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Spectroscopic studies of NO reduction on Pt/TiO_2 catalysts

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Abstract

2 wt.% Pt/TiO_2 catalyst was prepared by photochemical deposition (PCD) method with UV irradiation on an aqueous TiO_2 suspension containing hexachloroplatinic acid. The prepared catalyst exhibits nano-particles of Pt (~3 nm) uniformly dispersed on TiO_2 surface as evidenced by TEM. In situ FT-IR spectroscopic studies indicated that the catalyst exhibits high capacity for chemisorption of NO that led to highly catalytic activity for NO reduction. The temperature programmed desorption profile of NO indicates that adsorption of NO was enhanced thermally and reduced to the major product of N_2 with minor N_2O on the prepared Pt/TiO_2 catalyst. Photodecomposition of NO was investigated by in situ DRIFT and EPR spectroscopy. The photocatalytic activity of the catalyst is highly dependent on its pretreatment. The catalyst after reduction in hydrogen at 300 °C is highly active for NO photodecomposition to N_2 and N_2O. The XPS spectra indicated the mixed valence-states of Pt (Pt^{n+} and Pt^0) presented on the catalyst surface that incorporated with reducible TiO_2 support to present the super catalytic property of the PCD-prepared Pt/TiO_2 catalyst.

Keywords: Pt/TiO_2; NO decomposition; FT-IR; XPS; EPR; UHV-TPD

1. Introduction

Titanium dioxide (or called titania) has been shown to be an excellent light mediator in several photocatalytic processes due to its n-type semiconducting property [1]. The bandgap irradiation of TiO_2 generates electron-hole pairs that can be exploited in various redox reactions [2]. An interesting application would be the photochemical selective recovery of noble metals for industrial wastes [2]. Since the photoreduced noble metals that deposited on the semiconductor particles can easily be separated from the slurry by centrifugation, such a technique has been applied to the preparation of TiO_2-supported noble metal catalysts as heterogeneous catalysts [3–5]. However, few details on catalytic properties were reported.

It is known that the high temperature reduced TiO_2-supported noble metal catalyst exhibits the so-called SMSI (strong metal-support interaction) characteristics [6]. In the SMSI state, titania itself can play an active role in increasing the metal-titania interfacial area, although its surface area is usually low. The SMSI catalyst suppresses in chemisorption of hydrogen and carbon monoxide, but enhances the catalytic activity of CO hydrogenation [7]. In our previous study [5], it has been discovered that the photochemical deposition of platinum onto titania remarkably improves in the Pt dispersion and such catalyst, even after high temperature reduction, shows considerable extent in chemisorption of H_2 and CO, that led to the high catalytic reactivity for CO hydrogenation. The behavior is somehow different from the SMSI characteristics.

Due to the fundamental importance in pollution control, catalytic reaction of NO-reduction or direct decomposition has been the subjects of extensive research in recent years [8]. Application of the photochemically prepared titania-supported Pt catalyst to such reactions, we found that, even after high temperature reduction, the catalyst exhibits a potent capability of NO adsorption, the NO decomposition and the NO/CO reactions. In the current study, the reduction of NO on Pt/TiO_2 catalyst was performed thermally or under UV irradiation that investigated by in situ spectroscopic methods including FT-IR, EPR, UHV-TPD and XPS.

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2. Experimental

2 wt.% Pt/TiO_2 catalyst was prepared by photochemical deposition (PCD) method as described previously [5]. Briefly, the aqueous suspension containing an appropriate amount of hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) and TiO_2 was deaereated by flowing argon and irradiated with UV lamps using a Rayonet Phochemical Reactor (model RPR-100). After completion of the photochemical deposition of metal complex ions onto TiO_2, the suspended substance was recovered by centrifugation and washed twice with distilled-deionized water and then dried in air and finally in an oven at 120 °C. The prepared Pt/TiO_2 catalyst after reduction in hydrogen exhibits well-dispersed nanosize Pt particles with particle size of ~3 nm on the TiO_2 surface as observed from TEM micrographs [5].

In the in situ FT-IR measurements, the dried catalyst powders was pressed into a thin self-supporting pellet and then put into a quartz high-pressure IR cell. Infrared spectra were taken on a Bomem DA-8 spectrometer. The in situ DRIFT (diffuse-reflectance infrared Fourier transform) measurements were carried out on a Bomem MB-100 spectrometer with a Harrick HVC-DR2 microreactor for facilitating photocatalytic reaction. In the in situ EPR experiments, the samples were reduced either under evacuating or in hydrogen followed by evacuating. After introduction of 1 Torr NO, the photoreactions were performed using a Rayonet Photochemical Reactor with UV source of 253.7 nm. All EPR spectra were recorded at 77 K using a Bruker X-band E500CW spectrometer. X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption of NO in an ultra-high vacuum system (UHV-TPD) were investigated on an Omicron ESCA spectrometer equipped with a Hiden residual gas analyzer.

3. Results and discussion

In our previous in situ FT-IR studies [5], it indicated that the Pt/TiO_2 catalyst prepared by the photochemical deposition (PCD) exhibit a high capacity for CO chemisorption that lead to a 100% conversion to form CO_2 at room temperature. Upon admission of 1 Torr CO to H_2-reduced Pt/TiO_2 catalyst at room temperature, the infrared spectra showed strong peaks at 2097 and 2085 cm^{-1} as well as a weak band at 1850 cm^{-1}. The signals are assigned to CO adsorbed linearly on Pt terrace sites and on Pt step sites, and bridge-bonded on Pt step sites [9], respectively. The intensity of linear CO adsorption decreased gradually and simultaneously appeared CO_2 signal at 2349 cm^{-1}. All the IR peaks due to CO adsorption completely disappeared in 12 hr and CO_2 formation at room temperature was evident [5].

Like CO, NO can act as a σ donor or π acceptor to form bondings with the transition metals [10]. The in situ IR spectroscopic study was carried out to investigate NO adsorption on the Pt/TiO_2 catalyst. The catalyst after being reduced at 500 °C in H_2 (HTR) shows higher intensity than the one reduced at 300 °C in H_2 (LTR). The IR spectra of NO adsorption on the HTR-Pt/TiO_2 are presented in Fig. 1. It is clear that as soon as an introduction of NO, there appeared strong NO adsorption peaks at 1735, 1683 and 1673 cm^{-1} as well as weak bands at 1607 and 1584 cm^{-1}. A trace of gas phase NO at 1877 cm^{-1} and N_2O at 2224 cm^{-1} were also observed. Bourane et al. [11] summarized that the adsorption of NO on Pt-containing solids leads to linear and bridged or bent NO adsorption species with IR bands in the ranges 1850–1650 cm^{-1} and 1650–1400 cm^{-1}, respectively. When NO adsorbed on single crystalline Pt (1 1 2), the two IR bands at 1794 and 1698 cm^{-1} were assigned to the linear adsorption on step and terrace sites, respectively, and IR bands at 1601 and 1441 cm^{-1} were due to the bridged adsorption on step and terrace sites, respectively [12]. Watson and Ozkan [13] investigated the NO adsorption on the hydrogen-reduced TiO_2 by DRIFT spectra, they assigned the 1618 cm^{-1} band to the bridged nitrate, and the bands at 1600, 1580 and 1241 cm^{-1} to the bidentate nitrate species formed on titanium oxide surfaces. Accordingly, the two IR bands at 1735 and 1673 cm^{-1}, as shown in Fig. 1, are assigned to the linear NO species on step and terrace sites of the Pt particles. The 1683 cm^{-1} peak was attributed to the linear NO species on defect sites in interaction with the adsorbed O or N species [11]. The two IR bands at 1607 and 1584 cm^{-1} is more likely due to the bidentate nitrate species

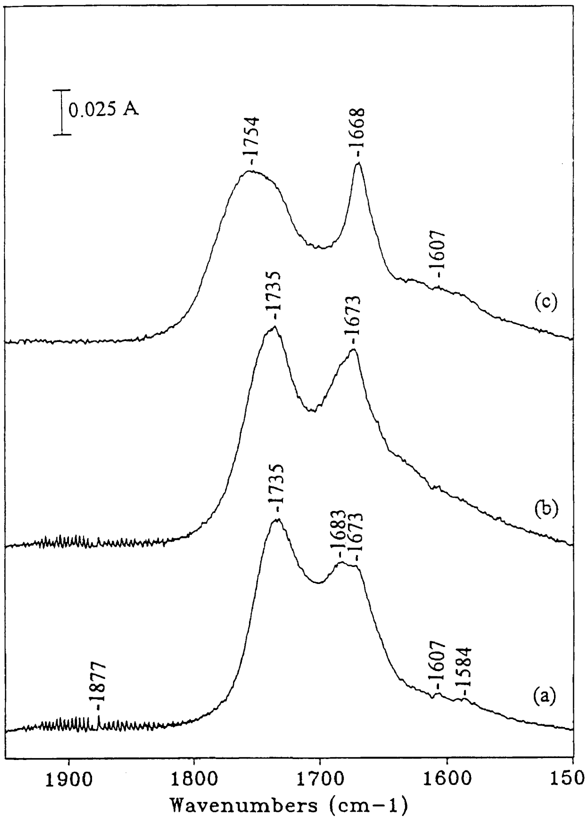

Fig. 1. FT-IR spectra of HTR-Pt/TiO_2 after exposure to 1 Torr NO for (a) 1 min, (b) 2 h, and (c) under evacuating at 1×10^{-3} Torr.

adsorbed on TiO_2 surface. It is reasonable to expect that the platinum surface contain a large number of defect sites due to the lack of long-range order at the surface [14]. Furthermore, NO will preferentially adsorb at these defect sites. The intensity of 1673 cm^{-1} peak showed slightly increase during the adsorption period of 2 h, as can be seen in Fig. 1(b). In the meantime, the peak of gaseous N_2O increased and that of gaseous NO decreased in intensity with time. After evacuating the IR cell, the gaseous NO and N_2O disappeared. The peaks of linearly bound NO became broader with the peak maximum shifting to 1754 cm^{-1}. The peak of linear NO on Pt terraces became sharper and slightly shifted to 1668 cm^{-1}. Although it was reported that the peak position of linear NO adsorbed on step sites of Pt foil is independent of NO exposure [14], the linear NO adsorption peaks remarkably shifted as the increasing in coverage. We conclude that the adsorbed NO species on the PCD-Pt/TiO_2 catalysts possess high surface mobility that caused the surface diffusion to step sites quite readily.

The temperature programmed desorption (TPD) of NO on Pt/TiO_2 catalyst in the in situ FT-IR system was then performed at a heating rate of 2 °C/min either under evacuating condition or in a closed cell after admission of 1 Torr of NO. Fig. 2 shows the IR-TPD spectra of NO on HTR-Pt/TiO_2 under evacuating. As the temperature was increased, the linear NO adsorption peak showed a gradual blue shift to 1774 cm^{-1}, which was due to the coupling interaction between the adjacent NO molecules at high temperature [15]. In the meanwhile, the band at 1668 cm^{-1} decreased in intensity with increasing in the bidentate nitrate signals at 1617, 1607 and 1588 cm^{-1}. All signals of NO adsorption completely disappeared as the temperature reached 190 °C. The variation of peak intensity versus temperature is shown in Fig. 3.

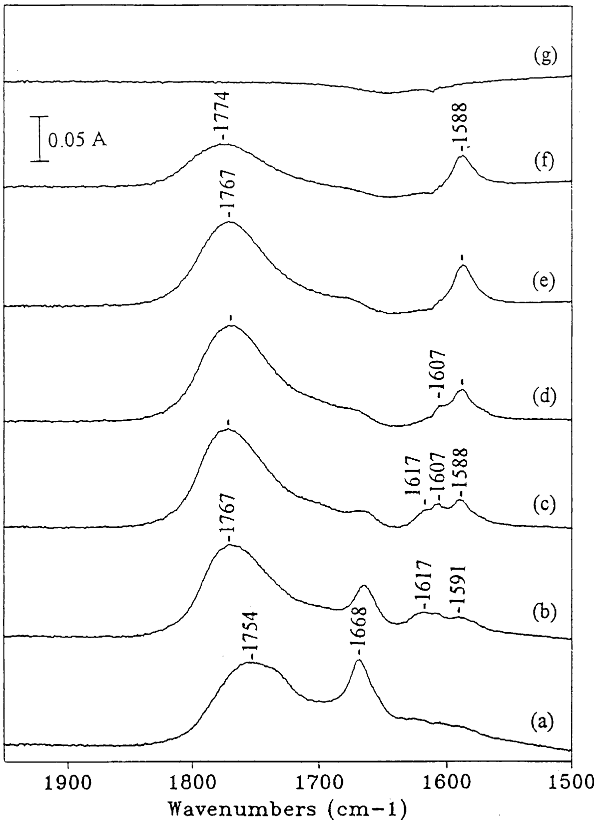

Fig. 2. FT-IR spectra of TPD of NO on HTR-Pt/TiO_2 under evacuating at (a) 30 °C, (b) 50 °C, (c) 70 °C, (d) 110 °C, (e) 150 °C, (f) 170 °C, and (g) 190 °C.

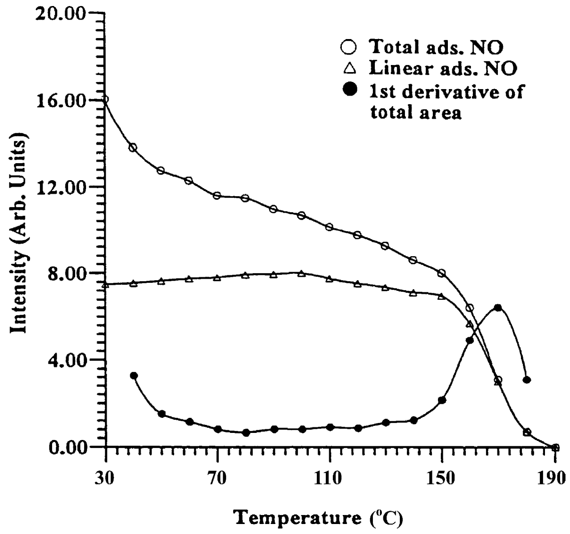

Fig. 3. The IR peak intensity of the adsorbed NO heated under evacuating.

When the temperature programmed desorption was performed under 1 Torr of NO, the intensity of linear adsorption is increased with temperature and reached to a maximum at 190 °C and then decreasing in intensity, as can be seen in Fig. 4. The thermal effect apparently enhanced the NO adsorption on the catalyst. All peaks of NO adsorption abruptly decreased at 230 °C and disappeared at 250 °C. The variation of peak intensity versus temperature is shown in Fig. 5. The peak of gaseous NO gradually decreased with temperature. In the meantime, the intensity of N_2O signal increased obviously as the increased temperature, as can be seen in Fig. 6. The results indicate that the Pt/TiO_2 catalyst is highly active for the thermal reduction of nitric oxide to nitrous oxide whether the formation of the N_2 products could not be detected by IR spectra.

When the TPD experiments were carried out in the UHV system of Omicron ESCA spectrometer equipped with a residual gas analyzer, the signal traces of $m/e = 30, 44$ and 28 were used to follow the desorption of NO, N_2O and N_2, respectively. The TPD profiles indicated that most of NO reduced to major product of N_2 and minor N_2O product, as can be seen in Fig. 7. N_2 and N_2O desorbed completely below 180 °C, which is in good agreement with the results of IR-TPD. The adsorbed NO dissociates to $N_{(a)}$ and $O_{(a)}$ followed by coupling of two $N_{(a)}$ to form N_2 [$2N_{(a)} \rightarrow N_{2(g)}$]. A competing reaction with this would be $N_{(a)} + NO_{(a)} \rightarrow N_2O_{(a)}$, followed by desorption of N_2O into the gas phase as a minor product. The O-product from NO desorption or decomposition was not detected in UHV-TPD profiles,

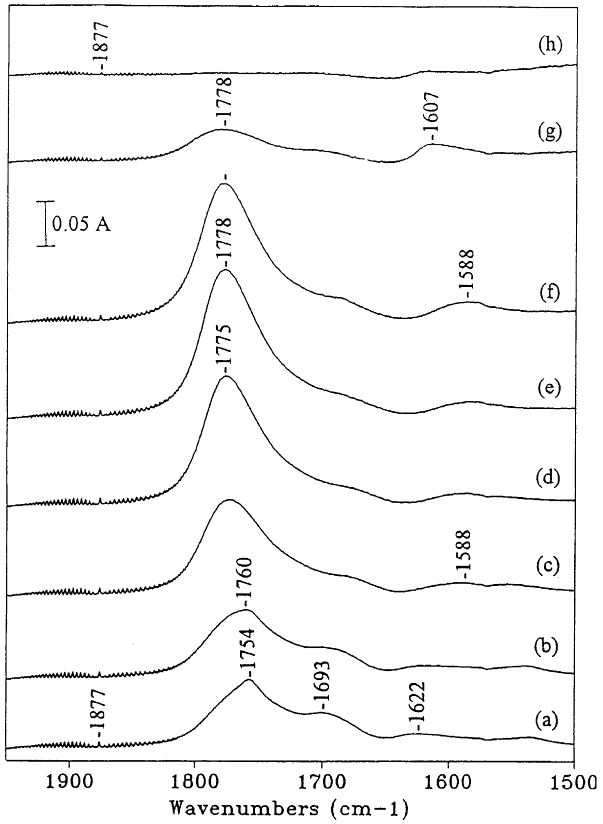

Fig. 4. FT-IR spectra of TPD of NO on HTR-Pt/TiO_2 under 1 Torr NO at (a) 50 °C, (b) 70 °C, (c) 110 °C, (d) 150 °C, (e) 190 °C, (f) 210 °C, (g) 230 °C, and (h) 250 °C.

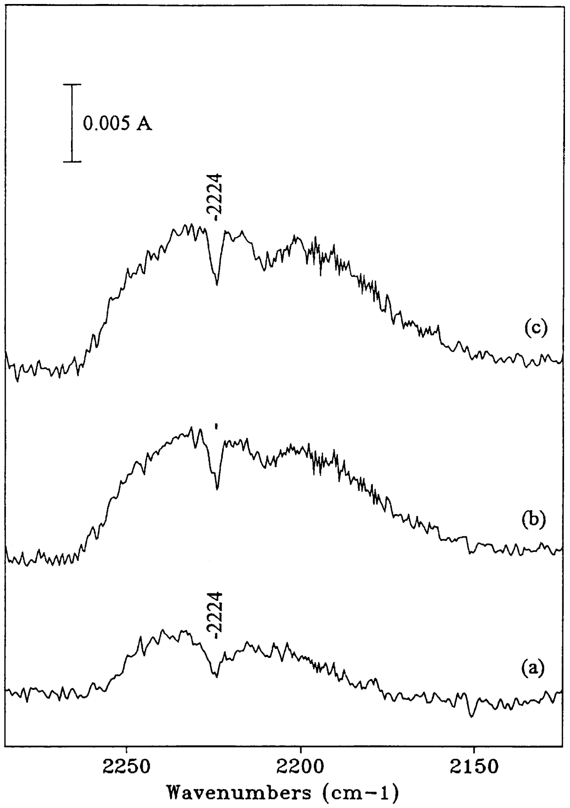

Fig. 6. FT-IR spectra of HTR-Pt/TiO_2 in the N_2O region (a) after exposure to 1 Torr NO, and TPD at (b) 230 °C and (c) 250 °C.

which indicated that the decomposed oxygen product might be retained at vacancies of TiO_2 and oxidized Ti^{3+} to Ti^{4+}.

The photodecomposition of NO on Pt/TiO_2 was investigated by the in situ DRIFT and EPR spectroscopic studies. In our previous studies [16] on the adsorption and photodecomposition of NO on Pt/TiO_2 as monitored by in situ DRIFT spectra, it indicated that the photocatalytic activity of Pt/TiO_2 is highly dependent on its pretreatment. The catalysts after either high temperature reduction in H_2 at 500 °C (HTR) or evacuating at 500 °C represented a highly capability to NO adsorption, but the adsorbed NO could not be decomposed by UV irradiation. However, the catalyst after low temperature reduction in H_2 at 300 °C (LTR) represented an intense NO adsorption that conducted a direct decomposition of NO to N_2 and O_2 under UV irradiation.

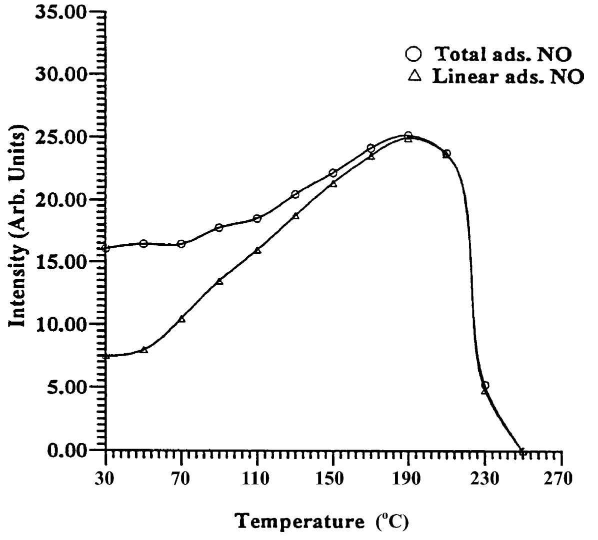

Fig. 5. The IR peak intensity of the adsorbed NO heated under a constant pressure of 1 Torr NO.

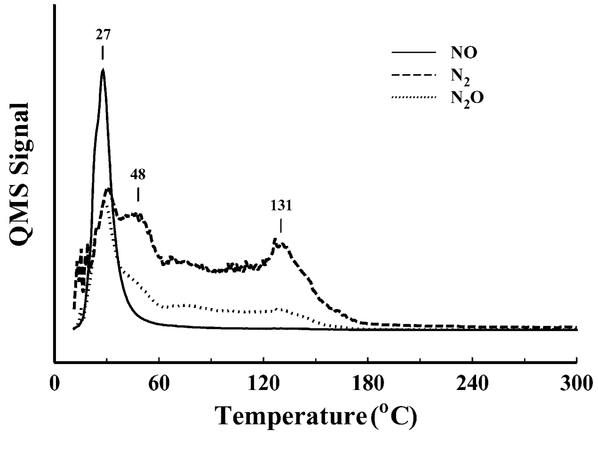

Fig. 7. UHV-TPD profiles of different species desorbed from the H_2-reduced Pt/TiO_2 after exposure to NO.

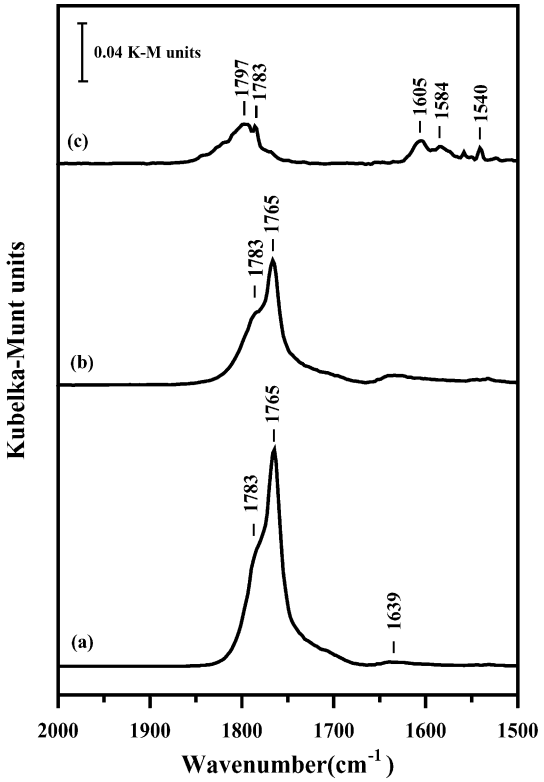

Fig. 8. DRIFT spectra of LTR-Pt/TiO$_2$ after exposure to 10 Torr NO for (a) 1 min, (b) 20 min, and (c) continued UV irradiation for 40 min.

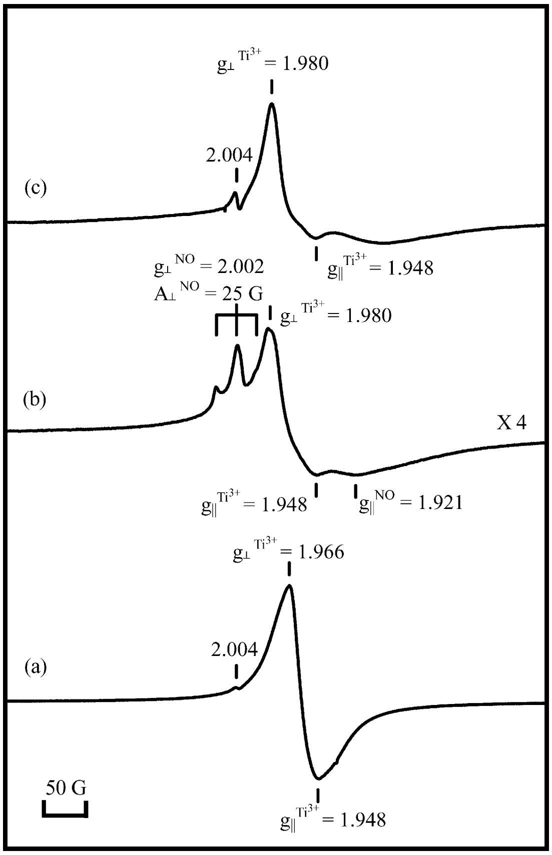

Fig. 9. EPR spectra at 77 K of HTR-TiO$_2$: (a) after hydrogen-reduction followed by evacuation, (b) exposure to 1 Torr NO, and (c) UV irradiation at 253.7 nm for 2 h.

The DRIFT spectra represented a peak of the linear-bonded NO on the Pt sites at 1765 cm^{-1} and a weak peak of the bridged nitrates on Pt step site at 1639 cm^{-1} after admission of NO, as can be seen in Fig. 8(a). The peaks of NO adsorption gradually decreased in intensity accompanied with the formation of N_2O with increasing the exposure time. Upon UV irradiation, the IR peaks of adsorbed NO almost disappeared and the peak of N_2O also decreased remarkably. It was noticed that the milder the reduction temperature of the Pt/TiO$_2$ catalyst, the higher the photocatalytic activity of NO decomposition. For catalyst after being reduced in H_2 at 200 °C, it showed weaker IR peaks of NO adsorption but quickly disappeared in intensity upon UV irradiation. As the irradiation time was increased, N_2O was further photocatalytically decomposed to N_2 and O_2 on Pt/TiO$_2$ catalyst as detected by residual gas analyzer.

In situ EPR experiments were carried out to investigate the adsorption and photocatalytic decomposition of NO on HTR-Pt/TiO$_2$ (Degussa P25) catalyst. Fig. 9(a) shows the EPR spectra at 77 K of the hydrogen-reduced TiO$_2$ that exhibits a strong Ti^{3+} signal at $g_\perp = 1.966$ and $g_{||} = 1.948$ and a F-center signal at 2.004. After introduction of 1 Torr NO to the reduced sample, the EPR spectrum represents a signal at $g_\perp = 2.002$ and $g_{||} = 1.921$ with a hyperfine constant $A_\perp$ = 25 G due to N ($I = 1$), which is attributed to adsorption of NO (see Fig. 9(b) and Fig. 10(a)). The Ti^{3+} signal decreased in intensity significantly. After UV irradiation with wavelength of 253.7 nm for 2 h, the EPR signal of NO adsorption completely disappeared and left the Ti^{3+} signal. The in situ EPR cell was then connected to a residual gas analyzer, and the gaseous products containing major N_2 and minor N_2O were detected. The EPR spectrum of Pt/TiO$_2$ catalyst after hydrogen-reduction showed an intense EPR signal of NO adsorption at $g_\perp = 2.002$ and $g_{||} = 1.921$ with a hyperfine constant $A_\perp$ = 27 G, as shown in Fig. 10(b). The Ti^{3+} signal decreased in intensity and was not clearly resolved. The EPR signal of NO adsorption completely disappeared under UV irradiation for 2 h, which was similar to the results of TiO$_2$. It indicated that the deposition of nanosize platinum particles on TiO$_2$ surface significantly enhanced the capacity for NO adsorption and the photocatalytic activity for NO decomposition. In comparison, the catalyst after evacuating at 500 °C represented a weak signal of NO adsorption. Pt/TiO$_2$ catalyst after heating at 500 °C in O_2 showed a stronger EPR signal of NO adsorption (Fig. 10(c)) than that of reduced one, and the adsorbed NO was completely decomposed under UV irradiation. It was evidenced that the oxidized Pt/TiO$_2$ also represents high photocatalytic activity for NO decomposition. The IR and EPR results indicate that both Pt and Ti^{3+} species play as the active sites for NO adsorption. The deposition of platinum on TiO$_2$ surface enhances NO adsorption and plays as an important role on NO photodecomposition. Both in situ DRIFT and EPR

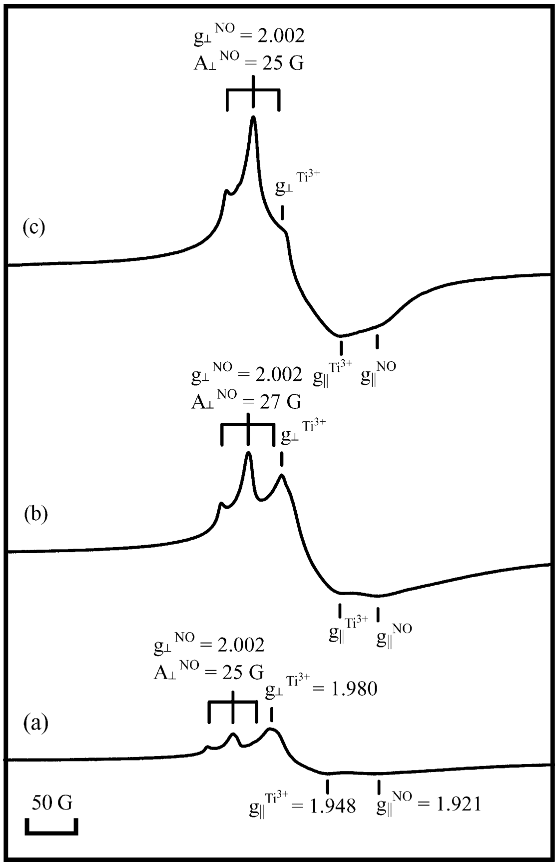

Fig. 10. EPR spectra at 77 K of the catalysts after exposure to 1 Torr NO: (a) TiO_2 after HTR, (b) Pt/TiO_2 after HTR, and (c) Pt/TiO_2 after heating in O_2 at 500 °C.

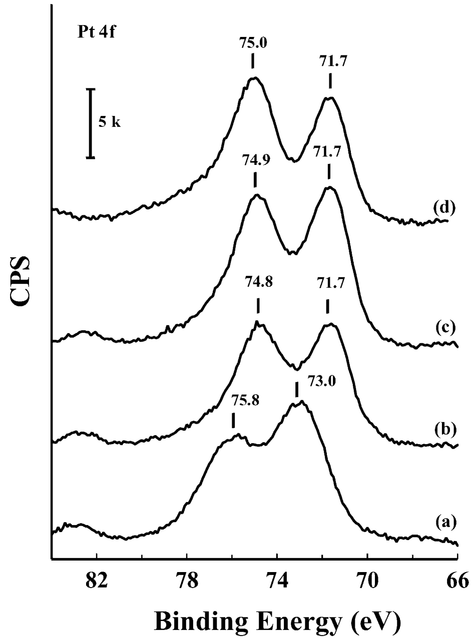

Fig. 11. Pt 4f XPS spectra of (a) as-prepared Pt/TiO_2 and that (b) after LTR, (c) after admission of NO and (d) after UHV-TPD.

spectra indicated that the hydrogen-reduced Pt/TiO_2 catalyst exhibits a higher catalytic activity for NO photodecomposition as compare to the high temperature reduced catalyst.

The surface states of the catalysts were investigated by XPS. The Pt 4f spectra of the as-prepared Pt/TiO_2 catalyst and that after LTR (reduction in H_2 at 300 °C), after admission of NO and after UHV-TPD were shown in Fig. 11(a–d). The as-prepared catalyst represented a doublet of Pt 4f peaks at 73.0 ($4f_{7/2}$) and 75.8 eV ($4f_{5/2}$). After reduction in H_2 at 300 °C, the Pt 4f peaks shifted to 71.7 ($4f_{7/2}$) and 74.8 eV ($4f_{5/2}$), and the relative intensity of the two doublet peaks was changed significantly. For a given oxidation state of Pt, the correct intensity ratio of $4f_{7/2}$ and $4f_{5/2}$ lines should be about 4:3. The spectra indicated that there exhibited the mixed valence state of Pt. The peak deconvolution was carefully carried out using the reported binding energies of $4f_{7/2}$ electron for Pt^0, Pt^{2+} and Pt^{4+} as 71.6, 73.0 and 74.5 eV [17], respectively. Fig. 12 shows the deconvolution spectra for the LTR samples. The deconvolution results corresponding to the Fig. 11(a–d) were listed in Table 1. The as-prepared Pt/TiO_2 contained mainly Pt^{2+} (64.1%) and a few Pt^0 (15.5%) and Pt^{4+} (20.3%). After reduction in hydrogen at 300 °C, most of the Pt^{2+} reduced to Pt^0 (67.7%), with a few Pt^{2+} (13.9%) and Pt^{4+} (18.4%) appeared on the sample. The results indicate that there are various mixed valances of Pt^{n+} retained on the surface of the catalyst and the surface Pt was not fully reduced after reduction. When NO adsorbed on Pt/TiO_2, the binding energy of Pt 4f peaks seemed not shift obviously but varied in relative intensities. The results of peak deconvolution given in Table 1 indicated that about 5% of platinum was oxidized upon NO adsorption due to the back-donation of electron transfer from Pt to NO. After UHV-TPD of NO, platinum was further oxidized where the amount of Pt^0 was decreased to 60.6%. The corresponding

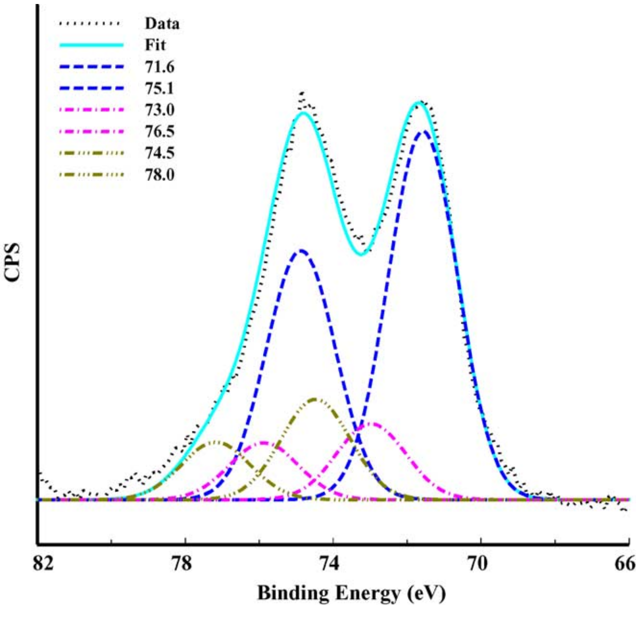

Fig. 12. The deconvolution of Pt 4f XPS spectra of LTR-Pt/TiO_2.

Table 1
The results of peak deconvolution from XPS studies of Pt/TiO_2 catalyst

	Pt $4f_{7/2}$ (eV)		
	Pt^0 (71.6) (%)	Pt^{2+} (73.0) (%)	Pt^{4+} (74.5) (%)
As-prepared	15.5	64.1	20.3
After LTR	67.7	13.9	18.4
Adsorbed NO	62.7	20.9	16.3
After UHV-TPD	60.6	18.8	20.6

Ti 2p XPS spectra of samples given in Fig. 11(a–d) represented no significant variation, the Ti^{3+} signal could not be clearly resolved from Ti^{4+} accordingly.

4. Conclusion

In summary, it is concluded that the photochemically prepared Pt/TiO_2 catalysts exhibits nano-particles of Pt (~3 nm), with the co-existing Pt^0 and Pt^{n+} mixed valence-states, uniformly dispersed on the TiO_2 surface. The catalyst exhibits high capacity for chemisorption and decomposition of NO at room temperature. The thermal effect enhanced NO adsorption and decomposition to N_2 and N_2O. It was evidenced that the catalytic activity for thermal reduction and photodecomposition of NO is highly dependent on the catalyst pretreatment. From in situ IR results, the catalyst reduced at 500 °C represented higher activity for thermal decomposition of NO than that reduced at 300 °C. In situ DRIFT and EPR results indicated that the catalyst after moderate reduction is highly active for NO photodecomposition to N_2 and N_2O. The unusual catalytic activity of the catalyst could be attributed to the mixed valence-states of Pt (Pt^{n+} and Pt^0) on surface of the catalyst, which incorporated with reducible TiO_2 support.

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