Effects of synthesis methods on catalytic activities of CoO<sub>x</sub>−TiO<sub>2</sub> for low-temperature NH<sub>3</sub>-SCR of NO

Li Zhu**, Yiqing Zeng**, Shule Zhang*, Jinli Deng, Qin Zhong*

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

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Introduction

NO<sub>x</sub> including NO and NO<sub>2</sub>, emitted from stationary sources, causes a variety of harmful effects on the ecological environment and human health, such as ozone depletion, photochemical smog and acid rain (Liu et al., 2011a; Gao et al., 2011; Bu et al., 2014). Selective catalytic reduction of NO by NH<sub>3</sub> (NH<sub>3</sub>-SCR) is known as one of the most efficient technologies for removing nitrogen oxides (Zhu et al., 2000; Klimczak et al., 2010). The well-known commercial catalyst for power plant NO<sub>x</sub> emissions is vanadium–titanium catalytic system, e.g., V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> based catalysts promoted by WO<sub>3</sub> and/or MoO<sub>3</sub> (Parvulescu et al., 1998). Unfortunately, some inevitable drawbacks are presented during the industrial applications, such as the toxicity of vanadium species, the high oxidation of SO<sub>2</sub> to SO<sub>3</sub>, and the poor activity at low-temperature regions (Liu et al., 2011b; Dunn et al., 1998). Generally, in order to avoid the catalyst deactivation caused by the high concentration of ash and SO<sub>2</sub> poison, the SCR equipment is installed at the downstream of the electrostatic precipitator and desulfurizer (Gao et al., 2011; Koebel et al., 2000; Pourkhalil et al., 2013). As a result, the temperature of flue gas is usually below 270°C or even lower. Therefore, the development of the SCR catalysts that can exhibit high activity at low temperatures (100–270°C) for avoiding the high cost of reheating the flue gas has attracted lots of attention from the scientific academy.

In the past few years, many efforts have been made to study transient metal-based catalysts for the low-temperature SCR of NO<sub>x</sub>. Peña et al. (2004a) reported catalysts of TiO<sub>2</sub>-supported first row transition-metal oxides, which showed effective for NH<sub>3</sub>-SCR. Boningari studied the effects of co-doping the transition-metal on Mn/TiO<sub>2</sub> catalyst for low-temperature SCR of NO<sub>x</sub> (Boningari, 2001). In this work, a series of cobalt doped TiO<sub>2</sub> (Co-TiO<sub>2</sub>) and CoO<sub>x</sub> loaded TiO<sub>2</sub> (Co/TiO<sub>2</sub>) catalysts prepared by sol–gel and impregnation methods respectively were investigated on selective catalytic reduction (NH<sub>3</sub>-SCR) of NO. It was found that Co-TiO<sub>2</sub> catalyst showed more preferable catalytic activity at low temperature range. From characterization results of XRD, TEM, Raman and FT-IR, Co species were proved to be doped into TiO<sub>2</sub> lattice by replaced Ti atoms. After being characterized and analyzed by NH<sub>3</sub>-TPD, PL, XPS, EPR and DRIFTS, it was found that the better NH<sub>3</sub>-SCR activities of Co-TiO<sub>2</sub> catalysts, compared with Co/TiO<sub>2</sub> catalyst, were ascribed to the formation of more oxygen vacancies which further promoted the production of more superoxide ions (O<sup>2-</sup>). The superoxide ions were crucial for the formation of low temperature SCR reaction intermediates (NO<sub>3</sub><sup>-</sup>) by reacting with adsorbed NO molecule. Therefore, these aspects were responsible for the higher low temperature NH<sub>3</sub>-SCR activity of Co-TiO<sub>2</sub> catalysts.
NH₃-SCR (Thirupathi and Smirniotis, 2011). Researchers also reported the relation of surface properties of TiO₂-supported transition-metal oxide catalysts and their NH₃-SCR activities (Boningari et al., 2015). Because of the advantages of cobalt species, such as good oxidizing ability to NO, inexpensive and lasting activity, some cobalt containing catalysts have been studied. Wang et al. (2010) reported CoOₓ/TiO₂ catalysts synthesized by sol–gel method which showed good NO catalytic oxidation behaviors. It has been reported that oxygen vacancies and superoxide ions (O₂⁻) were important to low-temperature NH₃-SCR (Zhang et al., 2014). And Wang et al. (2001) reported the effects of O₂ for SCR reaction of cobalt-based catalysts. Therefore, the paper tried to improve the promotion effect of O₂ by different synthesis methods and proposed preparing catalysts by sol–gel and impregnation methods. The TiO₂ support is commonly used in the SCR of NO with NH₃. Considering the reasons above, we put forward the idea of using TiO₂ as the support of cobalt species. Thus, the catalyst can be applied in the low-temperature NH₃-SCR reaction.

In this study, Co/TiO₂ and Co-TiO₂ catalysts were prepared by sol–gel and impregnation methods, respectively. And compared with Co/TiO₂ catalysts, Co-TiO₂ catalysts showed higher low-temperature SCR catalytic activities. A series of test methods were used to investigate the promoting effect of Co species doping and redox behaviors. It would contribute to a better understanding of the low-temperature SCR processes over Co species doped TiO₂ catalysts.

1. Experimental

1.1. Catalyst preparation

The Co species doped TiO₂ catalysts were prepared by sol–gel method, specifically as follows: A stoichiometric amount of Co(NO₃)₂·6H₂O was dissolved into 1.37 mol ethanol and 0.058 mol tetrabutyl titanate (C₁₆H₃₆O₄Ti) was added under vigorous stirring at 30°C to obtain solution A, and 0.14 mol acetic acid and 0.34 mol ethanol were dissolved in 0.45 mol deionized water to obtain solution B. Subsequently, the solution B was dropped into the solution A under vigorous stirring to obtain transparent sol. The transparent sol was kept at 30°C for 1 day, and then transformed to gel. Then the gel was dried at 120°C for 12 hr and calcined in muffle furnace at 500°C for 3 hr.

CoOₓ loaded TiO₂ catalysts were prepared by a sol–gel method for the TiO₂ support preparation, followed by impregnation of CoOₓ. Specific steps are as follows: The TiO₂ obtained from sol–gel method above was used as the support to prepare CoOₓ loaded TiO₂ catalysts by impregnation method. 2.0 g TiO₂ support was added to a 100 mL crucible containing a stoichiometric amount of Co(NO₃)₂·6H₂O and 2.78 mol deionized water with continuous heating at 30°C and stirring for 2 hr. The impregnated sample was dried in an oven at 120°C for 6 hr and followed by calcination in air at 500°C for 3 hr. Finally, the CoOₓ loaded TiO₂ catalysts were obtained. The catalyst was denoted as CoₓTiO₂−y, where y represents the molar percentage of Co/Ti element. All catalysts were ground and sieved to 40–60 mesh for activity evaluation. Hereafter we chose Co-TiO₂-5 and Co/TiO₂-5 as primary study objects, which were named as Co-TiO₂ and Co/TiO₂.

1.2. Catalytic activity tests

The SCR activity measurements were carried out at 120–275°C in a fixed-bed flow reactor (i.d. 6.8 mm) under atmospheric pressure. The simulated flue gas containing 500 ppm NO, 600 ppm NH₃, 5 vol% O₂ and balanced with N₂ at a total flow rate of 150 mL/min, which was corresponded to a gas hour space velocity (GHSV) of 41,000 hr⁻¹. 0.3 g of catalyst was placed in the center position of the reactor. The mixed gases were firstly controlled by a mass flow controller, and then entered the reactor through a preheater. The reaction temperature was measured by a type K thermocouple inserted into the catalyst bed. Each catalyst was adsorbed by the reaction gas before the reaction in order to avoid errors caused by NO adsorption on the catalyst. The concentrations of NO and NOₓ were continually monitored by a Flue Gas Analyzer (Germany ECOM-JZKN). For each temperature, the activity of the catalyst was determined after 1 hr reaction time before the concentration analysis. The NO removal efficiency was calculated by the following equation:

\[
\text{NO conversion} = \frac{\text{NO(in)} - \text{NO(out)}}{\text{NO(in)}} \times 100\%
\]

where NO(in) and NO(out) were the NO inlet and outlet.

1.3. Catalyst characterization

X-ray diffraction (XRD) was performed on a XD-3 diffractometer using Cu-Kα radiation (\(\lambda = 0.15406 \text{ nm} \)) in the 2θ interval 5–80° (Beijing Purkinje General Instrument Co., Ltd., China). The scanning speed is 8°/min and the step value is 0.04°.

Oxygen vacancies were characterized by photoluminescence (PL) spectra at room temperature using a Labram-HR 800-typespectro-photometer (Jobin Yvon Co., France) with a He–Cd laser (\(\lambda = 325 \text{ nm} \)) as the light source.

The micromorphology of the catalysts was examined on a JEOJEM-2100 transmission electron microscope (TEM), and the sample was deposited on a copper mesh by means of dipcoating. The acceleration voltage is 200 kV.

Raman spectra were recorded on a Renishaw Invia RamanMicroscope with Ar⁺ radiation (514 nm). The laser light was focused onto the samples by using a microscope equipped with a \(\times 50 \) objective lens.

The X-ray photoelectron spectroscopy (XPS) was conducted using a PHI Quantera II (ULVAC-PHI, Japan) XPS System equipped with monochromatic Al-Kα excitation. All binding energies (BE) were referenced to the adventitious C 1s at 284.8 eV. This reference gave BE values with an accuracy at ±0.1 eV. And the atomic surface ratios of the corresponding species were given with the accuracy at ±0.1%. The penetration depth of the XPS probe is 10 nm.

Ammonia temperature-programmed desorption (NH₃-TPD) and hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out on an automated chemisorption analyzer (Quanta-chrome Instruments). The amounts of NH₃
desorption and the consumption of H$_2$ in He was detected by a TCD. About 0.1 g sample was used. The NH$_3$-TDP experimental began with NH$_3$ adsorption under a flow rate of 70 mL/min at room temperature for 1 hr, and then the temperature was increased linearly at a rate of 10°C/min. In the H$_2$-TPR experimental, the sample was purged with 70 mL/min He at 50°C for 0.5 hr and then heating the sample to 800°C at a rate of 10°C/min after switched to a H$_2$/N$_2$ gas mixture (10% H$_2$, V/V) at a flow rate of 70 mL/min.

The Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements were performed on a Nicolet IZ10FTIR spectrometer equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. Each spectrum was recorded at 4 cm$^{-1}$ resolution with 32 accumulated scans. In the DRIFTS cell, the catalyst was pretreated at 300°C in He for 2 hr and then cooled to the 275°C. After the background spectrum was recorded with the flowing of He and was subtracted, the sample was exposed to NO and O$_2$ and the DRIFTS spectra were recorded.

Electron paramagnetic resonance (EPR) spectra were carried out on a Bruker EMX-10/12 X-band (9.7 GHz) spectrometer at room temperature.

2. Results and discussion

2.1. Catalytic activity tests

Fig. 1a shows NO conversions over various catalysts at different reaction temperatures. As we can see, the pure TiO$_2$ showed low catalytic activity and the NO conversion increased slowly with the rise of temperature. However, the samples Co-TiO$_2$-5 and Co/TiO$_2$-5 showed better catalytic performances and the NO conversion increased evidently with the rise of temperature in the low temperature range (120–275°C). It can be seen clearly that the introduction of Co species could significantly improve the NO conversion. Especially for Co-TiO$_2$-5, it had higher catalytic activity than Co/TiO$_2$-5 and pure TiO$_2$ in the low temperature range and the NO conversion reached 64.1% at 275°C, and 35.1% higher than that of Co/TiO$_2$-5 at 275°C. Thus, it is possible that different preparations of samples led to their different SCR performances.

Fig. 1b shows the NH$_3$-SCR performance of catalysts with different molar ratios of Co/Ti from 0.05 to 0.1 in the low temperature range. For all catalysts, NO conversion increased with the rise of temperature. The NO conversions was promoted with the increase of Co doping until the molar ratio of Co/Ti reached 0.08, and the NO conversion of Co-TiO$_2$-8 reached 74.2% at 245°C. A further increase the amount of the Co doping would result in the decline of catalytic activity. The reason might be the agglomeration of Co species at such a high molar content, which would be discussed at next section. Based on above results, it can be concluded that an appropriate amount of Co was conducive to improve the activity of the catalyst for low temperature NH$_3$-SCR of NO. Furthermore, the 5% H$_2$O was introduced to test the hydrothermal stability Co-TiO$_2$-5 catalyst at 22°C (shown in Fig. S1). The lowest NO conversion with H$_2$O was 50%. It was worth noting that as the H$_2$O cut off, the NO conversion could recovery to 56.5%. Therefore, the Co-TiO$_2$-5 had a good hydrothermal stability.

2.2. XRD and TEM analysis

In order to investigate the effect of Co species doping on the bulk structure of the catalysts, XRD test was carried out. Fig. 2 shows the XRD patterns of pure TiO$_2$, Co/TiO$_2$-5, Co/TiO$_2$-10, Co-TiO$_2$-5, Co-TiO$_2$-8 and Co-TiO$_2$-10 catalysts. As shown in Fig. 2, the characteristic peaks as attributive indicator of TiO$_2$ anatase phase were at about 25.2°, 37.79°, 47.97°, 53.85°, 62.73°, 70.2° and 75.2°, which corresponding to peaks of (101), (004), (200), (105), (204), (220), (215) (PDF-JCPDS 71-1166). All catalysts, except for Co/TiO$_2$-10 and Co-TiO$_2$-10, were in pure anatase form without any rutile peak and did not show any secondary phases, such as metallic cobalt, CoO, CoTiO$_3$, Co$_3$O$_4$. Furthermore, there no obvious cobalt oxide phase in Co/TiO$_2$-10 and Co-TiO$_2$-10, indicating that the Co species well dispersed when Co/Ti (molar) less than 0.1. It is worth noting that the (101) peak of Co-TiO$_2$-5, Co-TiO$_2$-8 and Co-TiO$_2$-10 shifted slightly to a lower angle when compared with the TiO$_2$. The doping of foreign species would shift the position of diffraction peak (Das et al., 2009). Therefore, the shift of (101) peak might be the consequence of the doping of Co species into TiO$_2$ lattice. Many studies (Das et al., 2008) have reported that the radius of cobalt ions is larger than that of Ti$^{4+}$ in TiO$_2$, and the XRD diffraction peaks of TiO$_2$ should be shifted to a lower diffraction angle after cobalt ions doping into the TiO$_2$ lattice. Thus, these results above confirmed well
incorporation of Co species into anatase lattice of TiO₂ and then changed the local structure around Ti ions. And compared with pure TiO₂, the corresponding d₁₀₁ value of Co-TiO₂-5, Co-TiO₂-8 and Co-TiO₂-10 was 0.3645 nm, 0.3723 nm and 0.3701 nm, which were larger than that of pure TiO₂ (0.3533 nm). The lattice parameters of all samples (Table 1), analysis by Rietveld refinement of the corresponding XRD data, showed that the doped samples have larger lattice parameters. Therefore, we can conclude that a certain amount of Co species were doped into the TiO₂ lattice for doping catalysts. Because of the small size of the particles, some Co species may sit on grain boundary instead of incorporating into the host lattice interior, this can be seen from the widening of the (101) peak with increasing dopant content (Choudhury and Choudhury, 2012). As we know, due to the different ionic charges oxygen vacancies (Vo) (Das et al., 2009; Choudhury and Choudhury, 2012). As we go on analyzing the FTIR spectra of all catalysts. In these spectra, the peaks coming at 3687.3 cm⁻¹ for all the samples were attributed to surface hydroxyl groups (Music et al., 1997) and the peaks appearing at 1615.8 cm⁻¹ were attributed to H–O–H bending vibration mode of physical adsorbed water (Choudhury and Choudhury, 2012). Generally, Ti–O frequency peaks appeared between 600 and 400 cm⁻¹ (Choudhury and Choudhury, 2012). Therefore, we can conclude that a certain amount of Co species were doped into the TiO₂ lattice for sample Co-TiO₂ and loaded on the surface of TiO₂ for sample Co/TiO₂. And this would support results of XRD and TEM.

The morphology of catalysts was investigated by TEM and HRTEM as shown in Fig. 3. The particle sizes were mainly in the range of 14–20 nm which were similar to results of Scherrer Equation. And Co-TiO₂ catalyst (Fig. 3b) was not clearly agglomerated. It can be seen from the TEM images that Co species doping inhibited the sintering of the particle seriously, resulting in particles behaved in the uniform morphologies, compared with that of the undoped samples. Additionally, according to the HRTEM images of catalysts, the lattice spacing of pure TiO₂ and Co/TiO₂ were determined to be 0.344 nm and 0.345 nm, which were assigned to the interplanar distance of anatase phase (101) plane. However, the Co-TiO₂ catalyst showed the lattice image with a lattice spacing of 0.35 nm, which was larger than of pure TiO₂ and Co/TiO₂. It might be that the introduction of foreign species expanded the interplanar spacing. These results were well consistent with the XRD results.

### Table 1 – Lattice parameters for all samples as a function of the XRD measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
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<tbody>
<tr>
<td>TiO₂</td>
<td>3.784</td>
<td>9.485</td>
<td></td>
</tr>
<tr>
<td>Co/TiO₂-5</td>
<td>3.784</td>
<td>9.486</td>
<td></td>
</tr>
<tr>
<td>Co/TiO₂-10</td>
<td>3.783</td>
<td>9.485</td>
<td></td>
</tr>
<tr>
<td>Co-TiO₂-5</td>
<td>3.789</td>
<td>9.486</td>
<td></td>
</tr>
<tr>
<td>Co-TiO₂-8</td>
<td>3.792</td>
<td>9.490</td>
<td></td>
</tr>
<tr>
<td>Co-TiO₂-10</td>
<td>3.793</td>
<td>9.514</td>
<td></td>
</tr>
</tbody>
</table>

XRD: X-ray diffraction.
These conformed well the formation of Co–O bond by substitution of Ti$^{4+}$ in the TiO$_2$ lattice (Choudhury and Choudhury, 2012). Thus, FTIR spectra can be taken as a tool to understand the formation of Co–O bond in the TiO$_2$ lattice and the formation of oxygen defects during the substitution of lattice Ti$^{4+}$ by Co species.

$$\text{TiO}_2 + q\text{Co}^{3+} \rightarrow \text{Ti}_{1-q}\text{Co}_q^{3+}\text{O}_2^{2-} + q/2\text{O}_2^- + q/2\text{Vo} + q\text{Ti}^{4+}$$  \hspace{1cm} (1)

### 2.4. PL analysis

Many studies (Liu et al., 2009; Ciardelli et al., 2004) have proved that nitro and nitrate groups were the intermediates in SCR reaction, which were beneficial to promote the SCR process at low-temperature. Oxygen vacancies can promote generating active oxygen species to promote the oxidation processes in SCR reaction. In this study, PL spectra were used to detect the oxygen vacancies in catalysts. The PL spectra of Co/TiO$_2$-5 (a), Co-TiO$_2$-5 (b) and pure TiO$_2$ (c) are shown in Fig. 6. The peak at 524 nm was assigned to the oxygen vacancy with one trapped electron, i.e., F$^+$ center (Lei et al., 2001; Saraf et al., 1998). And the peak at around 630 nm might be a consequence of the polarizability of the lattice ions surrounding the vacancy (Saraf et al., 1998). According to the reports, when the content of surface oxygen vacancies increased to a high level, the diversity of the surface state might slow the radiative recombination process of generating electrons and holes,
and thus decreased the intensity of the PL spectrum (Zhao et al., 2013; Xu et al., 2009; Kim et al., 2008; Yu et al., 2003). Therefore, compared to these three samples, Co/TiO$_2$-5 (a), Co-TiO$_2$-5 (b) and pure TiO$_2$ (c), it was found that the intensity of the PL peak for samples Co/TiO$_2$-5 (a) and pure TiO$_2$ (c) were much stronger than that of Co-TiO$_2$-5 (b), indicating that Co-TiO$_2$-5 had much more oxygen vacancies, especially the number of single-electron-trapped oxygen vacancy (F$^+$ center). Therefore, oxygen vacancies, generated due to the charge neutrality by Co species doping, could be reflected by the IR and PL spectra. It was reported that oxygen vacancies could absorb O$_2$ to form active chemisorbed oxygen (Nowotny et al., 2008), which was based on Eq. (2). Namely, the more oxygen vacancies, the more the chemisorbed oxygen was, which would be discussed in the next section. Surface chemisorbed oxygen, especially the superoxide radical, was the most active oxygen and plays an important role in oxidation reaction. This meant that Co-TiO$_2$ catalysts might have better activities for the better NO oxidation process.

\[
\text{VO}^+ + \text{O}_2 \rightarrow \text{absorbed oxygen}(\text{O}_2^\cdot, \text{O}_2^{\cdot-}) \tag{2}
\]

Based on contents above, the pulse transient studies were carried out to demonstrate the role of oxygen vacancies. According to results of the pulse transient studies (Fig. 7), catalytic activities of Co-TiO$_2$-5 and Co/TiO$_2$-5 reached stabilization at 275°C for 120 min, and decreased to minimum when the oxygen in the feed gas was cut off, and increased to maximum when oxygen was added again. However, the catalytic activity of Co-TiO$_2$-5 decreased slower when the oxygen flow was cut off and increased faster when the oxygen flow was added again compared with Co/TiO$_2$-5, which indicates that Co-TiO$_2$-5 had more oxygen vacancies which can adsorb oxygen and promote the SCR reaction decreasing slower to some extent at the moment of cutting the O$_2$ off. Similarly, oxygen vacancies could promote the activity increasing faster than catalyst Co/TiO$_2$-5. In this way, we can prove the promotion effect of oxygen vacancies.

Fig. 5 – Diffused reflectance infrared Fourier (FT-IR) spectra of the samples pure TiO$_2$, Co/TiO$_2$-5, Co-TiO$_2$-5 and Co-TiO$_2$-8.

Fig. 6 – PL spectra of samples (a) Co-TiO$_2$-5, (b) Co/TiO$_2$-5 and (c) pure TiO$_2$. PL: photoluminescence.

Fig. 7 – Pulse transient studies of samples Co/TiO$_2$-5 and Co-TiO$_2$-5. Conditions: 0.05% NO, 0.06% NH$_3$ at a total flow rate of 150 mL/min, GHSV-41000 hr$^{-1}$. GHSV: gas hour space velocity.
2.5. XPS analysis

The XPS was carried out to investigate the valence states of catalysts Co-TiO₂-5 and Co/TiO₂-5. And the XPS spectra of Co 2p, Ti 2p and O 1s in the mixed oxides are presented in Fig. 8.

Fig. 8a shows the Co 2p core level spectrum of catalysts Co/TiO₂-5 and Co-TiO₂-5. In the spectrum of Co-TiO₂-5 catalyst, four broad peaks in the Co 2p region were observed, the Co 2pₓ/₂ and Co 2pₜ/₂ peaks being at 781.4 and 797.3 eV, respectively, attributed to peaks of Co²⁺ (Manivannan et al., 2003). And the presence of strong shakeup satellites being at 786.32 and 803.2 eV on the high-energy side of the principal Co 2pₓ/₂ and Co 2pₜ/₂ lines were a typical characteristic of high-spin Co²⁺ (Jeong et al., 2004). Therefore, Co species were mainly in a bivalent state in Co-TiO₂-5. However, in the spectrum of Co/TiO₂-5 catalyst, the binding energy values of Co 2pₓ/₂ and Co 2pₜ/₂ appeared at 780.2 and 795.7 eV. The spectra were fitted with the Co²⁺ and Co³⁺ components, characterized by the binding energies at about 781.0 ± 0.2 and 779.1 ± 0.4 eV, respectively (Kang et al., 2003). Therefore, cobalt was mainly in the trivalent state in Co/TiO₂-5. Thus the presence of Co in a metallic state in both samples was completely ruled out, since the metallic Co 2pₜ/₂ had a peak position at 778.3 eV (Moulder et al., 1992). It is worth noting that the Co ions were mainly in a bivalent state in sample Co-TiO₂, while it was mainly in a trivalent state in precursor. Therefore, the interaction of Co ion with TiO₂ was strong over the Co-TiO₂-5 catalyst. The reason might be that the electron in the oxygen vacancies was captured by Co ions, resulting in decreasing of valence state. Therefore, the formation of Co²⁺ related to the generating of lots of single-electron-trapped oxygen vacancies. Thus, we can draw conclusions from the results of the XPS spectra that Co species doped in the TiO₂ lattice were mainly Co²⁺ and Ti⁴⁺ ions were substituted by Co²⁺ ions, which leads to the formation of oxygen vacancies in the Co doped samples. And based on the atomic ratios of the catalysts' surface determined from XPS analysis, we found that the atom ratios of Co/Ti was 0.239 and 0.06 (Table 2 Co atomic percentage/Ti atomic percentage) in Co/TiO₂-5 catalyst's surface and Co-TiO₂-5 catalyst's surface respectively, indicating that most Co species of Co-TiO₂-5 were doped into TiO₂ lattice compared with Co/TiO₂-5. Most of the heterogeneous reactions depend on the surface active components. However, Co-TiO₂-5 had a better catalytic activity with a lower surface Co species content compared with that of Co/TiO₂-5 on the basis of Table 2, indicating the oxygen vacancy and superoxide ions played an important role in the SCR reaction.

![Fig. 8 – XPS spectra of Co-TiO₂-5 and Co/TiO₂-5 (a): Co 2p, (b): Ti 2p, (c): O1s). XPS: X-ray photoelectron spectroscopy.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak (eV) Ti 2pₓ/₂</th>
<th>Atomic percentage (%) Ti 2pₓ/₂</th>
<th>Peak (eV) Ti 2pₜ/₂</th>
<th>Atomic percentage (%) Ti 2pₜ/₂</th>
<th>Peak (eV) Co 2pₓ/₂</th>
<th>Atomic percentage (%) Co 2pₓ/₂</th>
<th>Peak (eV) Co 2pₜ/₂</th>
<th>Atomic percentage (%) Co 2pₜ/₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/TiO₂-5</td>
<td>464.32</td>
<td>458.63</td>
<td>18.01</td>
<td></td>
<td>795.7</td>
<td>780.2</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Co-TiO₂-5</td>
<td>464.24</td>
<td>458.50</td>
<td>20</td>
<td></td>
<td>797.3</td>
<td>781.4</td>
<td>1.2</td>
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XPS: X-ray photoelectron spectroscopy.
Fig. 8b gives the XPS spectra of the core levels of Ti 2p3/2 and Ti 2p1/2 for Co/TiO2-5 to be approximately 458.63 and 464.32 eV, which were in excellent agreement with the values of Ti4+ in pure TiO2 (Moulder et al., 1992). The separation between Ti 2p3/2 and Ti 2p1/2 was 5.72 eV and the half-width of the peak of Ti 2p3/2 was 1.28 eV, which were consistent with 5.7 eV as the standard binding energy and 1.09 eV as the standard half-width, respectively (Das et al., 2009). However, the peaks corresponding to Ti 2p3/2 and Ti 2p1/2 of sample Co-TiO2-5 shifted to lower energies, being at 458.50 and 464.24 eV respectively, which suggested that the electron density of Ti4+ increased due to the introduction of cobalt ions. The cobalt intercalation also makes the binding energy of O 1s slightly shift toward a lower energy (Fig. 8c). These shifts can be attributed to the formation of Co–O between the host sheets and the guest cobalt species (Liu et al., 2013).

The binding energy of the O 1s peaks of Co/TiO2-5 and Co-TiO2-5 are shown in Fig. 8c. It was said that the binding energy of 529–530 eV was characteristic of lattice oxygen (Bensalem et al., 1995) (hereafter denoted as O0) and the binding energy of 531–533 eV might be assigned to defect oxide or the chemisorbed oxygen with low coordination situation (hereafter denoted as Oδ−)(Larachi et al., 2002). It could be seen that the O0 peak of Co/TiO2-5 shifted to lower binding energy, compared with that of Co/TiO2-5, indicating the increasing of electron cloud density of the lattice oxygen of sample Co-TiO2-5. Moreover, based on the area integral of the two peaks of O 1s photoemissions, the relative concentration ratio of Oδ−/(Oδ−+O0) was calculated. It can be seen that the ratio of Oδ−/(Oδ−+O0) was higher in Co-TiO2-5 catalyst than that of Co/TiO2-5 catalyst, which was calculated to be 29.87% and 22.64%, respectively. This result meant that the Co doping had a promoting effect on the formation of chemisorbed oxygen species. Researchers had proposed that the doped of Co species could make charge imbalance, promote generating vacancies and create unsaturated chemical bonds on the surface of catalysts, which would lead to the increase of chemisorbed oxygen on the catalyst surface (Zhang et al., 2014). Surface chemisorbed oxygen species have been reported to be the most active oxygen species and play an important role in oxidation reaction (Li et al., 2012). This meant that Co-TiO2-5 might have better activity for the better oxidation of NO than that of Co/TiO2-5.

2.6. NH3-TPD analysis

It was well known that surface acid sites that favor ammonia adsorption were important for NH3-SCR reaction. The strong surface acidity of catalyst was required to ensure sufficient NH3 adsorption and further activation (Xiong et al., 2013). Therefore, we compared the surface acidity of Co/TiO2-5, Co/TiO2-5 and pure TiO2 by NH3-TPD testing. As shown in Fig. 9, there was a broad peak for pure TiO2 from 200°C to 350°C, the typical NH3 desorption peak, which indicated that there were a certain amount of surface acid sites in pure TiO2 surface. Samples Co-TiO2-5 and Co/TiO2-5 showed broader NH3 desorption peaks from 300°C to 700°C, which were larger than that of pure TiO2, indicating that the introduction of Co species would increase catalysts’ surface acid sites. What’s more, it could also be seen that the intensity and corresponding area of the TPD peak of Co/TiO2-5 (area = 1113.34) were a little bit larger than that of Co/TiO2-5 (area = 1051.76), which meant that the Co/TiO2-5 had higher NH3 adsorption than that of Co-TiO2-5. This result implied that Co/TiO2-5 had more acid sites on the surface of catalyst compared with Co-TiO2-5. It was possible that the presence of Co3+ ions was responsible for this enhancement of the total acidity, due to its high tendency to form amino complexes (Moreno-Tost et al., 2002). Many studies have shown that the enhanced acidity was beneficial to the promotion of NH3 adsorption and activation (Peña et al., 2004b; Shan et al., 2012), which was believed to be crucial for the increase of the catalytic activity in NH3-SCR reaction. However, the NH3 adsorption of samples Co/TiO2-5 and Co-TiO2-5 were not consistent with their catalytic activities, which meant that the difference of catalytic activity might not due to the amount of acid sites. Thus, the performance of oxidation of NO would be focused in our study.

2.7. EPR analysis

The reaction mechanism involved the interaction of adsorbed ammonia (NH3) with gaseous NO for commercialized SCR processes at temperatures between 300 and 400°C. However, for low-temperature NH3-SCR process, Active NO3 (nitro and/or nitrate) groups are reported to be the intermediates that would react with adsorbed ammonia (Zhang and Zhong, 2013). Therefore, the formation of NO3 from gaseous NO was an essential process. As we know that NO3 groups were formed from NO and an adsorbed superoxide ions (Zhang and Zhong, 2013). Wang also proved that NO molecule could react with a superoxide ion to form NO3 in the SCR reaction (Wang et al., 2001). It followed the reaction as Eq. (3). Thus, Co/TiO2-5 might have better catalytic activity for higher amount of superoxide ions than that of Co/TiO2-5 catalyst. Therefore, we also investigated the content of superoxide ions on the catalysts’ surface.

\[ \text{NO} + \text{O}_2^− \rightarrow \text{NO}_3^- \]  

(3)

Fig. 10 shows EPR spectrum comparison of Co/TiO2-5, Co/TiO2-5 and pure TiO2. Based on the literature EPR data (Zhang and Zhong, 2013), the signals at g = 2.0061–2.0103 were assigned to the superoxide ions. We detected the signals at
\[ g = 2.0069 \] in this study. It could be seen in Fig. 10 that the intensity of \( g = 2.0069 \) of Co-TiO\(_2\)-5 and Co/TiO\(_2\)-5 was much higher than that of pure TiO\(_2\), indicating that the introduction of Co species would increase the amount of superoxide ions compared with pure TiO\(_2\). Furthermore, catalyst Co-TiO\(_2\)-5 had the stronger peak intensity which meant that it had more superoxide ions. It has been reported that oxygen vacancies generated by Co-doped could react with adsorbed O\(_2\) to form superoxide ions (Zhao et al., 2013). Thus, the sample Co-TiO\(_2\)-5 with more oxygen vacancies which had more superoxide ions could be concluded from PL and EPR results. These results suggested that the doping of cobalt species could improve the formation of superoxide ions on the catalyst. The catalytic activities of samples Co/TiO\(_2\)-5 and Co-TiO\(_2\)-5 were in good consistency with their corresponding EPR intensity.

### 2.8. H\(_2\)-TPR analysis

In NH\(_3\)-SCR reaction, the NO removal rate at low temperature largely depended on the redox properties of catalyst (Zhang et al., 2015). Therefore, the difference of catalysts in redox properties was investigated by H\(_2\)-TPR. As shown in Fig. 11, pure TiO\(_2\) displayed two peaks at 550-650\(^\circ\)C. For Co/TiO\(_2\)-5 catalyst, two new peaks were observed in spectra. Peak 1 might due to the dispersed Co species. For Co-TiO\(_2\)-5, two peaks, especially peak 1, had obviously shift to low temperature. And it was confirmed that the Co-TiO\(_2\)-5 catalyst possessed stronger redox properties. All of these well coincided with the results of EPR.

### 2.9. In-situ DRIFT spectra and the NO oxidation analysis

Fig. 12 shows in-situ DRIFT spectra of Co/TiO\(_2\)-5 and Co-TiO\(_2\)-5 catalysts exposed to 1000 ppm NO (1% in N\(_2\)) and O\(_2\) (20 mL/min) at 275\(^\circ\)C for various times (original spectra showed in Fig. S3). After pretreatment by N\(_2\), the IR spectra were recorded as a function of time, when NO + O\(_2\) was introduced. The DRIFT spectra of NO + O\(_2\) co-adsorption over Co/TiO\(_2\)-5 are shown in Fig. 11a. According to previous researches (Zhang et al., 2015; Yu et al., 2006), several peaks at 1602, 1529, 1480 and 1360 cm\(^{-1}\) could be assigned to bridging bidentate nitrates (1602 and 1530 cm\(^{-1}\)) and monodentate nitrates (1480 and 1360 cm\(^{-1}\)), respectively. However, as shown in Fig. 11b, five peaks at 1602, 1570, 1560, 1485 and 1360 cm\(^{-1}\) were observed in Co-TiO\(_2\)-5 spectra. The peaks at 1602 and 1570 cm\(^{-1}\) could be ascribed to bridging nitrates, the peaks at 1560 cm\(^{-1}\) could be assigned to...
chelating bidentate nitrates and the peaks at 1485 and 1360 cm\(^{-1}\) could be attributed to the monodentate nitrates. Simultaneously, the peak intensity of Co-TiO\(_2\)-5 located at 1650–1450 cm\(^{-1}\) and 1360 cm\(^{-1}\) much stronger than that of Co/ TiO\(_2\)-5 (Fig. S3). In addition, the peak intensity of Co/TiO\(_2\)-5 had no obvious change after NO + O\(_2\) adsorbed but that of Co-TiO\(_2\)-5 had a significant increase. It has been confirmed in the Section 2.4 (PL) that the doping sample (Co-TiO\(_2\)-5) had more oxygen vacancies, which promote the formation of more superoxide ions. Furthermore, it has been reported that the superoxide ions can react with NO to form nitrate species in the SCR reaction (Zhang et al., 2008). Thus, it indicated that the doping of Co species could more effectively promote the oxidation of NO to form nitrate species, which was in agreement with the results of H\(_2\)–TPR. Since that nitrate species could react with adsorbed NO to decompose to NO\(_2\) molecules in the SCR reaction which was beneficial to SCR (Wang et al., 2001). Therefore, the higher catalytic performance of Co-TiO\(_2\)-5 could be attributed to its strong oxidation abilities due to oxygen vacancies and superoxide ions.

Fig. 13 shows the NO conversion to NO\(_2\) for catalysts of Co/ TiO\(_2\)-5 and Co-TiO\(_2\)-5 at different O\(_2\) concentrations at 275°C. It could be seen that Co-TiO\(_2\)-5 showed higher oxidative activity at the O\(_2\) concentrations of 10%, 15%, 25% and 30% (volume ratio) than that of Co/TiO\(_2\)-5. And it reached the highest activity, which is 16.06% higher than that of Co/ TiO\(_2\)-5, at the O\(_2\) concentration of 10%. The above XPS, PL and EPR results indicated that Co doping was helpful to the formation of superoxide ions which could react with adsorbed NO to form nitrate species, and a further reaction with adsorbed NO to decompose to NO\(_2\) molecules in the SCR reaction. The result could prove that sample Co-TiO\(_2\)-5 possessed a better NO oxidation than sample Co/TiO\(_2\)-5, which might account for the better SCR activity of the doped sample to some extent.

3. Conclusions

In conclusion, Co-TiO\(_2\) and Co/TiO\(_2\) catalysts were respectively prepared by sol–gel and impregnation methods and the Co-TiO\(_2\) catalyst exhibited better catalytic activity than that of Co/TiO\(_2\) in low-temperature range. Through XPS, PL, EPR analysis, the excellent catalytic performance of doped catalysts were mainly attributed to the increasing amount of oxygen vacancies and superoxide ions, which were improved by the introduction of cobalt species. From the results of DRIFTS and NO oxidation test, it could be seen that the generating of superoxide ions could generate active nitrate species and promote the NO oxidation which could be good for SCR reaction. What was more important was that superoxide ions in chemisorbed oxygen, which were produced on oxygen vacancies, played a major role in the formation of nitrate species. All of the reasons above resulted in the improvement of SCR activity.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.jes.2016.09.014.

REFERENCES
