

04.4-7 SURFACE STRUCTURE OF SUPPORTED BIMETALLIC CATALYSTS. By P.L. Gai, B.C. Smith and W.G. Waddington, Department of Metallurgy, Oxford University, OX1 3PH, United Kingdom.

Supported bimetallic particle catalysts (with particle sizes a few nanometres) are being increasingly used in heterogeneous catalysis due to their enhanced selectivity introduced by changes in their surface and electronic structure. Cu-Pd supported on carbon is of interest to commercial methanol synthesis reactions. Using an in-situ 1 MeV EM fitted with a gas reaction cell, reactions in  $H_2$  and CO are monitored and different sintering behaviour has been obtained. Surface defect layers of up to only a few angstroms in the reacted catalysts have been observed by high resolution microscopy using a JEOL 200CX and a JEOL 4000EX HREMs. Particle structures are identified by convergent beam diffraction patterns. High precision microanalysis with probe sizes 3-5 nm has indicated preferential surface enrichment of Pd. The surface structure information is critical to the understanding of chemisorption of the synthesis gases and therefore, to activity. Based on the microanalysis and HREM results, calculations of these complex images have been carried out using 256x256 FFTs (arrays) in the multislice programmes. The calculations have been performed for both possible models: Pd at the surface and Cu at the surface as a function of thickness and defocus. The results have shown a marked difference in the image contrast between the two models and simulations using Pd-edge are in agreement with the experimental data. It is shown for the first time that even a monolayer coverage of a particular species on the nanometre size particles can be distinguished.

04.5-1 MOLECULAR SEPARATIONS BY LATTICE INCLUSION.

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This presentation is concerned with structural design and characterization of a series of new host-guest compounds which can be used for isolation and optical resolution of material by lattice-inclusion type complexation.

Lattice inclusion selectivity and guest discrimination has been observed in coordinato-clathrates formed by several functional hosts such as  $N,N'$ -ditritylurea [DTU], 1,1-di(p-hydroxyphenyl)cyclohexane [DHC] and 1,1'-bi-2-naphthol [BNL]. DTU is a versatile host, exhibiting properties of selective complexation towards guests of different functionality and molecular shape (Hart, Lin and Goldberg, Mol. Cryst. Liq. Cryst., 1986, 137, 277-286). The DHC host has been applied successfully to separations of cresols from a cresol mixture obtained from coal tar. Selectivity studies showed preferential complexation of this host with m-cresol > p-cresol > phenol > o-cresol, leading to 98.5% pure isolation of m-cresol from the mixture of isomers. Optical resolution of some phosphinates and phosphine oxides has been achieved by crystalline complexation with optically active BNL. 100% optically pure enantiomers of the phosphorous compound could be resolved separately from a racemic mixture by complexation with the corresponding enantiomer of BNL.

The above results confirm that crystalline inclusion is an excellent technique for molecular separations between species of nearly identical chemical and physical properties but containing a small structural variation. The close-packed crystal phase is very sensitive to the degree of spatial and functional complementarity between the interacting components, especially when they form a strongly bonded lattice as in the presented examples.

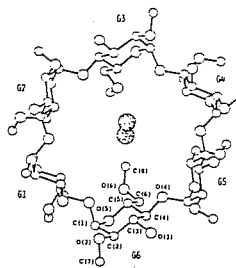
04.5-2 CRYSTAL STRUCTURES OF HEXAKIS(2,6-DI-O-METHYL)- $\alpha$ -CYCLODEXTRIN INCLUSION COMPLEXES

By Kazuaki Harata, Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305 Japan

Hexakis(2,6-di-O-methyl)- $\alpha$ -cyclodextrin (dimethyl- $\alpha$ -CDx), which is expected to have an intramolecular cavity wider than that of parent  $\alpha$ -CDx, forms inclusion complexes in the solid state and in solution. We have determined the crystal structures of three dimethyl- $\alpha$ -CDx complexes to investigate the effect of methylation on the macrocyclic conformation and the host-guest interaction. Crystallographic data are as follows:

(1) 1-Propanol complex;  $C_{48}H_{84}O_{30} \cdot C_3H_8O$ ,  $P2_1$ ,  $Z=2$ ,  
 $a=14.136(2)$ ,  $b=10.680(1)$ ,  $c=21.479(2)$  Å,  $\beta=106.00(1)^\circ$ ,  
 $R=0.058$ , (2) iodine complex;  $C_{48}H_{84}O_{30} \cdot I_2$ ,  $P2_1$ ,  $Z=2$ ,  
 $a=14.124(2)$ ,  $b=10.667(2)$ ,  $c=21.443(2)$  Å,  $\beta=106.29(1)^\circ$ ,  
 $R=0.077$ , (3) 3-iodopropionic acid complex;  $C_{48}H_{84}O_{30} \cdot C_3H_5O_2I$ ,  $P2_1 2_1 2_1$ ,  $Z=4$ ,  $a=10.707(1)$ ,  $b=14.564(3)$ ,  $c=41.448(4)$  Å,  $R=0.095$ .

The dimethyl- $\alpha$ -CDx molecule has a round shape which is maintained by intramolecular O(3)-H...O(2) hydrogen bonds. 3-Iodopropionic acid is located at the center of the host cavity, while iodine and 1-propanol molecules are shifted toward the wider O(2), O(3) side from the center of the cavity. Dimethyl- $\alpha$ -CDx molecules are arranged to form a typical "cage" type packing in the crystal.



Iodine complex

04.5-3 CHIRAL DISCRIMINATION AND THE CRYSTAL STRUCTURES OF PAIRS OF DIASTEREOISOMERIC SALTS.

By Sine Larsen, Department of Physical Chemistry, H.C. Ørsted Institute, University of Copenhagen, Denmark.

A commonly used method for separation of enantiomers in a racemic mixture is to add a suitable chiral reagent, that reacts (precipitates) with the racemate, e.g. R,R-tartaric acid is a widely used reagent for the resolution of optically active amines. The two different diastereoisomeric salts that may result from the reaction can differ so much in their relative solubilities that an almost quantitative separation of the enantiomers is achieved. To investigate the chiral discrimination, that is responsible for this difference in solubility, the crystal structures have been determined for pairs of diastereoisomeric salts.

As it is the aim to relate the differences between the intermolecular interactions in the structures to the difference in solubility, we have limited our studies to systems where the two diastereoisomeric salts have identical composition.

The crystal structures have been determined for the salts obtained when enantiomers of the organic amines 1-amino-2-propanol, 1-amino-2-butanol and 1-(2-pyridyl) ethylamine are resolved as hydrogentartrates and for two pairs of coordination compounds. A careful examination of the intermolecular interactions in these compounds shows that both hydrogen bonds and non-bonded interactions are important for the crystal packing.

A qualitative comparison between the intermolecular interactions in equivalent diastereoisomeric salts showed that the number and the strength of the hydrogen bonds in the structures are very similar and that the difference in solubility seems mainly to arise from differences in the non-bonded interactions. The results will be related to the thermodynamics of the resolution process.