Oxidation of nitric oxide to nitrogen dioxide over Ru catalysts

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ABSTRACT

A series of TiO₂ supported catalysts were prepared by impregnation method in a rotary evaporator and evaluated for the oxidation of NO to NO₂. Among all catalysts studied, Ru/TiO₂ catalyst exhibited the best activity and a maximal NO conversion of c.a. 94% could be achieved at c.a. 275 °C at a high GHSV of 180,000 h⁻¹. For ruthenium catalysts, the effects of supports, ruthenium loadings, pretreatment conditions and experiment conditions (feed gas composition, GHSV) on NO oxidation to NO₂ were investigated in detail. The ruthenium catalysts were characterized by means of X-ray diffraction (XRD), CO pulse chemisorption, transmission electron microscopy (TEM) and temperature-programmed reduction (TPR) techniques. The active ruthenium species for NO oxidation were discussed based on the catalytic and characterization results. Moreover, the reaction mechanism for NO oxidation over Ru/TiO₂ catalyst was studied by means of in situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS).

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1. Introduction

Nitrogen oxides (NOx), from stationary and transportation sources, are major air pollutants that greatly contribute to the formation of photochemical smog and acid rain. The removal of NOx is always a hot topic forever in the field of environmental catalysis and various techniques have been proposed for the abatement of NOx from anthropogenic sources. For example, selective catalytic reduction (SCR) and NOx storage-reduction (NSR) are two major techniques for NOx abatement in excess oxygen. In the research of SCR and NSR, it is well established that the oxidation of NO to NO₂ is a very important step for the whole reaction. For NSR, NO is first oxidized to NO₂ and then stored on the basic component of catalyst as nitrates [1]. For HC-SCR, NO is oxidized to NO₂, which subsequently reacts with hydrocarbon to give out N₂ [2]. In recent years, the so-called “fast” SCR reaction (4NH₃ + 2NO + 2NO₂ → 4N₂ + 6H₂O), in contrast to standard ammonia SCR reaction (4NH₃ + 4NO + O₂ → 4N₂ + 6H₂O), is receiving more and more attention [3-9]. The reaction between equimolar NO–NO₂ and NH₃ is c.a. 10 times faster than the reaction between NO and NH₃ at low temperatures (200–300 °C) [10]. Therefore, the fast SCR reaction is considered as a feasible means to boost the denitrification efficiency at lower temperatures as well as to reducing the catalyst costs of SCR system. It is also noted that most nitrogen oxides from exhaust emissions exist in the form of NO (>90%), so that an upstream pre-oxidation catalyst converting NO to NO₂ is absolutely necessary to realize fast SCR reaction.

In the research of catalysts for NO oxidation, much effort has been focused on supported platinum materials. Pt/SiO₂ [11-13] and Pt/Al₂O₃ [13,14] were reported to be highly active for NO oxidation. The catalytic kinetics and the effects of preparation parameters on activities had been investigated in detail [11-14]. Although supported platinum catalysts show considerable activity for NO oxidation, the high cost of noble metal platinum materials restricts the application of supported Pt catalysts to a great extent. Moreover, the activity loss of supported platinum catalyst in strong oxidizing conditions remains a problem to be solved. Other catalysts, such as supported cobalt catalysts, are now being investigated as alternative catalysts for NO oxidation [15-18].

During the past decades, supported ruthenium materials have been extensively studied as catalysts for a number of reactions, e.g. organic synthesis [19], partial oxidation of hydrocarbons [20], Fischer–Tropsch synthesis [21] and ammonia synthesis [22]. Recently, ruthenium catalysts have been applied in the reaction of wet air oxidation of various pollutants [23-25] and complete oxidation of volatile organic compounds [26]. The good redox behaviors of ruthenium catalysts have been proved in these reactions, and supported ruthenium materials are thus expected to be good catalysts for other oxidation reactions. However, up to now, few researches have been focused on the application of ruthenium catalysts in the oxidation of nitric oxide to nitrogen dioxide.

In the present study, the activities of different transition metal catalysts for NO oxidation are investigated and supported ruthenium catalysts are found to be very active for the first time.
The effects of supports, ruthenium loadings, pretreatment of catalysts and reaction conditions (feed gas composition, GHSV) on NO oxidation are investigated in detail. More important, the active ruthenium species for NO oxidation are discussed based on the catalytic and characterization results.

2. Experimental

2.1. Catalysts preparation

The following oxides were selected as catalyst supports: SiO2 (Sinopec), Al2O3 (Sinopec), ZrO2 (Sinopec), TiO2 (Degussa P25, 70% anatase, 30% rutile), TiO2-Anatase (denoted as TiO2-A, Fluka), TiO2-Rutile (denoted as TiO2-R, Degussa). Difficult metal salts of analytical agent grade (NH4VO3, CrCl3, MnSO4, FeCl3, CoCl2, NiCl2, CuCl2, PdCl2, RhCl3, RuCl3, H2PtCl6, HAuCl4) were used as sources for supported materials without further purification.

The catalysts were prepared by impregnating the supports with aqueous solution of metal salt in a rotary evaporator at the constant temperature. In a typical preparation process of Ru/TiO2, 20 mL RuCl3 aqueous solution (Ru concentration: 1.0 mg/mL) was added to 1 g TiO2 (P25) support. The impregnated sample was mixed well and then evaporated in a rotary evaporator at constant temperature of 80 °C. The as-prepared samples were carefully washed by distilled water, dried at 100 °C over night and then calcined at 450 °C in flowing air for 4 h. The Pt/TiO2 sample was further reduced in 5%H2/He at 450 °C for 1 h prior to catalytic test.

2.2. Catalyst characterization

The ruthenium contents in supported ruthenium catalysts were determined by ICP-AES using an Optima 2000 spectrometer. The surface areas of catalysts were analyzed by low temperature N2 adsorption/desorption using a Quantachrome NOVA-1200 gas absorption analyzer and the specific surface areas were calculated using the BET equation.

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°.

The dispersion of ruthenium on various supports 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/He (Chemisorb 2720, Micromeritics). In a typical experiment, c.a. 100 mg sample was placed in the quartz reactor (4 mm i.d.) and pretreated in 5%H2/He (5%H2/He for Pt/TiO2 sample) at 450 °C for 1 h. After cooling to 150 °C in He, the reactant gas mixture (400 ppm NO, 10% O2, He balance) was fed to the reactor. The total flow-rate of the gas mixture was kept at 450 mL min⁻¹, corresponding to a GHSV of 180,000 h⁻¹. The inlet and outlet gases were monitored on-line using a gas chromatograph (HP 6820 series, for N2 and N2O analysis) and a chemiluminescence NOx analyzer (Ecotech EC 9841, for NO and NO2 analysis).

2.4. In situ DRIFT study of NO and NO2 adsorption

In situ DRIFT studies were performed on the spectrometer (Bruker Tensor 27) with 128 scans at a resolution of 4 cm⁻¹. A self-supporting pellet (ca. 50 mg) made of the catalyst sample was placed in the IR flow cell and the background spectrum was taken at desired temperatures in flowing He. For NO adsorption, 1% NO in He was fed to catalyst cell at room temperature and a series of time-dependent DRIFT spectra of NO adsorption were sequentially recorded. For NOx/CO co-adsorption, the gas mixture (400 ppm NO, 10% O2, balance He) was fed to the sample cell at a total flow-rate of 60 mL min⁻¹ at 150 °C. After holding this temperature for 20 min, it was stepwise increased to the next designed temperature. The DRIFT spectra were recorded every 25 °C (from 150 to 350 °C) after 20 min of steady state reaction.

3. Results and discussion

3.1. NO oxidation activity over TiO2 supported catalysts

The temperature dependence of steady-state NO oxidation over a series of TiO2 supported catalysts is shown in Fig. 1. For reference, the thermodynamic equilibrium for NO–NO2 under given conditions is also shown in the figure (in dashed). The main product for NO oxidation was NO2, and the formation of other N-containing products (N2O, N2, etc.) could be neglected. The NO conversion to NO2 over catalysts was kinetically limited at low temperatures and equilibrium-limited at higher temperatures. After reaching thermodynamic equilibrium, if possible, the NO conversion to NO2 closely followed the thermodynamic equilibrium curve. Among TiO2 supported transition metal oxides investigated, the best activity was obtained over Co/TiO2 sample and the activity order was observed as Co/TiO2 > Mn/TiO2 > V/TiO2 > Cu/TiO2 > Fe/TiO2 > Cr/TiO2 > Ni/TiO2. Among TiO2 supported precious metal or metal oxides studied, Ru/TiO2 showed the best activity, followed by Rh/TiO2 and then Pd/TiO2 and Au/TiO2. The Pt/TiO2 catalyst showed good activity at low temperatures (<225 °C), however its activity at high temperatures was observed to be lower than Rh/TiO2. It should be mentioned that the Pt/TiO2 was pre-reduced before reaction, considering that Pt metal was reported more active than Pt oxides [11,14]. Ru/TiO2 was the most active catalyst among TiO2 supported catalysts for NO oxidation and a 50% NO conversion to NO2 was achieved at ca. 250 °C at a very high GHSV of 180,000 h⁻¹. The maximal NO conversion of c.a. 94% could be achieved at c.a. 275 °C.

The XRD patterns of TiO2 supported catalysts studied are shown in Fig. 2. Typical diffraction peaks of TiO2 support corresponding to anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) phase were observed, as marked in the XRD patterns. Besides, no diffraction peaks corresponding to the supported phases, neither in metal form nor in oxide form, could be observed. It is deduced that the supported phases are highly dispersed on TiO2 support. The TEM image of Ru/TiO2 catalyst is displayed in Fig. 3. It is seen that homogeneous nano-clusters with average diameters of below 5 nm are evenly dispersed on the surface of TiO2 support.
3.2. Effects of supports and Ru loadings on NO oxidation over Ru catalysts

The activities of Ru catalysts for NO oxidation are significantly dependent on the supports. The comparison of various supported Ru catalysts is shown in Fig. 4 and the activity order of these catalysts is observed as Ru/TiO$_2$ > Ru/TiO$_2$-R > Ru/ZrO$_2$ > Ru/SiO$_2$ > Ru/Al$_2$O$_3$ > Ru/TiO$_2$-A. Obviously, the BET surface areas of Ru catalysts do not play a decisive role on their activities (Table 1). Ru/TiO$_2$-R sample with lowest surface area (21.5 m$^2$/g) exhibited quite high activity while Ru/Al$_2$O$_3$ with highest surface area (95.3 m$^2$/g) exhibited the very low activity. It is also seen that rutile phase TiO$_2$ appears to be much better support than anatase phase TiO$_2$. TiO$_2$ P25 with both anatase and rutile is the best support for Ru since Ru/TiO$_2$ exhibited the best activity among Ru catalysts studied.

The XRD patterns of supported Ru catalysts are shown in Fig. 5. In the XRD patterns of Ru/TiO$_2$, Ru/TiO$_2$-A, Ru/TiO$_2$-R, Ru/ZrO$_2$ and Ru/SiO$_2$, only diffraction peaks corresponding to supports are observed and no peaks ascribable to ruthenium species can be observed. While in the case of Ru/Al$_2$O$_3$, clear diffraction peaks ascribable to RuO$_2$ were observed besides the diffraction peaks corresponding to supports. The appearance of diffraction peaks ascribable to RuO$_2$ phase in the XRD patterns indicates the formation of bulk RuO$_2$ with high crystallinity.

The dispersion of Ru on different supports was analyzed by means of CO chemisorption and the data obtained are listed in Table 1. As expected, great difference in the dispersion of Ru is observed on different supports. The highest Ru dispersion of 70.5% is obtained in the case of Ru/TiO$_2$-R, while the lowest Ru dispersion of 21.8% is obtained in the case of Ru/Al$_2$O$_3$. The properties of supports play a decisive role on the dispersion of Ru species. The formation of bulk RuO$_2$ on supports undoubtedly results in the low dispersion of Ru, e.g. in the case of on Ru/Al$_2$O$_3$. Moreover, the
crystal phase of support might have essential effect on Ru dispersion. The Ru dispersion was the highest (70.5%) on rutile phase TiO₂ while the Ru dispersion was rather low (24.7%) on anatase phase TiO₂. It is seen that the dispersion of Ru species on support relates to the activity of Ru catalysts to some extent. Generally, higher dispersion of Ru species in Ru catalysts corresponds to higher NO oxidation activity. For example, Ru/Al₂O₃ with lowest Ru dispersion of 21.8% exhibited the very low NO oxidation activity. While Ru/TiO₂-R catalyst with highest Ru dispersion of 71.5% exhibited quite good NO oxidation activity. It is known that the dispersion of metal is greatly related to the Ru species formed on different support. So, it is proposed that the different Ru species formed on the supports may be responsible for the activity difference in Ru catalysts.

The different Ru species on supports are investigated by means of temperature-programmed reduction and the H₂-TPR profiles of Ru catalysts, together with reference amorphous RuO₂ sample, are shown in Fig. 6. Since the support materials were almost irreducible from 100 to 250 °C, the reduction peaks in this temperature range correspond to the reduction of different kinds of ruthenium oxides. Particularly, the reduction peaks at ca. 180 and 230 °C are attributed to the reduction of crystallized RuO₂ to Ru⁰ in well-dispersed form and bulk form, respectively [26,27]. The reduction peak at 125 °C in the low temperature range is attributed to the reduction of poorly crystallized or so-called amorphous bulk RuO₂. The reduction peak at higher temperature of 150 °C is attributed to the reduction of amorphous RuO₂ with Ru–support interaction while reduction peak at the lower temperature of 105 °C is attributed to the reduction of highly dispersed amorphous RuO₂. The reduction peak at 75 °C in the TPR profile of reference amorphous RuO₂ sample should be attributed to the reduction of atomically dispersed Ru⁴⁺ [28]. As seen in Fig. 6, multiple H₂ reduction peaks are observed on Ru catalysts, indicating the formation of different kinds of ruthenium oxides. The TPR profiles are carefully deconvoluted and the amount of H₂ consumption of each reduction peak is summarized in Table 2. The total H₂ consumption indicated that most ruthenium oxides existed in the state of Ru⁴⁺, i.e. RuO₂. By comparing the TPR data in Table 2 with the activity data in Fig. 4, we easily find that ruthenium oxides reducible at lower temperature exhibited higher activity for NO oxidation. As for Ru/TiO₂, Ru/TiO₂-R and Ru/ZrO₂, only amorphous ruthenium oxides reducible at low temperature were formed on supports, so high NO oxidation activity were observed on these catalysts. In the case of Ru/Al₂O₃, a large proportion of ruthenium species existed in the form of bulk RuO₂ that could be reduced at relative high temperature (XRD patterns in Fig. 5 and TPR profiles in Fig. 6), so Ru/Al₂O₃ exhibited the lowest activity.

The effect of Ru loading (0.5–4%) in Ru/TiO₂ on the activity of NO oxidation was studied and the results are shown in Fig. 7. As expected, Ru/TiO₂-4% exhibited the highest activity while Ru/TiO₂-0.5% exhibited the lowest activity. However, it is also found that Ru/TiO₂-4% only showed a little higher activity than Ru/TiO₂-2% despite that the Ru loading was doubled from 2% to 4%. In this work, Ru/TiO₂-2% was the most suitable catalyst for NO oxidation taking both the activity and the cost of catalyst into account. For a further understanding of the effect of Ru loading on the activity of catalyst, temperature-programmed reduction experiments were conducted to explore the ruthenium species formed on TiO₂ with different Ru loadings. The TPR profiles in Fig. 8 reveal that Ru mainly exists in the form of amorphous RuO₂ with Ru–support interaction in Ru/TiO₂-0.5% and Ru/TiO₂-1% (listed in Table 2). In the case of Ru/TiO₂-2%, more than 50% of Ru exists in the form of highly dispersed amorphous RuO₂ (reduction peak at 105 °C, in
Table 2). This is the most active Ru species for NO oxidation, so Ru/TiO$_2$ exhibits quite higher activity than Ru/TiO$_2$-1%. The dispersion of Ru decreased from 68.5% to 57.4% with Ru loading increasing from 2% to 4%, and a large proportion of ruthenium species (>40%) existed in the form bulk amorphous RuO$_2$ in Ru/TiO$_2$-4% (Table 2). Since the amount of most active highly dispersed amorphous RuO$_2$ was similar in Ru/TiO$_2$-2% and Ru/TiO$_2$-4% (referred to the data of H$_2$ consumption in Table 2), Ru/TiO$_2$-4% only exhibited a little high activity for NO oxidation than Ru/TiO$_2$-2%.

3.3. Effects of experimental conditions on NO oxidation over Ru/TiO$_2$

We have investigated the effects of initial NO concentration in the gas stream on NO oxidation at a constant oxygen concentration of 10%. As shown in Fig. 9, the NO conversion to NO$_2$ decreases slightly with initial NO concentration increasing from 200 to 800 ppm. Particularly, the maximal NO conversion of ca. 95% is observed at 275 °C with initial NO concentration of 200 ppm while the maximal NO conversion of ca. 88% is observed at 300 °C with initial NO concentration of 800 ppm. Obviously, the oxidation of NO on Ru/TiO$_2$ catalyst is not an apparent first-order reaction under these reaction conditions.

### Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>First reduction peak</th>
<th>Second reduction peak</th>
<th>Third reduction peak</th>
<th>Total H$_2$ (μmol g$^{-1}$)</th>
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<tr>
<td></td>
<td>T (°C)</td>
<td>H$_2$ (μmol g$^{-1}$)</td>
<td>T (°C)</td>
<td>H$_2$ (μmol g$^{-1}$)</td>
</tr>
<tr>
<td>Ru/SiO$_2$</td>
<td>150</td>
<td>325.7</td>
<td>180</td>
<td>61.9</td>
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<tr>
<td>Ru/Al$_2$O$_3$</td>
<td>125</td>
<td>120.7</td>
<td>180</td>
<td>49.3</td>
</tr>
<tr>
<td>Ru/ZrO$_2$</td>
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<td>67.9</td>
<td>125</td>
<td>309.7</td>
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<tr>
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<td>69.8</td>
<td>190</td>
<td>317.5</td>
</tr>
<tr>
<td>Ru/TiO$_2$R</td>
<td>105</td>
<td>67.1</td>
<td>125</td>
<td>287.6</td>
</tr>
<tr>
<td>Ru/TiO$_2$</td>
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<td>205.8</td>
<td>125</td>
<td>73.5</td>
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<tr>
<td>Ru/TiO$_2$-0.5%</td>
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<td>4.7</td>
<td>150</td>
<td>99.2</td>
</tr>
<tr>
<td>Ru/TiO$_2$-1%</td>
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<td>5.2</td>
<td>125</td>
<td>24.7</td>
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<tr>
<td>Ru/TiO$_2$-4%</td>
<td>105</td>
<td>230.1</td>
<td>125</td>
<td>366.3</td>
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<td>250</td>
<td>177.2</td>
<td>280</td>
<td>154.3</td>
</tr>
</tbody>
</table>

* Theoretical value = Ru loadings (wt%) × 19.8 mmol g$^{-1}$ (RuO$_2$ + 2H$_2$ → Ru + 2H$_2$O).
The effects of GHSV on NO oxidation over Ru/TiO<sub>2</sub> are shown in Fig. 9. In this work, a very high GHSV of 180,000 h<sup>-1</sup> was generally employed to reduce the amount of catalysts needed, so as to reduce the cost of catalysts. From Fig. 9, it is seen that NO conversion to NO<sub>2</sub> decreases with increasing GHSV from 135,000 to 540,000 h<sup>-1</sup>. However, a maximal NO conversion of c.a. 84% could be obtained at 325°C even at the highest GHSV of 540,000 h<sup>-1</sup>. Also, it is possible to control the ratio of NO:NO<sub>2</sub> in the product, e.g. 1:1 for fast SCR, by changing the loadings of catalysts, i.e. adjusting the GHSV.

Since in a real NO emission source there are some SO<sub>2</sub> and water vapor in the stream, it is necessary to clarify their effects on NO oxidation. Water vapor in the reaction stream presents a negative impact on NO oxidation. As shown in Fig. 10, the presence of 2% H<sub>2</sub>O reduces the NO conversion by 20–30% at 250–275°C. The inhibition effect caused by water vapor is supposed to be due to the following reaction [29]:

2NO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O → 2OH<sup>-</sup> + NO + NO<sub>2</sub> + O<sub>2</sub>

The addition of water vapor accelerated the decomposition of nitrate species on catalysts, which produced both NO and NO<sub>2</sub>. As a result, NO conversion to NO<sub>2</sub> decreased slightly. The presence of 40 ppm SO<sub>2</sub> in the stream shows serious negative effect on N<sub>2</sub>O decomposition. As seen in Fig. 10, the maximal NO conversion decreases from c.a. 94% to c.a. 69% and the temperature for maximal NO conversion increases from 275 to 350°C with the addition of 40 ppm SO<sub>2</sub>. Moreover, higher concentration of SO<sub>2</sub> may cause more serious deactivation of Ru/TiO<sub>2</sub> for NO oxidation (not shown in this work). SO<sub>2</sub> poisoning is known as the most serious problem for NO catalytic oxidation since catalysts preferred to convert SO<sub>2</sub> to SO<sub>3</sub> (2SO<sub>2</sub> + O<sub>2</sub> → 2SO<sub>3</sub>) instead of oxidation of NO. The formed SO<sub>3</sub> may not only occupy the active sites for NO oxidation but also cover the support materials by forming sulfates [11]. In this work, we selected SO<sub>2</sub>-resistant TiO<sub>2</sub> as the support and tried to diminish the negative effect of SO<sub>2</sub> on NO oxidation. To our glad, Ru/TiO<sub>2</sub> appears to be relatively SO<sub>2</sub>-resistant and NO oxidation activity over Ru/TiO<sub>2</sub> is sustainable in the presence of SO<sub>2</sub> at below 40 ppm level. When 2% water vapor and 40 ppm SO<sub>2</sub> coexist in the stream, the total inhibition effects are approximately accumulative (as seen in Fig. 10). On a whole, Ru/TiO<sub>2</sub> exhibits considerable activity for NO oxidation even in the present of water vapor and SO<sub>2</sub>, i.e. the simulated condition of industrial NO emission sources.

### 3.4. Effects of catalysts pretreatment conditions on NO oxidation over Ru/TiO<sub>2</sub>

The effects of catalysts pretreatment conditions on NO oxidation over Ru/TiO<sub>2</sub> are shown in Fig. 11. It is seen that the pre-oxidized sample (O<sub>2</sub>, 450°C) is much more active than the pre-reduced sample (H<sub>2</sub>, 450°C), indicating that Ru in oxides form (Ru<sup>4+</sup>) was more active than Ru in metal form (Ru<sup>0</sup>). It is also seen that thermal treatment in O<sub>2</sub> at higher temperatures results in the serious deactivation of Ru/TiO<sub>2</sub>. For example, the maximal NO conversion decreased to c.a. 20% on sample treated at 750°C. As is known, thermal treatment of TiO<sub>2</sub> leads to the transformation of anatase TiO<sub>2</sub> phase to rutile TiO<sub>2</sub> phase [30]. In the case of Ru/TiO<sub>2</sub>, the transform of anatase to rutile caused by thermal treatment was suppressed to some extent by the addition of Ru, as indicated by XRD patterns in Fig. 5. Since rutile phase TiO<sub>2</sub> was better support than anatase TiO<sub>2</sub> (Section 3.2),
the transformation of anatase to rutile was not the main cause for the deactivation of Ru/TiO₂ by thermal treatment. The TPR profile of Ru/TiO₂-750 in Fig. 8 showed reduction peaks at 250 and 280 °C, while the TPR profile of Ru/TiO₂ sample shows multiple reduction peaks at below 200 °C. The relay of Ru reduction indicated the strong interaction between Ru and TiO₂ support in Ru/TiO₂-750 sample, probably RuO₂ going into the matrixes of TiO₂. Meanwhile, the dispersion of Ru species also decreased from 68.5% to 10.5% after thermal treatment (Table 1). In our opinion, the formation of Ru species reducible at much higher temperatures was responsible for the lower activity of Ru/TiO₂-750. Except for the formation of Ru species reducible at higher temperatures, it was also found that some Ru left the catalyst after thermal treatment at 750 °C (Table 1), due to the formation of volatile RuO₄ at above 700 °C (RuO₂ + O₂ → RuO₄) [31].

3.5. In situ DRIFT study of NO and NO–O₂ adsorption on Ru/TiO₂

Introduction of NO (1% in He) to Ru-TiO₂ sample at room temperature results in the appearance of several bands corresponding to various coordinated nitrites/nitrates, as displayed in Fig. 12. The bands at 1630 and 1320 cm⁻¹ are assigned to the bridging nitrates at Ru–TiO₂ interface [32]. The band at 1440 cm⁻¹ is assigned to mono-nitrite [33] while the band at 1350 cm⁻¹ is assigned to chelating nitrates [34]. The intensity of IR bands corresponding to nitrates/nitrites increased with increasing adsorption time, and new IR band corresponding to mono-dentate nitrate [35] at 1500 cm⁻¹ appeared after 9 min of NO adsorption. The surface species formed after NO adsorption on Ru/TiO₂ differ greatly from those on pure TiO₂ support reported by Hadjiivanov and Knozinger [36]. The modification of Ru to TiO₂ changes the oxidative activity and suppresses the formation of adsorbed nitrosyls (IR bands at 1966–1710 cm⁻¹). Since Ru/TiO₂ is able to oxidize NO to nitrite or nitrate species at room temperature, Ru/TiO₂ is expected as outstanding catalysts for NO oxidation at higher temperatures.

In situ DRIFT spectra obtained under reaction conditions over Ru/TiO₂ at different temperatures are shown in Fig. 12. At 150 °C, strong bands at 1630, 1600, 1500 and 1305 cm⁻¹ as well as weak bands at 1875 and 1370 cm⁻¹ have been observed. The bands at 1630 and 1600 cm⁻¹ are assigned to different kinds of bridging nitrates [32,33], while the band at 1305 cm⁻¹ is assigned to chelating nitrites [34]. The band at 1500 cm⁻¹ is assigned to mono-dentate nitrate and the band at 1370 cm⁻¹ is assigned to free nitrates [37]. The band at 1875 cm⁻¹ is assigned to adsorbed NO species [38], most probably on RuO₂.

With increasing temperature, the intensity of IR bands associated with free nitrates increased gradually, while the intensities of IR bands associated with chelating nitrates and mono-dentate nitrate decreased gradually. Meanwhile, the intensities of IR bands associated with bridging nitrates remained
nearly unchanged. As for the IR band associated with adsorbed NO species, the band intensity increased first to a maximum (at 250 °C) and then began to decrease with increasing temperature. Based on the in situ DRIFT spectra, the NO oxidation mechanism on Ru/TiO₂ catalyst is proposed as following. In the first step, gaseous NO adsorbs on the surface of RuO₂ as NO(g) + * → NO(•) (active sites). The adsorbed NO species reacts with active oxygen to produce gaseous NO₂, with the release of the active sites (-NO + O → NO₂(g) + *). In another possible way, the adsorbed NO can be further oxidized to various nitrates and migrate to the TiO₂ supports [39], known as -NO + 2O → NO₃⁻. The bridging nitrates are relative stable nitrates at below 350 °C [33], so that they almost keep unchanged with increasing temperature, as indicated by Fig. 12. The chelating nitrates and mono-dentate nitrates are unstable species and they may decompose to give out NO₂ [40]. There are two possible pathways for the formation of gaseous product NO₂: the direct oxidation of adsorbed NO and the decomposition of surface nitrates. It is quite difficult to distinguish exactly which is the main pathway for NO₂ formation. In our experiments, the oxidation of NO to nitrates/nitrates takes place at room temperature (FTIR results), while the obvious oxidation of NO to gaseous NO₂ can only be observed at >175 °C (catalytic results). From this point of view, we prefer that NO₂ be originated by the decomposition of surface nitrates in the way as following: 4NO₂(g) → 4NO(g) + 1O₂(g) + 2-O. At high temperatures of >275 °C, the catalytic decomposition NO₂ takes place accompanied by the oxidation of NO and as a result the NO conversion to NO₂ drops along the thermodynamic equilibrium.

4. Conclusion

The catalytic oxidation of NO over a series of TiO₂ supported catalysts prepared by impregnation method was studied. Ru/TiO₂ catalyst was found to be the most active among catalysts. The activities of Ru catalysts were related to support choice, Ru loadings, pretreatment conditions and reaction conditions. TiO₂ P25 with both anatase and rutile phase appeared to be the most suitable support of Ru and the optimal Ru loading was determined to be c.a. 2%. Increasing initial NO concentration and GHSV lowered the NO conversion to NO₂ over Ru/TiO₂ catalyst to some extent. Thermal treatment of catalyst at high temperature resulted in a severe deactivation of Ru/TiO₂ catalyst. The presence of H₂O and/or SO₂ in the reaction system showed obvious negative effects on NO oxidation over Ru/TiO₂. However, Ru/TiO₂ still exhibited considerable activity for NO oxidation even under the simulated condition of industrial NO emission sources. The formation of different kinds of RuO₂ species was observed on Ru catalysts and highly dispersed amorphous RuO₂ was proposed to be the most active Ru species.

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