

10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

(3) In reduced and used catalysts, we found a Cu-O coordination peak ($R=0.190\text{nm}$, $N=1$) in RSF. But another peak at $R=0.196\text{nm}$, belonging to Cu-Cu coordination in CuO, was not found in the same RSF. We consider that this is evidence of a strong interaction between metal and $r\text{-Al}_2\text{O}_3$.

(4) Because of $r\text{-Al}_2\text{O}_3$, the reasons of deactivation are different for CZ and CZA. For CZ, deactivation is caused by enlargement and increase of crystalline Cu. For CZA, the $r\text{-Al}_2\text{O}_3$ may prevent the enlargement of Cu crystals, and stabilize in this way the activity of CZA. The reason of deactivation is the change of the dispersed Cu to the crystalline phase in the catalytic reaction, which leads to the loss of active regions.

XRD graphics and RSF figures are shown below.

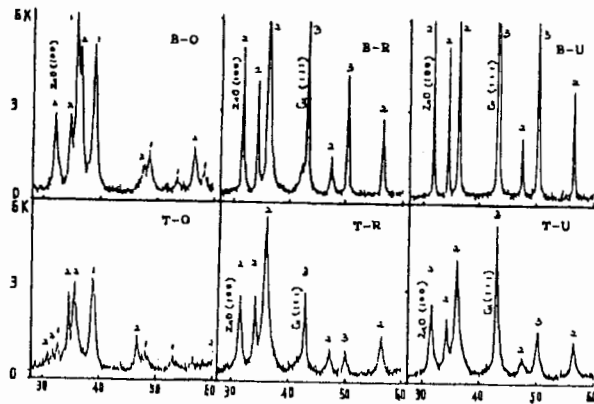


Fig.1 X-ray diffraction diagrams of the binary catalysts the ternary catalysts 1.CuO 2.ZnO 3.Cu

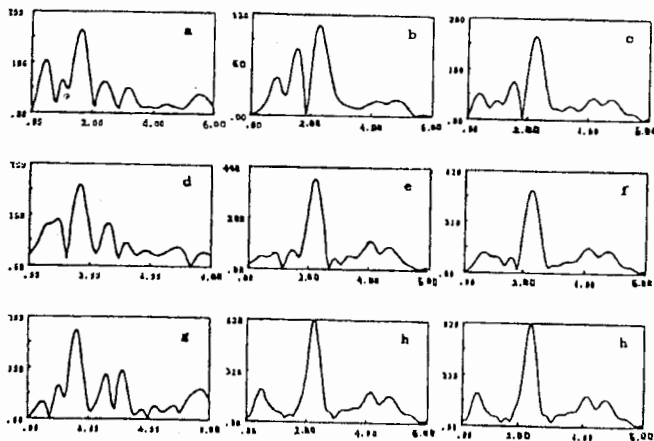


Fig.2 Cu-EXAFS a.T-oxidized b.T-reduced c.T-used d.B-oxidized e.B-reduced f.B-used g.CuO h.Cu

PS-10.03.07 ELECTRON DIFFRACTION STUDY OF THE SUBSTITUTION DISORDER OF THE Ti IONS IN $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$.

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The LiTi_2O_4 compound (spinel structure, space group $\text{Fd}\bar{3}\text{m}$, $a=8.41\text{Å}$, $Z=8$) is known to be superconducting with $T_c=11\text{K}$. In the spinel oxides containing lithium, it has been observed that the small Li^+ cations can move easily through vacant sites generated by the

titanium-oxygen network. Therefore, by removing or inserting lithium, the stoichiometry of the compound can be varied. In the case of LiTi_2O_4 , Capponi et al. have shown (Physica C, 1991, 185-189, 2721), that it is possible to extract lithium in a "soft" and controlled way by immersion in an HCl solution. In order to see if such a treatment induces any kind of disorder, crystals treated in HCl solution for several days have been studied by electron diffraction. A Philips EM 400T microscope operating at 120KV was used.

Besides Bragg reflections, the presence of pronounced diffuse scattering was readily observed, and its geometry was studied by tilting around a^* and a^*+b^* directions from the $[001]$ zone axis. Figure 1a shows an example of the diffuse scattering observed on the $[001]$ zone axis.

To interpret the diffraction patterns we have applied the theory of invariant clusters proposed by Brunel et al. (J. Phys. Chem. Solids, 1972, 33, 1927) and developed by Sauvage et al. (Acta Cryst., 1974, A30, 239). This theory establishes that, if the diffuse scattering is confined to a geometric locus in reciprocal space, the ordering state can be described by the regular arrangement of identical polyhedra having the average composition of the sample. In the present case, we suppose that the diffuse scattering is due to the substitution disorder of Ti ions over the two types of octahedral sites in the spinel structure (16d and 16c), the displacement of Ti ions from a full 16d site to an empty 16c one being possible after the departure of the two neighboring Li ions. Then, the relevant polyhedron is a cube of edge dimension $a/2$ whose corners and centers of the faces correspond to the center of the octahedral sites occupied either by a Ti atom or by a vacancy. The composition of the sample implies that the numbers of vacancies and Ti atoms in one such cube are equal. With this description, the equation of the surface of diffuse intensity is given by $\cos(\pi X/2)+\cos(\pi Y/2)+\cos(\pi Z/2)+4\cos(\pi X/2)\cos(\pi Y/2)\cos(\pi Z/2)=0$

The calculated intersections of this surface with different reciprocal planes are in agreement with the experimental diffraction patterns as shown in Figure 1b. This observation confirms the presence of a Ti cation disorder between the 16d and 16c octahedral sites in the case of large lithium deficiencies.

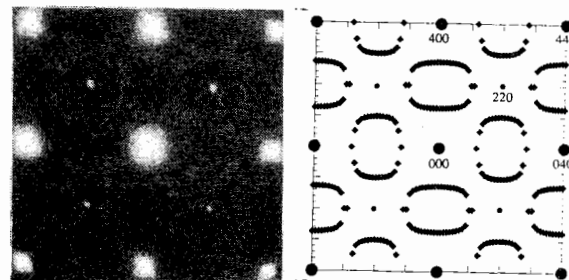


Figure 1. (a) Electron diffraction photograph along the $[001]$ zone axis showing the diffuse scattering due to Ti cation network disorder. (b) The intersection of the diffuse scattering surface calculated with the model described in the text and the $[001]$ reciprocal plane.

PS-10.03.08 STRUCTURAL ASPECTS OF THE CRYSTALLOGRAPHIC-MAGNETIC TRANSITION IN LaVO_3 AROUND 140 K by P.Bordet^{1*}, C. Chaillout¹, M. Marezio^{1,2}, Q. Huang^{3,4}, A. Santoro³, S-W. Cheong², H. Takagi², C.S. Oglesby², and B. Batlogg². ¹ Laboratoire de Cristallographie CNRS-UJF, BP 166, Grenoble Cedex 9, France. ² AT&T Bell Laboratories, Murray Hill, NJ07974, USA. ³ Reactor Division, NIST, Gaithersburg, MD 20899, USA. ⁴ Dept. of Physics, University of Maryland, College Park, MD 20742, USA