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EXAFS Study of $\text{Ti}_{0.98}\text{Pd}_{0.02}\text{O}_{2-\delta}$ Catalyst

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Abstract. To understand the higher catalytic properties, the structure of 2 at. % palladium supported on TiO_2 has been investigated by Extended X-ray absorption fine structure (EXAFS) spectroscopy. This nanocatalytic material of composition $\text{Ti}_{0.98}\text{Pd}_{0.02}\text{O}_{2-\delta}$ has been synthesized by solution combustion method. The analysis of EXAFS shows the oxide ion sublattice around Pd ions is destabilized in the solid solution. Instead of ideal six coordination, Pd ion has 4+2, coordinations creating long and short bonds. The long Pd–O bonds are at 2.52 Å which are much higher than average Ti–O bonds of 1.947 Å.

INTRODUCTION

In our programme on synthesis and study of structural properties of new catalytic materials, we have been pursuing the idea of noble metal ions as the active sites for catalytic oxidation–reduction reactions (1) and we have shown that the noble metal ions are stabilized by the substitution of noble metals in reducible oxides such as CeO_2 forming single phase $\text{Ce}_{1-x}\text{M}_x\text{O}_{2-\delta}$ (M = Ru, Rh, Pd, Pt) (1). Pd-substituted CeO_2 has been studied for activation of C–H bonds in CH_4 (2). TiO_2 is a nontoxic reducible oxide support and noble metal ions can be substituted in TiO_2 . Indeed, $\text{Ti}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$ ($x = 0.01$) where Pd is in +2 oxidation state showed high rates of NO_x reduction by CO (3), high rates of hydrogen – oxygen recombination at 40 – 50 °C (4), and good photo catalytic activity for CO oxidation (5).

Activation of lattice oxygen in TiO_2 with substitution of Au and noble metals in ZnO has been shown by DFT calculations. Earlier works (1-6) have shown that noble metal ion in CeO_2 activates the lattice oxygen. It has been also shown there that high rates of CO oxidation activity of $\text{Ti}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$ is due to activation of the lattice oxygen by the substitution of Pd^{2+} ion in TiO_2 from XRD, XPS and first-principles DFT calculations. In this investigation, we report our results on X-ray absorption spectroscopic study in one of the compounds of the series $\text{Ti}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$ namely $\text{Ti}_{0.98}\text{Pd}_{0.02}\text{O}_{2-\delta}$.

$\text{Ti}_{0.98}\text{Pd}_{0.02}\text{O}_{2-\delta}$ was prepared by solution combustion method. For this synthesis we have taken 9.8 mmol of $\text{TiO}(\text{NO}_3)_2$ solution, which is prepared by $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (sigma Aldrich), 0.2 mmol of $\text{Pd}(\text{NO}_3)_2$ (sigma aldrich), and 1.11 mmol of glycine (SD Fine Chem. Limited) as fuel in a 300 mL crystallizing dish. The components were fully dissolved in 15 mL of water. The solution was kept in preheated furnace at 350 °C. The combustion takes place after the dehydration and the solid product is left behind. This is used for our EXAFS study.

The material was characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM) and X-ray photoemission spectroscopy (XPS). The results of these XRD, TEM and XPS studies were reported by our group earlier (7). These earlier findings show that the material crystallizes in anatase-type structure having the average crystallite size of 13 ± 2 nm and that Pd^{2+} ions are substituted in highly ionic TiO_2 lattice.

X-ray absorption measurements were carried out in the NW10A beamline of the Photon Factory (High Energy Accelerator Research Organization, Tsukuba, Japan) using a ring energy of 6.5 GeV and a stored current of 442.6 - 440.9 mA for measurement of the Pd–K edge spectra. The X-ray absorption spectra were recorded in transmission mode at room temperature with a Si(311) two-crystal monochromator. X-ray absorption spectrum was scanned from

24.2 to 25.6 keV The photon energy was calibrated for each scan with the first inflection point of the absorption edge in Pd metal foil. Both the incident (I_0) and transmitted (I) synchrotron beam intensities were measured simultaneously using ionization chambers filled with appropriate gases. The absorber of the nanomaterial was made by pressing the fine powder sample into pellet of 10 mm diameter with boron nitride. To avoid the sample thickness effect, the total μx was restricted to a value ≤ 3 by adjusting the thickness of the absorber pellet where μ is the absorption coefficient and x is the sample thickness. EXAFS data analysis was done using IFEFFIT program. Details of this analysis procedure are given in Refs. 8 and 9.

RESULTS AND DISCUSSION

In Figure.1(a) X-ray K-edge absorption spectrum of Pd in the catalyst ($x = 0.02$) is shown. Figure. 1(b) shows background subtracted k^3 -weighted PdK EXAFS function with fit and its magnitude is displayed in Figure.1(c) in the catalyst sample.

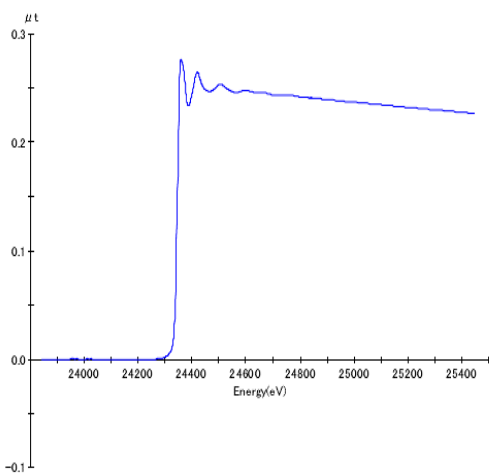


Figure. 1(a), X-ray K edge absorption edge of Pd catalyst with fine structure little more than 1000 eV

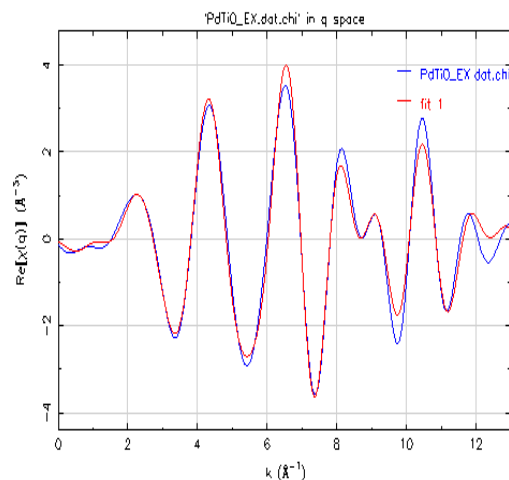


Figure1(b) background subtracted k^3 -weighted PdK EXAFS function with fit

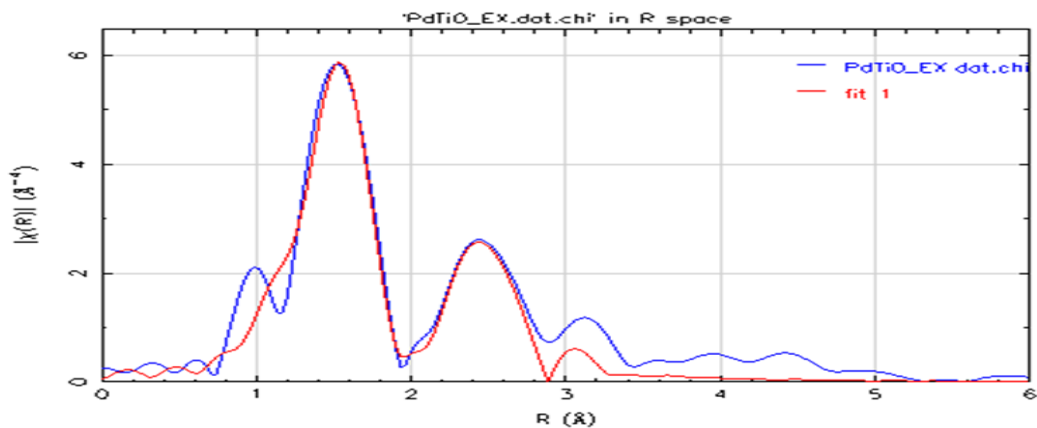


Figure 1(c). Backtransform EXAFS with fit and magnitude of FT of PdK edge in $\text{Ti}_{0.98}\text{Pd}_{0.02}$

In our earlier studies we have reported the results of EXAFS on Pd and PdO (8-9) and we have seen there that the FT of PdO shows three distinct peaks corresponding to four O ions at 2.02 Å and Pd ions at 2.67 and 3.08 Å with coordination numbers 2 and 4, respectively. The EXAFS spectrum of the catalyst is slightly similar to that of PdO, indicating Pd to be in +2 state. The phase corrected values of EXAFS data are given in Table 1.

TABLE 1. Curve-fitting analysis for Pd K edge EXAFS in $\text{Ti}_{0.98}\text{Pd}_{0.02}\text{O}_{2-\delta}$

Shell	CN	R(A ⁰)	$\Delta \sigma^2$ (Å ⁻²)
Pd-O	4.1(1)	2.026(2)	0.006(1)
Pd-O	1.9(1)	2.52(1)	0.006(2)
Pd-Pd	2.4(1)	3.22(3)	0.018(6)
Pd-Ti	1.3(1)	2.96 (1)	0.002(1)

As can be seen from the Fig. 1 (c), a strong peak at about 1.50 (phase shift uncorrected) is seen and it can be attributed to Pd – O correlation with a bond length of about 2.026 Å⁰. The coordination number obtained from this fitting is 4. Further there is a slight broad structure is observed extending from little over 2 to about 3.5 Å. This structure is different from the twin peak structure seen earlier in PdO both in terms of peak position and relative heights, indicating the local structure around the metal ion to be different in catalyst from that in PdO. Therefore, the EXAFS was fitted to a model wherein Pd substitutes Ti ion in distorted anatase structure. The fitting parameters obtained are presented in Table 1 and the fitted curve in the backtransformed k space is presented in Fig. 1(b). It can be seen that the first peak in the magnitude of FT of EXAFS spectra can be fitted with two Pd–O correlations at 2.026 and 2.52 Å, respectively. Furthermore, there are two more correlations corresponding to Pd–Ti and Pd–Pd interactions at 2.96 and 3.22 Å⁰ respectively. Total coordination number is very close to 4 which is expected for second coordination in anatase structure. This clearly confirms that in 2% Pd/CeTiO₂ Pd²⁺ ion substitutes Ti⁴⁺ in a distorted anatase structure. It may be mentioned here that the first-principles density functional theory (DFT) calculations of Mukri et al (7) also support our conclusion that this nanocatalytic compound has anatase TiO₂ type structure with Pd²⁺ ion in nearly square planar geometry with creation of oxygen ion vacancies.

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REFERENCES

1. M.S.Hegde, G. Madras, and K.C.Patil, *Acc. Chem. Res.* **42**, 704-712 (2009).
2. L.M.Misch, J.A.Kurzman, A.R.Derk, Y. Kim, R.Seshadri, H.Metiu, E.W.McFarland, and G.D.Stucky, *Chem. Mater.* **23**, 5432-5439 (2011).
3. S.Roy, T.Aarhi, and M.S.Hegde, G. Madras, *Ind. Eng. Chem. Res.* **46**, 5798-5802(2007).
4. S.Sharma, and M.S. Hegde, *Chem Phys Chem* **10** 637-640 (2009).
5. S. Roy, M.S.Hegde, N.Ravishankar, G.Madras, *J. Phys. Chem.C* **111**, 8153-5360(2007).
6. S. Sharma, and M.S.Hegde, *Catal. Lett.* **112**, 69-75 (2006).
7. Bhaskar DevuMukri,†Gargi Dutta,† Umesh V. Waghmare,‡ and M. S. Hegde, *Chem. Mater.* **24**, 4491-4502 (2012).
8. TinkuBaidya, K. R. Priolkar, P. R. Sarode, M. S. Hegde, K. Asakura, G. Tateno, and Y. Koike, *J. Chem. Phys.* **128**, 124711-124711-8 (2008).
9. K. R. Priolkar, Parthasarathi Bera, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, and N. P. Lalla, *Chem. Mater.* **14**, 2120 -2128(2002).