Catalytic oxidation of NO over TiO$_2$ supported platinum clusters I. Preparation, characterization and catalytic properties

Landong Li, Qun Shen, Jie Cheng, Zhengping Hao *

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

**ABSTRACT**

The oxidation of NO to NO$_2$ was studied on Pt/TiO$_2$ catalysts prepared by wet impregnation and photo-deposition method. Pt/TiO$_2$ prepared by photo-deposition exhibited quite higher activity for NO oxidation to NO$_2$ 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. SO$_2$ and H$_2$O in the stream, on NO oxidation were investigated in details. The different Pt/TiO$_2$ 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-TiO$_2$ electron-interaction was studied based on the characterization results and the role of Pt-TiO$_2$ electron-interaction on the catalytic performance of Pt/TiO$_2$ 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 NO$_2$, (2 NO + O$_2$ → 2 NO$_2$) is a key step for those NO$_x$ elimination techniques. In a NO$_2$ storage-reduction (NSR) process, NO is first oxidized to NO$_2$ 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 NO$_2$, which subsequently reacts with hydrocarbon to give out N$_2$ [2]. In the selective catalytic reduction with ammonia (NH$_3$-SCR), the SCR reaction rate can be greatly enhanced if a fraction of NO is converted to NO$_2$. For example, the reaction between equimolar NO-NO$_2$ and NH$_3$ via so-called “fast” SCR reaction (4NH$_3$ + 2NO + 2NO$_2$ → 4N$_2$ + 6H$_2$O) is ca. 10 times faster than the standard reaction between NO and NH$_3$ (4NH$_3$ + 4NO + O$_2$ → 4N$_2$ + 6H$_2$O) at low temperatures (200–300°C) [3–5]. In the continuously regenerating trap (CRT) for soot removal, NO is first oxidized to NO$_2$, which then oxidizes the soot collected on a diesel particulate filter [6]. Owing to the strong oxidation activity of NO$_2$, the reaction temperatures for soot oxidation by NO$_2$ are much lower than those for soot oxidation in the air.

The catalytic oxidation of NO to NO$_2$ 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 O$_2$ as reactants or in the presence of water and SO$_2$, 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/SiO$_2$, but it was less significant for Pt/Al$_2$O$_3$. Besides, the catalyst support was found to influence the NO oxidation rate greatly and SiO$_2$ was better support than Al$_2$O$_3$ and ZrO$_2$. However, Denton et al. [14] found that platinum particle size was key factor controlling the NO oxidation rate for both Pt/SiO$_2$ and Pt/Al$_2$O$_3$, 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 O$_2$ and NO$_2$ due to oxides formation in...
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 a 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 ± 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 Kα 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 Kα X-ray source (hv = 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 μm × 700 μm, 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 (ε=0.1 eV) were determined with respect to the position of the adventitious C 1s peak at 284.8 eV.

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 maxinal 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
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.

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
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 Pt/TiO$_2$-imp, platinum clusters with averages 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 Pt/TiO$_2$-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 Pt/TiO$_2$-imp, (b) Pt/TiO$_2$-imp pretreated in 5%H$_2$/He at 450 °C for 1 h, (c) as-prepared Pt/TiO$_2$-pho, (d) Pt/TiO$_2$-pho pretreated in 5%O$_2$/He at 450 °C for 1 h, (e) Pt/TiO$_2$-pho pretreated in 5%O$_2$/He at 650 °C for 1 h and (f) Pt/TiO$_2$-pho pretreated in 5%O$_2$/He at 750 °C for 1 h.](image-url)
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 PtII 4f7/2 and PtIV 4f5/2, 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 TiIV 2p3/2 and 2p1/2 in TiO2. The peaks at higher binding energies are tentatively assigned to the electron-deficient TiIV 2p3/2 and 2p1/2 in TiO2. With H2PtCl6 as Pt precursor, the platinum species should exist in the form of PtO2, and as a consequence the platinum dispersion on Al2O3 is much lower (32.6%) than that on TiO2 (59.8% or 72.7%).

As-prepared 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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt loading (wt%)</th>
<th>Surface area (m²/g)</th>
<th>Pt particle size (nm)</th>
<th>Pt dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/TiO2-imp</td>
<td>1.91</td>
<td>53.8</td>
<td>6.7</td>
<td>59.8</td>
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<tr>
<td>Pt/TiO2-pho</td>
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<td>51.7</td>
<td>4.2</td>
<td>72.7</td>
</tr>
<tr>
<td>Pt/Al2O3-imp</td>
<td>1.93</td>
<td>107.3</td>
<td>9.8</td>
<td>32.6</td>
</tr>
</tbody>
</table>

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

Table 1
Physical properties of platinum catalysts.

After O2/He or H2/He treatment on Pt/TiO2-pho at 450 °C for 1 h, Pt 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 PtIIO4 generally occurs at above 500 °C, the PtIIO4 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–, with the excess electrons donated by TiO2 support [32]. The surface electron-deficient TiIV 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 PtIV can only be reduced to Pt0 through the treatment in O2/He with less electrons accumulated on Pt species. If treated in H2/He, the PtIV and Pt0 in as-prepared Pt/TiO2-imp are all reduced to Pt0 (binding energy at 70.7 eV and 74.1 eV). Obviously, the Pt0 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 TiIV in surface TiO2 support is reduced to TiIII (binding energy at 456.2 eV and 461.8 eV) by hydrogen through H2/He treatment (Ti4+ + O2− + Hads → Ti3+ + OH−). The reduction of TiIV...
in TiO_2 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-TiO_2 electron-interaction in Pt/TiO_2-imp.

Based on the above XPS analysis results, following conclusions can be drawn. Firstly, Pt-TiO_2 electron-interaction exists in both as-prepared Pt/TiO_2-imp and as-prepared Pt/TiO_2-pho samples, and Pt-TiO_2 electron-interaction in as-prepared Pt/TiO_2-pho is stronger than that in Pt/TiO_2-imp. Secondly, platinum oxides on Pt/TiO_2-pho are reduced to Pt^0 through the treatment in O_2/He or H_2/He, with Pt-TiO_2 electron-interaction preserved. Finally, Pt^{IV} is reduced to Pt^0 in Pt/TiO_2-imp through treatment in O_2/He while Pt^0 is further reduced to Pt^0 by hydrogen through treatment in H_2/He, with Pt-TiO_2 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/TiO_2-pho and Pt/TiO_2-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 TiO_2 support. Treatment of as-prepared Pt/TiO_2 in O_2/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/TiO_2-pho to 4.03% and Pt/TiO_2-imp to 4.73%). Treatment of as-prepared Pt/TiO_2-pho in H_2/He at 450 °C also results in the enrichment of surface platinum (increase to 3.39%) while treatment of as-prepared Pt/TiO_2-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/TiO_2-pho in O_2/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 TiO_2 support during high temperature O_2/He treatment at 750 °C.

3.3. Catalytic performance for NO oxidation

The temperature dependence of steady-state NO oxidation over Pt/TiO_2 catalysts prepared by different methods and model Pt/Al_2O_3 catalyst is shown in Fig. 7. For reference, the thermodynamic equilibrium for NO-NO_2 under given conditions is also shown in the figure (in dashed). The major product for NO oxidation is NO_2, and the formation of other N-containing product (e.g. N_2O and N_2) can be neglected. Among the catalysts pre-treated in H_2/He, Pt/TiO_2-pho exhibits the best NO oxidation activity followed by Pt/Al_2O_3 and then Pt/TiO_2-imp. For Pt/TiO_2 prepared by impregnation, the sample pre-treated in H_2/He exhibits a little higher activity than the sample pre-treated in O_2/He. While for Pt/TiO_2 prepared by photo-deposition, the sample pre-treated in O_2/He exhibits a little higher activity than the sample pre-treated in H_2/He. As revealed by XPS results in Fig. 4, the Pt/TiO_2-pho pre-treated in O_2/He mostly contains Pt^0, 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 Pt^0 in Pt/TiO_2-pho samples under different pre-treated conditions, so both Pt/TiO_2-pho pre-treated in O_2/He and Pt/TiO_2-pho pre-treated in H_2/He exhibit quite high activity for NO oxidation. Pt/TiO_2-pho sample pre-treated in O_2/He exhibits a little higher activity than that pre-treated in H_2/He, probably due to its higher surface Pt loading as determined by XPS analysis. It should be noticed that Pt/TiO_2-pho, both treated in H_2/He and treated in O_2/He, exhibited quite higher activity for NO oxidation than the Pt/TiO_2-imp treated in H_2/He. As revealed by XP spectra in Fig. 4, great Pt-TiO_2 electron-interaction exists in Pt/TiO_2-pho after treated in H_2/He or O_2/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/TiO_2-pho, though platinum exists in the form of Pt^0 after H_2/He treatment, the Pt-TiO_2 electron-interaction is greatly weakened. The small platinum clusters on TiO_2 with weak Pt-TiO_2 electron-interaction are easily oxidized during reaction under strong oxidizing conditions [22], leading to the serious decrease in NO oxidation activity.

The Pt/TiO_2-pho pre-treated in O_2/He is the most active catalyst among all catalysts studied and a 50% NO conversion to NO_2 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 94% at ca. 275 °C it becomes equilibrium limited. In fact, the Pt/TiO_2-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/TiO_2 prepared by wet-impregnation showed a decrease in conversion to...
NO\textsubscript{2} with the time during NO oxidation and the deactivation was ascribed to formation of platinum oxides. In this study, no deactivation of Pt/TiO\textsubscript{2} 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\textsubscript{0})\textsuperscript{+} 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-TiO\textsubscript{2} electron-interaction, as discussed above.

The effects of catalysts pretreatment conditions on NO oxidation over Pt/TiO\textsubscript{2}-pho are shown in Fig. 8. It is seen that the NO oxidation activity is slightly improved after thermal treatment of sample in O\textsubscript{2}/He at 550 °C or 650 °C. A possible explanation is that the Pt-TiO\textsubscript{2} 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 lost of Pt/TiO\textsubscript{2}-pho after thermal treatment is also associated with the change in Pt-TiO\textsubscript{2} 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 TiO\textsubscript{2} support), as indicated by the surface analysis data in Fig. 8. The lack of available surface platinum sites should be a main reason for the deactivation of Pt/TiO\textsubscript{2}-pho after thermal treatment at 750 °C. Based on the above results, it is seen that thermal treatment of Pt/TiO\textsubscript{2}-pho in O\textsubscript{2}/He with well-controlled temperature may be useful means to improve the catalytic activity for NO oxidation. Moreover, the good thermal stability of Pt/TiO\textsubscript{2}-pho under oxidizing conditions makes it quite suitable for industrial applications.

The effects of SO\textsubscript{2} 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 SO\textsubscript{2} 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 SO\textsubscript{2}. Increasing the concentration of SO\textsubscript{2} to 320 ppm only causes a bit more serious deactivation of Pt/TiO\textsubscript{2} for NO oxidation. The negative effect of SO\textsubscript{2} is due to the oxidation of SO\textsubscript{2} to SO\textsubscript{3} (2SO\textsubscript{2} + O\textsubscript{2} \rightarrow 2SO\textsubscript{3}). The formed SO\textsubscript{3} 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 SO\textsubscript{2} is generally observed on catalysts for NO oxidation [36–38]. In this work, SO\textsubscript{2}-resistant TiO\textsubscript{2} is selected as the support for platinum and the formation sulfates on support is greatly prohibited. Correspondingly, Pt/TiO\textsubscript{2}-pho exhibits quite good activity for NO oxidation even in the presence of high concentration of SO\textsubscript{2}. A detail mechanism study on NO oxidation in the presence of SO\textsubscript{2} will be presented in the next contribution.

4. Conclusion

The catalytic oxidation of NO over TiO\textsubscript{2} supported platinum nano-clusters prepared by photo-deposition is studied. Pt-TiO\textsubscript{2} electron-interaction is formed in as-prepared Pt/TiO\textsubscript{2} sample with electrons transfer from surface TiO\textsubscript{2} to platinum sites and the electron-interaction is well-preserved after treatment in O\textsubscript{2}/He or H\textsubscript{2}/He at 450 °C. The Pt-TiO\textsubscript{2} electron-interaction can protect platinum nano-clusters against oxidation and as expected, over 90% NO is oxidized to NO\textsubscript{2} at a high GHSV of 180,000 h\textsuperscript{−1}. The presence of H\textsubscript{2}O in the stream shows slight negative effects on NO oxidation over Pt/TiO\textsubscript{2} while the presence of SO\textsubscript{2} shows serious negative effects. Nevertheless, Pt/TiO\textsubscript{2} prepared by photo-deposition exhibits remarkable activity for NO oxidation with high concentration of SO\textsubscript{2} in the stream.

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