

among the B-family DNA polymerases, which include all eukaryotic replicative DNA polymerases, *E. coli* DNA pol II and eukaryotic pol  $\zeta$  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  $\eta$  will be discussed. The key to the specificity of DNA polymerases, whether in high-fidelity replication or translesion synthesis, appears to be two Mg<sup>2+</sup> 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

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### Effects of local structure on electrocatalytic behavior of doped RuO

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Recent theoretical works [1,2] on electrocatalytic O<sub>2</sub> and Cl<sub>2</sub> 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 RuO<sub>2</sub> host by 3d metals such as Fe, Co, Ni or Zn. In particular, Ru<sub>1-x</sub>Ni<sub>x</sub>O<sub>2</sub> and Ru<sub>1-x</sub>Zn<sub>x</sub>O<sub>2</sub> 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 RuO<sub>2</sub> based oxides.

In this work local structure of Ru<sub>1-x</sub>M<sub>x</sub>O<sub>2</sub> (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 RuO<sub>2</sub>, 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<sub>1-x</sub>Ni<sub>x</sub>O<sub>2</sub> 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 RuO<sub>2</sub> 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 RuO<sub>2</sub>.

[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

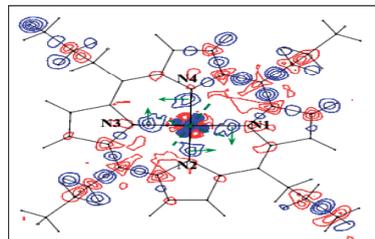
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### Implication to the catalytic process of heme proteins

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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 $\pi$ -p $\pi$  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 3<sup>rd</sup> 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.<sup>1-4</sup>



[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,

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T. Ozeki, M. Nakamura, *Chem. Commun.* **2006**, 1935-1937. [4] A. Ikezaki, M. Takahashi, M. Nakamura, *Angew. Chem. Int. Ed.*, **2009**, *48*, 6300-6303.

**Keywords:** charge density, spin-crossover, hemeprotein

### MS31.P11

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#### Cation order and magnetic structure of $\text{SbVO}_4$ catalyst

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$\text{SbVO}_4$  series of compounds could be used as a catalyst for the production of 20% cheaper acrylonitrile by the ammoxidation of propane compared to current method producing  $8 \times 10^6$  ton/year. In the non-stoichiometric series described as  $\text{Sb}_{0.9}\text{V}_{0.9+x}\square_{0.2-x}\text{O}_4$  ( $0 \leq x \leq 0.2$ ), cation vacancies ( $\square$ ) are introduced in the basic rutile type-structure following the mechanism:  $4\text{V}^{3+} \longrightarrow 3\text{V}^{4+} + \square$ , while antimony remains as  $\text{Sb}^{5+}$ . The reduced phase richest in  $\text{V}^{3+}$  has been reported to be  $\text{Sb}_{0.9}\text{V}_{1.1}\text{O}_4$ , which shows by electron diffraction superlattice reflections characteristic of a 2-fold rutile superstructure along  $c$ . However the X-ray powder diffraction pattern showed only basic rutile reflections ( $a_r = 4.6085(1)$ ,  $c_r = 3.0867(1)$  Å, S.G.  $P4_2/mnm$ ). The careful reciprocal lattice study by electron diffraction has revealed the following unit cell for the rutile superstructure:  $a = \sqrt{2}a_r$ ,  $b = \sqrt{2}b_r$ ,  $c = 2c_r$ . (subindex  $r$  refers to the basic rutile unit cell). Its space group,  $I4_1md$ , was determined by means of CBED. A structural model based on alternating Sb and V cations ordering along  $c$  in the chains of edge-sharing octahedra was proposed. No cation vacancies have been observed for this reduced phase, while for the compounds synthesized in oxidizing conditions the presence of vacancies has been confirmed. In fact, electron diffraction experiments have shown that vacancies order in the basic rutile structure giving rise to a modulated structure on the other end member of the series, namely  $\text{Sb}_{0.9}\text{V}_{0.9}\text{O}_4$ . On the other hand, our magnetic susceptibility studies indicate for the first time possible magnetic ordering. Thus for the magnetic structure determination we performed the study of 3 different samples of the series  $\text{Sb}_{0.9}\text{V}_{0.9+x}\square_{0.2-x}\text{O}_4$  by using neutron diffraction: **1)** a reduced phase rich on  $\text{V}^{3+}$  which shows the nuclear superstructure by Sb-V ordering. **2)** an oxidized phase rich on  $\text{V}^{4+}$  which shows the vacancies ordering. **3)** an intermediate phase which shows Sb-V disorder. In this way, we try to determine the magnetic structure of reduced  $\text{SbVO}_4$  coming from the ordering of vanadium magnetic moments, which certainly takes place at  $T_N \sim 50\text{K}$ , and to study how the substitution of  $\text{V}^{3+}$  ( $S=1$ ) by  $\text{V}^{4+}$  ( $S=1/2$ ), while the synthesis conditions become more oxidizing, affects the spin arrangement in  $\text{Sb}_{0.9}\text{V}_{0.9+x}\square_{0.2-x}\text{O}_4$ . This order seems to be destroyed by the appearance of vacancies and the chemical disorder in the cations positions. To follow the evolution of the order parameter we carried out neutron diffraction experiments ranging at temperatures from room (RT) to 1.5K. Another aim is to confirm the model of nuclear superstructure that we proposed based on the electron diffraction and HRTEM data, as far as it is not possible to measure the intensity in an absolute scale with the mentioned technique, and due to the higher contrast for the cations involved which is achievable with neutron diffraction compared with X-rays. The fact that V coherent scattering length for neutrons is rather small give us an obvious advantage to determine the superstructure due to alternating Sb-V occupation of two sites split from the substructure. To measure the samples at RT we used high resolution neutron powder diffraction. Due to the unique property of the neutrons to interact with ordered magnetic moments, the magnetic scattering coming from the V spins could be constrained to its crystallographic position, giving more information than at first glance could be expected by its almost

null nuclear scattering. Weak reflections could be associated to the vacancies modulation in the oxidized sample.

**Keywords:** catalyst structure; neutron, X-ray, electron diffraction

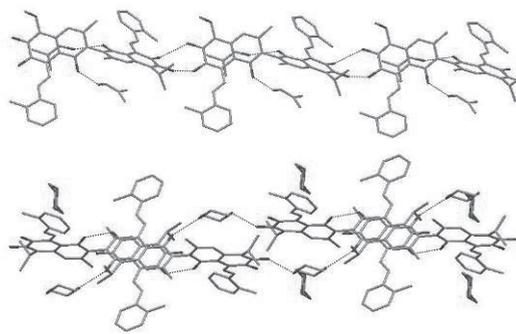
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#### H-bonding in clathrates bis-p-toluidine gossypol with DMFA and 1,4-dioxane

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Gossypol and its products of condensation with some amines (Schiff's base type derivative) are versatile hosts, capable to trap within the crystal structure the numerous types of guest species [1]. The studied clathrates of bis-p-toluidinegossypol with DMFA (1) and dioxane (2) were prepared by reaction of condensation between gossypol and p-toluidine in the corresponding solvents. The crystal of (1) – brown plate, Sp.gr.  $P2_1/n$ , cell parameters:  $a=15.8157(6)$  Å,  $b=15.9752(9)$  Å,  $c=18.8890(9)$  Å,  $\beta=102.940(4)^\circ$ ,  $V=4651.3(4)$  Å<sup>3</sup>, the host/guest ratio is 1:2. Host and guest molecules through hydrogen bonding are formed 1D supramolecular associate in the  $a$ -axis direction. The crystal of (2) – brown prism, Sp. gr.  $P-1$ ,  $a=9.3027(3)$  Å,  $b=12.6333(4)$  Å,  $c=20.5659(5)$  Å,  $\alpha=93.249(2)^\circ$ ,  $\beta=96.086(2)^\circ$ ,  $\gamma=109.954(3)^\circ$ ,  $V=247.90(10)$  Å<sup>3</sup>. Host/guest ratio is 1:2. In this structure host molecules form centrosymmetric dimers *via* H-bonds and together with 1,4-dioxane molecule of the first type form host-guest matrix, which running as 1D chain in the  $c$ -axis direction. Second type of 1,4-dioxane molecules are located in channels of the crystal structure without any H-bonding. Thermal stability of the obtained clathrates has been studied by TG-DSC method.



[1] B.T. Ibragimov, S.A. Talipov. *Gossypol in Encyclopedia of Supramolecular Chemistry*, Eds. Jerry L. Atwood & Jonathan W. Steed. Dekker. New York, **2004**, 606-614

**Key words:** crystal engineering, hydrogen bonding, supramolecular assemblies

### MS31.P13

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#### New molecular conductors with iron bis(dicarbollide) anion - synthesis, crystal structure and electrical conductivity

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