

Reversible Structural Transformation of Palladium Catalyst Supported on La–Al₂O₃ Probed with X-ray Absorption Fine Structure

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Reversible transformation of the palladium catalyst during thermal cycling was investigated with X-ray absorption fine structure. PdO was transformed to Pd at 850 °C upon when the air temperature was increased while the reverse transformation occurred at 680 °C. On-line TGA/MS measurements combined with EXAFS/XANES showed oxygen generation at 680 °C, indicating that the metal–support interaction stabilizes the catalyst, by transforming to the surface attached PdO and further to Pd metal agglomerates at 850 °C. Thermal stability of the Pd metal agglomerate was also improved by coating the Pd catalyst with TiO₂.

Introduction

Pd catalysts have been used extensively in catalytic combustion. By using Pd catalysts in the combustion process, the combustion temperature can be lowered to 1200 °C. The generation of thermal NO_x is thereby suppressed dramatically below 3 ppm since high combustion temperature, ca. 1500 °C, increased the rate of the formation of NO_x from O₂ and N₂ in air.¹

However, the Pd catalyst is evaporated readily at such a high temperature, resulting in the loss of catalytic activity.² Several combustion systems have been proposed to inhibit deactivation of the Pd catalyst. Catalytically stabilized combustion with post combustion zone, allows the catalyst zone to maintain its temperature, 900 °C.³

It has been suggested that reversible transformation of the Pd catalyst between PdO and Pd occurs during the thermal cycling in the combustion reaction.⁴ Farrauto et al. proposed the model for the reversible transformation of Pd catalyst during thermal cycling based on the weight change from TGA measurement.⁵ During thermal cycling, PdO converted to Pd and the resulting Pd metal agglomerate transformed back to PdO at 550–650 °C. They suggested a correlation between the methane combustion activity and the weight change. Electron microscopic study of Pd catalysts under controlled atmosphere showed the microscopic features of thermal behavior.⁶ This study suggested the formation of a compound like PdAlO_x above 800 °C that might cause the deactivation.

However, the information on the change of atomic structure of Pd catalyst during the thermal cycling was very limited. In the present work, we report the investigation of X-ray absorption fine structure (XAFS) on the Pd catalyst under thermal treatment in ambient air in conjunction with the on-line TGA/MS measurement. Also, the effect of the metal–support interaction between TiO₂ and Pd catalyst on the thermal stability has been investigated using XAFS.

Experiment

Pd(NO₃)₂ (Heesung Engelhard Corp., 19.9% Pd) was impregnated into La-doped Al₂O₃ (2 mol % La–Al₂O₃) supplied

from Condea Inc. Its surface area was 90 m²·g^{−1}. The activation procedure was the calcination in oxygen at 550 °C for 6 h followed by the reduction with hydrogen at 550 °C for 4 h. The Pd loading of the catalyst was 2 wt % on dry basis. The obtained Pd catalyst was denoted as Pd/La–Al₂O₃.

The preparation of TiO₂ sol following the procedure reported in the literature is briefly.⁷ Titanium tetraisopropoxide (Aldrich, 97%) was hydrolyzed in doubly distilled water. Upon the addition of concentrated HCl, the precipitates were dissolved to give clear transparent sol. This sol was impregnated onto Pd/La–Al₂O₃ and subsequently reduced at 800 °C for 6 h without calcination. The TiO₂-coated Pd catalyst was also denoted as TiO₂/Pd/La–Al₂O₃.

X-ray absorption measurement was carried out in ambient air using Beamline 10B at the Photon Factory in Tsukuba. For high-temperature measurements, a specially designed XAFS cell with Kapton window (DuPont, 125 μm) was used. The temperature was raised from room temperature to 900 °C. The extended X-ray absorption fine structure (EXAFS) data was analyzed using XFIT and Feff6. The details of EXAFS data analysis can be found elsewhere.⁸ Thermogravimetric analysis (TGA) was carried out with a TA instrument from 30 to 950 °C. Oxygen evolution from the catalyst was monitored with an on-line mass spectrometer (Genesys, Baltzers) after the removal of water using acetone/dry ice trap.

Results and Discussion

TGA spectra of the Pd catalyst coupled with on-line MS spectrum are presented in Figure 1. Pure La–Al₂O₃ showed monotonic decrease of weight with the increase of temperature at a rate of 10 °C·min^{−1}. There was negligible weight gain of the sample upon subsequently decreasing the temperature. Thus, the monotonic decrease of weight seemed to come from the desorption of adsorbed water.

Pd/La–Al₂O₃ showed decreases in weight at two distinct temperatures, namely at 680 and 880 °C. However, subsequent cooling caused the catalyst to gain weight. The weight changes at 680 °C can be ascribed to the evolution of oxygen, as shown by the peak at around 680 °C in the on-line MS spectra of oxygen (*m/e* = 32). There was no oxygen evolution at 880 °C where the weight change in TGA spectrum occurred. This

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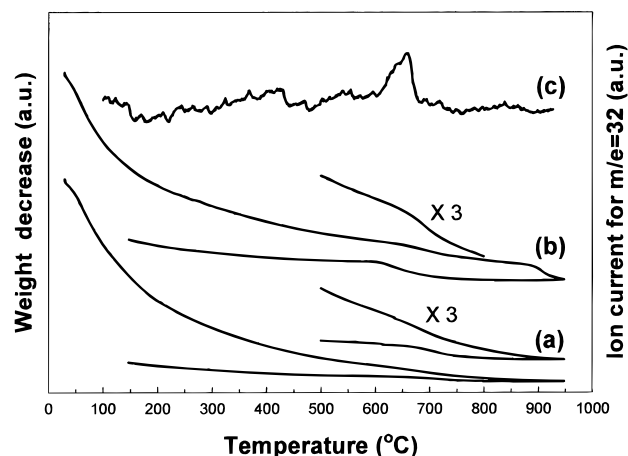


Figure 1. TGA spectra of (a) La-Al₂O₃ and (b) Pd/La-Al₂O₃, and the MS spectrum ($m/e = 32$) of (c) Pd/La-Al₂O₃. The ramping rate in TGA experiment was 10 °C·min⁻¹. The effluent gas stream in mass spectroscopic measurement was passed through the dry ice/acetone trap to remove water.

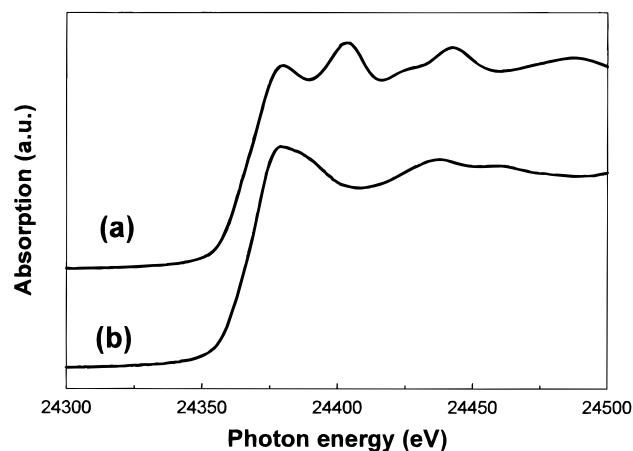


Figure 2. Near-edge spectra of X-ray absorption at the Pd K edge for (a) Pd foil and (b) PdO. The spectra were measured at room temperature.

change might be attributed to the evolution of H₂O due to dehydroxylation.

The temperature for the decomposition of PdO to Pd is widely distributed from 650 to 800 °C in the literature depending on the support, the presence of dopant like La³⁺ or metal oxide like NiO, metal particle size, etc. Widjaja et al. studied the reduction-oxidation property of Pd catalyst supported on Al₂O₃ using TPD of oxygen.⁹ They ascribed the desorption at 700 °C to the decomposition of PdO and the desorption over 700 °C from Al₂O₃. Incorporation of NiO into Pd/Al₂O₃ led to a change of the TPD profile: the appearance of the peak at 750 °C. Groppi et al. report the TPD/TPO measurements over 2.5% Pd/La-Al₂O₃ (5 wt % La doping).¹⁰ Their result showed that oxygen is evolved at 700–750 °C.

Figure 2 shows the X-ray absorption near-edge structure (XANES) of Pd foil and PdO at the Pd K edge. At the Pd K edge, the absorption transition at 24 348 eV is 1s → 4d dipole forbidden transition according to the selection rule, $\Delta l = 1$ and $\Delta j = 1$, where l and j are the orbital angular momentum and the total angular momentum of the local density of states, respectively.¹¹ Thus, this transition intensity is suppressed greatly as shown in Figure 2a. The absorption cross section in the K edge region of transition metals is strongly influenced by d-s,p hybridization because the unoccupied bands are d bands. Thus, in system where the d-s,p hybridization is strong, the p-like

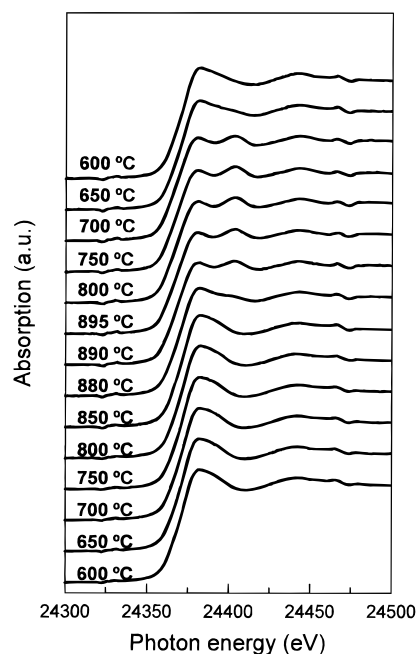


Figure 3. Near-edge spectra of X-ray absorption at the Pd K edge for the Pd/La-Al₂O₃ as a function of heating temperature in ambient air from the bottom to top.

density of states is strongly enhanced and the absorption can be increased like the second and third absorption peak in the XANES spectrum of Pd foil. The XANES spectra of PdO in Figure 2b shows the strong absorption at the Pd K edge since the d-p hybridization of Pd²⁺ increased significantly the absorption cross section, compared with that of Pd foil.

The XANES feature is known to be very sensitive to the long-range order up to 10 nm due to a large mean free path of the photon electron in the energy range of 1–100 eV above the absorption edge.¹² The reference Pd and PdO spectra thus have a characteristic XANES features which are sensitive to the change of physicochemical environment of the absorbing atom, such as the change of oxidation state, hydrogen chemisorption, the formation of bimetallic particles, etc.¹³ Therefore, the reversible transformation of Pd catalyst during the thermal cycling in ambient air can be monitored using XANES at the Pd K edge.

Figure 3 shows XANES spectra as a function of the heat treatment temperature. A rather broad strong single peak characterized as the PdO was maintained up to 850 °C. Upon further increase of the temperature above 850 °C, a single peak became split into two peaks characterized as the Pd, which suggests the transformation of the PdO structure to Pd. The data analysis of Pd XANES of the Pd/La-Al₂O₃ indicated that there was no change of the PdO entity around 680 °C where the oxygen was evolved. The results suggest that the spread of Pd over the surface occurs upon desorption of oxygen from PdO. Koningsberger and Gates suggested that the metal support interaction over Al₂O₃ was very strong.¹⁴ They claimed the EXAFS contribution of a long metal-oxygen distance as a direct evidence for the metal support interaction. Needle, rod, or planar shape of the particle on the catalyst support is believed to maximize the metal-support interaction. Planar shape of the Pt particle under vacuum and helium was reported inside the channel of zeolite KL, which might indicate the substantial metal-support interaction.¹⁵ Rodriguez et al. observed that the needlelike shape was a result of the interaction between Pd and oxygen at 840 °C.⁶ They suggested that the reduced Pd particle over γ -Al₂O₃ converted to PdO in the range of 350–650 °C

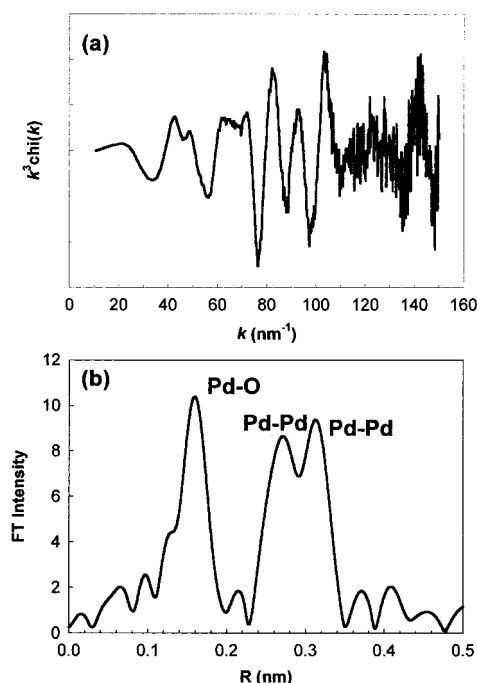


Figure 4. (a) Typical k^3 -weighted EXAFS spectrum and (b) its corresponding Fourier transformation of the Pd/La–Al₂O₃. The phase shift was uncorrected.

TABLE 1: Structural Parameters from the Best Fit of EXAFS Spectra of the Pd Catalyst at the Pd K Edge Using XFIT and Feff6

sample	pair	<i>N</i>	<i>R</i> (nm)	σ^2 (pm ²) ^a
Pd/La–Al ₂ O ₃	Pd–O	3.5	0.201	16.7
	Pd–Pd	4.8	0.305	57.6
	Pd–Pd	4.2	0.343	41.6
TiO ₂ /Pd/La–Al ₂ O ₃	Pd–O	3.7	0.201	21.2
	Pd–Pd	4.9	0.304	68.0
	Pd–Pd	4.2	0.342	40.0
	Pd–Ti	(4.7)	(0.361)	(79.6)
Aged at 1200 °C for 4 h				
Pd/La–Al ₂ O ₃	Pd–Pd	10.6	0.274	56.0
TiO ₂ /Pd/La–Al ₂ O ₃	Pd–O	1.7	0.202	~ 0
	Pd–Pd	5.3	0.275	47.8
	Pd–Pd	6.4	0.342	84.4

^a The Debye–Waller factor.

and subsequently PdAlO_x above 800 °C. Further, the coexistence of PdO and Pd over the surface was claimed for heavy metal loading, ~10%. In the present work, the Pd metal loading was controlled to 2 wt %, far from heavy loading.

Upon decreasing the temperature, the two split peaks combined to give the single feature characterized as PdO at 650–700 °C. This reverse transformation from Pd to PdO was consistent with the weight gain occurred at 680 °C in TGA spectra. Thus, the results of XANES suggested that the reversible transformation between PdO and Pd did not follow the same pathway upon increasing and decreasing the temperature.

Typical k^3 -weighted EXAFS spectrum and the corresponding Fourier transformation are shown in Figure 4. Three distinct peaks at 0.20, 0.30, and 0.34 nm corresponded to Pd–O, Pd–Pd, and Pd–Pd bond, respectively, which were identified from the comparison of amplitude and phase functions with those of the standards. The results of data analysis of EXAFS are shown in Table 1. The many-body reduction factor, $S_0^2 = 0.90$, was obtained from the curve fitting of Pd foil. The refinement of the model structure of the Pd catalyst was performed through an iterative refinement of model structure for the simulation of

theoretical EXAFS with Feff6 and the subsequent curve fitting of the experimental EXAFS spectrum using the simulated amplitude and phase function of EXAFS spectrum.

The best fit of the model structure of PdO is shown in Figure 5. The obtained tetragonal PdO structure consisted of four oxygen atoms at 0.203 nm, eight palladiums at 0.300 nm, and four palladiums at 0.340 nm. The difference in the CN in the second shell was due to the small size of PdO particle. The reduced Pd particle has the coordination number of Pd–Pd, 8.8 at 0.272 nm, indicating the formation of 1–2 nm Pd particle.

Figure 6 shows the change of the coordination distance (*R*) and the coordination number (CN) of the first shell appeared in *r* space. The *R* at 0.20 nm and the CN ca. 4 did not change up to 850 °C, indicating that the PdO structure was stabilized on the La–Al₂O₃ support. At 850 °C, the atomic structure of the Pd catalyst changed suddenly to Pd metallic state, referred from the *R* at 0.27 nm and the CN ca. 6–8. At high temperatures, the large thermal vibration may hinder an accurate estimation of the CN. The *R* may better indicate the change of the atomic structure. Consistent with the result of XANES, it was found from the results of EXAFS data analysis that the reversible transformation between PdO and Pd occurred at 850 and 680 °C with the increase and decrease of the temperature, respectively.

Based on the results from the TPD/MS experiment, and XANES and EXAFS of the Pd catalyst, the structural model for the reversible transformation can be suggested as shown in Figure 7. The weight change of the Pd catalyst at 680 °C estimated from TG measurement corresponded to the decomposition of PdO to Pd, ~0.25% ± 0.10%, close to the calculated value, 0.3%. However, the XANES feature did not show the change of the oxidation state corresponding to the change of PdO to Pd at the same temperature region. Thus, the fresh PdO was believed to convert into the surface attached PdO at 680 °C.

The other supporting evidence for the formation of the surface attached PdO species was found in the change of the Pd–Pd CN at 0.30 nm. This Pd–Pd CN changed suddenly from 3.0 to 1.6 with the increase of the temperature from 650 to 700 °C. Below 650 °C, the Pd–Pd CN at 0.30 nm decreased gradually from 4.8 at room temperature to 3.0 at 650 °C. Above 700 °C, the Pd–Pd CN also decreased gradually and disappeared at 850 °C. This CN change cannot be the subject of rigorous XAFS data analysis. However, the sudden change of Pd–Pd CN at 650–700 °C may be qualitatively interpreted as the change of the PdO size, that is, the reconstruction of the initial PdO into rather platelike particle by forming the surface attached PdO upon the desorption of oxygen.

The surface-attached PdO underwent the further structural change to Pd metal at 880 °C, losing PdO's character. Both results from EXAFS and XANES on Pd catalyst supported this structural change. It has hitherto been suggested that the conversion of the PdO to Pd is responsible for the decrease of the catalytic activity in methane combustion. Iglesia reported that the PdO decomposition to Pd metal above 830 °C led to very low methane oxidation rates and to very low apparent PdO dispersions.¹⁶ Similarly, Groppi et al. showed that the activity of methane combustion over the Pd catalyst declined significantly upon the complete conversion of PdO to Pd metal.¹⁰ Sekizawa et al. also reported that the methane combustion activity depended on the dispersion and oxidation states of the palladium through the interaction with the support.¹⁷

The present model for the reversible transformation of Pd catalyst further suggests the direct transformation from Pd metal

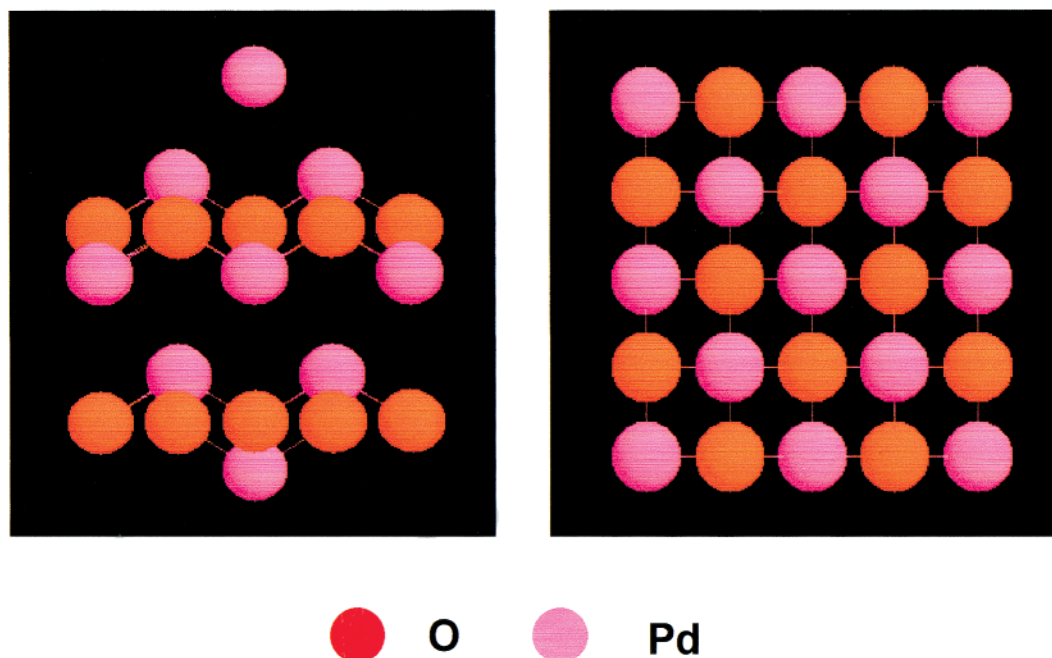


Figure 5. Cluster model of PdO obtained through the iterative refinement of the model structure for the simulation of theoretical EXAFS with Feff6 and the subsequent curve fitting of the experimental EXAFS spectrum to the obtained theoretical EXAFS spectrum.

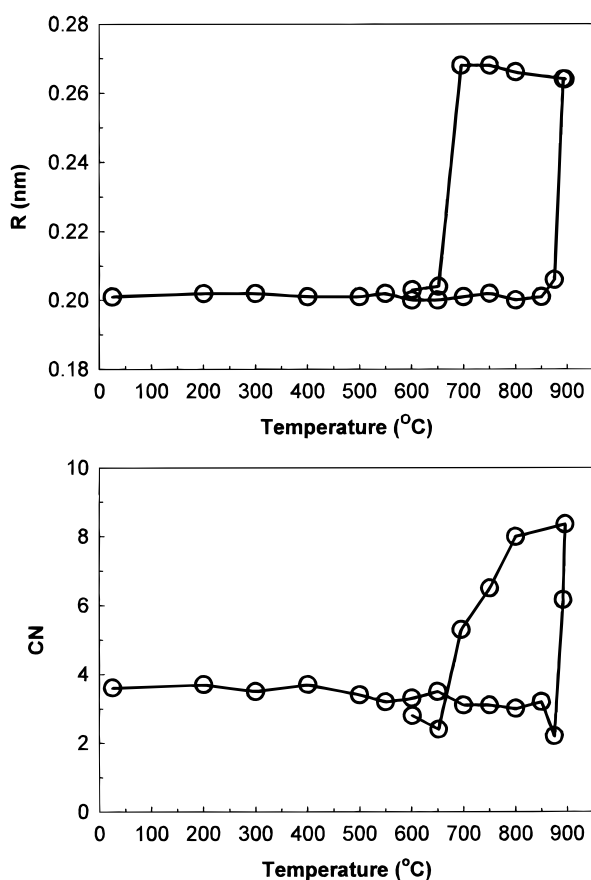


Figure 6. Coordination number and coordination distance of the first shell in r space plotted as a function of heating temperature. The distances of Pd–O in the palladium oxide reference and Pd–Pd in Pd metal foil reference are 0.20 and 0.27 nm, respectively.

to PdO at around 680 °C since there was no reoxidation of Pd metal and adsorption of oxygen before that temperature. In other words, the Pd metal agglomerate did not spread to form the surface attached PdO but converted to PdO upon reoxidation.

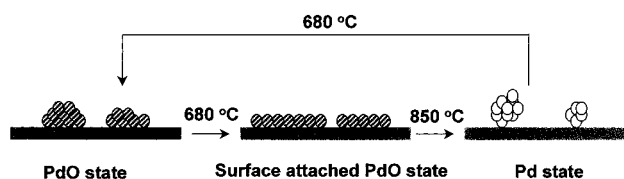


Figure 7. Proposed structural model for the reversible transformation of Pd catalyst in this work. The PdO seems to spread upon the desorption of oxygen and to agglomerate to form Pd metal particle upon heating to 850 °C. The reverse transformation of the Pd metal occurred to PdO at 680 °C.

It was expected that the Pd agglomerate might sinter to form large bulk Pd metal upon excessive heating above 1000 °C. We have thereby examined the suppression of Pd metal sintering using metal oxide coating like TiO₂ which is known to have the strong metal–support interaction.¹⁸ Asakura suggested the strong metal–support interaction between Pd and TiO₂ using EXAFS.¹⁹ It was found that the reducibility of Pd on TiO₂ was suppressed, which was ascribed to the metal–support interaction.

The TiO₂ sol used as the coating agent in the present work was initially prepared for the synthesis of titanium incorporated microporous and mesoporous zeolite.⁷ Catalytic reaction test proved that the zeolite contained the incorporated titanium in the framework. The size of the TiO₂ particles measured by SAXS was ~10 nm, indicating the presence of polymeric species in the sol, that is, *nano-sol*.²⁰ Investigation on the mechanism of the incorporation using EXAFS and XANES suggested that the dissolved Ti precipitates converted to polymeric Ti species with a simultaneous partial substitution of isopropyl ligands with chloride ion and water.²¹ This polymeric Ti species may further break down during the zeolite synthesis.

Figure 8 compares the Fourier transforms of the EXAFS spectra of the Pd catalyst with and without TiO₂ incorporation. Incorporation of TiO₂ onto Pd catalyst led to an increase of the third shell intensity corresponding to the Pd–Pd bond at 0.34 nm. Significant change in intensity can be regarded as the Pd–Ti scattering contribution. Table 1 also summarized the result of the curve fit of the EXAFS spectra above the Pd K edge.

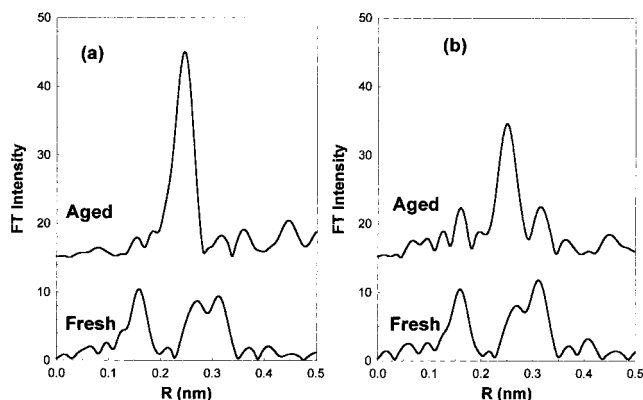


Figure 8. Comparison of the Fourier transformation of the Pd/La- Al_2O_3 and $\text{TiO}_2/\text{Pd/La-Al}_2\text{O}_3$ catalyst (a) before and (b) after the thermal aging at 1200 °C for 4 h. The phase shift was uncorrected

The Ti contribution in the TiO_2 -coated Pd catalyst appeared at 0.36 nm, of which the estimation of the Pd-Ti CN and the Debye-Waller factor may be ambiguous due to multiple scattering effect. However, the distance information appeared to be reliable to indicate the presence of Ti at the outer shell.

Thermal aging of the Pd catalyst at 1200 °C for 4 h affected remarkably the Fourier transformation of EXAFS spectrum. The best-fitted structural parameters were almost the same as that of bulk Pd foil except for the smaller Pd-Pd CN, 10.6, suggesting the irreversible transformation of PdO to Pd metal upon heating at 1200 °C. Meanwhile, the same thermal aging treatment of the TiO_2 -coated Pd catalyst at 1200 °C for 4 h did not affect the Fourier transform of EXAFS spectra as much as for the Pd catalyst. As shown in Figure 8, the tetragonal PdO structure was still present after such a severe sintering condition. The obtained structural parameters were also partly consistent with those of tetragonal PdO. It was thus concluded that TiO_2 coating ameliorated the thermal stability of the Pd catalyst.

Conclusion

The structural model for the reversible transformation has been proposed using EXAFS and XANES combined with TGA/

MS spectroscopy. The atomic structure of the fresh Pd catalyst was best fitted to the tetragonal palladium oxide. The PdO appears to spread at 680 °C over the surface of La- Al_2O_3 to maximize the metal-support interaction and to transform into the Pd metal agglomerate upon further heating above 850 °C. The Pd metal agglomerate was reoxidized to the PdO directly at 680 °C without the formation of the surface-attached PdO. The thermal stability of the Pd catalyst has been improved with the coating of TiO_2 probably due to metal-support interaction.

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