The Role of Water in Zeolitic Encapsulation: the Cs,Na-A(O₂) Case

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Three low-temperature peaks are generated during the temperature programmed diffusion of O_2 from gradually rehydrated Cs,Na-A(O₂) encapsulates; these peaks are associated with molecular jumps through 6-rings blocked by tetrahedral Na^+ ions in co-ordination with zeolitic water apparently at various stages of clustering.

Conflicting evidence exists on the effect of water in zeolitic encapsulation of simple non-polar gases. Treatment of encapsulates with water is known as a method of releasing trapped gases, *e.g.*, from zeolite 3A.[1] 'Superficial rehydration' after encapsulation has been claimed to improve zeolite retentivity for various gases, *e.g.*, Kr in zeolite M.[2] Yet, a third report mentions the appearance of a low-temperature desorption peak upon decapsulating Ar from 3A zeolite using water-saturated He carrier gas.[3] In the course of our study on the diffusional behaviour of encapsulated O_2 in Cs,Na-A,[4] we have noticed the appearance of more than one temperature programmed diffusion (TPD) peak due to β-cage decapsulation. We suspected that this might be related to the presence of zeolitic water and have undertaken a rigorous investigation on the role of water in zeolitic encapsulation. This paper is concerned with the effect of deliberate rehydration of Cs,Na-A(O₂) encapsulates on the mechanism of O_2 motion within the microcrystalline zeolitic structure.

A series of representative differential TPD chromatograms, obtained as described in the preceding communication,[4] are given in Figure 1 for selected degrees of Cs exchange (Cs$_z$). As shown in Figure 1(a), Na$_{12}$-A (Cs$_z$ 0) exhibits two peaks in its dehydrated form, marked (i) and (ii) with relative areas of *ca.* 2 and 1, respectively. Upon rehydration, peak (i) decreases and peak (ii) increases, and a third, lower-temperature peak, marked (iii) appears. The last chromatogram of Na-A shows a fourth peak, (iv) as the most intense peak. We conclude that peak (i) is due to an O_2 jump through a 6-ring in the dehydrated form, having a trico-ordinated Na^+ ion bound to the three O-3 framework oxygens. This ring, designated $6R_{Na}^d$ is the most effectively closed 6-window. The three new peaks, (ii)—(iv) resulting from gradual rehydration† are believed to represent hydrated 6-windows. In such windows the Na^+ ion is bound to four oxygens, three framework O-3 atoms and one belonging to a water molecule. This tetraco-ordinated Na^+ is pushed slightly away from the 6-ring plane toward the large α-cavity thereby creating a slightly distorted tetrahedral I-site position. Such a picture has been already confirmed by X-ray diffraction studies of Na-A[5] and Cs$_7$Na$_5$-A,[6] although in both cases only *fully* hydrated structures were analysed. We believe that the transition from a trigonal to a tetrahedral Na^+ at site I is responsible for the diminishing effectiveness of the 6-ring as a closed window. Furthermore, the fact that rehydration generates (at least) three TPD peaks suggests that there might

be several distinct tetrahedral I-site positions for Na^+, depending on the degree of rehydration. Possibly, peak (ii) is due to decapsulation *via* 6-windows of partially hydrated zeolites ($6R_{Na}^{ph}$) with an isolated H_2O molecule bonded to the Na^+ ion, whereas peaks (iii) and (iv) could be correlated with the presence of windows having Na^+ co-ordinated to H_2O at a certain stage of clustering. As more water positions within the α-cage are filled up, Na^+ is probably pulled more strongly toward the centre of this cage and the 6-window becomes more open for O_2 diffusion. A recent powder X-ray diffraction
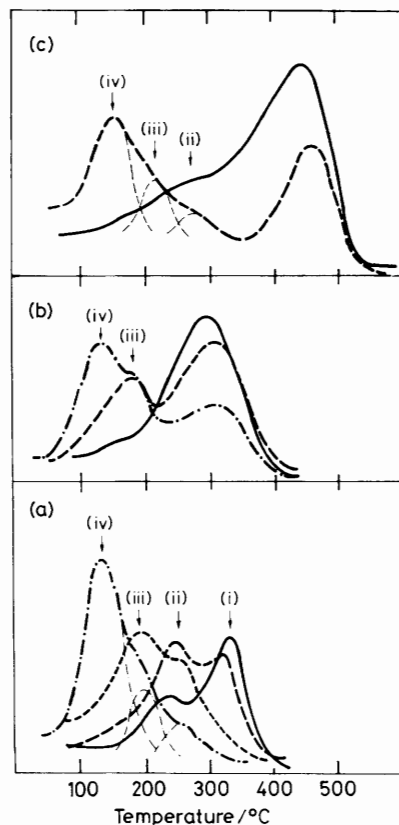

Figure 1. O_2 TPD chromatograms for Cs,Na-A(O₂) obtained at a heating rate of 0.533 °C s⁻¹. (a) Cs$_z$ 0; ——, dehydrated form; — —, 5.3 water molecules added per *pseudo*-cell upon rehydration; – – – –, 7.4; – · –, 25.5. (b) Cs$_z$ 3.0; ——, dehydrated form; — —, 5.3; – · –, 9.8. (c) Cs$_z$ 4.5; ——, dehydrated form; — —, 25.2.

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† The presence of peak (ii) at 'zero rehydration' is apparently because of residual water in dehydrated Na-A.

study of Ca-A at different dehydration stages has revealed, for the fully hydrated form, two Ca^{2+} sites near the 6-ring, one close to the ring plane, the other well inside the α cavity.[7] The multiplicity of co-ordination concluded for hydrated Ca-A (involving 4- and 6-co-ordination) seems, however, inappropriate for Na-A because Na^+ is apparently incapable of co-ordinating with more than four neighbouring atoms.[8] Peak (iv) might be attributed to the fully hydrated zeolite ($6R_{Na}^{fh}$) at which the eight I-site Na^+ ions per pseudo-cell are co-ordinated to eight 'II type' H_2O molecules of the dodeca-hedral water cluster characterizing fully hydrated Na-A.[5] The activation energy for O_2 diffusion calculated from this peak is 41 ± 1 kJ mol^{-1}, about half the value obtained for peak (i),[4] in accord with the foregoing discussion.

Figure 1(b) gives chromatograms of O_2 decapsulation from $Cs_{3.0}$-A. As seen, rehydration produces the same low-temperature peaks as in Na-A [Figure 1(a)]. A similar trend is observed with $Cs_{4.5}$-A [Figure 1(c)]. Since both cases are concerned primarily with α-cage decapsulation,[4] this indicates that upon rehydration the α,α diffusion mode is apparently replaced by the α,β mode. A plausible explanation is that unlike the rather dramatic decrease in the efficiency of $6R_{Na}$ as a closed window on rehydration, the $8R_{Cs}$ ring[4] is only very slightly influenced by H_2O, as reflected by crystallographic data.[6]

Our results do not conform with the early observation[2] that rehydration enhances zeolite retentivity for trapped gases although this disagreement may arise from structural differences between the different zeolite types studied. Also, these results do not seem to support the view that the reason for the easy decapsulation upon rehydration is displacement of the

trapped gas by the more strongly sorbed water;[1] at least this is not the case at low loading of ca. one gas molecule per α-cage. The changing chemical environment of zeolitic cages when filled with water molecules may, however, have an influence on the location and energetics of trapped gas molecules. Finally, the reported decapsulation behaviour of 3A(Ar) when performed under a wet He stream[3] resembles the pattern of decapsulation for $Cs_{3.0}$-A(O_2) at an intermediate rehydration state [Figure 1(b)].

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