Catalytic oxidation of NO over TiO₂ supported platinum clusters I. Preparation, characterization and catalytic properties

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ABSTRACT

The oxidation of NO to NO₂ was studied on Pt/TiO₂ catalysts prepared by wet impregnation and photo-deposition method. Pt/TiO₂ prepared by photo-deposition exhibited quite higher activity for NO oxidation to NO₂ than that prepared by wet impregnation and over 90% NO conversion could be achieved at below 250 °C at a high GHSV of 180,000 h⁻¹. The effects of catalysts pretreatment conditions and feed gas composition, i.e. SO₂ and H₂O in the stream, on NO oxidation were investigated in details. The different Pt/TiO₂ samples were characterized by means of X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) techniques. The Pt-TiO₂ electron-interaction was studied based on the characterization results and the role of Pt-TiO₂ electron-interaction on the catalytic performance of Pt/TiO₂ was further discussed.

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1. Introduction

The removal of NO_x is always a hot topic in the field of environmental catalysis and various techniques have been developed for the elimination of NO_x from anthropogenic sources. The catalytic oxidation of NO to NO₂ (2 NO + O₂ → 2 NO₂) is a key step for those NO_x elimination techniques. In a NO_x storage-reduction (NSR) process, NO is first oxidized to NO₂ over the noble metal component and then stored as nitrates or nitrites on the basic component [1]. In the selective catalytic reduction with hydrocarbons (HC-SCR), NO is partially oxidized to NO₂, which subsequently reacts with hydrocarbon to give out N₂ [2]. In the selective catalytic reduction with ammonia (NH₃-SCR), the SCR reaction rate can be greatly enhanced if a fraction of NO is converted to NO₂. For example, the reaction between equimolar NO-NO₂ and NH₃ via so-called “fast” SCR reaction (4NH₃ + 2NO + 2NO₂ → 4N₂ + 6H₂O) is ca. 10 times faster than the standard reaction between NO and NH₃ (4NH₃ + 4NO + O₂ → 4N₂ + 6H₂O) at low temperatures (200–300 °C) [3–5]. In the continuously regenerating trap (CRT) for soot removal, NO is first oxidized to NO₂, which then oxidizes the soot collected on a diesel particulate filter [6]. Owing to the strong oxidation activity of NO₂, the reaction temperatures for soot oxidation by NO₂ are much lower than those for soot oxidation in the air.

The catalytic oxidation of NO to NO₂ is thus established as a very important reaction and much effort has been focused on

developing eligible catalysts for NO oxidation. Platinum catalysts have been extensively investigated in the past years [7–14] and up to now platinum catalysts are still regarded as model catalysts for NO oxidation. The catalytic and kinetic results for NO oxidation over platinum catalysts under different feed composition, e.g. containing only NO and O₂ as reactants or in the presence of water and SO₂, have been reported [7–10,12]. The impact of preparation parameters, e.g. platinum loadings, supports, platinum dispersion, on NO oxidation over platinum catalysts has also been studied in details. Xue et al. [7] found that platinum particle size (or platinum dispersion) influenced the NO oxidation rate, suggesting the reaction is structure sensitive. When the dispersion decreased, giving larger particles, the oxidation capacity of platinum increased. They reported that the particle size was very important for Pt/SiO₂, but it was less significant for Pt/Al₂O₃. Besides, the catalyst support was found to influence the NO oxidation rate greatly and SiO₂ was better support than Al₂O₃ and ZrO₂. However, Denton et al. [14] found that platinum particle size was key factor controlling the NO oxidation rate for both Pt/SiO₂ and Pt/Al₂O₃, while the impact of support was negligible. Further study of Olsson and Fridell [9] confirmed that NO oxidation rate decreased with decreasing platinum particle size and they explained this as small platinum particles more easily formed oxides. It is well known that platinum oxides are much less active for NO oxidation than metallic platinum. However disappointedly, the reaction of NO oxidation is carried out under strong oxidizing conditions and the deactivation of platinum catalysts due to the formation of platinum oxides sometimes is unavoidable. The catalytic deactivation of platinum catalysts by O₂ and NO₂ due to oxides formation in

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the reaction has been proved and investigated in details [9–12]. In the research of support effect on the state of platinum catalysts, Yoshida et al. [15] suggested that electrophilic acidic support suppress the formation of platinum oxides through electrons donation from support to platinum. The electron-interaction between platinum and support may be considered as promising tool to suppress the formation of platinum oxides.

Despite of the numerous researches on NO oxidation, eligible catalysts with high activity and stability under simulated practical conditions (high GHSV, with water and SO₂ in the feed) are still being researched. As for model platinum catalysts, it has not yet been quite certain about what is the key factor controlling NO oxidation rate. In the past, Pt/Al₂O₃ and Pt/SiO₂ have been the most popular platinum catalysts for NO oxidation. However, much less attention has been paid on Pt/TiO₂ catalyst. TiO₂ is proved to be good catalyst support (also SO₂-resistant) and Pt/TiO₂ exhibited quite good activities in a number heterogeneous catalytic reactions [16]. In this work, Pt/TiO₂ catalyst prepared by photo-deposition method is studied as promising catalysts for NO oxidation under different conditions. The Pt-TiO₂ electron-interaction in Pt/TiO₂ is analyzed by means of XPS and the role of electron-interaction on the catalytic properties of Pt/TiO₂ in NO oxidation is discussed.

2. Experimental

2.1. Catalysts preparation

Pt/TiO₂-imp and Pt/Al₂O₃-imp samples were prepared by impregnation method. TiO₂ (Degussa P25, 70% anatase, 30% rutile) and γ -Al₂O₃ (Sinopec Co.) were impregnated with certain amount of 2 mM H₂PtCl₆ aqueous solution under vigorous stirring. After impregnation, the as-prepared samples were dried at ambient conditions over night.

Pt/TiO₂-pho was prepared by so-called photo-deposition method as described in literature [17,18]. In a typical synthesis, 100 mL H₂PtCl₆ solution (containing 10 mg Pt), 500 mg of TiO₂ and 10 mL of ethanol were added into a round-bottom quartz flask under vigorous stirring to form slurry. The slurry was adjusted to pH 10.5 $\pm$ 0.5 using either 1 M HCl or 1 M NaOH aqueous solutions and irradiated by a high-pressure mercury light with the main wavelength of 365 nm for 6 h under vigorous stirring. After 6 h of irradiation, the particles were filtered, washed, and dried at ambient conditions.

2.2. Catalyst characterization

The X-ray diffraction patterns of samples were recorded on a Rigaku powder diffractometer (D/MAX-RB) using Cu K α radiation (λ = 0.15418 nm) at a scanning rate of 4°/min in 2θ = 5–80°.

Transmission electron microscopy images of samples were acquired on a JEOL 2010 transmission electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the catalyst sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

Raman analysis was carried out on a Renishaw InVia Raman spectrometer and spectra were obtained with the green line of an Ar-ion laser (514.53 nm) in micro-Raman configuration.

The dispersion of platinum in platinum catalysts was determined by CO pulse adsorption on a chemisorption analyzer (Chemisorb 2720, Micromeritics). In a typical experiment, ca. 100 mg sample in the quartz reactor was first reduced in 5%H₂/Ar at 350 °C for 1 h and then treated in He at 350 °C for 1 h to remove H₂ adsorbed on the surface of samples. After cooling down to room temperature in flowing He, pulses of CO were injected to the reactor every 1 min until no further changes in intensity of outlet CO. The dispersion of platinum was calculated assuming the equimolar adsorption of CO on platinum.

X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra DLD spectrometer with a monochromated Al K α X-ray source ($h\nu$ = 1486.6 eV), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). All spectra were recorded using an aperture slot of 300 μ m $\times$ 700 μ m, survey spectra were recorded with a pass energy of 160 eV and high-resolution spectra with a pass energy of 40 eV. Accurate binding energies ($\pm$ 0.1 eV) were determined with respect to the position of the adventitious C 1s peak at 284.8 eV.

2.3. Catalytic oxidation of nitric oxide

The catalytic oxidation of NO was performed in a fixed-bed flow microreactor at atmospheric pressure. Typically, 150 mg sample (sieve fraction of 0.17–0.25 mm, small enough to exclude mass transfer limitations) was placed in a quartz reactor (4 mm i.d.) and pretreated in 5%O₂/He or 5%H₂/He at desired temperature for 1 h. After cooling to 150 °C in He, the reactant gas mixture (400 ppm NO, 10% O₂, 0–5% H₂O, 0–320 ppm SO₂, He balance) was fed to the reactor. The total flow rate of the gas mixture was 450 mL min^{−1}, corresponding to a GHSV of 180,000 h^{−1}. The steady-state tests were conducted isothermally every 25 °C from 150 °C to 450 °C and the gas products (after 30-min reaction) were analyzed on-line using a gas chromatograph (HP 6820 series, for N₂ and N₂O analysis) and a chemiluminescence NO_x analyzer (Ecotech EC 9841, for NO and NO₂ analysis).

3. Results and discussion

3.1. NO oxidation over unsupported platinum clusters

Based on the calculation results by density function theory (DFT) [19,20], the oxidation of NO is energy preferred on flat Pt{1 1 1} surface than on stepped Pt{2 1 1} surface. Since Pt{1 1 1} surface dominates in large platinum particles, it is proposed that large platinum particles are more active for NO oxidation than small particles. This is well supported by most experimental results reported [7,12,14]. In our opinion, however, the accessibility of Pt{1 1 1} in platinum catalysts is another very important issue to be considered. Although large platinum particles contain more Pt{1 1 1} than small particles, a great proportion of Pt{1 1 1} is buried inside the large particles and is not accessible during the reaction. As a result, the accessible Pt{1 1 1} in large particles may be even less than that in small particles. To make a direct view, we calculate the accessible Pt{1 1 1} surface in platinum particles (assuming that only the Pt{1 1 1} surface in the shell is accessible) with different particle diameters based on the model of magic cluster. In the magic cluster, a platinum nano particle is treated as a central platinum atom surrounded by closed shells of identical atoms [21].

As seen in Fig. 1, on one side, the percentage of accessible Pt{1 1 1} surface in shell atoms increases with increasing platinum particle diameters. On the other side, the percentage of shell atoms in total platinum atoms decreases with increasing platinum particle diameters. As an integrated result, the percentage of accessible Pt{1 1 1} in total platinum atoms first increases to a maximal and then begins to decrease gradually. Based on the data presented, unsupported platinum clusters of ca. 3 nm (2–5 nm) should be most active for NO oxidation.

While for supported platinum clusters, the actual circumstances may change to some extent due to the difference between the actual clusters and magic cluster model. Nevertheless, it can be concluded that large platinum particles are not always preferred to obtain high NO oxidation rates. The reason for low activity of small platinum clusters should be that small platinum clusters are highly susceptible to formation oxides, as suggested by Xu et al. [22]. As is

Fig. 1. Percentage of accessible plat Pt(111) surface in platinum clusters as a function of platinum particle diameter.

discussed, high NO oxidation rate can be obtained on supported platinum nano-clusters and the most important issue is to protect the platinum clusters against oxidation under oxidizing conditions.

3.2. Characterization of Pt/TiO₂ prepared by different methods

The commercial TiO₂ support used in this study contains both anatase phase (ca. 70%) and rutile phase (ca. 30%). In Fig. 2, typical diffraction peaks of TiO₂ support corresponding to anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) phase are observed. The as-prepared Pt/TiO₂ sample by impregnation and photo-deposition also show diffraction peaks quite similar to TiO₂ support. Besides, no diffraction peaks corresponding to the supported platinum species, either in metal form or in oxide form, can be observed.

Fig. 2. XRD patterns of TiO₂ and different Pt/TiO₂ samples. (a) TiO₂ P25, (b) as-prepared Pt/TiO₂-imp, (c) Pt/TiO₂-imp pretreated in 5%H₂/He at 450 °C for 1 h, (d) as-prepared Pt/TiO₂-pho, (e) Pt/TiO₂-pho pretreated in 5%O₂/He at 450 °C for 1 h, (f) Pt/TiO₂-pho pretreated in 5%O₂/He at 550 °C for 1 h, (g) Pt/TiO₂-pho pretreated in 5%O₂/He at 650 °C for 1 h and (h) Pt/TiO₂-pho pretreated in 5%O₂/He at 750 °C for 1 h. R: rutile TiO₂; A: anatase TiO₂.

Treatment in H₂/He on Pt/TiO₂-imp sample at 450 °C or treatment in O₂/He on Pt/TiO₂-pho at 450 °C does not bring any change in the corresponding XRD patterns. While thermal treatment on Pt/TiO₂-pho in O₂/He at higher temperatures (up to 750 °C) results in the phase transformation of TiO₂ support from anatase to rutile. Meanwhile, no diffraction peaks corresponding to supported platinum species can be observed. A large proportion of anatase in pure TiO₂ P25 (~70%) can be transformed to rutile phase during thermal treatment at 750 °C [23], while in this work the phase transformation is greatly suppressed by the addition of platinum.

The surface phase composition of Pt/TiO₂ samples and TiO₂ support is analyzed by means of Raman spectroscopy. As seen in Fig. 3, strong bands at 143, 196, 395, 516 and 639 cm⁻¹ are observed for TiO₂ P25 support, corresponding to the Raman-active modes of anatase with the symmetries of E_g, E_g, B_{1g}, A_{1g}, and E_g, respectively [24]. Besides, a very weak at 446 cm⁻¹ is also observed corresponding to the E_g mode of rutile phase [25]. The introduction of Pt on TiO₂ support by impregnation or photo-deposition results in the appearance of band at 170 cm⁻¹, overlapped by the bands corresponding to anatase phase at 143 and 196 cm⁻¹. For Pt/TiO₂ samples prepared by photo-deposition, the bands corresponding to anatase phase (196, 395, 516 and 639 cm⁻¹) become weaker and broader while the band corresponding to rutile phase (446 cm⁻¹) nearly disappears. These may be resulted from the electron-interaction between Pt and TiO₂ and corresponding changes in the electron environment of TiO₂ [26]. The electron-interaction is well preserved after H₂/He or O₂/He treatment at 450 °C, as proved by the unchanged Raman spectra. For Pt/TiO₂ samples prepared by impregnation, the weakening and broaden of bands corresponding to anatase phase are observed on as-prepared Pt/TiO₂. After O₂/He treatment at 450 °C, the recover of bands corresponding to anatase and rutile phase is observed, indicating the weakening of Pt-TiO₂ electron-interaction. Treatment in H₂/He at 450 °C results in more serious weakening of Pt-TiO₂ electron-interaction in Pt/TiO₂-imp.

It is seen that treatment of Pt/TiO₂-pho in O₂/He at 750 °C only results in the appearance of very weak Raman bands corresponding to rutile phase. In contrast, obvious phase transformation from anatase to rutile phase through similar thermal treatment is

Fig. 3. Raman spectra of TiO₂ and different Pt/TiO₂ samples. (a) TiO₂ P25, (b) as-prepared Pt/TiO₂-pho, (c) Pt/TiO₂-pho pretreated in 5%O₂/He at 450 °C for 1 h, (d) Pt/TiO₂-pho pretreated in 5%H₂/He at 450 °C for 1 h, (e) as-prepared Pt/TiO₂-imp, (f) Pt/TiO₂-imp pretreated in 5%O₂/He at 450 °C for 1 h, (g) Pt/TiO₂-imp pretreated in 5%O₂/He at 450 °C for 1 h and (h) Pt/TiO₂-pho pretreated in 5%O₂/He at 750 °C for 1 h. R: rutile TiO₂; A: anatase TiO₂.

proved by XRD analysis, as seen Fig. 2. These might be explained from the aspect that Raman spectroscopy detects the surface region of samples while XRD techniques detect bulk region. The introduction of platinum to TiO_2 by photo-deposition greatly suppresses the anatase-rutile transformation in the surface phase.

The TEM images of Pt/TiO_2 prepared by different methods are shown in Fig. 4 and it is seen that platinum tends to form small clusters on TiO_2 support. In the image of $\text{Pt/TiO}_2\text{-imp}$, platinum clusters with averages diameters of ca. 6.5 nm are observed to evenly disperse on the support. Hydrogen reduction at 450 °C does not

result in obvious change in the particle size of platinum clusters. As for $\text{Pt/TiO}_2\text{-pho}$, homogeneous platinum clusters of ca. 4.0 nm are well dispersed on the support. The average diameter of platinum clusters increases slightly from ca. 4.0 nm to ca. 4.7 nm after thermal treatment in oxygen at 650 °C. Thermal treatment at 750 °C causes a further increase in the cluster diameter to ca. 5.6 nm. Besides, the expansion and aggregation of TiO_2 support can be observed after thermal treatment at 750 °C. The agglomeration and sintering of platinum particles during operation is a serious problem leading to the deactivation of platinum catalysts. In this work, sintering

Fig. 4. TEM images of different Pt/TiO_2 samples. (a) As-prepared $\text{Pt/TiO}_2\text{-imp}$, (b) $\text{Pt/TiO}_2\text{-imp}$ pretreated in 5% H_2 /He at 450 °C for 1 h, (c) as-prepared $\text{Pt/TiO}_2\text{-pho}$, (d) $\text{Pt/TiO}_2\text{-pho}$ pretreated in 5% O_2 /He at 450 °C for 1 h, (e) $\text{Pt/TiO}_2\text{-pho}$ pretreated in 5% O_2 /He at 650 °C for 1 h and (f) $\text{Pt/TiO}_2\text{-pho}$ pretreated in 5% O_2 /He at 750 °C for 1 h.

Table 1

Physical properties of platinum catalysts.

Catalyst	Pt loading (wt%) ^a	Surface area (m ² /g)	Pt particle size (nm) ^b	Pt dispersion (%)
Pt/TiO ₂ -imp	1.91	53.8	6.7	59.8
Pt/TiO ₂ -pho	1.82	51.7	4.2	72.7
Pt/Al ₂ O ₃ -imp	1.93	107.3	9.8	32.6

^a Determined by ICP (IRIS Advantage, TJA solution).^b Average particle size, determined by TEM.

inhibition of platinum clusters is observed on Pt/TiO₂-pho and this kind of sintering inhibition may be ascribed to formation of Pt–TiO₂ electron-interaction, as discussed in following sections.

The physical properties of Pt/TiO₂ and reference Pt/Al₂O₃ samples are summarized in Table 1. With the similar platinum loading of ca. 2%, the platinum particles on Al₂O₃ support are much larger (ca. 9.8 nm) than those on TiO₂ support (4.2 nm or 6.7 nm), and as a consequence the platinum dispersion on Al₂O₃ is much lower (32.6%) than that on TiO₂ (59.8% or 72.7%).

Fig. 5 shows the XP spectra of Ti 4f and Pt 4f region of Pt/TiO₂ samples prepared by different methods and pre-treated under different conditions. For as-prepared Pt/TiO₂-pho sample, the peaks of binding energy are observed at 72.4 eV and 75.7 eV in Pt 4f region corresponding to the Pt^{II}O 4f_{7/2} and Pt^{II}O 4f_{5/2}, respectively [27]. Meanwhile, peaks of binding energy at 458.5 eV, 460.2 eV, 464.2 eV and 465.9 eV are observed in the Ti 2p region. The peaks at 458.5 eV and 464.2 eV are easily assigned to the Ti^{IV} 2p_{3/2} and 2p_{1/2} in TiO₂. The peaks at higher binding energies are tentatively assigned to the electron-deficient Ti^{IV} 2p_{3/2} and 2p_{1/2} in TiO₂. With H₂PtCl₆ as Pt precursor, the platinum species should exist in the form of PtO₂ under alkaline condition if not reduced. However, the electron-interaction between Pt species and TiO₂ are formed and electrons are donated from TiO₂ support to Pt species. Moreover, the apparent transport of electrons from semiconductor TiO₂ to Pt is greatly promoted under UV irradiation, motivated by the difference in the work function between Pt and TiO₂ [28]. As a result, much excess electrons are thus accumulated on the surface of Pt species in Pt/

TiO₂, leading to the reduction of Pt^{IV} to Pt^{II}. Similar circumstances occur on as-prepared Pt/TiO₂-imp. But much excess electrons are thus accumulated on the surface of Pt species without UV irradiation and the electrons donated by TiO₂ are not enough to reduce all Pt^{IV} to Pt^{II} in Pt/TiO₂-imp. As a consequence, platinum species exist in the form of both Pt^{II} (binding energy at 72.4 eV and 75.7 eV) and Pt^{IV} (binding energy at 73.7 eV and 77.1 eV). It should be mentioned that the Pt–TiO₂ electron-interaction reported here is differ from the strong metal-support interaction (SMSI) induced by high temperature (>450 °C) reduction treatments [29,30].

After O₂/He or H₂/He treatment on Pt/TiO₂-pho at 450 °C for 1 h, Pt⁰ is observed as the only platinum species on TiO₂ (binding energy at 70.2 eV and 73.6 eV), indicating the reduction of Pt species during treatment. It is surprising to see the reduction of Pt species even in excess oxygen. Since the thermal decomposition of Pt^{II}O generally occurs at above 500 °C, the Pt^{II}O should be reduced by the excess electrons accumulated on the surface of Pt species. Here, elevated temperatures is the key point for the further reduction of Pt species and atmosphere for treatment does not play a significant role. Moreover, the Pt⁰ peaks shift slightly to lower binding energy compared to metal platinum (binding energy at 70.9 eV and 74.3 eV [31]). Actually, the Pt on TiO₂ support may exist in the form of (Pt)_n^{σ−} with the excess electrons donated by TiO₂ support [32]. The surface electron-deficient Ti^{IV} in Pt/TiO₂-pho cannot be observed any more after O₂/He or H₂/He treatment due to the electron transfer in TiO₂ during thermal treatment, probably from bulk phase TiO₂ to surface TiO₂. As for Pt/TiO₂-imp, the Pt^{IV} can only be reduced to Pt^{II} through the treatment in O₂/He with less electrons accumulated on Pt species. If treated in H₂/He, the Pt^{IV} and Pt^{II} in as-prepared Pt/TiO₂-imp are all reduced to Pt⁰ (binding energy at 70.7 eV and 74.1 eV). Obviously, the Pt^{II} is reduced to Pt⁰ by the hydrogen in the stream. Based on changes in the binding energy corresponding to Pt⁰, we propose that the Pt–TiO₂ electron-interaction in Pt/TiO₂-imp is greatly weakened after H₂/He treatment. As displayed in Fig. 5, a small proportion of Ti^{IV} in surface TiO₂ support is reduced to Ti^{III} (binding energy at 456.2 eV and 461.8 eV) by hydrogen through H₂/He treatment (Ti⁴⁺ + O^{2−} + H_{ads} → Ti³⁺ + OH[−]). The reduction of Ti^{IV}

Fig. 5. XPS of Ti 2p and Pt 4f region of different Pt/TiO₂ samples. (a) As-prepared Pt/TiO₂-pho, (b) Pt/TiO₂-pho pretreated in 5%O₂/He at 450 °C for 1 h, (c) Pt/TiO₂-pho pretreated in 5%H₂/He at 450 °C for 1 h, (d) as-prepared Pt/TiO₂-imp, (e) Pt/TiO₂-imp pretreated in 5%O₂/He at 450 °C for 1 h and (f) Pt/TiO₂-imp pretreated in 5%H₂/He at 450 °C for 1 h.

in TiO₂ is promoted by the existence of Pt [33] and the Ti^{IV} adjacent to Pt is preferentially reduced. Unfortunately, the reduction of Ti^{IV} to Ti^{III} results in the weakening of Pt–TiO₂ electron-interaction in Pt/TiO₂-imp.

Based on the above XPS analysis results, following conclusions can be drawn. Firstly, Pt–TiO₂ electron-interaction exists in both as-prepared Pt/TiO₂-imp and as-prepared Pt/TiO₂-pho samples, and Pt–TiO₂ electron-interaction in as-prepared Pt/TiO₂-pho is stronger than that in Pt/TiO₂-imp. Secondly, platinum oxides on Pt/TiO₂-pho are reduced to Pt⁰ through the treatment in O₂/He or H₂/He, with Pt–TiO₂ electron-interaction preserved. Finally, Pt^{IV} is reduced to Pt^{II} in Pt/TiO₂-imp through treatment in O₂/He while Pt^{II} is further reduced to Pt⁰ by hydrogen through treatment in H₂/He, with Pt–TiO₂ electron-interaction greatly weakened.

Other important information we can obtain from XPS analysis is the surface composition of tested samples in the depth up to 5 nm and surface platinum loadings are displayed in Fig. 6. It is seen that the platinum loadings in as-prepared Pt/TiO₂-pho and Pt/TiO₂-imp are 1.75% and 1.81%, respectively. These values are closed to the designed platinum loading of 2% and the analysis results by ICP (Table 1), indicating the relative homogeneous dispersion of platinum in bulk TiO₂ support. Treatment of as-prepared Pt/TiO₂ in O₂/He at 450 °C results in the transfer of platinum from bulk phase to the surface as proved by the distinct increase of surface platinum loadings (Pt/TiO₂-pho to 4.03% and Pt/TiO₂-imp to 4.73%). Treatment of as-prepared Pt/TiO₂-pho in H₂/He at 450 °C also results in the enrichment of surface platinum (increase to 3.39%) while treatment of as-prepared Pt/TiO₂-imp under identical conditions results in the transfer of platinum from surface to bulk phase as indicated by the decrease surface platinum loading to 1.43%. Moreover, treatment of as-prepared Pt/TiO₂-pho in O₂/He at 750 °C leads to a serious transfer of platinum from surface to bulk phase and surface platinum loading decreases to 0.54%. It is thus deduced platinum species go into the matrix of TiO₂ support during high temperature O₂/He treatment at 750 °C.

3.3. Catalytic performance for NO oxidation

The temperature dependence of steady-state NO oxidation over Pt/TiO₂ catalysts prepared by different methods and model Pt/Al₂O₃ catalyst is shown in Fig. 7. For reference, the thermodynamic

Fig. 6. Surface Pt loadings in different samples determined by XPS. (a) As-prepared Pt/TiO₂-pho, (b) Pt/TiO₂-pho pretreated in 5%O₂/He at 450 °C for 1 h, (c) Pt/TiO₂-pho pretreated in 5%H₂/He at 450 °C for 1 h, (d) as-prepared Pt/TiO₂-imp, (e) Pt/TiO₂-imp pretreated in 5%O₂/He at 450 °C for 1 h, (f) Pt/TiO₂-imp pretreated in 5%H₂/He at 450 °C for 1 h and (g) Pt/TiO₂-pho pretreated in 5%O₂/He at 750 °C for 1 h.

Fig. 7. Catalytic activities for NO oxidation on supported platinum catalysts. Reaction conditions: 0.15 g catalyst, 400 ppm NO, 10% O₂ and the balance He, GHSV = 180,000 h⁻¹.

equilibrium for NO–NO₂ under given conditions is also shown in the figure (in dashed). The main product for NO oxidation is NO₂, and the formation of other N-containing product (e.g. N₂O and N₂) can be neglected. Among the catalysts pre-treated in H₂/He, Pt/TiO₂-pho exhibits the best NO oxidation activity followed by Pt/Al₂O₃ and then Pt/TiO₂-imp. For Pt/TiO₂ prepared by impregnation, the sample pre-treated in H₂/He exhibits quite higher activity than the sample pre-treated in O₂/He. While for Pt/TiO₂ prepared by photo-deposition, the sample pre-treated in O₂/He exhibits a little higher activity than the sample pre-treated in H₂/He. As revealed by XPS results in Fig. 4, the Pt/TiO₂-imp pre-treated in O₂/He mostly contains Pt^{II}O, which is much less active than metallic platinum [9,10], so it exhibits quite low activity for NO oxidation. In contrast, platinum exists in the form of Pt⁰ in Pt/TiO₂-pho samples under different pre-treated conditions, so both Pt/TiO₂-pho pre-treated in O₂/He and Pt/TiO₂-pho pre-treated in H₂/He exhibit quite high activity for NO oxidation. Pt/TiO₂-pho sample pre-treated in O₂/He exhibits a little higher activity than that pre-treated in H₂/He, probably due to its higher surface Pt loading as determined by XPS analysis. It should be noted that Pt/TiO₂-pho, both treated in H₂/He and treated in O₂/He, exhibited quite higher activity for NO oxidation than the Pt/TiO₂-imp treated in H₂/He. As revealed by XP spectra in Fig. 4, great Pt–TiO₂ electron-interaction exists in Pt/TiO₂-pho after treated in H₂/He or O₂/He and this kind of electron-interaction can protect catalyst against being oxidized during reaction under strong oxidizing conditions. Moreover, the excessive electrons associate with platinum may play a positive role on NO oxidation due to the promotion effect on oxygen dissociation [34]. As for Pt/TiO₂-pho, though platinum exists in the form of Pt⁰ after H₂/He treatment, the Pt–TiO₂ electron-interaction is greatly weakened. The small platinum clusters on TiO₂ with weak Pt–TiO₂ electron-interaction are easily oxidized during reaction under strong oxidizing conditions [22], leading to the serious decrease in NO oxidation activity.

The Pt/TiO₂-pho pre-treated in O₂/He is the most active catalyst among all catalysts studied and a 50% NO conversion to NO₂ can be achieved at ca. 200 °C at a very high GHSV of 180,000 h⁻¹. The NO oxidation over catalyst is kinetically limited at low temperatures, and after reaching the maximal NO conversion of ca. 94% at ca. 275 °C it becomes equilibrium limited. In fact, the Pt/TiO₂-pho is the most active catalyst for NO oxidation under comparable reaction conditions [10–12]. In an early study of Olsson et al. [35], Pt/TiO₂ prepared by wet-impregnation showed a decrease in conversion to

NO₂ with the time during NO oxidation and the deactivation was ascribed to formation of platinum oxides. In this study, no deactivation of Pt/TiO₂ prepared photo-deposition is observed during reaction and the activity data are well duplicated after each run. XPS results (not shown here) indicate that the Pt species preserve in the form of (Pt)_n^{o-} after reaction. The difference between our catalyst and literature results is attributed to the photo-deposition method employed for catalyst preparation and the corresponding Pt-TiO₂ electron-interaction, as discussed above.

The effects of catalysts pretreatment conditions on NO oxidation over Pt/TiO₂-pho are shown in Fig. 8. It is seen that the NO oxidation activity is slightly improved after thermal treatment of sample in O₂/He at 550 °C or 650 °C. A possible explanation is that the Pt-TiO₂ interaction is enhanced during the thermal treatment. However, after thermal treatment at 750 °C for 1 h, the activity of catalyst is completely lost. As revealed by Raman analysis in Fig. 3, the anatase-rutile surface phase transformation is not so serious to cause the deactivation. Tentatively, the activity loss of Pt/TiO₂-pho after thermal treatment is also associated with the change in Pt-TiO₂ interaction. Thermal treatment at 750 °C leads to the serious transfer of platinum clusters from surface to bulk phase (probably Pt go into the matrix of TiO₂ support), as indicated by the surface analysis data in Fig. 6. The lack of available

surface platinum sites should be a main reason for the deactivation of Pt/TiO₂-pho after thermal treatment at 750 °C. Based on the above results, it is seen that thermal treatment of Pt/TiO₂-pho in O₂/He with well-controlled temperature may be useful means to improve the catalytic activity for NO oxidation. Moreover, the good thermal stability of Pt/TiO₂-pho under oxidizing conditions makes it quite suitable for industrial applications.

The effects of SO₂ and water vapor in the reaction stream on NO oxidation are investigated and the results are present in Fig. 8. It is seen that water vapor shows a mild negative impact on NO oxidation. For example, the presence of 2% water vapor reduces the NO conversion by 10% at 225 °C. Increasing the concentration of water vapor to 5% results in a bit more serious negative effect on NO oxidation and NO conversion at 225 °C further decreases from ca. 70% to ca. 60%.

The presence of SO₂ in the stream shows serious negative effect on NO oxidation. As seen in Fig. 8, the maximal NO conversion decreases from ca. 94% to ca. 79% and the temperature for maximal NO conversion increases from 250 °C to 300 °C with the addition of 80 ppm SO₂. Increasing the concentration of SO₂ to 320 ppm only causes a bit more serious deactivation of Pt/TiO₂ for NO oxidation. The negative effect of SO₂ is due to the oxidation of SO₂ to SO₃ (2SO₂ + O₂ → 2SO₃). The formed SO₃ may not only occupy the active sites for NO oxidation but also cover the support materials by forming sulfates. As a result, serious deactivation by SO₂ is generally observed on catalysts for NO oxidation [36–38]. In this work, SO₂-resistant TiO₂ is selected as the support for platinum and the formation sulfates on support is greatly prohibited. Correspondingly, Pt/TiO₂-pho exhibits quite good activity for NO oxidation even in the presence of high concentration of SO₂. A detail mechanism study on NO oxidation in the presence of SO₂ will be presented in the next contribution.

4. Conclusion

The catalytic oxidation of NO over TiO₂ supported platinum nano-clusters prepared by photo-deposition is studied. Pt-TiO₂ electron-interaction is formed in as-prepared Pt/TiO₂ sample with electrons transfer from surface TiO₂ to platinum sites and the electron-interaction is well-preserved after treatment in O₂/He or H₂/He at 450 °C. The Pt-TiO₂ electron-interaction can protect platinum nano-clusters against oxidation and as expected, over 90% NO is oxidized to NO₂ at a high GHSV of 180,000 h⁻¹. The presence of H₂O in the stream shows slight negative effects on NO oxidation over Pt/TiO₂ while the presence of SO₂ shows serious negative effects. Nevertheless, Pt/TiO₂ prepared by photo-deposition exhibits remarkable activity for NO oxidation with high concentration of SO₂ in the stream.

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Fig. 8. Effects of pretreatment condition and feed composition on NO oxidation activity over Pt/TiO₂-pho. Reaction conditions: 0.15 g catalyst, 400 ppm NO, 10% O₂, 0–320 ppm SO₂, 0–5% H₂O and the balance He, GHSV = 180,000 h⁻¹.

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