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Highly dispersed iron vanadate catalyst supported on TiO₂ for the selective catalytic reduction of NO_x with NH₃

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1. Introduction

Selective catalytic reduction (SCR) of NO_x with NH₃ over V₂O₅-WO₃ (MoO₃)/TiO₂ catalysts is a well-established system for the removal of NO_x from stationary sources, such as coal-fired power plants and industrial boilers [1,2]. The vanadium-based catalysts have also been successfully used in the deNO_x process for heavy duty diesel engines in 2005 using urea as an efficient reductant [3]. However, although it has been utilized industrially for several decades, some disadvantages still remain for this catalyst system, such as a narrow operation temperature window, low N₂ selectivity, and sublimation of V_2O_5 at high reaction temperatures [1,4,5], which greatly restrict its further application in the $deNO_x$ process for mobile sources. Accordingly, the in-depth study and improvement of vanadium-based catalysts for the NH₃-SCR process is still of great concern in the field of environmental catalysis [5–13].

Nowadays, much attention has also been paid to the investigation of non-vanadium NH₃-SCR catalysts worldwide, including Feand Cu-exchanged zeolite catalysts (e.g., Fe-ZSM-5, Fe-BEA, Cu-ZSM-5, Cu-SSZ-13, etc.) [14-22] and Fe-, Cu-, Mn-, and Ce-based oxide catalysts (e.g. γ -Fe₂O₃, FeTiO_x, Fe₂(SO₄)₃/TiO₂, Fe₂O₃/WO₃/ ZrO_2 , CuO_x/WO_x - ZrO_2 , MnO_x/TiO_2 , CrO_x - MnO_x , $(Fe_{3-x}Mn_x)_{1-\delta}O_4$,

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ABSTRACT

An iron vanadate (FeVO₄) catalyst supported on TiO₂ with high dispersion has been developed and applied in the selective catalytic reduction (SCR) of NO_x with NH_3 , showing high activity, N_2 selectivity, and H_2O/SO_2 durability in medium temperature range. The formation of Fe³⁺–O–V⁵⁺ linkages with low coordination number of vanadium atoms was evidenced by EXAFS, indicating the presence of abundant surface defects for reactant adsorption and activation. The XPS showed that the FeVO₄ phase was surfaceenriched with VO_x species acting as true active sites, and thus, high NH₃-SCR activity and H₂O/SO₂ durability could be preserved similar to that of V_2O_5/TiO_2 . Additionally, the presence of electronic inductive effect between Fe^{3+} and V^{5+} as confirmed by XANES and XPS could effectively decrease the unwanted NH₃ unselective oxidation, thus resulting in high N₂ selectivity at high temperatures. This FeVO₄/TiO₂ catalyst is a potential candidate for the deNO_x process for stationary flue gas or diesel exhaust.

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CeWO_x, CeO₂-WO₃/TiO₂, etc.) [23-32]. All the above-mentioned catalysts show relatively high deNO_x efficiency in different temperature ranges, and the Fe-based catalysts among them usually show good NH₃-SCR activity, N₂ selectivity, and H₂O/SO₂ durability at medium or high temperatures above 200 °C [23,29,30]. Therefore, it is promising to combine the advantages of vanadium species and iron species for the NH₃-SCR process into one catalyst, such as an FeVO₄ catalyst, to enlarge the operation temperature window and enhance the N₂ selectivity at high temperatures. The introduction of the Fe component into the V₂O₅-TiO₂ catalyst system has already been reported by Yang et al. [33,34], who found that Fe-Ti-V spinel and V₂O₅/Fe₂O₃-TiO₂ catalysts exhibited good NH₃-SCR performance in the medium temperature range. They did not observe the formation of the FeVO₄ phase in their catalysts, probably due to the different preparation methods used or the limitation of detection accuracy using XRD, yet the importance of the FeVO₄ phase for NH₃-SCR reaction is highly worthy of investigation. The promoting effect of Fe doping on the low temperature NH₃-SCR activity over ErVO₄/TiO₂-WO₃-SiO₂ catalysts was also observed by Sagar et al. [35], where the existence of the FeVO₄ phase might also be an important factor influencing the deNO_v efficiency. Besides, it is interesting that the FeVO₄ phase has a much higher melting point (ca. 850 °C) than that of V_2O_5 (ca. 690 °C) [36,37], thus possessing higher thermal stability, which is beneficial for use in NO_x removal from diesel engines, especially when the SCR converter is installed downstream of the diesel particulate





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filter (DPF) in view of the timed thermal shock (~ 800 °C) in the regeneration processes of DPF systems.

In this study, an FeVO₄ catalyst supported on TiO₂ with high dispersion was prepared using a facile co-impregnation method and applied as an NH₃-SCR catalyst for the first time. The high SCR activity, N₂ selectivity, and H₂O/SO₂ durability of this catalyst in the medium temperature range were demonstrated. Based on combined characterizations using XRD, Raman spectra, X-ray absorption spectra (XAS), and XPS, the microstructure of the active FeVO₄ phase was determined, in which an electronic inductive effect was found to exist between Fe³⁺ and V⁵⁺ species that was beneficial for the retention of high deNO_x efficiency and N₂ selectivity simultaneously. The conclusions drawn from this study are important for understanding the structure–activity relationships of FeVO₄/TiO₂ catalyst in the NH₃-SCR reaction and guiding its possible practical use.

2. Experimental

2.1. Catalyst synthesis

Iron vanadate catalysts supported on TiO₂ with different loading amounts were prepared by the conventional co-impregnation method using Fe(NO₃)₃·9H₂O and NH₄VO₃ as precursors, which are denoted as x wt.% FeVO₄/TiO₂. Firstly, a mixed solution of Fe(NO₃)₃, NH₄VO₃, and oxalic acid in distilled water was prepared according to the calculated stoichiometric ratio with Fe:V = 1:1 on a molar basis. Then, a certain amount of anatase TiO₂ support (DT-51) purchased from Millennium Inorganic Chemicals was added into the mixed solution and continuously stirred for 1 h. Thereafter, the excess water was removed in a rotary evaporator at 80 °C with the help of a vacuum pump. Finally, the sample was desiccated in an oven at 120 °C for 12 h, followed by calcination in a muffle furnace at 400 °C for 6 h in air. For comparison, 9 wt.% FeVO₄/Al₂O₃ (PURALOX SBa-90, SASOL Germany GmbH), 9 wt.% FeVO₄/WO₃-TiO₂ (DT-52 with 10 wt.% WO₃, Millennium Inorganic Chemicals), 9 wt.% Fe₂O₃/TiO₂, and 9 wt.% V₂O₅/TiO₂ catalysts were also prepared by the same co-impregnation or impregnation method using Fe(NO₃)₃·9H₂O and NH₄VO₃ as precursors. To further test the thermal stability of 9 wt.% FeVO₄/TiO₂ catalyst, different calcination temperatures were also used, i.e. 500, 600, 650, 700, and 800 °C for 6 h in air condition.

As reference material, the commercial TiO₂ support was calcined in a muffle furnace at 400 °C for 6 h in air. FeVO₄ was prepared by direct evaporation of a mixed solution of Fe(NO₃)₃, NH₄VO₃, and oxalic acid with molar ratio Fe:V = 1:1, followed by desiccation at 120 °C for 12 h and calcination at 400 °C for 6 h. Pristine Fe₂O₃ was prepared by a precipitation method using Fe(NO₃)₃. •9H₂O as precursor and standard NH₃·H₂O (25 wt.%) aqueous solution as precipitator, in which process the precipitate was washed by distilled water, desiccated at 120 °C for 12 h and calcined at 400 °C for 6 h in sequence. Pristine V₂O₅ was prepared by direct decomposition of NH₄VO₃ at 400 °C for 6 h in air.

2.2. Activity testing

The steady-state NH₃-SCR activity over the series of x wt.% FeVO₄/TiO₂ catalysts as well as 9 wt.% FeVO₄/Al₂O₃, 9 wt.% FeVO₄/WO₃-TiO₂, 9 wt.% Fe₂O₃/TiO₂, and 9 wt.% V₂O₅/TiO₂ catalysts was tested in a fixed-bed quartz tube reactor at atmospheric pressure, and the reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, 200 ppm SO₂ (when used), 5 vol.% H₂O (when used), and N₂ balance; 0.6 ml catalyst, 20–40 mesh if not noted (to check if the internal diffusional limitation was present, the smaller particle sizes of 9 wt.% FeVO₄/TiO₂ catalyst were

also used including 40–60 mesh and 60–80 mesh); total flow rate of 500 ml/min and gas hourly space velocity (GHSV) of 50,000 h^{-1} . The effluent gas was continuously analyzed using an FTIR spectrometer (Nicolet Nexus 670) equipped with a heated, low volume multiple-path gas cell (2 m).

2.3. Characterization

The N₂ adsorption-desorption isotherms over x wt.% FeVO₄/ TiO₂, 9 wt.% Fe₂O₃/TiO₂, and 9 wt.% V₂O₅/TiO₂ catalysts and corresponding reference samples were obtained at -196 °C using a Quantachrome Autosorb-1C instrument. Prior to the N₂ physisorption, all samples were degassed at 300 °C for 4 h. Surface areas were determined by the BET equation in the 0.05–0.35 partial pressure range. Pore volumes and average pore diameters were determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the isotherms.

The powder XRD measurements of *x* wt.% FeVO₄/TiO₂, 9 wt.% Fe₂O₃/TiO₂, and 9 wt.% V₂O₅/TiO₂ catalysts and corresponding reference samples were carried out on a computerized PANalytical X'Pert Pro Diffractometer with CuK_{α} radiation source (λ = 0.15406 nm). The data for 2 θ from 10° to 80° were collected at 8°/min with the step size of 0.07°.

The Raman spectra of *x* wt.% FeVO₄/TiO₂, 9 wt.% Fe₂O₃/TiO₂, and 9 wt.% V₂O₅/TiO₂ catalysts and corresponding reference samples were collected at room temperature on a Spex 1877 D Triplemate spectrograph with the spectral resolution of 2 cm⁻¹. A 532 nm DPSS diode-pumped solid-state semiconductor laser was used as the excitation source, and the power output was about 30 mW. Before measurements, the samples were well ground and mounted into a spinning holder to avoid thermal damage during the scanning. In order to eliminate the impact of color change in catalysts with different FeVO₄ loadings on the variation of Raman signals, we used white CaCO₃ powder as internal reference (with the ratio of target sample to CaCO₃ being 2.5:1) to normalize the Raman bands of TiO₂ for more reasonable comparison. The Raman signals were collected with conventional 90° geometry. All Raman spectra used in this paper are unsmoothed.

The XAS of Fe and V K-edges were measured in a transmission mode at room temperature on the BL-7C beam line, Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (IMSS-KEK), Japan and the BL14W1 beam line, Shanghai Synchrotron Radiation Facility (SSRF). The storage ring was operated at 2.5 GeV with 300 mA as an average storage current for the BL-7C beam line and 3.5 GeV with 200 mA as an average storage current for the BL14W1 beam line. The synchrotron radiation beam line was monochromatized with a Si (111) double crystal monochromator, and mirrors were used to eliminate higher harmonics. The incident and transmitted beam intensities were monitored using ionization chambers filled with pure N₂. Before measurements, all samples were crushed and sieved to 200 mesh or finer and then diluted with flour powder at appropriate ratios and pressed into thin disks. XAS data were analyzed using the REX2000 program (Rigaku Co.). XANES spectra of Fe, V K-edges were normalized with the edge height, and then, the first-order derivatives were taken to compare the variation in absorption edge energies. Since the strong absorption of Ti was present in V-Ti-containing samples, it was too difficult to obtain V K-edge EXAFS with good S/N. The EXAFS oscillation $\chi(k)$ of the Fe K-edge was extracted using spline smoothing with a Cook-Sayers criterion [38] and weighted by k^3 in order to compensate for the diminishing amplitude in the high k range due to the decay of the photoelectron wave. Thereafter, the filtered k^3 -weighted $\chi(k)$ was Fourier transformed into R space in the k range of 2.5– 13 $Å^{-1}$ with a Hanning function window. In the curve-fitting step,

the possible backscattering amplitude and phase shift were calculated using FEFF8.4 code [39].

The XPS of FeVO₄/TiO₂, Fe₂O₃/TiO₂, and V₂O₅/TiO₂ catalysts and corresponding reference samples were recorded on an Imaging Photoelectron Spectrometer (Axis Ultra, Kratos Analytical Ltd.) using Al K_{α} radiation (1486.7 eV). Binding energies of Fe 2p, V 2p, and Ti 2p were calibrated using the C 1s peak (BE = 284.8 eV) as standard.

2.4. Density functional theory (DFT) calculation

The geometry optimization of the three kinds of stoichiometric Fe_2O_3 , V_2O_5 , and $FeVO_4$ crystals was carried out using CASTEP module in Materials Studio software package. The generalized gradient approximation (GGA) with PBE functional was used to describe the exchange–correlation effect. The electron–ion interaction was described by the ultrasoft potential in the reciprocal space. A tight convergence of the plane-wave expansion was obtained with a kinetics energy cutoff of 300 eV.

The Brillouin zone using the Monkhorst–Pack scheme was sampled by $3 \times 3 \times 2$, $1 \times 4 \times 3$, and $2 \times 2 \times 1$ for Fe₂O₃, V₂O₅, and FeVO₄, respectively. For all calculations, the convergence in energy and force was set to 2×10^{-5} eV and 0.05 eV/Å. The atomic charges were calculated using the Hirshfeld approach. The electron density difference of the investigated crystal models was also analyzed.

3. Results and discussion

3.1. NH₃-SCR activity

Fig. 1A and B shows the NO_x conversion and N₂ selectivity over the series of x wt.% FeVO₄/TiO₂ catalysts (20–40 mesh) as a function of temperature in the NH₃-SCR reaction. As shown in Fig. 1A, the pristine TiO₂ was inactive for NO_x reduction below 350 °C. Only ca. 30% NO_x conversion was obtained at 400 °C over TiO₂. With a small amount of FeVO₄ supported onto TiO₂, such as over 1.5 wt.% FeVO₄/TiO₂ catalyst, the NO_x conversion showed a marked increase, especially in the temperature range of 200-400 °C. With the increase of FeVO₄ loading amount from 1.5 to 9 wt.%, the SCR activity below 300 °C showed a monotonic increase. Further increasing the FeVO₄ loading amount to 15 wt.% led to no significant enhancement of SCR activity at low temperatures, but resulted in some decrease of NO_x conversion above 350 °C. In addition, as presented in Fig. 1B, the N₂ selectivity showed a monotonic decrease above 350 °C with the increase of FeVO₄ loading amount, which was mainly due to the occurrence of unselective catalytic oxidation of NH₃. Therefore, the 9 wt.% FeVO₄/TiO₂ is an optimal catalyst with the appropriate FeVO₄ loading for the NH₃-SCR reaction, showing high activity and N₂ selectivity simultaneously. It is noteworthy that the pristine FeVO₄ exhibited a relatively narrow operation temperature window for NO_x reduction and also the lowest N2 selectivity, indicating that the sufficient dispersion of FeVO₄ onto TiO₂ support was very important for the NH₃-SCR reaction, which might influence the electronic state of the active phase due to interaction with TiO₂ support. Furthermore, as the results shown in Fig. S1 of Supporting information, not only the NO_x conversion but also the N₂ selectivity in NH₃-SCR reaction over 9 wt.% FeVO₄/TiO₂ catalysts with different particle sizes (20-40, 40-60, and 60-80 mesh) were guite similar to each other, indicating that the adopted catalyst particle size of 20-40 mesh in NH₃-SCR activity tests of this study had already eliminated the internal diffusional limitations. To further investigate the effect of FeVO₄ loading amount onto TiO₂ support on the SCR reaction, the reaction rates normalized by surface area at 175 °C (at which the NO_x conversion over all catalysts could be kept below 40% to



Fig. 1. (A) NO_x conversion and (B) N₂ selectivity in NH₃-SCR reaction as a function of temperature over *x* wt.% FeVO₄/TiO₂ catalysts; (C) the NH₃-SCR reaction rates normalized by surface area at 175 °C over *x* wt.% FeVO₄/TiO₂ catalysts.

eliminate the influence of mass and thermal transformation) were calculated, as the results shown in Fig. 1C. With the increasing of FeVO₄ loading amount from 1.5 to 9 wt.%, the rate constants for deNO_x process showed a monotonic increase, implying that the FeVO₄ species assembled gradually on the TiO₂ surface in this process supplying more catalytically active sites for NH₃-SCR reaction. Further increasing the FeVO₄ loading amount did not result in the obvious increase of reaction rates which maintained at ca. 3.0×10^{-9} mol s⁻¹ m⁻², indicating that above 9 wt.% loading amount, the FeVO₄ species might have already exceeded the monolayer dispersion limit leading to a surface convergence on TiO₂ support. This point of view will be discussed in detail in the following characterization sections.

It is reasonable that, with the monolayer dispersion of FeVO₄ species on TiO₂ support, the exposed active sites for SCR reaction have already reached the maximum, and at the same time, the roles of TiO₂ support in FeVO₄/TiO₂ catalysts interacting with Fe or V species to influence their electronic state and also working as efficient NH₃ reservoir would not be weakened. Therefore, the optimal deNO_x efficiency could be obtained over 9 wt.% FeVO₄/TiO₂ catalyst without needing the formation of multiple FeVO₄ layers at higher loadings. This also means in another aspect that, even with the similar monolayer dispersion of FeVO₄ species, the

property of catalyst supports could also greatly influence the NH₃-SCR activity. To prove this assumption, another two catalysts including 9 wt.% FeVO₄/Al₂O₃ and 9 wt.% FeVO₄/WO₃-TiO₂ were prepared using the supports with similar surface areas as that of TiO₂, and their activity test results are shown in Fig. 2. As we clearly see, the 9 wt.% FeVO₄/Al₂O₃ catalyst showed the lowest NH₃-SCR activity in the whole temperature range although with the highest N₂ selectivity. Comparing with the 9 wt.% FeVO₄/TiO₂ catalyst, the 9 wt.% FeVO₄/WO₃-TiO₂ showed higher NH₃-SCR activity at low temperatures probably due to the higher surface acidity induced by WO₃ and a little lower NH₃-SCR activity above 350 °C, with very similar N₂ selectivity in the whole temperature range. Therefore, besides of the dispersion degree of FeVO₄ species, the property of catalyst support could indeed greatly influence its catalytic performance for SCR reaction, which is worthy to be investigated in the near future. In the following studies, we mainly used anatase TiO₂ support to elucidate the structure-activity relationship of FeVO₄ catalyst for the deNO_x process.

Fig. 3 shows the NO_x conversion and N_2 selectivity over 9 wt.% Fe₂O₃/TiO₂, 9 wt.% V₂O₅/TiO₂, and 9 wt.% FeVO₄/TiO₂ catalysts (20-40 mesh) for comparison. Compared with the $9 \text{ wt.\% } V_2 O_5/$ TiO₂ catalyst, the 9 wt.% FeVO₄/TiO₂ catalyst showed lower SCR activity to a certain extent below 250 °C, but much higher SCR activity and N₂ selectivity above 350 °C. It is noteworthy that only ca. 70% N₂ selectivity was obtained over the 9 wt.% V₂O₅/TiO₂ catalyst at 400 °C, due to the formation of a large amount of N_2O . Compared with the 9 wt.% Fe₂O₃/TiO₂ catalyst, the SCR activity of the 9 wt.% FeVO₄/TiO₂ catalyst below 300 °C was much higher, and the operation temperature window was also much wider. Furthermore, the presence of vanadium species in addition to iron species in the 9 wt.% FeVO₄/TiO₂ catalyst did not result in any noticeable decrease in N2 selectivity over the whole temperature range. These results indicate that the interaction between iron and vanadium species in the FeVO₄/TiO₂ catalyst possibly led to the formation of a new active phase, which was different from those in the Fe_2O_3/TiO_2 and V_2O_5/TiO_2 catalysts. This point of view can be confirmed by the activity test result of the physically mixed 9 wt.% Fe₂O₃/TiO₂ + 9 wt.% V₂O₅/TiO₂ catalysts, as also shown in Fig. 3. It is obvious that the physically mixed catalysts only showed an intermediate SCR activity at low temperatures between 9 wt.% Fe₂O₃/TiO₂ and 9 wt.% V₂O₅/TiO₂, and a similar SCR activity at high



Fig. 2. (A) NO_x conversion and (B) N₂ selectivity in NH₃-SCR reaction as a function of temperature over 9 wt.% FeVO₄/Al₂O₃, 9 wt.% FeVO₄/TiO₂, 9 wt.% FeVO₄/WO₃-TiO₂ catalysts.



Fig. 3. (A) NO_x conversion and (B) N₂ selectivity in NH₃-SCR reaction as a function of temperature over 9 wt.% Fe_2O_3/TiO_2 , 9 wt.% V_2O_5/TiO_2 , 9 wt.% Fe_2O_4/TiO_2 and 9 wt.% $Fe_2O_3/TiO_2 + 9$ wt.% V_2O_5/TiO_2 physically mixed catalysts.

temperatures as that of 9 wt.% V₂O₅/TiO₂ (which was lower than that over 9 wt.% FeVO₄/TiO₂). The N₂ selectivity over the physically mixed catalysts also showed an intermediate state, higher than 9 wt.% V₂O₅/TiO₂ but lower than 9 wt.% Fe₂O₃/TiO₂ and 9 wt.% FeVO₄/TiO₂. These catalytic results again suggest that, different from the physically mixed effect, the synergistic effect between Fe and V species must exist in FeVO₄ catalyst, which can be explained by the subsequent characterization results.

3.2. SO₂/H₂O durability

In practical use, the SCR reaction atmosphere usually contains some fractions of SO₂ and water vapor. Therefore, we also tested the SO₂/H₂O durability of the 9 wt.% FeVO₄/TiO₂ catalyst in the NH₃-SCR reaction. Fig. 4A shows the NO_x conversion over 9 wt.% FeVO₄/TiO₂ catalyst as a function of time in the presence of 200 ppm SO₂ at 190 and 240 °C under the GHSV of 50,000 h^{-1} . As we can see, with increasing reaction time, the NO_x conversion at 190 °C showed a slow decrease from 50% to 40% for the first 24 h and then maintained at 40% for the next 12 h. This activity decline might be caused by the deposition of ammonium sulfate/bisulfate on the catalyst surface, blocking some active sites for NH₃-SCR reaction. At 240 °C, the introduction of 200 ppm SO₂ into the reaction atmosphere did not result in any decrease of NO_x conversion for the 36 h test, indicating the high resistance of the FeVO₄/TiO₂ catalyst to SO₂ poisoning. Afterward, we further increased the GHSV to 100,000 h^{-1} to test the SO₂/H₂O durability of 9 wt.% FeVO₄/TiO₂ catalyst at 240 °C. The stability test results in Fig. 4B showed that even at higher GHSV, this catalyst still showed rather good resistance to SO₂ poisoning without observing the apparent decline of SCR activity in the long term operation. However, in the presence of 5 vol.% H_2O , the NO_x conversion decreased from the initial 90% to ca. 50%, which was possibly due to the blocking of some active sites on the catalyst surface for reactant adsorption. After the cutting-off of H_2O inlet, the NO_x conversion over 9 wt.% FeVO₄/TiO₂ catalyst rapidly recovered to 90%, indicating a reversible inhibition effect of H₂O on the SCR activity. To further confirm the influence of reaction temperature on the inhibition effect of H_2O , we also recorded the NO_x conversion in NH₃-SCR reaction with 5 vol.% H₂O over 9 wt.% FeVO₄/TiO₂ catalyst at 290 °C. To



Fig. 4. NO_x conversion as a function of time over 9 wt.% FeVO₄/TiO₂ catalyst in NH₃-SCR reaction (A) at 190 and 240 °C in the presence of 200 ppm SO₂ under the GSHV of 50,000 h⁻¹; (B) at 240 °C in the presence of 200 ppm SO₂ or 5 vol.% H₂O under the GSHV of 100,000 h⁻¹; (C) at 290 °C in the presence of 5 vol.% H₂O under the GSHV of 200,000 h⁻¹; (D) NO_x conversion as a function of temperature over 9 wt.% FeVO₄/TiO₂ TiO₂ catalysts after sulfation at 190 and 240 °C and over fresh 9 wt.% FeVO₄/TiO₂ catalyst in the absence and presence of 5 vol.% H₂O under the CSHV of 50,000 h⁻¹.

ensure the initial NO_x conversion below 100%, the GHSV was raised to 100,000 h^{-1} for this test. As presented in Fig. 4C, although the NO_x conversion at 290 °C still decreased from 90% to ca. 70% upon H₂O addition, this reversible inhibition effect of H₂O on the SCR activity was actually mitigated at this temperature comparing with that at 240 °C. It is therefore inferred that this inhibition effect of H₂O will eventually vanish at higher temperatures. Finally, the SCR activities of the FeVO₄/TiO₂ catalysts sulfated at different temperatures in Fig. 4A, and the fresh FeVO₄/TiO₂ catalyst in the presence of H₂O as a function of reaction temperature were also tested under the GHSV of 50,000 h^{-1} . As shown in Fig. 4D, after sulfation in the NH₃-SCR reaction at 190 and 240 °C for 36 h, the 9 wt.% FeVO₄/TiO₂ catalyst still presented high efficiency for NO_x removal from 200 to 400 °C, similar to that of the fresh catalyst. The addition of 5 vol.% H₂O into the reaction atmosphere led to some decrease of NO_x conversion (ca. 15%) below 250 °C. Above 250 °C, the inhibition effect of H₂O on NO_x conversion was totally absent under this GHSV. Therefore, in short summary, this novel FeVO₄/

TiO₂ catalyst can retain high NH₃-SCR activity in the presence of SO_2/H_2O if the reaction temperature is higher than 250 °C under the typical GHSV (such as 50,000 h⁻¹) which can fulfill the using demands in deNO_x process for both stationary and mobile sources.

3.3. N₂ physisorption results

Table 1 shows the textural parameters of x wt.% FeVO₄/TiO₂, 9 wt.% Fe₂O₃/TiO₂, 9 wt.% V₂O₅/TiO₂ catalysts and corresponding reference samples derived from N2 physisorption results. With the increase of FeVO₄ loading onto TiO₂, the BET surface area showed some decrease to a certain extent due to pore blocking of TiO₂ by the active phase. It is interesting that the pore volume of 1.5 wt.% FeVO₄/TiO₂ and 3 wt.% FeVO₄/TiO₂ catalysts showed some decrease compared with that of pristine TiO₂; however, when the FeVO₄ loading amount was above 4.5 wt.%, the pore volume rebounded to the original level. This is probably due to the formation of some extra pores induced by the FeVO₄ species. From the average pore diameter data, all x wt.% FeVO₄/TiO₂ catalysts exhibited pore sizes in the range of 10-20 nm, indicating that this series of catalysts prepared by the co-impregnation method were all present as mesoporous materials. Although the textural parameters of FeVO₄, Fe₂O₃, and V₂O₅ reference samples showed some obvious discrepancies, the loaded-type catalysts including 9 wt.% $FeVO_4/TiO_2$, 9 wt.% Fe_2O_3/TiO_2 , and 9 wt.% V_2O_5/TiO_2 with the same loading amount possessed similar surface area, pore volume, and pore diameter. These results indicate that the textural parameters, especially the specific surface areas, are not the main reasons for the SCR activity differences between different loaded-type catalysts.

3.4. XRD results

To investigate the crystal structure of the active phase in the different catalysts, the XRD patterns of *x* wt.% FeVO₄/TiO₂, 9 wt.% Fe₂O₃/TiO₂, 9 wt.% V₂O₅/TiO₂ catalysts and corresponding reference samples were recorded, with the results shown in Fig. 5. With the increase of FeVO₄ loading from 1.5 wt.% to 15 wt.%, as shown in Fig. 5A, the XRD patterns of x wt.% FeVO₄/TiO₂ catalysts showed no significant variation and were similar to that of pristine TiO₂ with the typical anatase structure. No diffraction peaks attributed to FeVO₄ species were observed at all. This result clearly suggests that the loaded active phase FeVO₄ did not enter the crystal lattice of TiO₂ to form a solid solution resulting in lattice shrinkage or lattice expansion, only existing on the surface of the TiO₂ support in amorphous or crystallite state. Similarly, in Fig. 5B, the XRD patterns of 9 wt.% FeVO₄/TiO₂, 9 wt.% Fe₂O₃/TiO₂, and 9 wt.% V₂O₅/ TiO₂ were also identical to that of anatase TiO₂, without formation of crystallized FeVO₄, Fe₂O₃, and V₂O₅ or corresponding solid solutions. Summarizing the above-mentioned results, it is concluded that all the catalysts prepared by co-impregnation or single impregnation methods in this study are present as supported-type materials, which should be characterized by other methods besides XRD, such as the following Raman spectra.

3.5. Raman spectra

Fig. 6 shows the visible Raman spectra of x wt.% FeVO₄/TiO₂, 9 wt.% Fe₂O₃/TiO₂, 9 wt.% V₂O₅/TiO₂ catalysts and corresponding reference samples. As we can see in Fig. 6A, with the increase of FeVO₄ loading from 1.5 wt.% to 9 wt.%, the bands corresponding to the typical Raman shifts of anatase TiO₂ (E_g at 156, 641 cm⁻¹, B_{1g} at 396 cm⁻¹ and A_{1g} at 521 cm⁻¹) [40] showed a monotonic decrease in intensity due to the coverage of the TiO₂ surface by FeVO₄ species or the color change in samples with different FeVO₄ loading amounts. To eliminate the influence of color change on the

Table	1
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Textural parameters of x wt.% FeVO₄/TiO₂, 9 wt.% Fe₂O₃/TiO₂, 9 wt.% V₂O₅/TiO₂ catalysts and corresponding reference samples derived from N₂ physisorption results.

Samples	$S_{BET}^{a} (m^2 g^{-1})$	Pore volume ^b ($cm^3 g^{-1}$)	Pore diameter ^c (nm)
TiO ₂	84.1	0.33	15.7
1.5 wt.% FeVO ₄ /TiO ₂	84.2	0.24	11.4
3 wt.% FeVO ₄ /TiO ₂	80.8	0.25	12.7
4.5 wt.% FeVO ₄ /TiO ₂	78.7	0.39	19.5
6 wt.% FeVO ₄ /TiO ₂	78.3	0.34	17.3
7.5 wt.% FeVO ₄ /TiO ₂	77.0	0.38	19.6
9 wt.% FeVO ₄ /TiO ₂	75.0	0.36	19.2
10.5 wt.% FeVO ₄ /TiO ₂	75.9	0.36	18.4
12 wt.% FeVO ₄ /TiO ₂	73.6	0.35	18.8
13.5 wt.% FeVO ₄ /TiO ₂	76.7	0.36	18.6
15 wt.% FeVO ₄ /TiO ₂	71.0	0.33	18.2
FeVO ₄	17.7	0.16	34.8
Fe ₂ O ₃	42.5	0.21	19.4
9 wt.% Fe ₂ O ₃ /TiO ₂	73.3	0.37	20.0
V ₂ O ₅	10.2	0.13	51.4
9 wt.% V ₂ O ₅ /TiO ₂	74.4	0.37	19.9

^a BET surface area.

^b BJH desorption pore volume.

^c Average pore diameter.



Fig. 5. Powder XRD patterns of (A) x wt.% FeVO₄/TiO₂ catalysts; (B) 9 wt.% Fe₂O₃/TiO₂, 9 wt.% V₂O₅/TiO₂, 9 wt.% FeVO₄/TiO₂ catalysts and corresponding reference samples.

variation of Raman signals, the Raman peak ascribed to the v_1 vibration mode of CaCO₃ at 1073 cm⁻¹ [41] was used as internal reference (Fig. 6B). By adjusting the integral area of this Raman peak to be the same for all samples, the Raman signals of TiO₂ was accordingly normalized for rational comparison, as shown in Fig. 6C. The gradual coverage of the TiO₂ surface by FeVO₄ species can be further confirmed by the integrated area of the TiO₂ vibration bands at 641 cm⁻¹ as indicted by the short dashed rectangle, and the corresponding results about the integrated areas are shown in Fig. 6D. When the FeVO₄ loading was increased from 0 wt.% to 9 wt.%, the integrated area of the relevant TiO₂ band nearly showed a linear decrease, indicating that the FeVO₄ species may have monolayer dispersion on the TiO₂ support below this loading amount. Above 9 wt.% loading (i.e. from 10.5 wt.% to 15 wt.%), no notable change in the integrated area of the TiO₂ band of interest can be observed, suggesting that the FeVO₄ species may already have the surface convergence forming multiple layers or small FeVO₄ particles at high loadings and the 9 wt.% was the threshold value for the total coverage of the TiO₂ surface. This also

explained the decrease of NH₃-SCR activity and N₂ selectivity at high temperatures when the FeVO₄ loading was above 9 wt.% (Fig. 1). According to the previous work by Giakoumelou et al. [42], the 5 wt.% V_2O_5 loading for V_2O_5/TiO_2 catalyst have already reached the monolayer limit. However, in the case of FeVO₄ in our study, the loading amount for monolayer limit was actually 9 wt.% possibly due to the totally different microstructure and existing conformation of FeVO₄ species from that of V₂O₅ on TiO₂ surface. Because of the relatively strong Raman signal of the TiO₂ support, the Raman shifts of the surface FeVO₄ species (which should appear in the ranges of 300-400 cm⁻¹ and 700-1000 cm⁻¹) cannot be well discriminated. Therefore, the enlargement of the Raman spectra of 9 wt.% FeVO₄/TiO₂ catalyst is shown in Fig. 6E. As we can see, besides the typical TiO₂ bands, there were indeed some surface species formed on the 9 wt.% FeVO₄/TiO₂ catalyst in the range of 700–1000 cm⁻¹, which can be further confirmed as the surface FeVO₄ phase by comparing with the standard Raman spectra [43]. As for the 9 wt.% Fe₂O₃/TiO₂ and 9 wt.% V₂O₅/TiO₂ catalysts, on which no active phases can be de-



Fig. 6. (A) Raman spectra of x wt.% FeVO₄/TiO₂ catalysts; (B) normalized Raman peak ascribed to the v_1 vibration mode of CaCO₃ at 1073 cm⁻¹ as internal reference; (C) normalized Raman signals of x wt.% FeVO₄/TiO₂ catalysts; (D) the integrated area of TiO₂ vibration bands at 641 cm⁻¹; Raman spectra of (E) 9 wt.% FeVO₄/TiO₂, (F) 9 wt.% Fe₂O₃/TiO₂ (inset: the enlargement of spectra in the range of 1100–1550 cm⁻¹); (G) 9 wt.% V₂O₅/TiO₂ catalysts and corresponding reference samples.

tected by XRD either, the presence of surface Fe₂O₃ and V₂O₅ species were also verified, respectively, by comparing their Raman spectra with those of standard materials (Fig. 6F and G) [43,44]. In the following sections, the electronic property and local structure of the surface active species on the supported-type catalysts will be investigated using XAS and XPS methods.

3.6. XAS results

Fig. 7A and B shows the normalized XANES spectra of the Fe Kedge in Fe-containing samples and the corresponding first-order derivatives, respectively. The 9 wt.% Fe₂O₃/TiO₂ catalyst showed a single pre-edge peak similar to that of pristine Fe₂O₃ at ca. 7110.2–7111.2 eV, confirming the formation of surface Fe₂O₃ species as indicated by Raman spectra. The post-edge region of Fe–K XANES for the 9 wt.% Fe₂O₃/TiO₂ catalyst was much smoother than that of pristine Fe₂O₃, indicating the much smaller particle size of surface Fe₂O₃ species due to their dispersion on the TiO₂ support. As for the FeVO₄ sample, two characteristic peaks at 7110.5 and 7115.4 eV in the pre-edge region were clearly observed, and its post-edge region was totally different from that of Fe₂O₃, probably due to the scattering of emitted photoelectrons by surrounding vanadium atoms. Both the 9 wt.% FeVO₄/TiO₂ and 15 wt.% FeVO₄/ TiO₂ catalysts showed very similar XANES patterns to that of the FeVO₄ reference, validating the formation of surface FeVO₄ species again. It is noteworthy that the absorption edge energy (i.e. the corresponding energy relative to the maximum of the first-order derivatives) of Fe-K in pristine Fe₂O₃ was 7123.1 eV, while the corresponding values in 9 wt.% Fe₂O₃/TiO₂, FeVO₄ reference, 9 wt.% FeVO₄/TiO₂ and 15 wt.% FeVO₄/TiO₂ were shifted to 7123.4 eV toward the higher energy range. In our previous study [45,46], we concluded that an electronic inductive effect between Fe and Ti species was clearly present in Fe-Ti-containing catalysts, leading to the deviation of electron cloud from Fe³⁺ to Ti⁴⁺. Based on our experience, in XANES results, this electronic inductive effect can be observed through the shift of the adsorption edge energy of a specific element, while in XPS results through the shift of the corresponding binding energy [45–47]. In this study, besides the electronic inductive effect between Fe and Ti species in 9 wt.% Fe₂O₃/ TiO₂ catalyst, a similar phenomenon was also observed between Fe and V species in the FeVO₄ reference, 9 wt.% FeVO₄/TiO₂ and 15 wt.% FeVO₄/TiO₂ catalysts. It is inferred that the electronic cloud around Fe³⁺ species may deviate toward V⁵⁺ in FeVO₄ phase, thus resulting in the increase of average valence of Fe species to a certain extent. If so, the average valence of V species in FeVO₄ phase will decrease to a certain extent to meet the charge balance. This



Fig. 7. (A) Normalized XANES spectra of Fe K-edge in Fe-containing samples and (B) corresponding first-order derivatives; (C) normalized XANES spectra of V K-edge in V-containing samples and (D) corresponding first-order derivatives.

point of view can be well verified by the following V-K XANES results and also the subsequent XPS and DFT calculation results.

Fig. 7C and D shows the normalized XANES spectra of the V Kedge in V-containing samples and corresponding first-order derivatives, respectively. As we can see, the V-K XANES patterns of the 9 wt.% V₂O₅/TiO₂ catalyst were guite similar to that of pristine V₂O₅, although the post-edge region was much smoother due to the small particle size of the supported active phase. Owing to the possible existence of an electronic inductive effect between V and Ti species, the adsorption edge energy of the V K-edge in the 9 wt.% V₂O₅/TiO₂ catalyst (5482.1 eV) was lower relative to that in pristine V_2O_5 (5482.8 eV). It is interesting that, as we expected, compared with the pristine V_2O_5 , not only the pre-edge peak position but also the adsorption edge energy of the V K-edge in FeVO₄ reference, 9 wt.% FeVO₄/TiO₂ and 15 wt.% FeVO₄/TiO₂ catalysts shifted toward the lower energy range. This can be easily explained by the reverse electronic inductive effect by the surrounding Fe³⁺ species, similarly to the Fe K-edge case. In short summary, a relatively strong electronic interaction between Fe³⁺ and V⁵⁺ species was present in the FeVO₄ active phase for NH₃-SCR, resulting in the increase and decrease of the average valence of Fe^{3+} and V^{5+} species to a certain extent, respectively. The enhancement of the oxidation ability of Fe³⁺ species was beneficial to the improvement of SCR activity, while the weakening of the oxidation ability of V⁵⁺ species was favorable for the improvement of N₂ selectivity at high temperatures. This electronic inductive effect must occur through the $Fe^{3+}-O-V^{5+}$ linkage, as can be verified by the following EXAFS results.

Fig. 8 shows the EXAFS spectra of the Fe K-edge in Fe-containing samples, including the Fourier transforms of filtered $k^3 \cdot \chi(k)$ into *R* space (Fig. 8A) and filtered $k^3 \cdot \chi(k)$ in the *k* range from 2.5 to 13 Å⁻¹ (Fig. 8B). The curve-fitting results in *R* space and *k* space using the scattering pathways from FEFF calculations are also presented by red dashed lines and dotted lines, respectively. As shown by the

R factor from Table 2, a rather high fitting degree can be obtained when using Fe₂O₃ and FeVO₄ as references to simulate the experimental data. For pristine Fe₂O₃ and the 9 wt.% Fe₂O₃/TiO₂ catalyst, the first coordination shell was attributed to Fe-O and the second coordination shell to Fe-O-Fe₁ plus Fe-O-Fe₂ with different bond lengths. The Fe–O coordination numbers for the first shell (ca. 6.0) in both samples were similar to each other, while the Fe-O-Fe₁ plus Fe-O-Fe₂ coordination numbers for the second shell in 9 wt.% Fe₂O₃/TiO₂ catalyst was much smaller than those in pristine Fe₂O₃ which was mainly due to the decreased particle size of Fe₂O₃ after dispersion to TiO₂ support. By contrast, for the FeVO₄ reference, 9 wt.% FeVO₄/TiO₂ and 15 wt.% FeVO₄/TiO₂ catalysts, the first coordination shell was also attributed to Fe-O, while the second coordination shell to Fe-O-Fe plus Fe-O-V. For all FeVO₄-containing samples, the Fe-O coordination numbers for the first shell were similar to each other, which was ca. 4.0. However, the peak intensity of the second coordination shell of the supported FeVO₄/TiO₂ catalysts was much lower than that of pristine FeVO₄, and especially the coordination number of Fe-O-V in 9 wt.% FeVO₄/TiO₂ catalyst was only 1.3 ± 0.6. This was an unsaturated coordination state for Fe-O-V linkage, and the corresponding coordination number increased to 2.1 ± 0.9 with 15 wt.% FeVO₄ loading which was probably responsible for the decrease of SCR activity. These results again clearly indicate the high dispersion of active FeVO₄ species onto the TiO₂ support at 9 wt.% loading, with very small particle size and abundant lattice defects for reactant adsorption and activation in the NH₃-SCR reaction.

3.7. XPS results

Fig. 9A–C shows the XPS results for Fe 2p in Fe-containing samples, V 2p in V-containing samples and Ti 2p in Ti-containing samples, respectively, and Table 3 shows the semi-quantitative analysis of surface atomic concentrations (% in molar ratio) over



Fig. 8. EXAFS spectra of Fe K-edge in Fe-containing samples: (A) Fourier transforms of filtered k^{3} . $\chi(k)$ into *R* space, where the red dashed lines correspond to the curve-fitting results; (B) filtered k^{3} . $\chi(k)$ in the *k* range of 2.5–13 Å⁻¹, where the red dotted lines correspond to the curve-fitting results. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Curve-fitting results of Fe K-edge EXAFS in 9 wt.% Fe₂O₃/TiO₂, 9 wt.% FeVO₄/TiO₂ and 15 wt.% FeVO₄/TiO₂ catalysts and corresponding Fe-containing reference samples.

Sample	Reference	Shell	CN ^a	R ^b (Å)	DW [∈] (Å)	R factor (%)
Fe ₂ O ₃	Fe ₂ O ₃	Fe-O Fe-Fe ₁ Fe-Fe ₂	6.0 ± 1.9 3.0 ± 0.8 3.0 ± 1.5	1.95 ± 0.03 2.98 ± 0.02 3.47 ± 0.02	0.098 0.085 0.045	2.6
9 wt.% Fe ₂ O ₃ /TiO ₂	Fe ₂ O ₃	Fe-O Fe-Fe ₁ Fe-Fe ₂	6.2 ± 1.0 1.1 ± 1.2 1.0 ± 1.2	1.96 ± 0.01 2.98 ± 0.06 3.48 ± 0.12	0.080 0.105 0.090	4.9
FeVO ₄	FeVO ₄	Fe-O Fe-Fe Fe-V	4.0 ± 0.6 1.0 ± 1.8 3.0 ± 5.1	1.97 ± 0.01 3.06 ± 0.09 3.46 ± 0.07	0.077 0.070 0.037	4.8
9 wt.% FeVO ₄ /TiO ₂	FeVO ₄	Fe-O Fe-Fe Fe-V	4.1 ± 0.7 0.8 ± 1.1 1.3 ± 0.6	1.98 ± 0.01 3.06 ± 0.09 3.46 ± 0.07	0.071 0.095 0.032	4.4
15 wt.% FeVO ₄ /TiO ₂	FeVO ₄	Fe-O Fe-Fe Fe-V	4.0 ± 0.7 0.8 ± 1.1 2.1 ± 0.9	1.98 ± 0.01 3.06 ± 0.09 3.46 ± 0.07	0.076 0.089 0.078	4.4

^a CN: coordination number.

^b *R*: bond distance.

^c DW: Debye–Waller factor.

different samples derived from the XPS data. As shown in Fig. 9A, two characteristic XPS bands attributed to Fe³⁺ 2p_{3/2} (710.6 eV) and Fe³⁺ 2p_{1/2} (724.1 eV) were observed on pristine Fe₂O₃ [48,49], while these bands shifted to 711.5 and 725.4 eV, respectively, on the FeVO₄ reference, mainly due to the above-mentioned electronic inductive effect between Fe³⁺ and V⁵⁺ species. On the 9 wt.% Fe₂O₃/TiO₂ catalyst, the bands of Fe³⁺ 2p_{3/2} and Fe³⁺ 2p_{1/2} only shifted to 710.9 and 724.8 eV, respectively, indicating that the electronic inductive effect between Fe³⁺ and Ti⁴⁺ species was actually not so strong as that between Fe³⁺ and V⁵⁺ species. Similarly to the pristine FeVO₄ case, on the FeVO₄ supported-type catalysts, the binding energies of both Fe 2p_{3/2} and Fe 2p_{1/2} were also higher than those on Fe₂O₃, which is in accordance with the Fe-K

XANES results. It is noteworthy that, with the increasing of FeVO₄ loading amount, the bands of Fe³⁺ $2p_{3/2}$ and Fe³⁺ $2p_{1/2}$ showed some shifts from 711.2 and 725.1 eV to 711.4 and 725.3 eV, respectively, and the latter binding energies were much closer to the values in pristine FeVO₄. These results also suggest that at relatively higher loadings, the surface FeVO₄ species indeed had a surface convergence on the TiO₂ support as we concluded above. The reverse electronic inductive effect of V⁵⁺ species by surrounding Fe³⁺ species can be clearly observed in Fig. 9B, in which the binding energies of both V⁵⁺ $2p_{3/2}$ and V⁵⁺ $2p_{1/2}$ [50–52] on the FeVO₄ reference and supported-type catalysts all shifted to the lower energy range compared with those on pristine V₂O₅. In order to further confirm the electronic inductive effect between Fe³⁺ and V⁵⁺ spe-



Fig. 9. XPS results of (A) Fe 2p in Fe-containing samples, (B) V 2p in V-containing samples and (C) Ti 2p in Ti-containing samples; (D) the calculated surface V/Fe molar ratios versus FeVO₄ loading amounts.

Table 3

Semi-quantitative analysis of surface atomic concentrations (% in molar ratio) over Fe₂O₃/TiO₂, V₂O₅/TiO₂ and FeVO₄/TiO₂ catalysts and corresponding reference samples derived from XPS data.

Samples	Fe (%)	V (%)	Ti (%)	0 (%)
TiO ₂	-	-	29.9	70.1
Fe ₂ O ₃	20.7	-	-	79.3
9 wt.% Fe ₂ O ₃ /TiO ₂	4.2	-	26.1	69.7
V ₂ O ₅	-	29.8	-	70.2
9 wt.% V ₂ O ₅ /TiO ₂	-	4.6	26.3	69.1
FeVO ₄	11.3	17.7	-	71.0
3 wt.% FeVO ₄ /TiO ₂	0.9	0.9	28.1	70.1
6 wt.% FeVO ₄ /TiO ₂	2.1	2.4	25.6	69.9
9 wt.% FeVO ₄ /TiO ₂	2.5	3.7	24.5	69.3
15 wt.% FeVO ₄ /TiO ₂	3.2	5.0	22.8	69.0

cies in FeVO₄ catalyst, the DFT calculation was conducted based on periodical model structures. The average Hirshfeld charge of Fe in stoichiometric Fe₂O₃ and FeVO₄ was calculated to be 0.27 and 0.33, while the value of V in V₂O₅ and FeVO₄ was calculated to be 0.54 and 0.53. In FeVO₄, the charge of Fe and V indeed increased and decreased to a certain extent comparing with that in pristine Fe₂O₃ and pristine V₂O₅, respectively. This trend can also be seen in the

electron density difference map, as shown in Fig. 10. The electron transfers from Fe to the coordinated oxygen and further to neighboring V atoms (Fig. 10C). Therefore, more charge accumulation (depletion) around V (Fe) can be obtained in FeVO₄ than that in V_2O_5 (Fe₂O₃), which is in well accordance with the XANES results in Section 3.6 and the XPS results in this section.

As for 9 wt.% V_2O_5/TiO_2 catalyst, the bands of $V^{5+} 2p_{3/2}$ and $V^{5+} 2p_{1/2}$ also shifted to lower energy range, suggesting that the electronic inductive effect between V^{5+} and Ti^{4+} species was also present resulting in the decrease and possible increase of the average valence of V^{5+} and Ti^{4+} species to a certain extent. The decrease of the average valence of V^{5+} species has already been confirmed by the V-K XANES results in Fig. 7C and D, and the increase of the average valence of Ti^{4+} species can be proved by the Ti 2p XPS results in Fig. 9C. Herein, we can conclude that the electronic inductive effect between different elements may universally exist in mixed oxides or supported-type catalysts, such as the Fe–Ti-containing materials in our previous study [45,46] and the Fe–V, V–Ti-containing materials in this study.

Back to Fig. 9B, it is interesting that, unlike the case of Fe 2p XPS results, with the FeVO₄ loading increasing from 3 to 15 wt.% the bands of both V^{5+} 2p_{3/2} and V^{5+} 2p_{1/2} on the supported-type catalysts showed some shifts (from the binding energies close to the



Fig. 10. Electron density differences of (A) Fe₂O₃, (B) V₂O₅ and (C) FeVO₄.

prsitine FeVO₄) to the binding energies at 517.4 and 525.0 eV, which were quite close to the corresponding values of V_2O_5/TiO_2 catalyst. This "abnormal" phenomenon indicates that, the FeVO₄/ TiO_2 catalysts may have a surface enrichment of VO_x species at relatively high FeVO₄ loadings, which can be verified by the semiquantitative analysis of surface atomic concentrations in Table 3 and the calculated V/Fe molar ratios versus FeVO₄ loading amounts in Fig. 9D. Although the theoretical molar ratio of Fe:V in FeVO₄ should be 1:1, the surface concentration of V^{5+} species (17.7%) was much higher than that of Fe^{3+} (11.3%). It was reported that the bulk FeVO₄ phase was actually surface-enriched with VO_x species, and the catalytic active sites for oxidation reactions (e.g. methanol oxidation) over the bulk FeVO₄ mixed oxide resided in the outermost surface layer but not in the bulk lattice structure [43]. For FeVO₄/TiO₂ catalysts, with the increasing of FeVO₄ loading amounts from 3 to 15 wt.%, the V/Fe molar ratios showed a monotonic increase from 1.00 to 1.56 approaching the value of 1.57 on pristine FeVO₄. These results clearly imply that at high FeVO₄ loadings especially exceeding the monolayer dispersion limit, the FeVO₄/TiO₂ catalyst surface was indeed surface-enriched by VO_x species. Therefore, it is concluded that the surface-enriched VO_x species on the FeVO₄/TiO₂ catalysts is responsible for the preservation of high NH₃-SCR activity plus H₂O/SO₂ durability, and the presence of Fe³⁺ species can effectively weaken the unselective oxidation of NH₃, thus resulting in high N₂ selectivity at high temperatures.

3.8. Thermal stability test of 9 wt.% FeVO₄/TiO₂ catalyst

In practical use, the NH₃-SCR catalysts should have good thermal stability in the long term deNO_x process for both stationary and mobile sources. Therefore, in the preparation process of 9 wt.% FeVO₄/TiO₂ catalyst, we also elevated the calcination temperature to 500, 600, 650, 700, and 800 °C to investigate the activity and structure change of this novel catalyst. As we can see in Fig. 11, the 9 wt.% FeVO₄/TiO₂ catalysts calcined at 400, 500 and 600 °C for 6 h showed quite similar NH₃-SCR activity, although the XRD patterns (Fig. 12) and N_2 physisorption results (Table 4) indicated that after calcination at 600 °C the anatase TiO₂ support showed higher crystallinity degree along with lowered surface area and pore volume. Further increasing the calcination temperature to 650, 700, and 800 °C resulted in an obvious and monotonic decrease of NH₃-SCR activity, which was mainly due to the phase transformation of anatase TiO₂ to rutile TiO₂ accompanying by the severe decrease of surface area and pore volume. It is



Fig. 11. NO_x conversion in NH_3 -SCR reaction as a function of temperature over 9 wt.% FeVO₄/TiO₂ catalysts calcined at different temperatures for 6 h.



Fig. 12. Powder XRD patterns of 9 wt.% $FeVO_4/TiO_2$ catalysts calcined at different temperatures for 6 h.

noteworthy that, even after the high temperature calcination, neither Fe species nor V species was detected in the XRD patterns, suggesting that the active FeVO₄ species could indeed exist on the TiO₂ support in a well dispersed state. In short summary, this FeVO₄/TiO₂ catalyst can only be stably used below 600 °C, which can completely meet the requirements for deNO_x process of sta-

Samples	$S_{BET}^{a} (m^2 g^{-1})$	Pore volume ^b ($cm^3 g^{-1}$)	Pore diameter ^{c} (nm)
9 wt.% FeVO ₄ /TiO ₂ -400 °C	75.0	0.36	19.2
9 wt.% FeVO ₄ /TiO ₂ -500 °C	77.8	0.32	16.3
9 wt.% FeVO ₄ /TiO ₂ -600 °C	47.7	0.28	23.8
9 wt.% FeVO ₄ /TiO ₂ -650 °C	21.7	0.09	18.2
9 wt.% FeVO ₄ /TiO ₂ -700 °C	11.3	0.03	10.8
9 wt.% FeVO ₄ /TiO ₂ -800 °C	7.5	0.01	7.8

Table 4

Textural parameters of 9 wt.% FeVO₄/TiO₂ catalysts with different calcination temperatures for 6 h derived from N₂ physisorption results.

^a BET surface area.

^b BJH desorption pore volume.

^c Average pore diameter.

tionary sources and also heavy duty diesel engines with Euro IV/V emission standards without the usage of DPF system. The SCR converter using this catalyst system cannot fulfill the needs for deNO_x process of diesel engines with higher emission standard such as Euro VI if the DPF system is installed upstream with timed thermal shock (~800 °C) in the regeneration processes. The deposition of FeVO₄ catalyst onto other alternative supports with much higher thermal stability than that of anatase TiO₂ is probably an efficient method to expand its application scope in the near future.

4. Conclusions

An iron vanadate catalyst supported on TiO₂ (9 wt.% FeVO₄/ TiO₂) was prepared using a facile co-impregnation method for NH₃-SCR of NO_x in the medium temperature range, with high deNO_x efficiency and H₂O/SO₂ durability. The FeVO₄ active phase did not enter the lattice structure of anatase TiO₂, and only existed on the support surface with a high degree of dispersion. The presence of Fe^{3+} –O–V⁵⁺ linkages with low coordination number of vanadium atoms related to large surface defects was evidenced by EXAFS results, and the electronic inductive effect between Fe³⁺ and V⁵⁺ species was confirmed by XANES and XPS results. The true catalytically active phase on the FeVO₄/TiO₂ catalyst was the surface-enriched VO_x species, which was responsible for the high NH₃-SCR activity and H₂O/SO₂ durability, while the presence of Fe³⁺ species could effectively decrease the unwanted NH₃ unselective oxidation at high temperatures, thus resulting in the observed high N₂ selectivity. This novel catalyst is promising for use in the deNO_x process of flue gas from coal-fired power plants or in diesel engine exhaust.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.08.003.

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