Cations and Cation Migration in Zeolitic Materials - I - Influence of temperature and water on the Ba migration in Faujasite

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BaY Material **: $Ba_{28}Al_{56}Si_{136}O_{384}.nH_2O$**

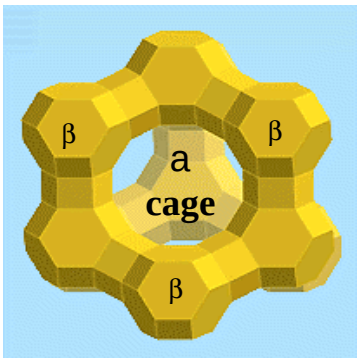

Fig.1 - The FAU structure type

Zeolites presenting the Faujasite structural type [1] (Fig.1,2) are widely used in petrochemical processes for selective gas separation, catalysis and detergent builders. NaY (Si/Al=2.42) zeolite has been totally Ba-exchanged and both its hydrated and dehydrated forms have been investigated by X-ray synchrotron powder diffraction (λ=0.79969Å). The samples have been filled into 0.9mm quartz capillaries, mounted on a specially designed atmosphere-controlled sample holder (Fig.3) and investigated in the 25-450 °C temperature range.

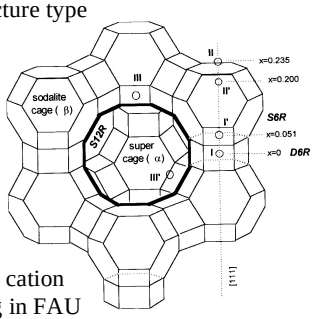

Fig.2 - cation labelling in FAU

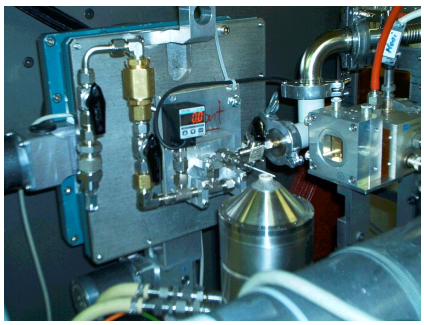

Fig.3 - Experimental setup

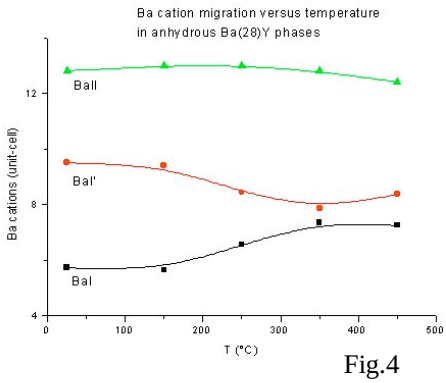

Fig.4

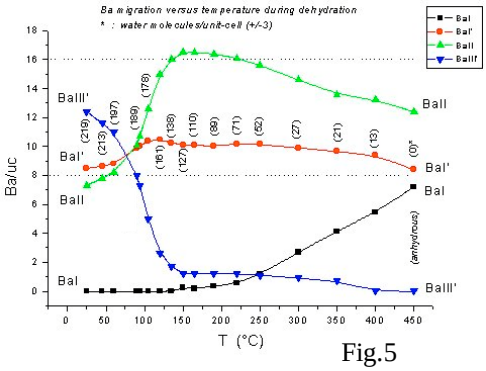

Fig.5

In the hydrated BaY samples four Ba sites (I,I',II and III') and five water sites have been identified. In Figure 5 the Ba cation migration versus temperature at different water fillings (in parenthesis) is represented. In the anhydrous BaY (Fig.4) only three I,I' and II Ba species are detected, and the Ba migration versus temperature is significantly less important than in the hydrated phases. These results correspond to the ***dehydration*** of BaY. In Figure 6 the distribution of the water molecules during dehydration is described : owI' in the sodalite cage (β) is bonded to BaI' - owII in the super-cage (α) is bonded to BaII - owIII' close to the twelve ring windows (S12R) are bonded to BaIII' cations - ow4 and ow5 are located close to the super-cage center and are in interaction with BaII and BaIII' cations. Unit-cell parameters of BaY in its hydrated and dehydrated forms are given versus temperature in Figure 7. Figure 8 is an example of a Rietveld plot corresponding to BaY at 50% dehydration.

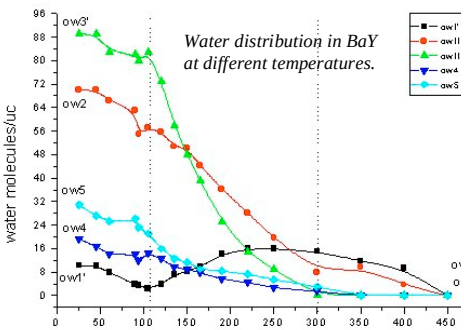

Fig.6

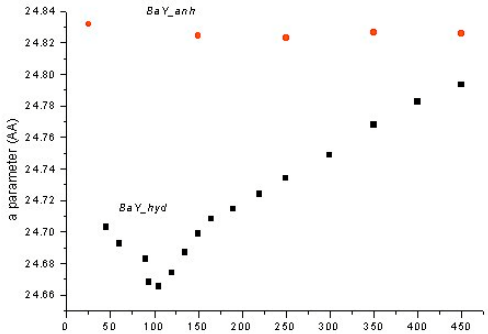

Fig.7

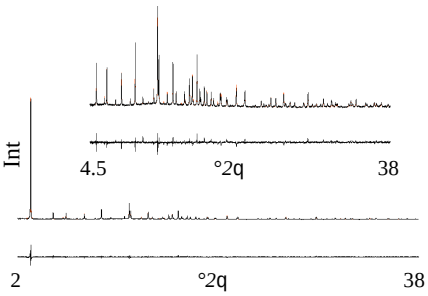

Fig.8
Rietveld-plot for
$BaY.120H_2O$

Data-collections corresponding to several ***partially rehydrated*** samples at ambient temperature show that the hydration process of BaY is ***very slow*** : *e.g.*, at a same overall water filling (24 water molecules/unit-cell) Ba and water migrate simultaneously and equilibrium is obtained after at least 12 hours. The study of the complete hydration process of BaY at ***ambient*** temperature is part of future work. Similar results have been observed in the case of partially Cs-exchanged NaY faujasites [2].

References

[1] - W.L. Meier and D.H. Olson, Atlas of Zeolite Structure Types, Butterworths (1987)
[2] - P. Norby, F.I. Poshni, A.F. Gualtieri, J.C. Hanson and C.P. Grey, J. Chem. Phys; B, **102** (1998) 839-856.