Resolved α- and β-Cage Decapsulation Peaks in the Temperature Programmed Diffusion of Oxygen in Cs,Na-A Type Zeolites

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Temperature programmed diffusion peaks due to α- and β-cage decapsulation are clearly resolved in the Cs,Na-A(O_2) system; the latter peak is independent of the degree of Cs exchange whereas the former peak shifts to higher temperature with increasing Cs content.

Encapsulation of small non-polar gas molecules in A-type zeolites can take place either in the α-cage or in the β-cage, or in both depending on the degree of exchange with a blocking univalent cation. This was previously concluded from the analysis of results obtained for the Cs,Na-A(H_2) system in terms of the change in encapsulation capacity, the change in peak temperature (T_M) generated during temperature programmed diffusion (TPD), and the change in activation energy for diffusion (E) as a function of the degree of Cs exchange (Cs_z).[1,2] However, H_2 decapsulation from Cs,Na-A always gave only one symmetrical TPD peak and no distinction could be made between α- and β-cage encapsulation based on the anticipated difference in T_M between the two corresponding modes of gas escape. Since O_2 (kinetic diameter, σ 0.34 nm) is a much larger molecule than H_2 (σ 0.289 nm), we expected the Cs,Na-A(O_2) system to exhibit sufficient difference between T_M's due to α- and those due to β-cage decapsulation, thus allowing effective peak separability. In this communication we report on preliminary TPD results with this system and on what appears to be the first successful resolution of α- and β-cage decapsulation peaks.

Encapsulation experiments were performed in the arrangement described previously.[1†] Decapsulation was performed either *in situ* affording integral curves [amount of gas released *vs.* time (temperature)], or in a separate apparatus generating differential curves [rate of gas release *vs.* time (temperature)]. The latter device employs a sample cell containing a Perkin-Elmer TGS-1 furnace, through which helium carrier gas flows to a gas chromatograph equipped with a drying column and a thermal conductivity detector. In general there was satisfactory agreement between results obtained in the differential measurements and those derived from the integral curves. Figure 1 shows representative differential TPD chromatograms obtained at various Cs_z values. Up to Cs_z 2.2 encapsulation is restricted to the β-cages, as confirmed by the change in peak area between Cs_z 2.2 and 2.4 as well as by the cut off in the integral decapsulation curve (not shown herein) at Cs_z *ca.* 2.25, in excellent agreement with

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† The zeolite sample was loaded at 350—450 °C with O_2 under pressure (11.3—12.3 MPa) to give upon cooling *ca.* one trapped O_2 molecule per α-cage, or per five β-cages.
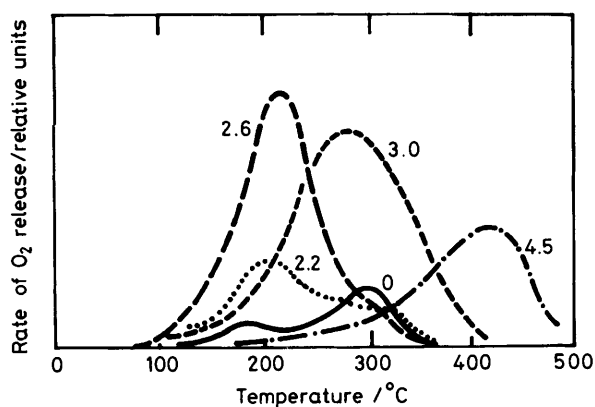
Figure 1. Normalized TPD chromatograms for the decapsulation of O_2 from Cs,Na-A at a heating rate of *ca.* 0.27 °C s^{-1}. (The number indicated near each curve is the corresponding Cs_z value.)
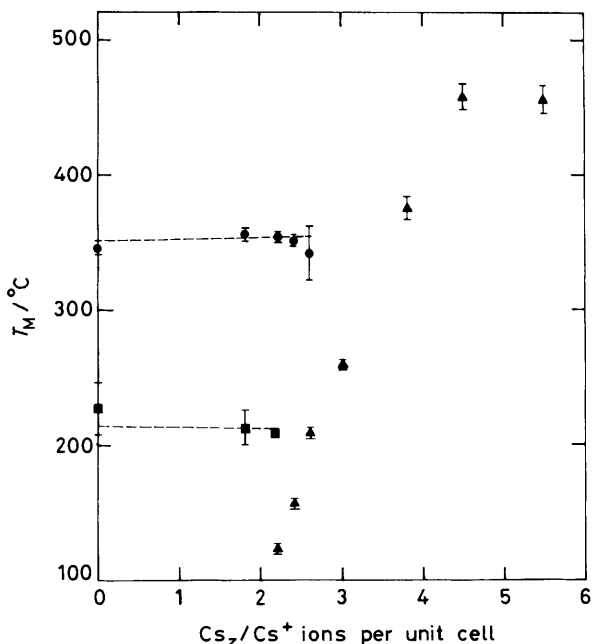

Figure 2. Change in T_M at a heating rate of *ca.* 0.2 °C s^{-1} as a function of the degree of Cs exchange. (Source of T_M values: integral curves; ●, β-cage decapsulation through $6R_{Na}{}^d$ windows; ■, β-cage decapsulation through $6R_{Na}{}^{ph}$ windows; ▲, α-cage decapsulation.)
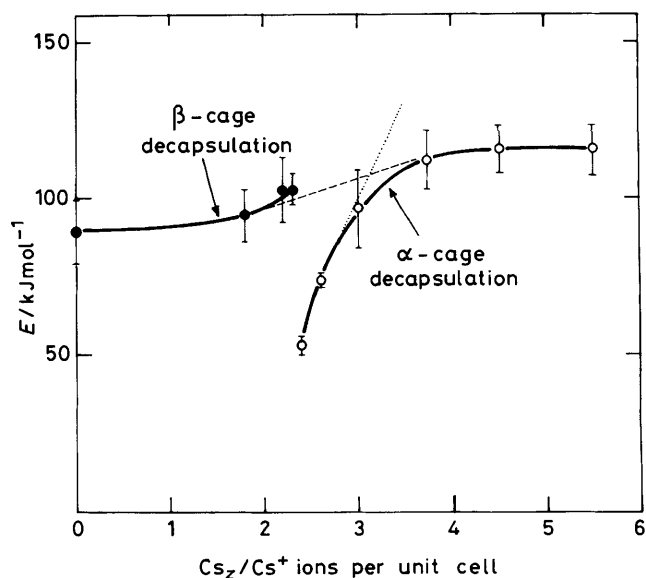

Figure 3. Change in activation energy for diffusion as a function of the degree of Cs exchange. (Results for β-cage decapsulation are based on T_M's associated with $6R_{Na}{}^d$ windows.)

the percolation theory and previous results with other gases in zeolite A.[2] The right-hand peak at Cs_z 0 (Na_{12}-A) is attributed to β-cage decapsulation through dehydrated Na$^+$-blocked 6-oxygen rings which we designate $6R_{Na}{}^d$. This peak is seen clearly in the exchange region Cs_z 0—2.6. The lower peak at Cs_z values of 0 and 2.2 is identified with molecular passages through partially hydrated 6-windows ($6R_{Na}{}^{ph}$) as discussed in detail in the subsequent paper.[3] Above Cs_z *ca.* 2.0, a third, more intense peak appears which shifts considerably to higher temperature with increasing Cs exchange, and is attributed to α-cage decapsulation through Cs$^+$-blocked octagonal ($8R_{Cs}$) windows. The behaviour of these three peaks as a function of Cs_z is further illustrated in Figure 2. β-Cage decapsulation through either $6R_{Na}{}^d$ or $6R_{Na}{}^{ph}$ windows is found to be

independent of Cs_z while, in contrast α-cage decapsulation through $8R_{Cs}$ windows is dramatically influenced by Cs_z, becoming gradually more difficult as Cs_z increases in the region 2.2—4.5.

E values for the Cs,Na-A(O_2) system derived from the resolved α- and β-cage decapsulation peaks, are plotted in Figure 3 as a function of Cs_z. These values were calculated from T_M's obtained from integral curves at various rates of heating in the range 0.067—0.533 °C s^{-1}, using the previously employed TPD equation.[1] The behaviour seen in Figure 3 generally resembles that predicted for the Cs,Na-A(H_2) system:[1] a constant E at low Cs content due to β-cage decapsulation through $6R_{Na}{}^d$ windows and an α-cage decapsulation curve increasing steeply at lower Cs level (2.4—*ca.* 3.5) then approaching a plateau. However, with the present system there is an indication of some increase in E due to β-cage decapsulation above Cs_z *ca.* 2.‡ Also, the plateau of the α-cage decapsulation curve is slightly above that of β-cage decapsulation. Therefore, the diffusion pathway of O_2 during decapsulation from Cs,Na-A cannot be concluded unequivocally. An α,α mode of molecular jump over the entire range of α-cage decapsulation, previously proposed for H_2, is one possibility. Alternatively, one may assume that E, due to α,α jumps, increases steadily at $Cs_z > 2.4$ (dotted line in Figure 3) but at Cs_z *ca.* 3.5 becomes so high that decapsulation starts to favour the α,β jump mode (*i.e.*, an indirect passage from one α-cage to the other, involving the β-cages). The dashed line in Figure 3 connects E values for β-cage decapsulation through $6R_{Na}{}^d$ windows with E values reflecting α-cage decapsulation possibly through the very same windows. The apparent increase in closure effectiveness of $6R_{Na}{}^d$ windows with increasing Cs exchange above Cs_z *ca.* 2.0 is as yet unexplained and certainly deserves further attention.

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‡ In fact, at Cs_z 2.6 a value of 123 ± 10 kJ mol^{-1} was obtained but because of peak separation difficulties when most of the gas is encapsulated in the α-cage, we doubt the accuracy of this value.

References

1 D. Fraenkel, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2029, and references therein.
2 D. Fraenkel, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2041.
3 D. Fraenkel, B. Ittah, and M. Levy, *J. Chem. Soc., Chem. Commun.*, following communication.