

Sulfur Resistance Enhancement by Grafted TiO_2 in SiO_2 -supported Pd Catalysts: Role of the Grafted TiO_2

Pd clusters on TiO_2 grafted SiO_2 (TiO_2 - SiO_2), SiO_2 , and TiO_2 particles were prepared via impregnation with palladium (II) acetate followed by air-calcination and hydrogen-reduction. The prepared catalysts were tested by tetralin hydrogenation with sulfur-poisoning reaction. The results show that Pd/ TiO_2 - SiO_2 presents highest activity maintenance. To investigate the role of the grafted TiO_2 in improving activity maintenance, the catalyst samples were characterized by FT-IR, EXAFS and XRD. The results indicated that layer-like TiO_2 clusters formed on SiO_2 helps anchor palladium oxides during air-calcination. This anchoring leads to a formation of relatively small Pd clusters having less electronic density as opposed to the other two catalysts. Combining structural characterization with kinetic study results, we concluded that the superior catalytic performance for Pd/ TiO_2 - SiO_2 could arise from the decrease of the affinity of Pd for H_2S and the increase of hydrogen reducibility for PdS_2 .

Beamlines

BL01C1 SWLS-EXAFS
BL01C2 SWLS-X-ray Powder Diffraction
BL17C1 W20-EXAFS

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The interactions between noble-metal clusters and non-reducible-metal-oxide carriers are critically important for supported-metal catalysts. The interactions and the catalytic properties of those materials could be modified by the addition of TiO_2 . However, little is known about the roles of TiO_2 in changing catalytic properties because of the difficulty in characterizing metal-support interface. In this research, the genesis of the formation of Pd clusters on TiO_2 grafted SiO_2 were explored by the unique use of X-ray absorption spectroscopy. The results indicated that TiO_2 help anchor PdO_x during air-calcination and maintain it in small ensembles during H_2 -reduction. This observation is expected to illuminate how TiO_2 on the catalyst support influences the structure and catalytic properties, specifically, sulfur resistance of the catalysts.

To facilitate this study, the material system is carefully designed. In the system, Pd is the metal of choice, because it is used widely as the active sites for catalytic reactions. Palladium (II) acetate was chosen because the Pd precursors readily undergo cleavage on metal-oxide carriers offering us opportunities to prepare highly dispersed Pd catalysts. TiO_2 grafted silica was chosen as the support (or carrier) because it presents high surface area, higher thermal stability than that of pure TiO_2 towards sintering at high temperature. Higher dose of Pd precursor and, in turn, Pd clusters can be expected to bond to TiO_2 on this composite support. Hence, the EXAF (Extended X-ray absorption fine structure) measurement can be performed in transmission mode, which presents much higher signal to noise ratio than in fluorescence mode; thus the contribution of TiO_2 - PdO_x interaction in EXAFS spectrum would not be affected significantly by noise. Moreover, since the catalyst samples are air and moisture sensitive, EXAFS measurements were carried out in an in-situ EXAFS cell, which are free of air and moisture.

In order to illustrate the merit of the grafted TiO_2 in catalysis, sensitivity to sulfur poisoning was tested because: (1) supported Pd catalysts are very sensitive to sulfur compound, (2) maintaining the required level of

sulfur to avoid deactivation in commercial operation is very expensive and millions dollars are lost every year in chemical and oil industries as a consequence of sulfur poisoning, and (3) several methods including the use of acidic supports, the addition of second metal, and the exchange of NaY support with polyvalent cations have been used to enhance sulfur resistance of supported metal catalysts, whereas no information regarding the use of TiO₂-SiO₂ supports has been reported.

Structure of Pd/TiO₂-SiO₂, Pd/SiO₂ and Pd/TiO₂

Fourier transformed EXAFS functions at the Pd *K*-edge provide the qualitative information about the structure of Pd clusters. As shown in Fig. 1, the Pd-Pd phase and amplitude corrected Fourier transformed-EXAFS functions in *r* space of the three hydrogen-reduced samples show that the peak corresponding to the first Pd-Pd shell (at about 2.7 Å) for the Pd/TiO₂-SiO₂ was much lower than that for Pd/SiO₂ and for Pd/TiO₂. Since the intensity of the Fourier transformed-EXAFS functions is proportional to the coordination number^[1], this result indicates that much smaller Pd clusters were formed on TiO₂-SiO₂. Detail analysis of the EXAFS data confirmed this result. The coordination number of the first Pd-Pd shell was 5.7, 7.8, and 10.2 for Pd/TiO₂-SiO₂, Pd/SiO₂, and Pd/TiO₂ respectively.

The higher-shell data provide a basis for the determination of Pd morphology. The Fourier transforms

indicated the presence of a peak at approximately 3.8 Å. The distance is consistent with the second shell of bulk fcc Pd, as reflected by crystallographic data and is an indication of the Pd clusters of three dimensional character^[2]. The results suggests Pd clusters with structures resembling spheres (sphere-like clusters) formed on support and the morphology of Pd clusters on support TiO₂-SiO₂ can thus be determined by 1st shell Pd-Pd coordination number. For Pd/TiO₂-SiO₂ catalyst, the Pd-Pd coordination number of 5.7 suggests that the average diameter of the Pd clusters is about 11 Å and fraction of atoms on surface is about 85%. If Pd clusters are bounded by a (111) face in the metal-support interface, a (111) interface only allow up to three Pd-O bonds per Pd interface atoms. The Pd-O_{support} coordination of 0.7 suggests about 20 % of Pd atoms existed at the interface between Pd clusters and TiO₂-SiO₂; if Pd clusters are bounded by a (100) face, fraction of Pd atoms at interface is about 17%.

The Pd/SiO₂ and Pd/TiO₂ samples are characterized by a first-shell Pd-Pd contribution with a coordination number of 7.8 and 10.2, respectively. These values with the evidence provided by the presence of 2nd shell Pd-Pd contribution suggest that the average cluster size and fraction of atoms on surface is about 22 Å and 64%, respectively, for Pd/SiO₂ and about 100 Å and 24%, respectively, for Pd/TiO₂. Moreover, no significant peak characterizing Pd-O_{support} contributions was observed, suggesting the metal-support interactions for these two catalysts are rather small.

Thermal stability of TiO₂ nano-particles and TiO₂-SiO₂: XRD results

PXRD patterns of anatase TiO₂ were measured at various calcinations temperatures as shown in Fig. 2. TiO₂ nano particles were prepared by hydrolysis of titanium (IV) butoxides in water at 70 °C. The particles were aggregated during calcination. The crystal grain sizes of TiO₂ calculated according to Scherrer's equation were 16, 19, 24, 36, and 80 nm for the sample calcined at 300, 350, 450, 550, and 650 °C in air for 2 h, respectively. Moreover, PXRD patterns clearly indicate that the material undergoes phase change at about 550 °C.

The TiO₂-SiO₂ support was calcined up to 900 °C. The PXRD patterns of TiO₂-SiO₂ show that the TiO₂ maintains its amorphous states at the temperature up to 600 °C (Fig. 3). Hence, highly dispersed Pd clusters could thus be

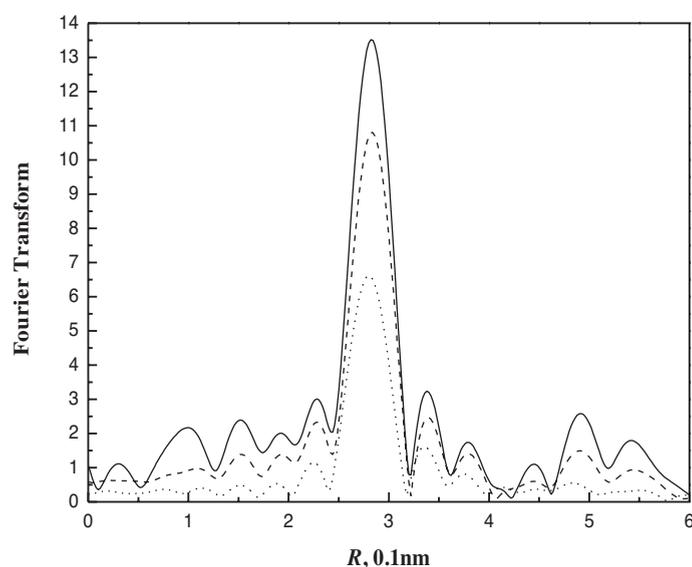


Fig. 1: Magnitude of the EXAFS Fourier transform ($3.5 < k^2 < 12.0$, Pd-Pd phase and amplitude corrected) for Pd/TiO₂ (solid line), Pd/SiO₂ (dashed line), and Pd/TiO₂-SiO₂ (dotted line).

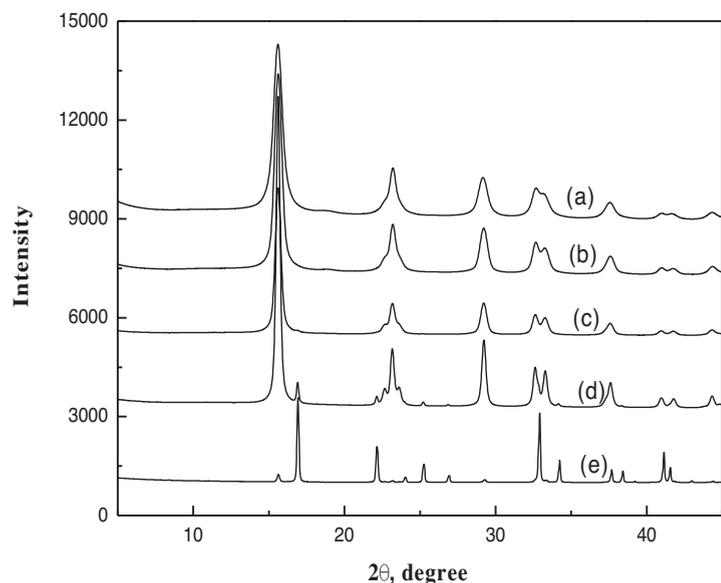


Fig. 2: Powder X-ray diffraction patterns of TiO_2 nano-particles prepared by hydrolysis of titanium butoxides and followed by calcination at various temperatures: (a) 300, (b) 350, (c) 450, (d) 550, and (e) 650 °C.

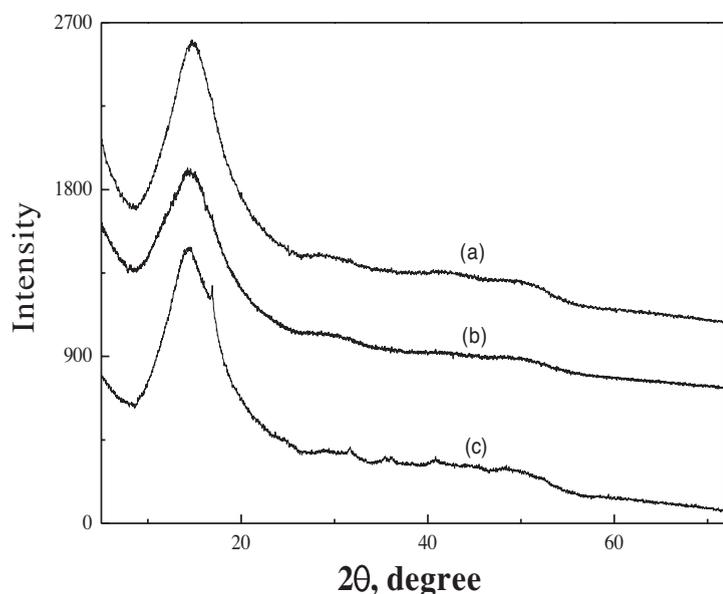


Fig. 3: Powder X-ray diffraction patterns of anatase TiO_2 in $\text{TiO}_2\text{-SiO}_2$ heated at various temperatures: (a) 450, (b) 600, (c) 900 °C.

prepared on $\text{TiO}_2\text{-SiO}_2$, which has high surface area and thermal stability.

Accelerated sulfur-poisoning catalyst deactivation

Total tetralin conversion for the sulfur-containing feed is shown as a function of time on stream in the flow reactor (Fig. 4). The conversion of Pd/TiO_2 dropped rapidly right after the test began and the catalyst lost all its activity at about the 3 h of run. Different from Pd/TiO_2 , two stages of deactivation were observed for $\text{Pd/TiO}_2\text{-SiO}_2$ and Pd/SiO_2 catalysts. The first stage starts right after the introduction of feed to the reaction system and extends until the time on stream at which the deactivation rate becomes lower. The second stage begins when the deactivation rate increases again with time on stream, which is about 3 and 5 h on stream for Pd/SiO_2 and $\text{Pd/TiO}_2\text{-SiO}_2$, respectively. Compared with Pd/SiO_2 , the first-stage deactivation for $\text{Pd/TiO}_2\text{-SiO}_2$ extended longer and in the nearly steady state (about 10 h on stream) the catalyst maintains higher activity.

The detail chemistry whereby grafted- TiO_2 enhances sulfur resistance remains to be elucidated. Our observation and the published results of Guenin et al.^[3] suggest a role of Pd cluster size. The layer-like TiO_2 clusters help anchor the Pd and/or increase the roughness of SiO_2 surface, thereby maintaining Pd in high dispersion. The decrease of Pd clusters decreases the affinity of H_2S for Pd clusters while increases hydrogen reducibility of PdS_2 , resulting in an increase of stability maintenance.

Experimental X-ray absorption spectroscopy

The X-ray absorption measurements of Pd K edge (24350 eV) were performed on the super-conducting wavelength shifter (SWLS) beamline BL01C1 at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan, with energy from 5 to 33 KeV. The monochromator employs double Si(111) crystals for energy selection with a resolution ($\Delta E/E$) better than 2.5×10^{-4} . It was detuned 20% at

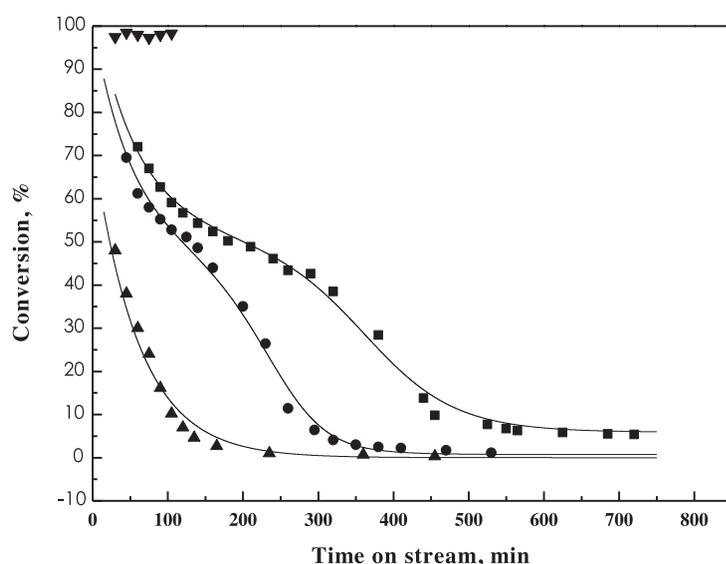


Fig. 4: Aging tests for Pd catalysts run at WHSV of 12.0, 200 °C, and 32 atm with 200 ppm-sulfur-containing-tetralin feed: ●, Pd/TiO₂-SiO₂; ▲, Pd/SiO₂; ■, Pd/TiO₂; solid line, data calculated from proposed model; ▼, pure tetralin feed catalyzed by Pd/TiO₂-SiO₂ for comparison.

$E_0 + 50$ eV to suppress higher harmonic radiation. The monochromator was scanned in energy from 200 eV below the palladium *K* absorption edge (24350 eV) to 1000 eV above the edge. Each sample was pressed into a self-supporting wafer in a N₂-filled glove bag and then placed into an EXAFS cell. The cell was connected to a vacuum/gas-handling manifold for in-situ treatment. All samples were measured in a transmission mode at room temperature. The transmission measurement geometry was arranged using gas-fill ionization chambers to monitor the intensities of incident and transmitted X-rays. To gain the proper absorption ratio for incoming X-rays, the gas composition in the ionization chamber were selected at argon to nitrogen mole ratio of 1/1 for the first chamber and pure argon for the second chamber, respectively.

X-ray absorption spectra of Ti *K* edge (4966 eV) were recorded on the wiggler beam line BL17C at NSRRC. Two Rh-coated mirrors (mainly for the purpose of collimating and focusing the synchrotron beam) to eliminate high energy components. However, the cut-off energy was set to 15 keV for both mirrors so that the third harmonics from Si(111)-crystal monochromator may not be completely rejected by the mirrors when the fundamental photon

energy was scanned around Ti *K*-edge (~ 5 keV). Accordingly, the higher X-ray harmonics were minimized by detuning at $E_0 + 50$ eV. The ion chambers used for measuring the incident (I_0) and transmitted (I) synchrotron beam intensities were filled with a mixture of N₂ and He gases and a pure N₂ gas, respectively.

Synchrotron XRD

Powder X-ray diffraction (PXRD) was performed at the BL01C2 beamline of the NSRRC, with the wavelength of 0.9537 Å (13 keV). Two dimensional diffraction patterns were recorded by a Mar345 imaging plate system, with a sample-to-detector distance of 300 mm. Diffraction angle was calibrated with Si powders (NBS640b) and silver behenate. One dimensional XRD profiles were integrated from selected fan-like areas of the symmetrical 2-D powder rings using the Fit2D program.

Experimental Stations

X-ray absorption spectroscopy end station
X-ray powder diffraction end station

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Publications

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