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



PS-10.03.04 X- RAY DIFFRACTION STUDIES OF ALKALI METAL DOPED Pd/$\gamma$-$Al_2O_3$ CATALYSTS. By J. Pielaszek*, J. Sobczak, Z. Juskovecs[1], M. Shymanska[1], Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland; [1]Institute of Organic Synthesis, Latvian Academy of Sciences, Riga, Latvia.

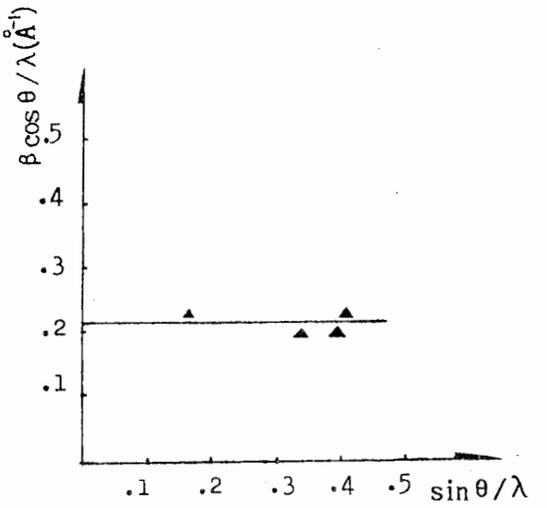
Palladium catalysts supported on $\gamma$-$Al_2O_3$ display dual reactivity with respect to the furan aldehydes in the vapour phase heterogeneous process . For example, furan and 2-methylfuran are produced from furfural, and 2-methylfuran and 2.5-dimethylfuran from 5-methylfurfural. This is the result of simultaneous reactions of decarbonylation and hydrogenation (Juskovecs, Z. G., Nekrasov, N. V., Kharson, M. S., Kostiukovski, M. M., Shimanska, M. V., Kiperman, S. L., *Kinetika i Kataliz*, 1983, 24, 1134 -1139). Introduction of alkaline promotors 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% $Na_2CO_3$ + 0.8 wt% $K_2CO_3$ ) 2.5 wt.% Pd/$\gamma$-$Al_2O_3$, 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 $\gamma$-$Al_2O_3$ 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 $Y_2O_3$-STABILIZED $ZrO_2$ POWDER BY X-RAY DIFFRACTOMETRY. By Mengxi Zhao, Xuanxuan Gao and Zengfu Ping, LuoYang Institute of Refractories Research, Ministry of Metallurgical Industry, China.

$Y_2O_3$-stabilized tetragonal $ZrO_2$ (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 $Y_2O_3$ in each particle is required. If $Y_2O_3$ is not contained homogeneously in $ZrO_2$ 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 $\theta$ is the Bragg angle, $\beta$ the integrated breadth, $\lambda$ the wavelength of X-rays, L the crystallite size and $\eta$ 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-$Al_2O_3$ 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/$Al_2O_3$(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 ($R_{Cu\text{-}O}$=0.196nm, $N_{Cu\text{-}O}$=4, $R_{Cu\text{-}Cu}$=0.290nm, $N_{Cu\text{-}Cu}$=4), ZnO powder ($R_{Zn\text{-}O}$ =0.215nm, $N_{Zn\text{-}O}$=4, $R_{Zn\text{-}Zn}$ =0.310nm; $N_{Zn\text{-}Zn}$=12) and Cu foil ($R_{Cu\text{-}Cu}$=0.255nm, $N_{Cu\text{-}Cu}$=12) were used as standards. Results are:

(1) In oxidized, reduced and used catalysts, the r-$Al_2O_3$ increases the dispersion of constituents in CZA, and r-$Al_2O_3$ 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.