

How intensities of specific reflections in XRD can be used as a finger print for the encapsulated complexes?

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This is always a question since the diffraction pattern of most of the zeolites are the same before and after encapsulation. The normal trend observed is that in the original sample the intensities of the following three lines have some information contained in them namely 331,311, and 220. Quayle and Lunsford suggested that a relationship exists between the relative intensities of 331,311,220 XRD peaks and cation distribution in faujasite-type zeolites [W.H.Quayle and J.H.Lunsford, *Inorg.chem.*, 21, 97 (1982)

Also see J M Thomas, C Williams and T Rayment, *JCSFaraday Trans*, 84,4647 (1988) and also Y Okamoto et al., *JCS Faraday Tans.*, 92,4647 (1996) some more recent references are given at the end of this presentation.

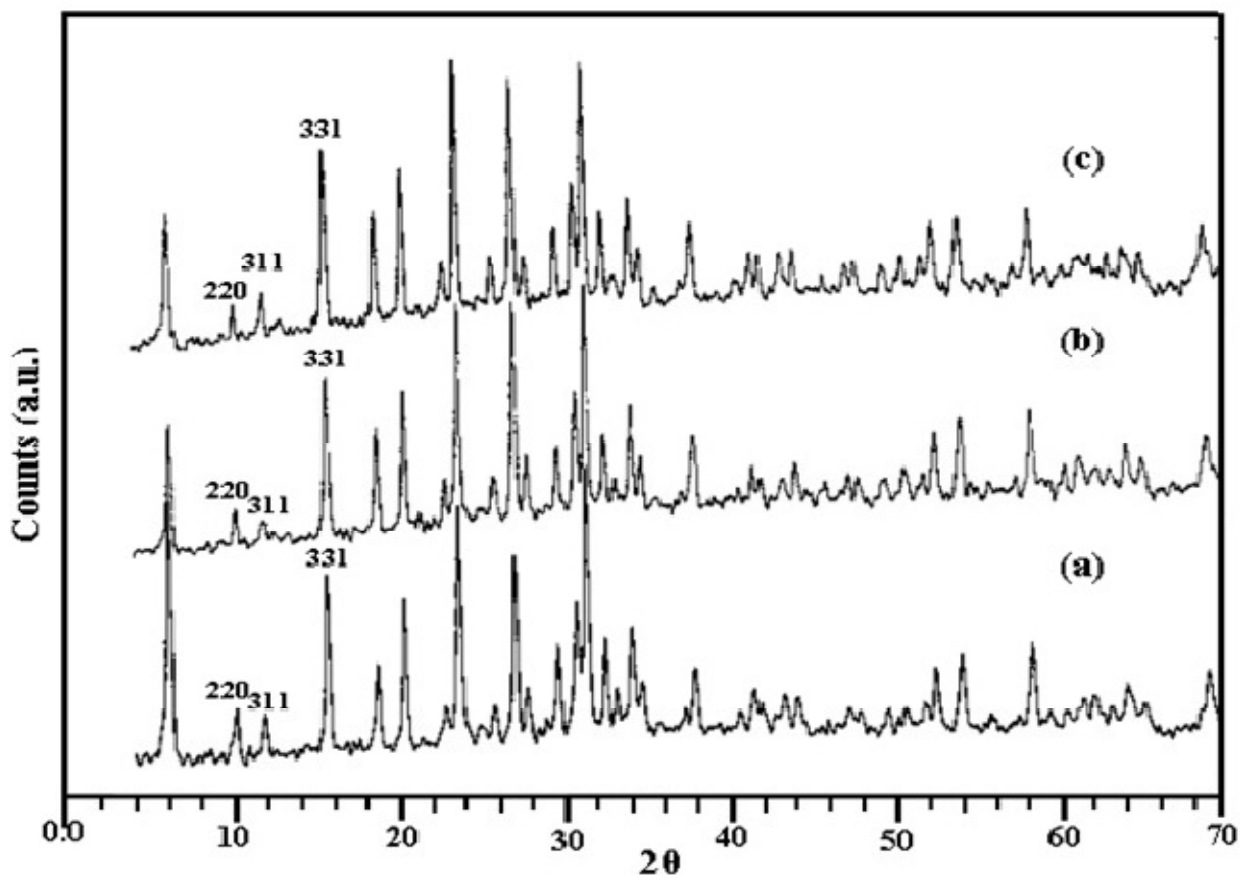
If the intensity ratio were to follow  $I_{331} > I_{220} > I_{311}$  sodium ions are randomly distributed and this can be the situation in the Na-Y type of zeolite.

If the cations were situated in type I' and II type sites then the intensity will follow the order  $I_{331} > I_{311} > I_{220}$  the larger cations have replaced the cations in the super cages from their original positions. Such intensity variations have been observed for a number of ship in bottle complexes and however there is no change in the pattern showing the basic zeolite unit is not changed. The absence of 222 line is indicative of the absence of antisymmetric arrangement of the cations in the supercage.

See also the following references

1. K.J.Balkus et al., *Appl.Catal.*, 143,159 (1996)
2. G.Vanko et al., *Chem.Comm*,785, 1996.

**XRD:** X-ray diffraction exhibits that the crystallinity and morphology of zeolite Y is preserved in spite of the inclusion of the Cu (II) ions or its complex (Fig. 3). This result is in good agreement with IR results obtained previously. Diffraction characteristic feature for any new phase in the diffractograms was not detected. From a comparison of patterns (a) with (b) it may be seen that little changed occurred in the relative intensities of the 331, 311 and 220 peaks upon introducing of exchanged metal ions. This means that the zeolite lattice retained its originally random sodium ion distribution after the exchanging process. In contrast, analysis of the patterns for the encapsulated complex indicated that significant cation redistribution occurred following complex formation within the zeolite supercages<sup>[26,29]</sup>. It is suggested that the formation of large Cu<sup>II</sup>(SBSH)/Y complex leads to disturb the random distribution of small extra framework cations. This change in location of small cations affects the relative intensities of 331, 311 and 220 peaks. Indeed, XRD clearly showed that the large complex displaced sodium ions from their random positions in the supercages to locations at sites II (located at the center of a single six-ring, S6R), I' (located in the sodalite cavity) and are placed inside the cages of zeolite Y.



**Fig. 3:** X-ray powder diffraction patterns of (a) NaY, (b) Cu<sup>II</sup>-Y and (c) Cu<sup>II</sup>(SBSH)/Y. [reference Journal of Applied Sciences Research, 3(12): 1663-1670, 2007]

Also see the following references

1. T. Joseph et al., Catalysis letters, 83,209(2002).
2. Inorganica Chimica Acta, vol. 337, 2002, p. 53-58
3. MAURYA Mannar R. ; CHANDRAKAR Anil K. ; CHAND Shri, Zeolite-Y encapsulated metal complexes of oxovanadium(VI), copper(II) and nickel(II) as catalyst for the oxidation of styrene, cyclohexane and methyl phenyl sulfide, Journal of molecular catalysis. A, Chemical 2007, vol. 274, n<sup>o</sup>1-2, pp. 192-201
4. *Clays and Clay Minerals*; February 2006; v. 54; no. 1; p. 54-61
5. The powder X-ray diffractions of the parent NaY, CoNaY and Cosalen/NaY are shown in Fig. 3. These samples displayed the expected pattern of hydrated NaY zeolite. It can be assumed that the zeolite framework was not affected to a measurable extent by the presence of the Co-exchanged ions or intrazeolitic complex formation.

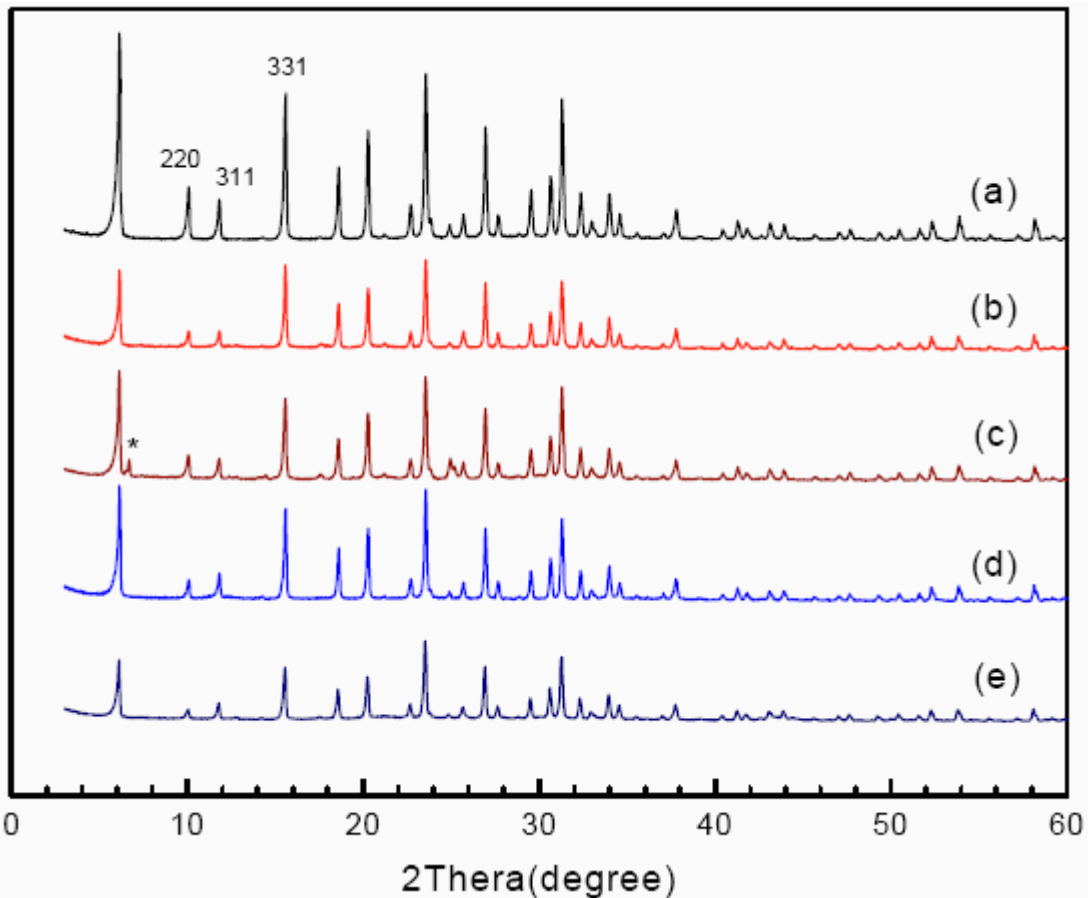


Fig. 3. XRD patterns of the sample. (a) Cosalen, (b) CoNaY, (c) Cosalen/NaY (IM), (d) Cosalen/NaY-A (FL), (e) Cosalen/NaY-B (FL)

It has been observed that empirical derived relationship (Kozlov *et al.*, 1998) exist between the relative 331, 311 and 220 peak intensities and cation location in faujasite type zeolites. Cations are randomly distributed within the lattice if  $I_{331} > I_{220} > I_{311}$ , but if  $I_{331} > I_{311} > I_{220}$ , the cations assume positions at sites I', II. Using these empirical criteria, the diffraction patterns suggest that the large Cosalen complex is probably displaced Co ions from their random positions within the NaY cavities to locations at sites I', II. Site I' is reported as being located in the sodalite cavity while site II at the center of a single six-ring or displaced from this point into a supercage. This would allow more effective coordination between Co ions and salen ligand groups extended into the large cages upon complexation. The XRD analysis proved that through flexible ligand method, the Cosalen has been encapsulated into the zeolite supercage. It is also found that the reduction in the intensities of the peaks was observed for Cosalen/NaY-B (FL) than that for Cosalen/NaY-A (FL). As to impregnated Cosalen/NaY, there is a new diffraction line close to the first line at  $6^\circ 2\theta$  (mark on asterisk) assigned to new phase were detected. Obviously, the impregnated sample posses Cosalen complex at the external surfaces

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Also see Chinese Chemical Letters Vol. 17, No. 3, pp 419-422, 2006

**Karl M Kadish, Roger Guilard, Kevin M Smith, The Porphyrin Hand book  
Vol 1 pp 262 and others.**

**For MCM materials see the reference** Solid State Sciences 7 (2005) 239–244