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follow the changing environments of nucleating sites during the formation of glass ceramics. In this context, Small Angle X-ray Scattering (SAXS) can give additional information on the intermediate nm scale, revealing details on the microstructures underlying crystallite growth. It is clearly valuable wherever possible to monitor XAFS and/or WAXS/SAXS in conjunction with X-ray diffraction in order that the degree of long range order is ascertained at each stage. This paper will discuss the various non-crystallographic X-ray techniques for obtaining structural information from disordered materials, describing typical experimental configurations and describing the latest developments where these techniques are being combined to facilitate novel twin detector experiments in which the varying degrees of order in a material can be characterised *in-situ*.

MS-16.01.05 Monolayer dispersion model of oxides and salts on supports as well as its EXAFS evidences

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The dispersion phenomenon of salts and oxides on supports with large specific surface area has been investigated widely. Quite a number of models, such as, forming surface compound (SC), cluster (CR), microcrystalline (MC), multilayer dispersion (MUD), solid solution (SS), and so on have been proposed already. But unfortunately, up to date, many problems about structure can not be well explained yet.

Recently, on the basis of investigation upon great deal of these systems, we find a interesting and quite common phenomenon that salts and oxides can disperse spontaneously in monolayer on the surface of a support and it have been confirmed by XRD, XPS, ESR, AES, ISS, SIMS, TEM, LRS, IR, UV, and Mossbauer spectroscopy etc. The principle has been applied successfully in the preparation of some commercial absorbents and catalysts.

The monolayer dispersion model takes into consideration of the possible effect of dispersion condition, (such as, loadings, surface behavior of support and atmosphere) on the structure, but most other models assume that the ions dispersed have its definite and characteristic structure. If the dispersion structure is described by coordination polyhedra of interested ions and their connection or distribution ways. Their differences might be summarized as follows:

dispersion models	definiteness of polyhedra	connect. of polyhedra	effect on loading	coordination of surface behaviors
MOD	not so marked	not so marked	marked	marked
MUD	marked	marked	not marked	not so marked
SC	marked	marked	not marked	not so marked
CR	marked	marked	not marked	not so marked
MC	marked	marked	not marked	not marked
SS	marked	rather marked	not marked	not marked

For most spectroscopies, it is very difficult to recognize structurally the dispersion state as a monolayer among above models. But for the EXAFS, it becomes much easier, since EXAFS can give out plenty of information about chemical bonds and geometry distribution of atoms around interested ions. Much EXAFS structure information in this paper about NiO/ γ -Al₂O₃, CuBr₂/ γ -Al₂O₃, CuCl₂/ γ -Al₂O₃, NiSO₄/ γ -Al₂O₃, and etc. shows that monolayer dispersion is a spontaneous and chemical process and the monolayer dispersion state has particular coordination features. The coordination state of monolayer dispersion is close correlative and changeable with the dispersion condition. It is very different from MC, CR, MC and other dispersion models, but well agrees with the monolayer dispersion model.

Reference

- [1] Youchang Xie and Youqi Tang, *Advance in Catalysis*, Vol. 37, 1 (1990)
- [2] Cai Xiaohai, Xie Youchang and et al, *Proceedings of 7th International Conference on X-Ray Absorption fine Structure*, Aug. 23-29, 1992, kobe, Japan

MS-16.01.06 EXAFS STUDY ON THE LOCAL STRUCTURE IN POTASSIUM TANTALATE. By Y. Nishihata*, O. Kamishima, A. Sawada and H. Maeda, Faculty of Science, Okayama University, Japan, and H. Kasatani and H. Terauchi, School of Science, Kwansai Gakuin University, Japan.

Many cubic perovskite crystals undergo phase transitions, where they transform to slightly distorted structures from the ideal perovskite structure. In KTaO₃, no phase transition occurs since long-range ordering of dipole moment is suppressed by the quantum fluctuation at very low temperatures. It was reported that the dielectric constant increases to a saturated value with decreasing temperature below 100 K (Samara & Morosin, 1973). An atomic vibrational analysis by the neutron diffraction implies that the mode of KTaO₃ at RT is of the Slater type (Harada, Axe & Shirane, 1970). A second-harmonic generation has been reported, although KTaO₃ is a centrosymmetric crystal (Vogt & Uwe, 1984). The purpose of the present work is to study a change of local structure from the ideal perovskite structure using the EXAFS technique.

EXAFS (Extended X-ray Absorption Fine Structure) measurements near the Ta-L_{III} edge of KTaO₃ at RT, 160, 80 and 32 K were carried out using the synchrotron radiation of the Photon Factory at the National Laboratory of High Energy Physics (KEK, Tsukuba). Figure 1 shows the x-ray absorption spectrum at 32 K. A well-defined EXAFS signal is found up to the Ta-L_{II} edge. The EXAFS function $\chi(k)$ was extracted from the spectrum in the usual way (Maeda, 1987). Figure 2 shows the radial structure function around the Ta atom at 32 K calculated by Fourier transform of $k\chi(k)$ in the range of $3.5 \leq k \leq 17.5 \text{ \AA}^{-1}$. The correction of phase shift is not taken into account. These three peaks can be assigned to O, K and Ta atoms, respectively from the crystallographic values obtained by the diffraction data. The broad distribution of the O atom is notable in comparison with that of the Ta atom. This broad distribution at very low temperature results from a large Debye-Waller type factor or a displacement of Ta atom from the center of oxygen octahedron. We use the Fourier filtering technique and a non-linear least-squares fitting method to determine the structural parameters. Preliminary result shows that the EXAFS signal $\chi(k)$ cannot be reproduced well

by a 1-shell model because of the beat of $\chi(k)$. If we take the model that the Ta atom displaces from the center of oxygen octahedron along <001> directions; the peak of the O atom may consist of three shells and the peak of the K atom two shells. We will evaluate the direction of the atomic displacement and the distance from the center of the oxygen octahedron by the least-square calculations under restricted conditions.

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Fig. 1. X-ray absorption spectrum near the Ta-L_{III} edge of KTaO₃ at 32 K.

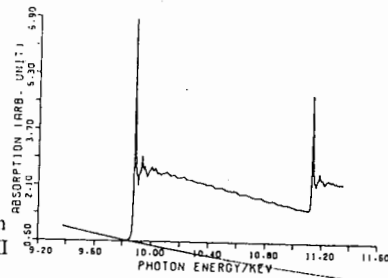
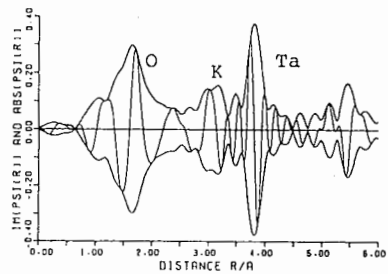


Fig. 2. Radial structure function around Ta atom at 32 K.



Harada, J., Axe, J. D. & Shirane, G. (1970). *Acta Cryst.* A26, 608.
Maeda, H. (1987). *J. Phys. Soc. Jpn.* 56, 2777.
Samara, G. A. & Morosin, B. (1973). *Phys. Rev.* B8, 1256.
Vogt, H. & Uwe, H. (1984). *Phys. Rev.* B29, 1030.

PS-16.01.07 RELATIONSHIP BETWEEN CATALYTIC ACTIVITY FOR WATER-GAS SHIFT AND STRUCTURE OF Co-Mo-Mg/Al₂O₃ CATALYST
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The deactivation of two commercial Co-Mo-Mg/Al₂O₃ WGS catalysts has been studied by XRD, ICP, IR, SEM, XPS etc. The results showed that formation sulfates, impurities, regenerative conditions and mechanical strength of catalyst have significant effect on the activity except ratio of steam/gas, H₂S content and operating temperature.

The Co-Mo-Mg/Al₂O₃ catalyst was prepared by incipient wetness impregnation on a γ-Al₂O₃ with a Mg(NO₃)₂ and calcined at 900°C for 2h after drying. Then this same material was impregnated with a Co(NO₃)₂ and (NH₄)₆Mo₇O₂₄ mixed solution.

A typical γ-Al₂O₃ XRD pattern was given by Co-Mo-Mg/γ-Al₂O₃ catalyst A in the oxidic state (P. J. Gajardo, *Less-Common Met.*, 1977, 54, 311). This implied that cobalt and molybdenum as well as magnesium had been well dispersed on the support. Catalyst B showed three XRD patterns consistent with MgO, Al₂O₃ and MgAl₂O₄. The crystal phases MgO and MgAl₂O₄ in the catalysts led to a gradual drop in activity (J. P. R. Visser, *Bull. Chim. Bdg.*, 1984, 93, 813). The spinel MgAl₂O₄ structure formation was observed with increasing the calcination temperature, so it is correlated with the procedure of catalyst preparation.

The specific surface areas of oxide state catalyst (>150m²/g) decrease to about 100m²/g as the catalyst converted to sulfided state. It was about 70m²/g after the catalyst used for a year, and the catalyst mechanical strength decreased to 1/3 after regeneration, comparing with new one.

The Co, Mo and Mg in catalyst were not lost after it used for four years. The ICP results of catalyst A and B are shown in Fig. 1. There was a small part of impurity K⁺ and Na⁺ in catalyst lost. The inorganic impurities in feed gas are mainly Fe, Ca, Pb and K etc. the activity is decreased with its deposition on the surface of the catalyst and it is reconverted after regeneration.

The deactivation is mainly due to the formation of sulfates, increasing of MoS₂ and MgAl₂O₄, the active center Co-Mo-S is destroyed. over-heating in the regeneration, sulfidation and operation process enhance formation of inactive MgO, MgAl₂O₄ and crystal phase MoS₂. The higher ratio of steam/gas and the higher concentration of SO₂ etc enhance also the sulfates formation.

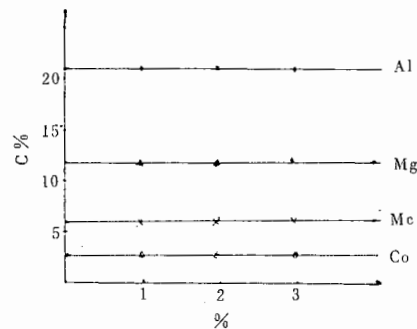


Fig. 1. ICP results of catalyst A and B.

PS-16.01.08 CRYSTAL STRUCTURE AND HALOGEN NQR OF DIAMMONIUMALKANE HALIDES. By Shi-qi Dou*, Helmut Paulus and Alarich Weiss, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr.20, D-6100 Darmstadt, Germany.

The crystal structures of the isomorphous compounds 1,3-diammoniumpropyl- dibromide and - diiodide are reported. Monoclinic, P2₁/n, Z=4. Lattice constants in pm. (H₃N(CH₂)₃NH₃)²⁺ 2Br⁻: a= 1343.8(5), b=457.9(1), c=1347.1(5), β=109.14(1)°; (H₃N(CH₂)₃NH₃)²⁺ 2I⁻: a=1421.3(5), b=478.0(2), c=1419.6(5), β=110.10(1)°. The diammoniumpropyl cations are centrosymmetric and there are two crystallographic independent anions and two independent cations in the unit cell. The positive (H₃N(CH₂)₃NH₃)²⁺ cations and halogen anions are proportionate distributed in the lattice. Weak hydrogen bonds N-H...X-, X=Br, I are observed. The discrepancy in the ⁷⁹Br and ¹²⁷I NQR spectra, respectively, [1] from which isomorphism was denied, is removed by reinvestigation of the spectra. Additionally to the already known ⁹¹Br line at 22.95MHz a second line at 12.07MHz was found at room temperature. Structures and NQR spectra are compared and discussed.

[1]; J. Hartmann, S.-q. Dou, and Al. Weiss, *Z. Naturforsch.* 44a, 41 (1989)

PS-16.01.09 N-TRICHLORO- AND DICHLOROACETYL AMINO ACIDS AND COMPOUNDS OF AMINO ACIDS WITH HALOGENO ACETIC ACIDS. ⁵¹CL NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY; CRYSTAL STRUCTURE OF N-TRICHLOROACETYL-GLYCINE, -DL-ALANINE, AND -L-ALANINE. By Shi-qi Dou*, Armin Kehrner, Armin R. Ofial, and Alarich Weiss, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, D-6100 Darmstadt, Germany