

among the B-family DNA polymerases, which include all eukaryotic replicative DNA polymerases, *E. coli* DNA pol II and eukaryotic pol ζ are exceptional and specialized for translesion and mutagenic DNA synthesis (2). In this presentation, different mechanisms of translesion synthesis by a B-family member and the Y-family human DNA pol η will be discussed. The key to the specificity of DNA polymerases, whether in high-fidelity replication or translesion synthesis, appears to be two Mg²⁺ ions essential for the catalysis.

Keywords: Metal ion, catalysis, nucleic acid enzymes

[1] C. Biertuempfel, Y. Zhao, et al., W. Yang, *Nature*, **2010** 465, 1044-1048. [2] F. Wang, W. Yang, *Cell* **2009**, 139, 1279-1389.

MS31.P09

Acta Cryst. (2011) A67, C427

Effects of local structure on electrocatalytic behavior of doped RuO

¹Valery Petrykin,^a Maki Okube,^b Katerina Macounova,^a Petr Krtil,^a ^aJ. Heyrovsky Institute of Physical Chemistry, ASCR, Prague (Czech Republic). ^bMaterials and Structures Laboratory, Tokyo Institute of Technology, Yokohama (Japan). E-mail: valery.petrykin@jh-inst.cas.cz

Recent theoretical works [1,2] on electrocatalytic O₂ and Cl₂ evolution on rutile-type oxides link the activity and selectivity in those processes to the cation stacking along the direction of c-axis. This order can be effectively altered by substitution of Ru in RuO₂ host by 3d metals such as Fe, Co, Ni or Zn. In particular, Ru_{1-x}Ni_xO₂ and Ru_{1-x}Zn_xO₂ materials exhibit opposite trends in terms of selectivity of chlorine and oxygen production, presenting interesting examples of local and electronic structures effects on catalytic performance of the materials. At the same time, the nature of "active sites" in both materials for both gas evolution processes is poorly understood due to the lack of structural information for these doped RuO₂ based oxides.

In this work local structure of Ru_{1-x}M_xO₂ (M=Ni and Zn; x=0.0-0.3) materials was examined by X-ray absorption spectroscopy (XAS) using the data collected on Ru-K, Ni-K and Zn-K edges at NW-10A and BL-12C beam lines of Photon Factory (KEK, Japan) and X18B line of National Synchrotron Light Source (BNL, USA). Visual comparison of the EXAFS functions revealed that the local structure around Ru core atoms undergoes only little change with increase of a dopant concentration. At the same time, the variation of Ni and Zn content results in rather dramatic evolution of Ni- and Zn- EXAFS functions and appearance of new features in the spectra that cannot be interpreted in terms of atomic arrangement in conventional rutile structure.

Full-profile refinement of EXAFS spectra revealed that for low Ni concentration the materials structure can be described in terms of Ni substitution into Ru site of RuO₂, which conforms to rutile structure. Ni tends to occupy metals sites along the diagonal of rutile unit cell, and the deviation of site occupancy from the statistically expected values indicates possible tendency of Ni towards clustering. For Ru_{1-x}Ni_xO₂ materials with x>0.1 Ni concentration, local structure around Ni cannot be explained in terms of substitution only, and one should assume formation of defects with rock salt motif in the vicinity of Ni. Such defects formation may be explained in terms of shear planes, which are common for the oxygen deficient rutile. The materials with Zn doping were found to be metastable with respect to the decomposition and at high zinc concentration they tend to realize another type of Zn-rich defect regions, which conform to the ilmenite structure within RuO₂ host. The revealed differences in the architecture around doped cations helped to explain the differences in the selectivity of those materials in the parallel electrochemical evolution of chlorine and oxygen that is connected with the formation of different type of intermediate oxo- and

peroxo-species on the active surface of doped RuO₂.

[1] J. Rossmeisl, Z.W. Qu, H. Zhu, G.J. Kroes, J.K. Nørskov, *J. Electroanal. Chem.* **2007**, 607, 83-89. [2] H.A. Hansen, I.C. Man, F. Studt, F. Abild-Pedersen, T. Bligaard, J. Rossmeisl, *J. Phys. Chem. Chem. Phys.* **2010**, 12, 283-290.

Keywords: catalyst, electrochemistry, EXAFS

MS31.P10

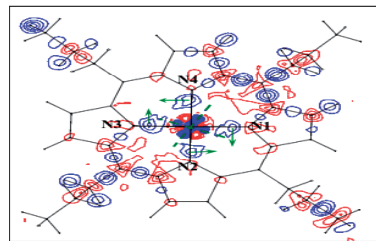
Acta Cryst. (2011) A67, C427-C428

Implication to the catalytic process of heme proteins

Yoshiki Ohgo,^{a,b,c} Daisuke Hashizume,^d Kazuyuki Takahashi,^e Hatsumi Mori,^e Shinya Hayami,^f Motoyasu Fujiwara,^g Saburo Neya,^h Yukiko Namatameⁱ and Mikio Nakamura,^{a,c} ^aDepartment of Chemistry, School of Medicine, Toho University, Tokyo, (Japan). ^bToho University Advanced Medical Research Center. ^cDivision of Chemistry, Graduate School of Science, Toho University, Funabashi. ^dMolecular Characterization Team, RIKEN, Wako, (Japan). ^eInstitute for Solid State Physics, The University of Tokyo. ^fDepartment of Chemistry, Graduate School of Science and Technology, Kumamoto University. ^gInstitute for Molecular Science. ^hDepartment of Physical Chemistry, Faculty of Pharmaceutical Sciences, Chiba University ⁱRIGAKU. E-mail: yohgo@med.toho-u.ac.jp

Investigations to clarify the orbital interactions or the nature of the chemical bonds between metals and ligands in the metalloproteins are quite important not only for understanding their functional activation mechanisms, but also for the development of the related catalysts or functional materials. For example, in the case of heme proteins, the catalytic activation mechanisms are closely connected with the electronic structures of central heme. Thus, the d π -p π interactions among iron(III) d-orbitals, frontier orbitals of porphyrin ring and axial ligands should be the essential manipulators in the functional activation mechanisms of the heme proteins.

In the course of the study, we and others clarified that the non-planarity of the heme, which is induced by the protein environment, is one of the key-factors to control the functions in these catalytic cycles, because the non-planarity of the heme largely changes their electronic structure. Since it is generally quite difficult to examine the systematic studies on the subject such as correlation between the non-planarity and the electronic structures in bio-system, the model complexes studies are necessary in most cases. A number of the spectroscopic studies together with the quantum chemical calculations have been reported so far, but there are little studies that actually see chemical bonds in valence electron level experimentally. Although this is mainly because of the deficiency in the power of the X-ray source in the past, recent 3rd generation synchrotron X-ray light source make us possible to carry out the charge density study by single crystal X-ray method. Here we report the experimental electronic structure observation in the model of the nonplanar heme, which can be considered as the models for the various heme proteins, by means of the single crystal synchrotron X-ray structure analysis at the valence electron level. We also describes the "Spin-crossover Triangle" system, which are closely connected with the catalytic process of the heme proteins, that respond to the external stimuli.¹⁻⁴



[1] T. Ikeue, Y. Ohgo, T. Yamaguchi, M. Takahashi, M. Takeda, M. Nakamura, *Angew. Chem. Int. Ed.*, **2001**, 40, 2617. [2] Y. Ohgo, T. Ikeue, M. Nakamura, *Inorg. Chem.*, **2002**, 41, 1698. [3] Y. Ohgo, Y. Chiba, D. Hashizume, H. Uekusa,