XAFS study on the chemical structure of gold catalyst loaded on titanium dioxide.

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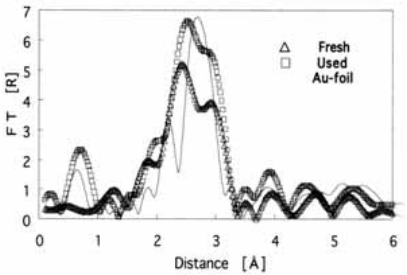
Propylene oxide is a basic chemical, but it is produced mainly by the co-product method. Therefore, establishment of the direct-produced method where only propylene oxide is produced is desired strongly.

Nippon Shokubai Co., Ltd. has developed a catalyst, which comprises ultra-fine Au particles dispersed on TiO2 by the special deposit precipitation technique. By utilizing the catalyst, it has developed a high selective vapor-phase oxidation method, which produces propylene oxide directly from propylene in the presence of hydrogen. However, the catalyst is greatly subject to deterioration by reaction pass time. The examination of causes of deterioration is needed to improve the catalytic performance to the industrially-used level. We have measured XAFS on Spring-8 to explicate the correlation of the catalytic performance and the chemical structure of Au at BL19B2 with XAFS using Si(111) monochrometer.

The Au-L3 absorption edge was measured by transmission mode with the Au 1wt%/TiO2 15wt%/SiO2 catalyst which were prepared in according to (1) at high sensitive ion-chamber type detector. From XANES analysis, the Au in catalysts were 0 valence. The EXAFS analysis also shows that the peaks for Au-Au distance of both fresh and used catalysts are shifted and split which were not found before and after in ordinary metals while the peak for Au-Au distance of Au-foil was single at 2.6 Å. This indicates that the catalysts demonstrated new catalytic performance, which was not seen before. We suppose the used catalyst bring about the crystal growth by the cohesion of loaded Au, because the EXAFS pattern is similar to Au-foil, for example 4, 0.6 Å emphasized.

(1) Journal of Catalysis 178,566-575(1998)



Precise structure analysis of complex hydrides of light elements

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Complex hydrides of light elements, such as $LiBH_4$, are recently investigated as hydrogen storage materials because of the large amount of hydrogen content ($LiBH_4$:18.5mass%). For practical use, it is necessary to lower the dehydrogenation temperature of $LiBH_4$. We found that the mixture of $LiBH_4$ and $LiNH_2$ is dehydrogenated at lower temperature than $LiBH_4$ single phase[1)]. In this mixing and dehydrogenating process, three phases are created.

$$LiBH_4+2LiNH_2 \rightarrow Li_3BN_2H_8$$
$$Li_3BN_2H_8 \rightarrow Li_3BN_2H_x+(4-x/2)H_2$$
$$Li_3BN_2H_x \rightarrow \alpha\text{-}Li_3BN_2+x/2H_2$$

The crystal structure of α-Li_3BN_2 is known[2)], but $Li_3BN_2H_8$ and $Li_3BN_2H_x$ are unknown. Therefore, the precise crystal structure analysis has been performed for the clarification of bonding state in these unknown phases.

The mixture sample was prepared by mechanically milling of $LiBH_4$ and $LiNH_2$ reagent using planetary mill. The dehydrogenation of mixture sample was preformed by heat-treating in argon atmosphere at temperature 423K, 523K, 723K, and 823K.

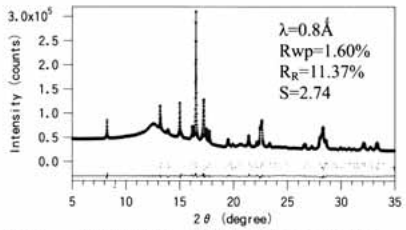

Fig.1 Rietveld analysis pattern of the $LiBH_4$+2$LiNH_2$ mixture sample after dehydrogenation at 723K.

The powder x-ray diffraction was measured at room temperature (295K) using incident x-ray wavelength 0.80Å. The measurement data were collected with a 0.01° step from 3.0° to 73.0° in 2θ. Crystal structure analysis of unknown phase was accomplished by ordinary method, namely indexing of peaks, decision of space group and so on. Finally, the structure was refined by Rietveld method (program RIETAN).

Rietveld analysis pattern for the sample, which was dehydrogenated at 723K, are shown in Fig.1. This sample includes $Li_3BN_2H_x$, LiH, α-Li_3BN_2, Li_2O and amorphous-like phase. The analyzed crystal structure of $Li_3BN_2H_x$ (Fig.2) is tetragonal system (space group: $I4_1md$) and the lattice constants are a= 6.583(2), c= 10.326(2) Å. $Li_3BN_2H_x$ is the ionic crystal which consists of Li^+ and $(N\text{-}B\text{-}N)^{3-}$ like α-Li_3BN_2. The result of thermal desorption spectroscopy shows that the value of x in $Li_3BN_2H_x$ is very small, because hydrogen was almost desorbed from the sample by dehydrogenation at 723K.

1) M. Aoki et al., Appl. Phys. A, in press
2) H. Yamane et al., J. Solid State Chem., **71** (1987) 1

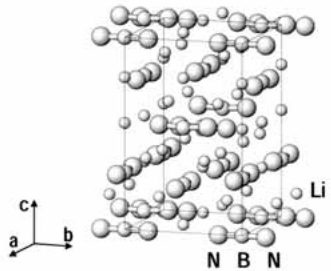

Fig.2 Crystal structure of $Li_3BN_2H_x$.