

04.2-4 THE FORMATION, AND ORDERING, OF CRYSTALLOGRAPHIC SHEAR PLANES IN NON-STOICHIOMETRIC TiO_2 . By A.N. Cormack, NYS College of Ceramics, Alfred University, USA and C.R.A. Catlow and C.M. Freeman, Department of Chemistry, University of Keele, UK.

It is well known that, on reduction, TiO_2 forms extended planar defects, known as Crystallographic Shear (CS) Planes, that accommodate the non-stoichiometry. Further, these CS Planes interact over large distances (100Å or more) to form regular, or nearly regular arrays in an otherwise perfect crystal. It has been shown, by theoretical computer based atomistic simulation studies that extensive structural relaxation around the CS Plane is responsible for its stability over point defect formation, even in composition regions very close to stoichiometry.

In this paper, we will elaborate on these earlier findings, and show how our computer simulation studies correctly predict, firstly, the formation of the Magnetic phases, Ti_2O_{3-4} in regions far from stoichiometry and, secondly, the coexistence of both CS Planes oriented on (121) and (132) rutile lattice planes.

The formation of CS Planes from point defects, the mechanism of which must depend on the nature of the intrinsic disorder in rutile TiO_2 , is still a subject which is under close study, since there is no consensus as to the nature of the intrinsic disorder. Both Schottky and anion Frenkel disorder have been proposed and there exists experimental data to back each claim. We will comment on this point using calculated defect formation energies to discuss the nature of the intrinsic disorder predicted from our theoretical model. We will also consider the energetics of some more complex defect species, such as those postulated by Bursill and co-workers, in an attempt to bridge the gap between the two schools of thought concerning intrinsic disorder.

04.2-5 STRUCTURAL INVESTIGATIONS OF ORGANOMETALLIC CATALYSTS, CATALYST PRECURSORS AND LIGANDS. K. Angermund and C. Krüger, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 4330 Mülheim/Ruhr, Federal Republic of Germany.

Structural investigations of several catalytically active organometallic compounds were undertaken to study possible correlations between the molecular structure in conjunction with the spatial electron distribution about transition metal centers and the chemical reactivity of these compounds.

The experimentally determined (X-X - method) electron deformation densities of several organometallic compounds with various ligand arrangements and of some potential ligand molecules will be shown. Recent improvements of experimental techniques as well as of data handling will be discussed briefly.

Electronic reaction control of homogeneous catalysis at the active metal may be supplemented by sterical properties of ligands. We use Molecular Modelling techniques to gain insight into possible sterical reasons for product differentiation of catalysts with optical active phosphines as ligands. It is found that small differences within the ligand framework of phosphine-modified nickel catalysts used for stereoselective dimerisation reactions of olefins cause remarkable changes in selectivity as well as in reactivity of the catalysts. Results of these investigations will be presented.

04.2-6 MOLECULAR STRUCTURE OF THE INTERMEDIATE OF THE STAUDINGER REACTION. By A.N. Chernega, M.Yu. Antipin and Yu.T. Struchkov, Institute of Organic Chemistry of the Ukrainian Academy of Sciences, Kiev and Institute of Organoelement Compounds of the USSR Academy of Sciences, Moscow, USSR.

The Staudinger reaction (1) as a route to phosphazoderivatives II is known for about 70 years. However, all assumptions about its possible mechanism were not conclusive because no structural data on the intermediates of this reactions, viz. phosphazides I, were available. The present X-ray structural study of two such intermediates III and IV with different substituents R and X allowed to establish unequivocally that the nitrogen atoms in phosphazides I form an unbranched $=N-N=N-$ chain with the E,E-configuration. The anomalously high thermal stability of IV in comparison with III and other known phosphazides is defined by electronic (a significant contribution of the bipolar $\overset{+}{P}-N=N-\overset{-}{N}$ form increasing the N^1-N^2 bond order) as well as by steric factors. The latter do not allow the free rotation by 180° around the N^1-N^2 bond, which is necessary for realization of the cyclic transition state (A) in the second stage of the Staudinger reaction. In order to find out the direction of electrophilic attack on the phosphazide I the structure of the alkylation product V has been determined, proving that alkylation occurs at the N^3 atom.

