

X-ray Absorption spectroscopy Characterization of Nano-scale Catalysts for Improving Sulfur Resistance

J.-R. Chang¹(0009076), Y.-F. Wang¹(0009077), S.-H. Lee¹(0014357), J.-F. Lee²(0006016)

¹Department of Chem. Eng., National Chung-Cheng University, Chia-Yi, Taiwan, R.O.C.

²National Synchrotron Radiation Research Center, Hsinchu, Taiwan, R.O.C.

The catalytic properties of supported metal catalysts can be markedly changed by interacting with the support, e.g. the sulfur resistance of Pt catalysts for aromatics reduction is improved by using zeolite instead of alumina as the support. Among noble metal catalysts, supported Pd catalysts are unique for partial oxidation reaction, whereas catalyst deactivation caused by strong adsorption of CO hampers its application. The drawbacks of the catalysts can also be remedied by modifying catalyst support. In our previous paper, we have reported that the CO₂ yield during partial oxidation catalyzed by V₂O₅/MCM-41 was reduced by grafting TiO₂ on MCM-41 and proved that this TiO₂ grafting MCM-41 mesoporous framework has high potential for use as a mesoporous TiO₂ support [1]. In comparing the catalytic properties between Pd and V₂O₅ catalysts, we found that the Pd catalysts present much less CO₂ formation than that for V₂O₅ [2]. Hence, it is of great interest to explore the role of grafted TiO₂ in changing the morphology of Pd clusters and the catalytic properties. In order to implement the research goals, two catalyst samples, Pd/SiO₂ and Pd/TiO₂/SiO₂ were prepared and characterized by EXAFS. The EXAFS results are depicted as follows.

Figure 1 shows the preliminary EXAFS results of the formation of Pd clusters on Pd/SiO₂ and Pd/TiO₂/SiO₂. The results indicated that Pd clusters on TiO₂/SiO₂ are much smaller than those on SiO₂, suggesting TiO₂ retards the migration of Pd clusters thereby inhibiting the agglomeration of Pd clusters. Moreover, as shown in Figure 2, after air calcination of Pd(II) acetate on both supports, a significant peak at about 3.1 Å was observed for the Pd/SiO₂ sample, whereas no significant peaks have been observed for Pd/TiO₂/SiO₂. The results suggest that TiO₂ can anchor the Pd precursors during the decomposition of acetate ligands. Further study will be focused on the detail mechanism of the formation of Pd oxides on supports and

the role of TiO₂ on CO adsorption. In-situ FT-IR and EXAFS will be used to characterize the surface species.

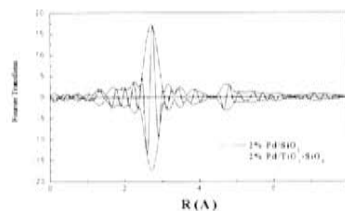


Figure 1. Imaginary and magnitude of Fourier transform (k^3 weighted, $4 < k < 13$, Pd-Pd phase and amplitude corrected) for Pd/SiO₂ and Pd/TiO₂/SiO₂ samples (samples prepared from Pd(II) acetate/support after 450 °C calcination and 450 °C hydrogen reduction).

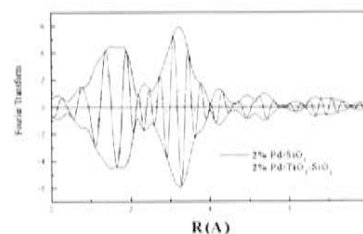


Figure 2. Imaginary and magnitude of Fourier transform (k^3 weighted, $4 < k < 13$, Pd-Pd phase and amplitude corrected) for PdO_x/SiO₂ and PdO_x/TiO₂/SiO₂ samples (samples prepared from Pd(II) acetate/support after 450 °C calcination).

Reference:

1. Lin, Hsiu-Mei; Kao, Sheng-Tsang; Lin, Kuo-Min; Chang, Jen-Ray; and Shyu, Shin-Guang "Grafting TiO₂ on MCM-41 as a TiO₂ Support for Vanadia for Catalytic Oxidation of Ethanol—EXAFS and XANES Analysis of Vanadium" *J. Catal.*, in press.
2. Lee, J.-F.; Zheng, F.-S.; Chang, J.-R. "Structural Investigation of Solid-Acid-Promoted Pd/SDB Catalysts for Ethyl Acetate Production from Ethanol" *J. Phys. Chem. B*, 105, 3400 (2001).

Gracing-incident structural characterization of supported composite porous thin films

(Characterization of Ru, Pd/zeolites by using XAS and PXRD)

Chao Kuei-jung^{*} (0007584), Liu Pang-hung (0007537), Huang Kuo-Ying (0008691) and Chiu Chien-Yang (0008690)

Department of Chemistry, National Tsinghua University, Hsinchu

Samples of the Ru nanosized catalysts in zeolites were offered by Weitkamp's group in German. By using different preparation methods, these samples were found to have different catalyzing ability.

Ru K-edge XAS were employed to characterize the local structure of Ru atoms and to infer the morphology of Ru metal in the molecular sieves. In this experiment, transmission mode XAS at Ru K-edge was employed using a Ru metal powder standard for reference and measured simultaneously with the samples so that energy calibration can be done for every scan. F.T. transformations of these spectra have been done and needed for further fitting.

For the Pd samples, Pd nanometal was introduced into the 3-dimensional channels of mesoporous MCM-48. It was observed under TEM that Pd metal particles are very small and uniform. The size of Pd nanoparticles was estimated to be about 1 nm. Therefore, high flux and high energy X-ray source was used for retrieving higher quality and more diffraction peaks.

In the following figure, the sample (c), which has the highest Pd content, was detected to have sharper and stronger peaks. Its particle size of Pd can be estimated to be about 2–3 nm. In samples (a) and (b), the most intense peak Pd(111) was still observable but others were too broad to tell. From the Pd(111) peak, the particle sizes of Pd nanoparticles in samples (a) and (b) should be

only 1 nm. However, the sizes of Pd metal in samples (d) and (e) are too small and therefore, its diffraction peaks are very broad and very difficult to calculate. In all these Pd/MCM48 samples, we can suppose most of Pd metal particles in the samples are in uniform sizes and large particles were not found in the homogeneous powder diffraction patterns. We also try to deconvolute the patterns and want to get some information between particle sizes and parameters of cell dimensions.

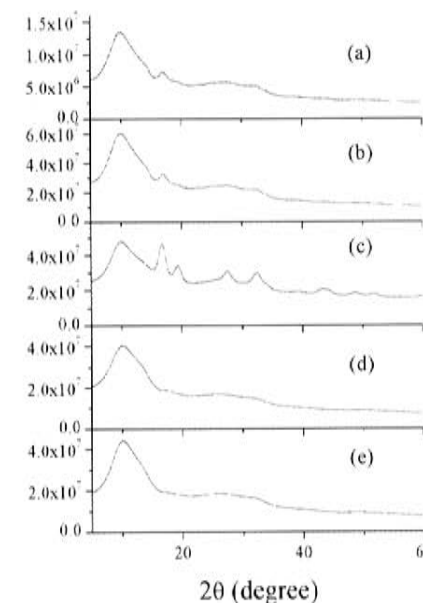


Figure PXRD patterns of Pd/MCM48 with different Pd contents.