

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

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PS-10.03.04 X-RAY DIFFRACTION STUDIES OF ALKALI METAL DOPED Pd/ γ -Al₂O₃ CATALYSTS. By J. Pielaszek*, J. Sobczak, Z. Juskovecs¹, M. Shymanska¹, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland; ¹Institute of Organic Synthesis, Latvian Academy of Sciences, Riga, Latvia.

Palladium catalysts supported on γ -Al₂O₃ display dual reactivity with respect to the furan aldehydes in the vapour phase heterogeneous process. For example, furan and 2-methylfuran are produced from furfural, and 2-methylfuran and 2,5-dimethylfuran from 5-methylfurfural. This is the result of simultaneous reactions of decarbonylation and hydrogenation (Juskovecs, Z. G., Nekrasov, N. V., Kharsan, M. S., Kostjukovski, M. M., Shimanska, M. V., Kiperman, S. L., *Kinetika i Kataliz*, 1983, 24, 1134 -1139). Introduction of alkaline promoters such as sodium or potassium results in the suppression of the hydrogenation reaction. This improves significantly selectivity for decarbonylation, stability of the catalyst, and increase in its lifetime.

Structure of both fresh and used (deactivated), pure and doped (0.2 wt% Na₂CO₃ + 0.8 wt% K₂CO₃) 2.5 wt.% Pd/ γ -Al₂O₃ catalysts was studied. Measurements were performed *in-situ* by X-ray diffraction in a gradientless catalytic reactor (Zieliński, J. & Borodziński, A., *Appl. Catal.*, 1985, 13, 305). Diffraction profiles originating from the metal phase were obtained by subtraction of background (support) from the diffraction profile of a catalyst. The choice of the proper support for background subtraction was found to be of paramount importance in XRD catalyst studies (Pielaszek, J., in "X-Ray and Neutron Structure Analysis in Material Science", Ed. J. Hasek, Plenum, USA, 1989). For this purpose, special low-loaded (0.1 wt % of Pd) catalysts were prepared and treated in the same way as the catalysts under study. The amount of metal in these samples was beyond the range of detectability by X-ray diffraction. For comparison, pure γ -Al₂O₃ was also studied.

The smoothing of the data was performed by iteration with the cubic spline method (Pielaszek, J., *Z. Kristallogr.*, 1988, 185, 703). Analysis of the as-registered and subtracted diffraction profiles showed that the Pd crystallite size in the fresh, non-doped catalysts is very small and increases with the deactivation process to about 200Å (sintering occurs). In contrast, the particle size in fresh, doped catalyst is about 200Å and does not change during use. Comparison of diffraction profiles from differently treated catalysts and supports, and their appropriate subtraction showed that the deactivation of the catalyst is accompanied by a change in the crystallinity of the support itself. This effect is dependent not only on the doping of the catalyst with alkali metals, but on the concentration of the active metal as well.

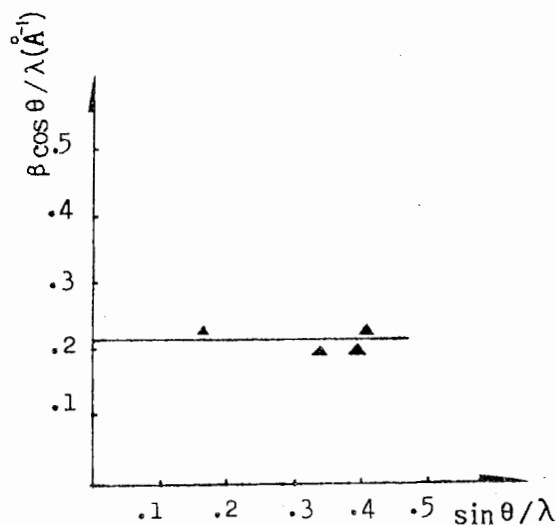
PS-10.03.05 MEASUREMENT OF HOMOGENEITY OF ULTRAFINE Y₂O₃-STABILIZED ZrO₂ POWDER BY X-RAY DIFFRACTOMETRY. By Mengxi Zhao, Xuanxuan Gao and Zengfu Ping, LuoYang Institute of Refractories Research, Ministry of Metallurgical Industry, China.

Y₂O₃-stabilized tetragonal ZrO₂ (Y-TZP) ceramics have many applications exploiting their high fracture toughness. The TZP powder was prepared by the method of chemical coprecipitation. In this case, uniform distribution of Y₂O₃ in each particle is required. If Y₂O₃ is not contained homogeneously in ZrO₂ grains, local stresses or microcracks will occur around these grains during the tetragonal-to-monoclinic martensitic transformation. The ultrafine Y-TZP (3.4 mol%) powder which was prepared by the coprecipitation method, and calcined at 850°C for 1 hour was

examined by XRD. The tetragonal (004) and (400) peaks were clearly separated from each other. The homogeneity of the powder was measured by X-ray profile analysis. The Williamson Hall plot ($\beta \cos \theta / \lambda$ vs $\sin \theta / \lambda$) is used to examine compositional fluctuation of powders. The broadening of peaks is mainly due to crystallite size and to lattice strain. Hall showed that both influences could be separated by the equation:

$$\beta \cos \theta / \lambda = 1/L + \eta \sin \theta / \lambda,$$

where θ is the Bragg angle, β the integrated breadth, λ the wavelength of X-rays, L the crystallite size and η the lattice strain. As the powder was prepared by coprecipitation, the lattice strain due to external stress can be ignored. Therefore, it was considered that the main cause of lattice strain would be the compositional fluctuation. From the figure below, the crystallite size L is obtained from the intercept of the linear plot on the vertical axis, and the lattice strain from its slope. This slope was approximately zero, and it is therefore concluded that compositional fluctuation was essentially absent from the TZP.



PS-10.03.06 EFFECTS OF r-Al₂O₃ ON STRUCTURES AND PROPERTIES OF CATALYST Cu/ZnO. By Wei Huang, Guoshun Shi, Lidun Ma*, Research Centre of Analysis and Measurement, Fudan University, 220 Handan Road, Shanghai, 200433, China.

The catalysts Cu/ZnO (CZ) and Cu/ZnO/Al₂O₃ (CZA) were studied in oxidized, reduced and used forms by XRD and EXAFS. The Cu edge and Zn edge were measured. The data were processed by the program package FXEA-III. Pure CuO powder ($R_{Cu-O}=0.196$ nm, $N_{Cu-O}=4$, $R_{Cu-Cu}=0.290$ nm, $N_{Cu-Cu}=4$), ZnO powder ($R_{Zn-O}=0.215$ nm, $N_{Zn-O}=4$, $R_{Zn-Zn}=0.310$ nm; $N_{Zn-Zn}=12$) and Cu foil ($R_{Cu-Cu}=0.255$ nm, $N_{Cu-Cu}=12$) were used as standards. Results are:

(1) In oxidized, reduced and used catalysts, the r-Al₂O₃ increases the dispersion of constituents in CZA, and r-Al₂O₃ itself is not seen in XRD graphics.

(2) In reduced and used catalysts, the Cu contents is seen in two forms: a crystallized phase and a dispersed phase. More crystalline Cu is observed in used catalysts than in reduced ones. We consider that the dispersed phases of Cu are the main active constituents.

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(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.

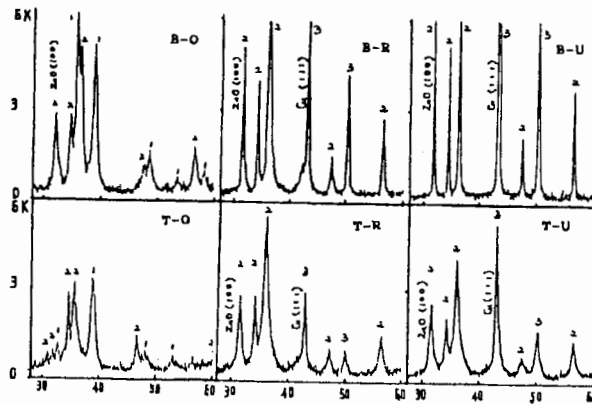


Fig.1 X-ray diffraction diagrams of the binary catalysts the ternary catalysts 1.CuO 2.ZnO 3.Cu

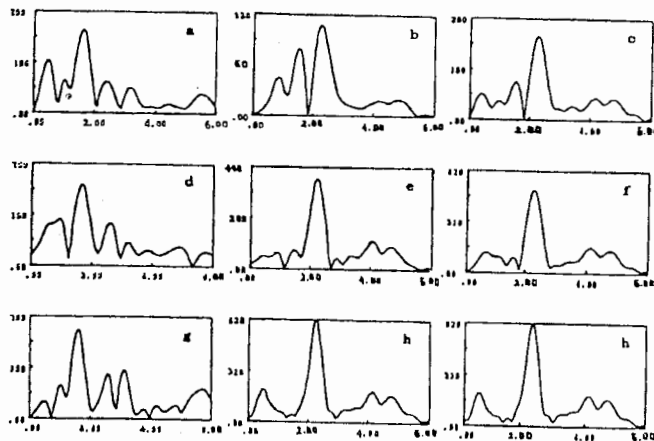


Fig.2 Cu-EXAFS a.T-oxidized b.T-reduced c.T-used d.B-oxidized e.B-reduced f.B-used g.CuO h.Cu

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.

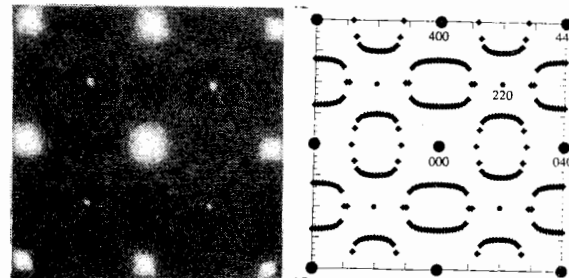


Figure 1. (a) Electron diffraction photograph along the $[001]$ zone axis showing the diffuse scattering due to Ti cation network disorder. (b) The intersection of the diffuse scattering surface calculated with the model described in the text and the $[001]$ reciprocal plane.

PS-10.03.07 ELECTRON DIFFRACTION STUDY OF THE SUBSTITUTION DISORDER OF THE Ti IONS IN $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$. By C. Chaillout, E. Moshopoulou, P. Bordet and J.J. Capponi, Laboratoire de Cristallographie, CNRS-UJF, BP 166, 38042 Grenoble cedex 09, France

The LiTi_2O_4 compound (spinel structure, space group $\text{Fd}\bar{3}m$, $a=8.41\text{Å}$, $Z=8$) 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

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