{3+} clusters are formed within the sodalitic cage of the Y-zeolite and of other faujasite type aluminosilicates [5,6], while the ionized Na^+ is located in the supercage.

As to the method for the obtaining of the paramagnetic clusters only an alternative route to the metal evaporation has been proposed which consists in the impregnation of the dehydrated zeolite with a solution of sodium azide (NaN_3) in methanol followed by the thermal decomposition of the azide at 520–600 K [7].

The present communication deals with a novel low temperature method of Na_4^{3+} generation based on the interaction of the dehydrated Y-zeolite with a

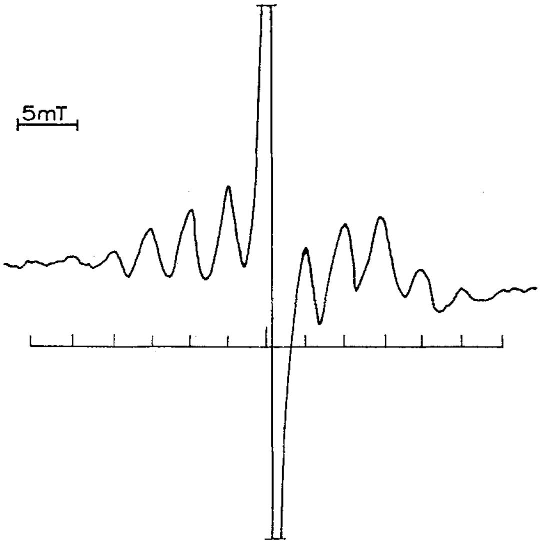

Fig. 1. EPR spectrum of the Na/Y zeolite contacted with a sodium solution in liquid ammonia.

solution of sodium in liquid ammonia i.e. a system containing solvated electrons and sodium ions [8]. The spectral features and stability of the system prepared by this new procedure are, however, slightly different from those obtained by the classic metal evaporation.

The solution of sodium in liquid ammonia has been obtained by trapping NH_3 vapours in a suitable manifold containing a small amount of metallic sodium. The solution is deep blue and exhibits, when frozen at 77 K, an intense, slightly asymmetric, EPR spectrum at about $g = 2.0020$. By contacting a zeolite sample (outgassed at 673 K) with the ammonia solution (at a temperature of about 240 K) the solid turns to blue and then, by increasing the temperature to 298 K, to red. Cooling again at 77 K, the solid exhibits the EPR spectrum reported in fig. 1. The spectrum is basically due to the superposition of two signals. The first one is the classic 13-lines multiplet centered about at $g = 2.0001$ and due to the Na_4^{3+} cluster located in the sodalitic cage of the zeolitic framework, as shown by computer graphics in fig.2. The hyperfine separation is the same observed by Kasai in Na^+/Y zeolites [1–3] i.e. 3.25 mT (1 T = 10000 G). The second signal is an intense and symmetric line at $g = 2.0014$ that overlaps the central line of the multiplet. The latter one, in fact, is expected to be only slightly more intense than the two neighbouring lines as the theoretical intensity ratio for the first seven lines of the multiplet is $1:4:10:20:31:40:44$. The intensities observed in the spectrum in fig. 1 unambiguously indicate, therefore, that a second signal is superimposed to the 13-lines multiplet. Solvated electrons in the supercage of the zeolite could be responsible of this latter signal. However, since the signal is definitely different from that of the frozen solution of sodium in ammonia, solvated electrons hosted in the sodalite cage can be invoked as well, as it has

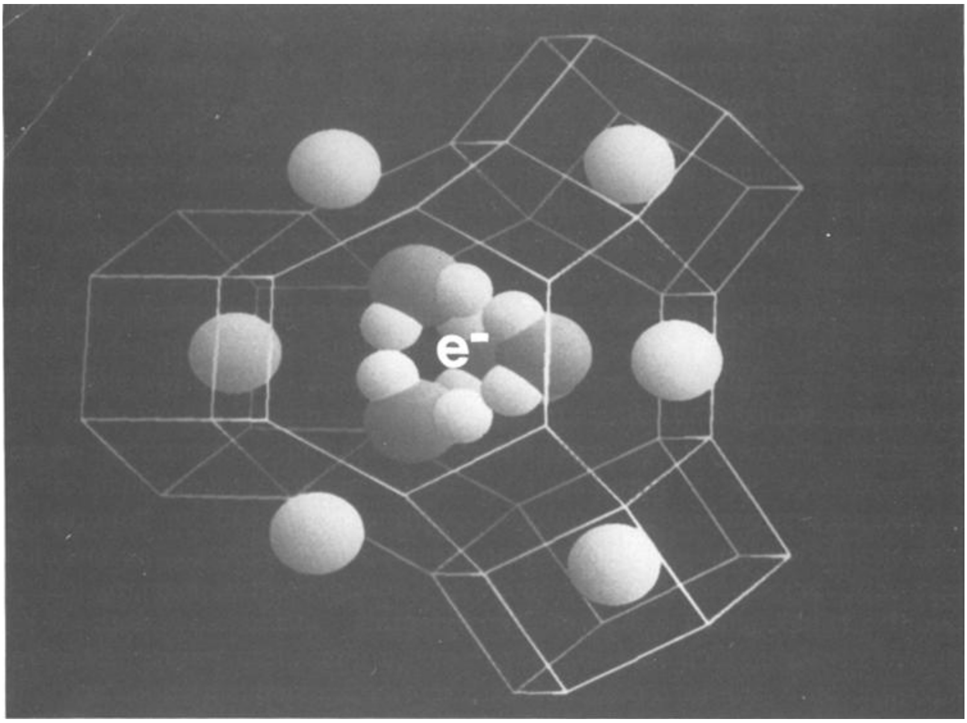

Fig. 2. Computer graphics picture of a Na_4^+ cluster into the sodalitic cage.

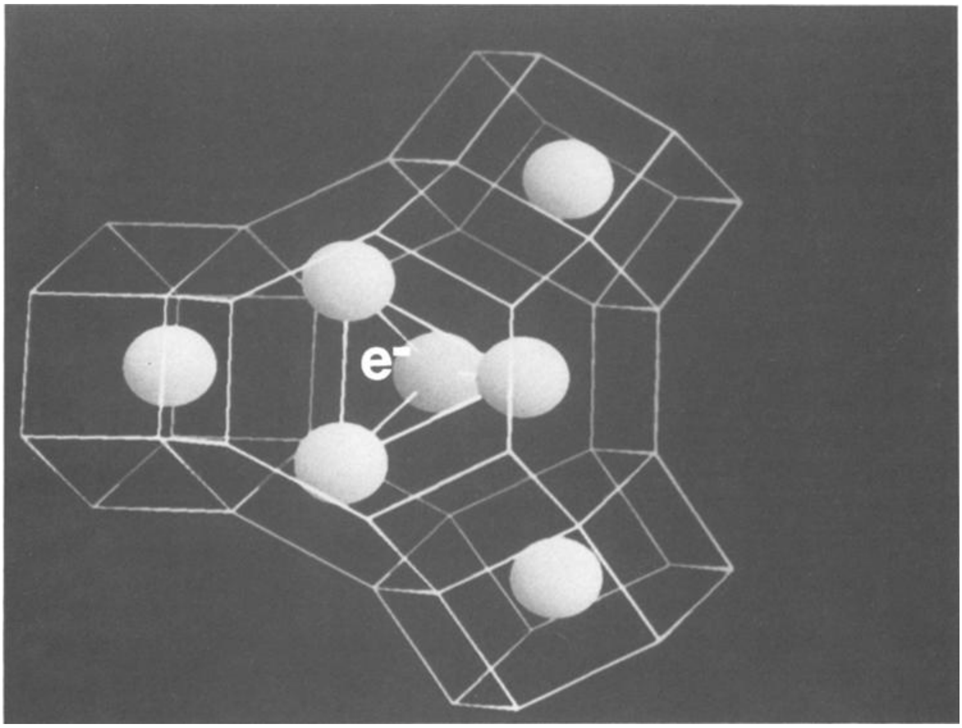

Fig. 3. Computer graphics picture of a $(NH_3)_4^-$ cluster into the sodalitic cage.

been shown that ammonia molecules can easily enter the sodalite cage [9]. The most commonly accepted model for solvated electrons in ammonia is an electron surrounded by four NH_3 molecules in tetrahedral symmetry [10,11]; computer graphics (fig. 3) shows that such a cluster can fit in the sodalite cage with distances between sodalitic sodium ions and nitrogen close to those found for ammonia adsorbed on sodium in zeolites [12].

Differently from other examples [1–3,5–7] the EPR signal of the system above described is stable in a limited range of temperature as it slowly decomposes at room temperature in the presence of gaseous ammonia and disappears by evacuation at 373 K.

The system is very reactive towards oxygen. By contact with this gas at room temperature the red colour suddenly disappears and the spectrum reported in fig. 1 is replaced by a new EPR signal typical of the superoxide radical ion O_2^-. The g_{zz} parameter which is usually considered the finger print of the adsorbed superoxide is 2.1210. This value coincides with that reported by Kasai [1] for superoxide ions in γ-irradiated Na^+/Y and is typical of an interaction of the radical species with Na^+ ions.

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