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The characterization and activity of F-doped vanadia/titania for the selective catalytic reduction of NO with NH_3 at low temperatures

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ABSTRACT

A F-doped vanadia/titania catalyst has been developed by partly substituting the lattice oxygen of the catalyst with fluorine, using NH_4F as a precursor. The aim of this novel design was to promote the activity of a catalyst with low vanadia loading in the low-temperature selective catalytic reduction of NO with NH_3. Analysis by N_2 physisorption, XPS, ICP, XRD, ESR and PL spectra showed that fluorine doping facilitated the formation of V^{4+} and Ti^{3+} ions mainly by charge compensation, promoted the distribution of vanadium on the catalyst surface, and increased the amount of surface superoxide ions. The catalytic activity of NO removal was promoted by F-doping. And the catalyst with $[F]/[Ti] = 1.35 \times 10^{-2}$ showed the highest NO removal efficiency in SCR reaction at low temperatures.

1. Introduction

Nitrogen oxides (NO_X) emitted from automobiles and stationary sources are major causes of acid rain as well as photochemical smog through their reactions with hydrocarbons. Selective catalytic reduction (SCR) of NO_X using NH_3 as a reductant is now widely used for the treatment of waste gases from stationary sources. The commercial catalyst for this deNO_X process is V_2O_5–WO_3 (MoO_3)/TiO_2 (anatase) with less than 1% V_2O_5 loading. The high operating temperature of this catalyst, typically 573–673 K, makes it necessary to locate the SCR unit upstream of the precipitator in order to avoid reheating the flue gas. Consequently, the life of the catalyst is shortened because of corrosion and abrasion from the high concentration of ash. When the temperature of the flue gas is above the operating temperature of the catalyst, the catalyst itself can become sintered and deactivated. In addition, the high temperature may cause side reactions, such as oxidation of NH_3 into NO and formation of N_2O [1]. However, this could be avoided by locating the SCR unit downstream of the precipitator and even downstream of desulfurizer, through the development of a low-temperature (<523 K) SCR. The end results of temperature reduction are an increase in the operational lifetime of the catalyst relative to existing configurations, as well as a lowering of investment costs.

The core of low-temperature SCR technology is the existence of a catalyst that is suitable for low-temperature flue gas conditions. For presently available vanadia/titania catalysts, performance of low-temperature SCR could be promoted by increasing the vanadia loading [1–4]. However, this has the shortcoming of decreasing the selectivity and lifetime of the catalyst as it facilitates SO_2 oxidation [5] and N_2O formation [2]. Recently, efforts have been made to promote low-temperature SCR performance of vanadia catalysts through the use of promoters such as 1%CrO_3–6%V_2O_5/TiO_2 [3] and 1%MO_x (M = Fe, Mn, Cu or Cr)–3%V_2O_5/mesoporous carbon-coated monoliths [6]. Other approaches have changed the support to materials such as 3–8%V_2O_5/carbon-coated monoliths [7–9], 1–7%V_2O_5/activated carbon fibers [10], 2.35%V_2O_5/carbon nanotubes [11], 1.7%V_2O_5/WO_X or SO_4^{2-}/ZrO_2 [12], 8%V_2O_5/TiO_2–SiO_2–MoO_3 [13], 3–7%VO_x ($x < 2.5$)/TiO_2 (supports obtained from different companies) [14]. However, these catalysts were unable to reduce the vanadia loading.

The aim of this study was to approach the problem from a different angle, by targeting the non-metal part of the catalyst. We describe a novel F-doped vanadia/titania catalyst formed by partly substituting the lattice oxygen of the catalyst with fluorine. In previous applications, F-doped and fluorinated TiO_2 has been used as a photocatalyst under visible light irradiation [15–20]. However, it has not previously been used as a support for a vanadia catalyst. Narayana et al. [21] revealed that the V^{4+} species increased with an increase in V_2O_5 loading over V_2O_5/AlF_3. Scheurell et al. [22–24], studying the selective oxidative dehydrogenation of propane (ODH), found that VO_x doped onto AlF_3 showed better redox ability of active vanadium species and more acid sites than

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did VO_x doped onto Al_2O_3. However, to the best of our knowledge, F-doped vanadia/titania catalysts for low-temperature SCR of NO with ammonia have not yet been studied.

The present study focuses on the structural and surface properties of a new catalyst formed by fluorine doping, which was characterized by N_2 physisorption, XPS, ICP, XRD, ESR and PL spectra. We also investigated the SCR activity of the catalyst at low temperatures, as well as the activity when H_2O and SO_2 existing. This information would contribute to a better understanding of the low-temperature SCR processes over a vanadia/titania catalyst.

2. Experimental

2.1. Catalyst preparation

The F-doped vanadia/titania catalyst was prepared by a sol–gel method for F-doped titania preparation, followed by impregnation for vanadia loading. The detailed procedure for F-doped titania preparation has been described elsewhere [15], specifically as follows: $Ti(OC_4H_9)_4$ (0.064 mol) was stabilized by adding 0.128 mol acetylacetone. A color change of the solution from pale yellow to orange occurred under continuous stirring. The solution was diluted with 50 mL of NH_4F ethanolic solutions [15]. After stirring for 2 h at room temperature, the sol was concentrated in a 333 K water bath and subsequently dried at 393 K for 6 h. The gel was calcined at 773 K for 3 h in air, and then sieved (0.701–0.833 mm). After impregnation in ammonium metavanadate solution (plus HNO_3 at pH 1) [25] in a 333 K water bath and refluxing for 4 h, the sieved titania was dried at 393 K for 6 h and subsequently calcined at 623 K for 4 h. Finally, the F-doped vanadia/titania catalyst was obtained. In the present study, the catalyst and the carrier were denoted as VTiF *x* and TiF *x*, respectively. For example, VTiF 1.35 meant the catalyst with fluorine content calculated as $[F]/[Ti] = 1.35 \times 10^{-2}$, and TiF 1.35 meant the carrier with the same fluorine content.

2.2. Catalyst characterization

The S_{BET} measurement was carried out in a Micrometrics ASAP 2000 apparatus at 77 K, using N_2 as the adsorption gas. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALB MK-II with Mg Kα source, calibrated by the C 1s peak at 284.6 eV with an accuracy of ±0.2 eV. The approximate content of vanadium was determined by inductively coupled plasma (ICP) spectroscopy (Thermo Electron; Model IRIS Interepid II XDL). The electron spin resonance (ESR) measurements were made at room temperature using a Bruker EMX-10/12-type spectrometer in the X-band. The photoluminescence (PL) spectra were conducted at room temperature using a Labram-HR800-type spectrophotometer (Jobin Yvon Co., France) with a He–Cd laser (λ = 325 nm) as the light source. The X-ray diffraction (XRD) analysis was obtained by a XD-3 diffractometer (Beijing Purkinje General Instrument Co., Ltd, China).

2.3. Activity tests

Catalytic activity tests of NO reduced by NH_3 were carried out at 393–513 K in a fixed-bed flow reactor (i.d. 6.8 mm) under atmospheric pressure. The gas flow was controlled by mass flow meters. The reaction temperature was measured by a K type thermocouple inserted directly into the catalyst bed. The used mass of the catalyst was 0.8000 g with quartz sand as inert. A reaction mixture containing 500 ppm NO + 600 ppm NH_3 + 5 vol.% O_2 + 600 ppm SO_2 (when used) + 2% or 4% H_2O (when used) balanced with N_2 at a flow rate of 150 mL min^{-1} was used, corresponding to a gas hour space velocity (GHSV) of 14,580 h^{-1}. Prior to the reaction, the catalyst sample was pre-adsorbed by the reaction mixture, to avoid a decrease of NO caused by adsorption on the catalyst. Analysis of reactants and products was carried out after a steady reaction of more than 1 h at each testing point. Concentrations of NO and SO_2 were analyzed by a MRU VARIO PLUS flue gas analyzer (Germany) after passing through concentrated phosphoric acid to avoid the influence of NH_3 on NO analysis. The N_2O was monitored by a Gasmet Dx-4000 FT-IR gas analyzer (Germany). The selectivity to N_2 is defined as N_2 divided by ($N_2 + N_2O$) on a N-atom basis. The NO conversion is defined as:

$$X = \frac{NO_{in} - NO_{out}}{NO_{in}} \quad (1)$$

The NO reaction rate was expressed by means of the following equation:

$$r = kP_{NO} \quad (2)$$

for which first order in NO partial pressure and zero order in NH_3 partial pressure was assumed. In order to compare the activities of different vanadium-loading catalysts, the rate constants k_m could be evaluated as follows:

$$k_m = -\frac{F^0_{NO}\ \ln(1-X)/w_m}{P^0_{NO}} \quad (3)$$

where P^0_{NO} is the NO partial pressure, F^0_{NO} is the inlet NO molar flux, and w_m is the vanadium mass [26].

3. Results and discussion

3.1. Characterization of the F-doped catalysts

3.1.1. Valences of titanium and vanadium

Lee et al. [14] revealed that the participation of lattice oxygen in the reduction of nitrogen oxide and the re-oxidation of gaseous oxygen into lattice oxygen were closely related to the electrons generated due to the valence change of vanadium. They suggested that the non-stoichiometric vanadium oxide produced on the catalyst could activate the electron transfer, thus improving the reduction and/or re-oxidation properties of the catalyst. For a F-doped vanadia/titania catalyst, considering the difference between fluorine and oxygen, we expected that the valences of titanium and vanadium would be influenced by fluorine doping. This was confirmed by the ESR and XPS characterizations of the samples.

The amounts of Ti^{3+} and V^{4+} ions present in both surface and bulk samples have been examined by ESR at room temperature (as shown in Fig. 1). Since the amount of vanadium loaded onto the catalyst was low (as shown in Table 1), the spectrum of the V^{4+} ion was not well-resolved. The spectra of F-doped samples showed a strong

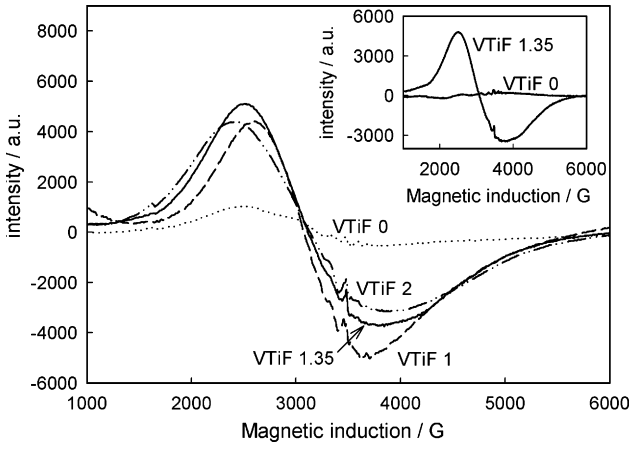

Fig. 1. ESR spectra of the catalysts at room temperature. Insert: ESR spectra of VTiF 0 and VTiF 1.35 after subtracting the ESR spectra of their supports, respectively.

Table 1
Vanadia content, BET specific area and the kinetic constants of the catalysts.

	V_2O_5 (wt.%)	S_{BET} ($m^2\ g^{-1}$)	k_m (483 K) ($\times 10^{-9}$ mol NO(g V)$^{-1}$ Pa^{-1} s^{-1})	k_m (513 K) ($\times 10^{-9}$ mol NO(g V)$^{-1}$ Pa^{-1} s^{-1})
VTiF 0	0.8	28.77	0.96	2.17
VTiF 1	1.2	20.93	10.51	15.64
VTiF 1.35	0.8	23.55	11.36	43.02
VTiF 2	0.9	27.66	4.81	9.84

and broad peak, related to the Ti^{3+} ion, which significantly reduced the spectral resolution of V^{4+} ion. Through an integral of this strong and broad peak, we could obtain that the peak area decreased as following order: VTiF 1.35 > VTiF 1 > VTiF 2 > VTiF 0. Within the detection depth of XPS, It shows that the binding energies of Ti 2p3/2, V 2p3/2, and O 1s of VTiF 1.35 shifted by 0.3, 0.35, and 0.45 eV, respectively, toward the low binding energy direction (as shown in Fig. 2), when compared with those of VTiF 0. Thus, there was a decrease in electrons both lost by Ti and V and gained by O, indicating that the valence states of Ti and V were not entirely +4 and +5, respectively. However, the F 1s was not observed, due to the low F-doping content (more details about the fluorine content in VTiF 1.35 evaluated from XPS are shown in the Supporting Information). The chemical states were analyzed in detail by deconvolution using Lorentzian–Gaussian mixture peak fitting. The deconvoluted XPS spectra (not shown) showed that the Ti^{3+}/Ti^{4+} ratios were 0.57 and 1.22 for VTiF 0 and VTiF 1.35, respectively. The V^{4+}/V^{5+} ratios were 0.79 and 1.19 for VTiF 0 and VTiF 1.35, respectively. The presence of V^{4+} was related to the condition of vanadia impregnation [25] and was promoted by F-doping. From the ESR and XPS characterizations, we can conclude that the samples in this study contained mixed valences of Ti and V, and that the amounts of V^{4+} and Ti^{3+} ions were promoted by F-doping. This indicated an improvement in the reduction and/or re-oxidation properties of the catalyst [21–24].

By subtracting the corresponding support spectrum (as shown in the insert of Fig. 1), the Ti^{3+} ion of the VTiF 0 sample was completely formed at the support preparation stage. In contrast, the Ti^{3+} ion of the F-doped sample VTiF 1.35 was formed primarily at the vanadium loading stage. Previous studies [27,28] have revealed that V^{4+} ions could be included as dopants inside a TiO_2 matrix, leading formally to a $V_xTi_{1-x}O_2$ solid solution. The cationic vacancies formed by Ti^{3+} moving to interstitial sites were considered to be the prerequisites for the introduction of V^{4+} ions into the TiO_2 matrix. Since Ti^{3+} ions were produced during heat-treatment due to the decomposition of organic compounds, the existence of Ti^{3+} and V^{4+} ions could be inferred. However, the amount of Ti^{3+} ion in the F-doped sample increased after vanadium loading, which indicated the existence of another process for the formation of V^{4+} ion in addition to the formation of $V_xTi_{1-x}O_2$. Therefore, it is reasonable to propose that there might be a charge compensation process [29,30] between vanadium and titanium, as in the following equations:

$$TiO_2 + qF^- \rightarrow Ti_q^{3+}Ti_{1-q}^{4+}O_{2-q}^{2-}F_q^- + q/2O^{2-} \quad \text{(I)}$$

$$Ti_q^{3+}Ti_{1-q}^{4+}O_{2-q}^{2-}F_q^- + p/2V_2O_5 \rightarrow V_p^{5+}Ti_{q+p}^{3+}Ti_{1-q-p}^{4+}O_{2-q-2p}^{2-}F_q^- \quad \text{(II)}$$

$$Ti_q^{3+}Ti_{1-q}^{4+}O_{2-q}^{2-}F_q^- + p/2VO_2 \rightarrow V_p^{4+}Ti_{q+p}^{3+}Ti_{1-q-p}^{4+}O_{2-q-3/2p}^{2-}F_q^- \quad \text{(III)}$$

$$Ti_q^{3+}Ti_{1-q}^{4+}O_{2-q}^{2-}F_q^- + (1-p)/2\,V_2O_5 \rightarrow V_{1-2p}^{5+}V_p^{4+}Ti_{q+p}^{3+}Ti_{1-q-p}^{4+}O_{9/2-q-7/2p}^{2-}F_q^- \quad \text{(IV)}$$

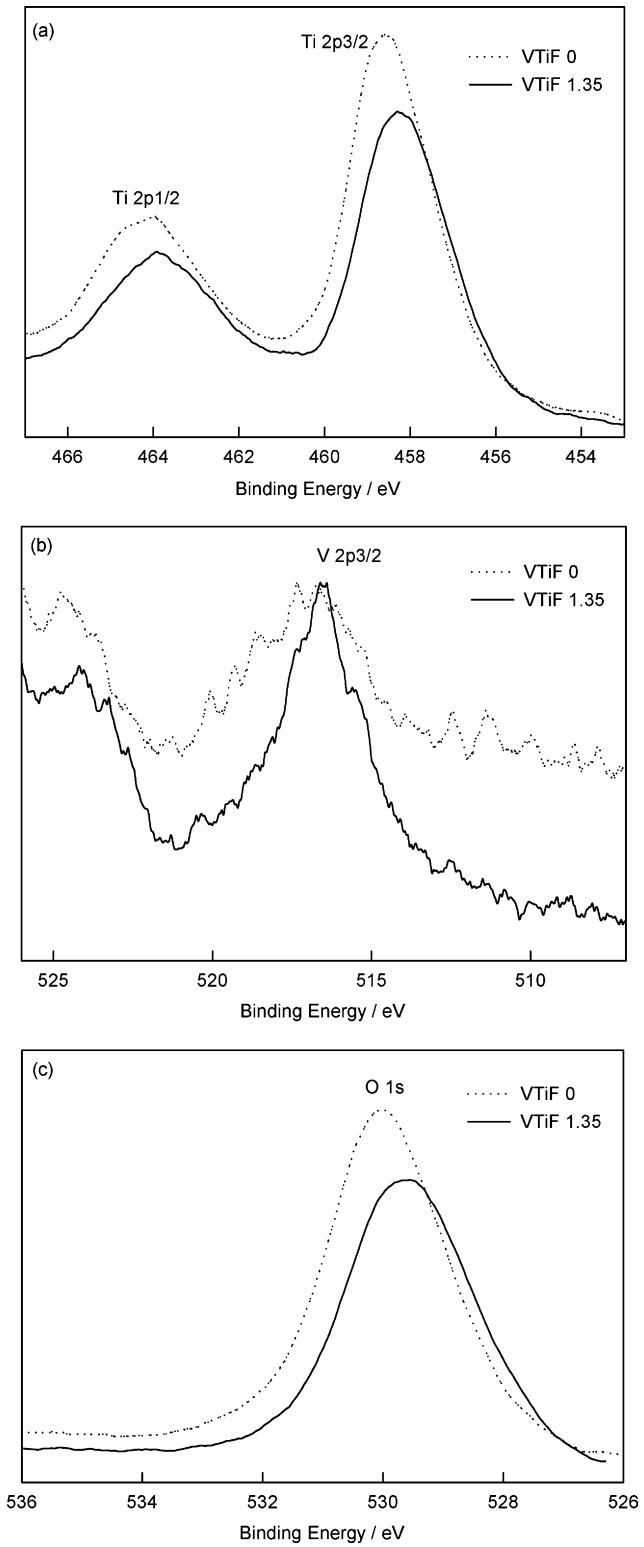

Fig. 2. XPS spectra of VTiF 0 and VTiF 1.35 catalysts: (a) Ti, (b) V, and (c) O.

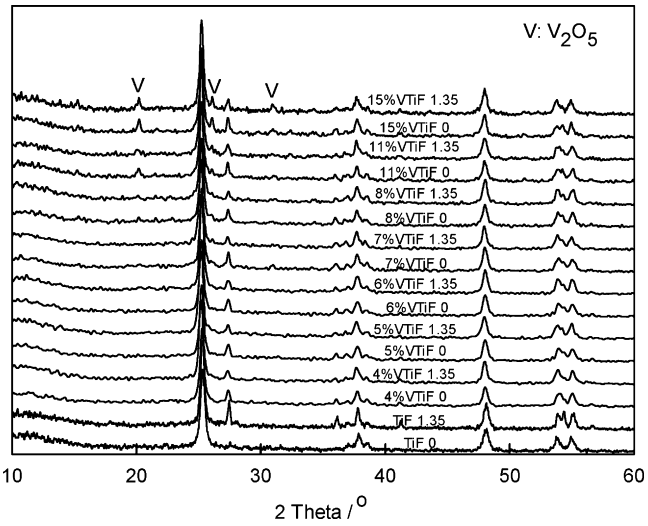

Fig. 3. X-ray diffraction patterns for 4–15 wt.% V_2O_5 content catalysts supported both on F-doped and undoped titania.

or

$$TiO_2 + qF^- \rightarrow Ti^{4+}O_{2-q/2}{}^{2-}F_q{}^- + q/2O^{2-} \quad (V)$$

$$Ti^{4+}O_{2-q/2}{}^{2-}F_q{}^- + p/2V_2O_5 \rightarrow V_p{}^{5+}Ti_p{}^{3+}Ti_{1-p}{}^{4+}O_{2-q/2+2p}{}^{2-}F_q{}^- \quad (VI)$$

$$Ti^{4+}O_{2-q/2}{}^{2-}F_q{}^- + p/2VO_2 \rightarrow V_p{}^{4+}Ti_p{}^{3+}Ti_{1-p}{}^{4+}O_{2-q/2+3/2p}{}^{2-}F_q{}^- \quad (VII)$$

$$Ti^{4+}O_{2-q/2}{}^{2-}F_q{}^- + (1-p)/2\,V_2O_5 \rightarrow V_{1-2p}{}^{5+}V_p{}^{4+}Ti_p{}^{3+}Ti_{1-p}{}^{4+}O_{9/2-q/2-5p}{}^{2-}F_q{}^- \quad (VIII)$$

3.1.2. Distribution of vanadium

Vanadium, as an active component, is the adsorption site for ammonia in the low-temperature SCR process [31]. Hence, promoting the distribution of vanadium increases the amount of effective vanadium that can participate in a low-temperature SCR reaction, which in turn facilitates the reaction. Within the detection depth of XPS, the F-doped sample VTiF 1.35 appeared to present more vanadium atoms (0.57%) than did the undoped sample VTiF 0 (0.21%). Moreover, to compare the distribution of vanadium over F-doped titania and undoped titania, we prepared 4–15 wt.% V_2O_5 content catalysts supported on TiF 1.35 and TiF 0. The samples were characterized by XRD (as shown in Fig. 3). When the V_2O_5 content was below 7%, it did not detect V_2O_5 for both F-doped and undoped samples. However, when the V_2O_5 content was 8%, the peak of V_2O_5 appeared (pdf 41-1426) for both samples. The difference of XRD patterns between the F-doped and undoped sample was that the peak of V_2O_5 over F-doped sample was weaker than that over undoped sample. This difference existed even when the V_2O_5 content was up to 15%. Therefore, F-doping could make vanadia well-dispersed over the support.

3.1.3. Surface superoxide ions

For commercialized SCR processes at temperatures between 573 and 673 K, it is agreed that the reaction mechanism involves the interaction of adsorbed ammonia (NH_4^+) with gaseous NO [31]. However, for SCR process at low temperatures, increasingly more studies [32–35] are revealing that reactive NO_y (nitro and nitrate) groups are the intermediates that react with adsorbed ammonia (most probably adsorbed onto Lewis acid sites [1,36–38]). Thus, the formation of NO_y from gaseous NO is the key process. Wang et al. [39] have proposed that the NO_y groups are formed from NO and an adsorbed superoxide ion. This important role of superoxide ions in the low-temperature SCR process has been confirmed by other studies [40,41]. Therefore, we also investigated the superoxide ion content on the catalyst surface.

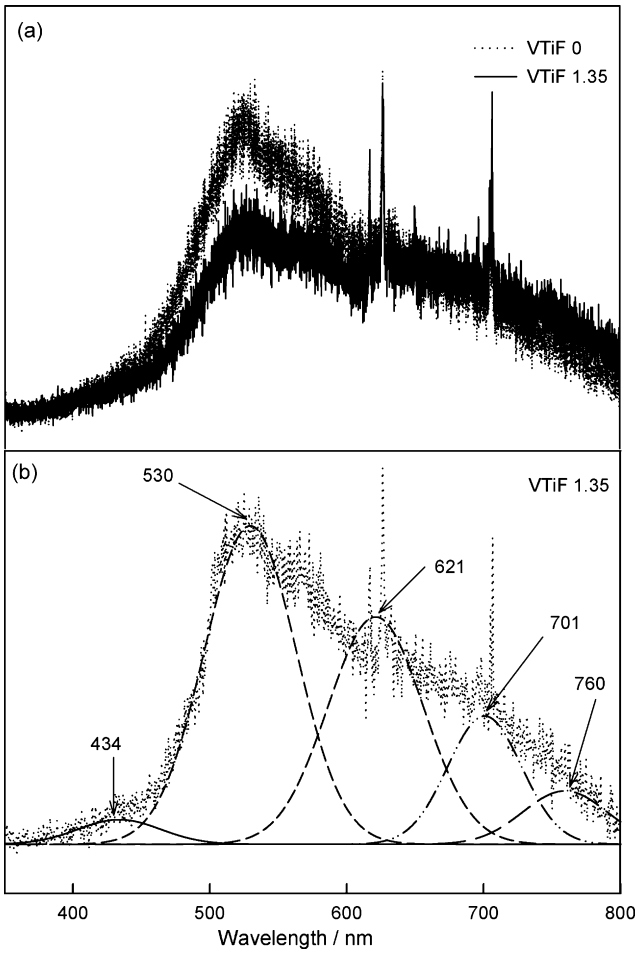

Fig. 4. PL spectra of VTiF 0 and VTiF 1.35 catalysts (a) and deconvolution of PL spectra of VTiF 1.35 (b) using Lorentzian–Gaussian peak fitting.

Superoxide ions could be formed by oxygen adsorption onto the surface color centers at low temperature [42]. These color centers or *F* centers could be characterized by photoluminescence (PL) spectra. Fig. 4 shows the PL spectra of VTiF 0 and VTiF 1.35 samples, from which we can observed color centers with one trapped electron at 530 nm [16,17] (more details are shown in Fig. S1 of the Supporting Information). Luminescence could be quenched by adsorption of oxygen [42], therefore the peak intensity at 530 nm of the F-doped sample was lower than that of the undoped one, which may represent a different adsorption capability for oxygen. In other words, a F-doped sample could adsorb more oxygen than an undoped sample. This was confirmed by ESR spectra of superoxide ions (g_{yy} = 2.0047 [42,43] as shown in Fig. 5). In overview, F-doping increased the amount of superoxide ions and the affinity for oxygen. Among the samples involved in the present study, VTiF 1.35 showed the most amount of superoxide ions, and then decreased as: VTiF 1 > VTiF 2 > VTiF 0. As the formation of superoxide ion over V^{4+} lead to the formation of V^{5+}–O_2^-, it also makes the decrease of the spectral resolution of V^{4+} ion, which has been discussed in Section 3.1.1. From the intensities of g_{yy} over VTiF 0, VTiF 1.35 and their carriers in Fig. 5, we can determine that the vanadia loading could facilitate the formation of superoxide ions.

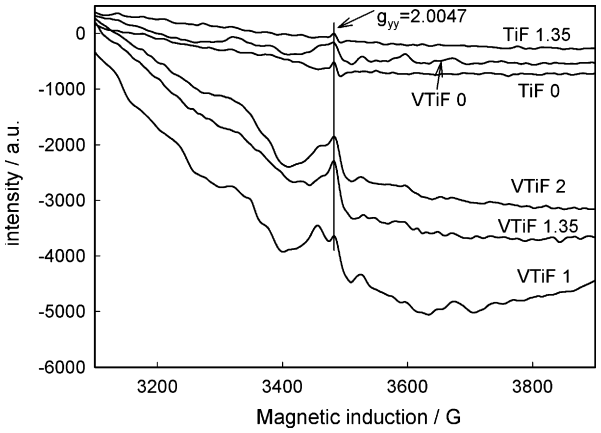

Fig. 5. ESR spectra of superoxide ions over the catalysts.

3.2. Low-temperature SCR activity of the catalysts

The NO removal efficiency of the catalysts at 483 and 513 K was shown in Table 1. It indicated that the rate constants of the catalysts were significantly increased by F-doping. The evolution of rate constants followed as: VTiF 1.35 > VTiF 1 > VTiF 2 > VTiF 0. Comparing the rate constants with those in Ref. [26], It can be seen that the catalysts developed in this work have a lower rate constant than the previously reported. This could be due to a lower specific surface area derived from the preparation method employed (as shown in Table 1). The formation of N_2O was <3 ppm for all the samples under our testing conditions, and thus the selectivity to N_2 was promising.

Moreover, we conducted a SO_2 and H_2O resistance experiment for the catalyst. This type of study is essential for initiating the practical use of vanadia/titania catalysts for NO_X removal with NH_3. Previous studies [44,45] have revealed that adding SO_2 could increase the activity of a vanadia catalyst, but H_2O could not. Moisture inhibited the SCR reaction of a vanadia catalyst, but this inhibition was reversible and decreased with increasing reaction temperature [10,36]. Fig. 6 shows the evolution of NO conversion and SO_2 concentration for a VTiF 1.35 sample with time on stream at 483 and 513 K. Adding SO_2 had almost no influence on NO conversion at 483 and 513 K, for the NO conversions were very high at both temperatures. However, adding H_2O without SO_2 inhibited the reaction and further deterioration was seen as the moisture content was increased (Fig. 6(b), point "C"). When both H_2O and SO_2 were added, the inhibition was more severe than the sum of inhibitions

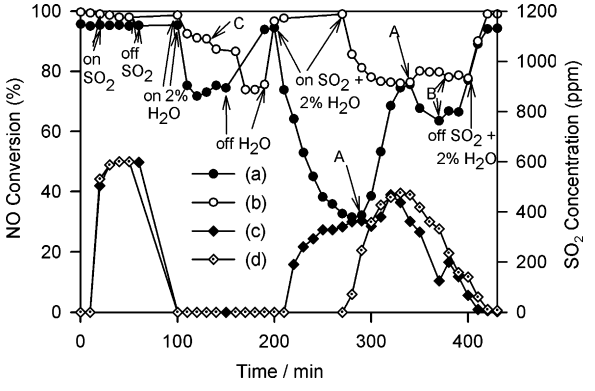

Fig. 6. The evolution of NO conversion and SO_2 concentration over VTiF 1.35 with time on stream at 483 and 513 K: (a) NO conversion at 483 K, (b) NO conversion at 513 K, (c) SO_2 concentration at 483 K, and (d) SO_2 concentration at 513 K. Point "A": changing ammonia concentration from 600 to 900 ppm, point "B": changing ammonia concentration from 900 to 1200 ppm, and point "C": changing water content from 2% to 4%.

observed when H_2O and SO_2 were added individually, indicating a synergistic inhibitory effect of H_2O and SO_2. However, this synergistic inhibition was alleviated, although not completely eradicated, by increasing the concentration of ammonia from 600 to 900 ppm (even to 1200 ppm, as shown in Fig. 6, point "A" and "B"). This suggested a competition for NH_3 between NO and SO_2, which could be seen when the evolution of NO removal efficiency and SO_2 concentration were compared (Fig. 6), and which was consistent with a previous study by Kasaoka et al. [46]. The above inhibitions could be reduced by increasing reaction temperature and were reversible, again in agreement with previous studies [10,36].

4. Conclusions

To improve the NO removal efficiency of low-vanadium-loading catalysts for low-temperature SCR, a novel fluorine doped vanadia/titania catalyst has been developed. In this catalyst, the lattice oxygen was partially substituted with fluorine using NH_4F as a precursor. In the present work, we characterized this catalyst and tested its catalytic activity in low-temperature SCR. When the valences of titanium and vanadium, the distribution of vanadium, and the surface superoxide ions of both the F-doped and undoped catalysts were examined, F-doping was found to facilitate the formation of V^{4+} and Ti^{3+} ions, to promote the distribution of vanadium on the catalyst surface, and to increase the amount of surface superoxide ions. The catalytic activity of NO removal was promoted by F-doping. In our study, The catalyst with [F]/[Ti] = 1.35×10^{-2} showed the highest rate constant in low-temperature SCR reaction. Although the changes in the catalyst caused after by F-doping were related to the improvement of NO removal efficiency, it still needs more in situ work to investigate the structure–activity relationships over this new catalyst. The further work is carrying out in our lab.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.07.039.

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