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Promotional effect of Fe and Ce co-doping on a V_2O_5 – WO_3 /TiO₂ catalyst for SCR of NO_x with high K and Pb resistance†

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There is an increasing demand to develop efficient SCR deNO_x catalysts with high resistance to alkali and heavy metals. In this study, a V_2O_5 – WO_3 /TiO₂ (denoted VWTi) catalyst modified with FeO_x and CeO_x in 0.05Fe/V and 1.5Ce/V molar ratio (denoted FeCeVWTi) showed enhanced SCR activity and resistance to K–Pb co-poisoning in the temperature range of 300–400 °C. The FeCeVWTi catalyst also presented outstanding tolerance to H₂O and SO₂. After K–Pb poisoning, the FeCeVWTi catalyst showed 92.7% NO_x conversion at 350 °C, much higher than that of the VWTi catalyst (70.6%). The Fe and Ce co-doping significantly improved the redox ability, V⁵⁺ ratio and surface chemisorbed oxygen ratio of the VWTi catalyst by the interaction between Fe, Ce and V. The cooperation between Fe and Ce slightly decreased the surface acidity but significantly enhanced the NO_x adsorption on the FeCeVWTi catalyst. Additionally, *in situ* DRIFTS revealed that the SCR reaction on VWTi followed an E–R mechanism, while Fe and Ce co-doping changed the reaction route and made the SCR reaction on FeCeVWTi follow both an E–R mechanism and an L–H mechanism. The enhanced redox ability and adsorption of NO_x played decisive roles in improving the alkali-heavy metal resistance of the FeCeVWTi catalyst.

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1 Introduction

The selective catalytic reduction of NO_x with ammonia (NH₃-SCR) is an effective technology for NO_x removal from stationary sources or diesel vehicle exhaust.^{1,2} Commercial V_2O_5 – WO_3 /TiO₂ (VWTi) catalysts exhibit excellent deNO_x efficiency between 300 °C and 400 °C, in which TiO₂ is the carrier supporting the main active component V₂O₅ and promoter WO₃. However, the severe deactivation of commercial catalysts by alkali and heavy metals is still a problem to be solved in practical industrial applications.^{3–5} Therefore, there is an increasing demand to develop efficient catalysts with high resistance to alkali and heavy metals in complex flue gas.

The deposition of alkali/heavy metals on VWTi catalysts in power plant flue gas mainly occupies acid sites to decrease the adsorption quantity of ammonia and reduce the redox ability simultaneously, which are the two primary factors in the deactivation of SCR catalysts.^{3,4} Some efficient

suggestions have been reported to enhance the acidity and redox property of metal oxide catalysts, such as modification with transition metals and rare earth metals, optimization of preparation methods, the creation of novel nanostructures, adjustment of morphology, and exposure of specific crystalline planes. Based on the principles of low cost and high efficiency in commercial applications, transition metals and rare earth metals were commonly used to modify the VWTi catalyst to improve the resistance to alkali and heavy metal poisoning. Highly efficient metal oxide catalysts generally contain main active components such as VO_x, MnO_x, CeO₂, Fe₂O₃, or CuO and promoters such as WO₃, TiO₂, ZrO₂, etc.⁴

In recent years, some researchers have improved the K-poisoning resistance of VWTi catalysts through bi-component doping, which showed much better performance than single-component modification due to the synergistic effect between the two components, such as a Ce(SO₄)₂ and Cu(NO₃)₂ co-modified VWTi catalyst⁶ and a CeO₂ and ZrO₂ co-doped VWTi catalyst.² Fe³⁺ and Zr⁴⁺ were used to modify a CeTiO_x catalyst, which provided additional reducibility and surface acidity, and it exhibited better K resistance than Fe³⁺ or Zr⁴⁺ doped CeTiO_x.⁷

Ceria has been reported in modifying SCR catalysts because of its excellent redox ability. Some researchers suggested that Ce addition could enhance the alkali metal

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resistance of the catalysts by promoting the surface acidity and redox ability. He *et al.*⁸ and Liu *et al.*⁹ introduced CeO₂ into V₂O₅-WO₃/TiO₂ and V₂O₅/TiO₂ catalysts to improve their K resistance. Fe₂O₃ has also been studied to enhance the NO conversion and SO₂ resistance of VWTi and VTi catalysts.^{10,11} The electronic inductive effect between Fe and V species was reported to improve the activity and N₂ selectivity of an Fe-V-Ti catalyst at high temperatures.¹² Moreover, it has been reported that there was a synergistic effect between Fe and Ce. The addition of Fe could increase the amount of Ce³⁺ and the formation of Fe-O-Ce species could lead to strong electron interaction between Fe³⁺-O-Ce⁴⁺ species,^{13,14} that could improve the SCR activity. Therefore, it is hypothesized that Fe and Ce co-doping may improve the SCR activity and K-poisoning resistance of a V₂O₅-WO₃/TiO₂ catalyst.

In previously reported work, many researchers have focused on ways to improve alkali-poisoning resistance but few studies have been reported about resistance to heavy metal and multi-element co-poisoning. Thus, it is meaningful to explore catalysts resisting alkali and heavy metal co-poisoning. For commercial V₂O₅-WO₃/TiO₂ catalysts, K is the most toxic alkali metal¹⁵ and Pb is a representative heavy metal. In this work, we synthesized a series of modified V₂O₅-WO₃/TiO₂ catalysts with cerium and ferric oxides *via* the impregnation method. Various characterization techniques were used to investigate the changes in chemical and physical properties over modified and poisoned catalysts and to study the effect of Fe and Ce oxides on improving the K-Pb-poisoning resistance. Further, the reaction mechanism was studied by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS).

2 Experimental

2.1 Catalyst preparation

The modified V₂O₅-WO₃/TiO₂ catalysts with cerium and ferric oxides were prepared by the impregnation method. First, ferric nitrate (Fe(NO₃)₃·9H₂O) and cerium nitrate (Ce(NO₃)₃·6H₂O) were mixed in deionized water with designed molar ratios (Fe/V = 0.05 and Ce/V = 1.5 chosen according to the pre-experiments presented in Fig. S1†). Fresh commercial V₂O₅-WO₃/TiO₂ SCR catalyst (1 wt% V₂O₅ and 3 wt% WO₃) was added to the above aqueous solution under stirring and then it was subjected to ultrasonic treatment for 30 min at room temperature, followed by aging for 12 h. Second, the mixtures were dried at 110 °C for 6 h and then calcined at 450 °C in air for 5 h. The obtained FeO_x-CeO_x-V₂O₅-WO₃/TiO₂ were abbreviated to FeCeVWTi. For comparison, CeO_x-V₂O₅-WO₃/TiO₂ catalyst was prepared by the same procedure and abbreviated to CeVWTi.

The K₂O and PbO_x co-poisoned catalysts were prepared with KNO₃ and Pb(NO₃)₂ aqueous solutions by the above procedure. The molar ratio of K/V and Pb/V was 0.5. Herein, K-Pb-poisoned catalysts are abbreviated to VWTi-K-Pb, CeVWTi-K-Pb and FeCeVWTi-K-Pb, respectively.

2.2 NH₃-SCR performance test

NH₃-SCR activity and H₂O + SO₂ tolerance were tested in a fixed-bed microreactor with a quartz tube (inner diameter = 7.5 mm), using 0.600 g of catalyst (40–60 mesh). The gas hourly space velocity (GHSV) was about 60 000 mL g⁻¹ h⁻¹. The total volume flow rate was 600 mL min⁻¹. The feed gas was a mixture of 500 ppm NO_x, 500 ppm NH₃, 5 vol% O₂, 500 ppm SO₂ (when used), 5 vol% H₂O (when used) and the balance was N₂. The concentrations of NO, NO₂, N₂O, NH₃ and SO₂ were continuously determined by a Fourier transform infrared (FTIR) gas analyzer (Antaris IGS, Thermo Fisher Scientific). The activity and N₂ selectivity were calculated as follows:

$$\text{NO}_x \text{ conversion} = (1 - [\text{NO}_x]_{\text{out}}/[\text{NO}_x]_{\text{in}}) \times 100\%$$

$$\text{N}_2 \text{ selectivity} = (1 - 2[\text{N}_2\text{O}]_{\text{out}}/([\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}})) \times 100\%$$

where [NO_x]_{in} and [NO_x]_{out} represent the inlet and outlet concentrations of NO_x (the sum of NO and NO₂). [NH₃]_{in} and [NH₃]_{out} are the inlet and outlet concentrations of NH₃, and [N₂O]_{out} is the outlet concentration of N₂O.

2.3 Catalyst characterization

The specific surface area and pore size of the catalysts were measured by N₂ adsorption-desorption at 77 K adopting the Brunauer-Emmett-Teller (BET) method using a Nova 2000e analyzer (Quantachrome Corp., USA) with pre-treatment of each sample at 300 °C for 3 h under vacuum. The content of each element in the catalysts was determined with an Axios Max X-ray fluorescence spectrometer (XRF, PANalytical B.V., Holland). Powder X-ray diffraction (XRD) patterns were collected with an X'Pert Pro XRD diffractometer (PANalytical B.V., Holland) with Cu Kα radiation. The surface element chemical state of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) that was performed on an AXIS Supra of Kratos Analytical Inc. The X-ray source was monochromatized Al Kα radiation (*hν* = 1486.6 eV), and it was referred to the contaminant carbon peak (C 1s = 284.8 eV) to calibrate the shift in binding energies.

The temperature-programmed reduction of H₂ (H₂-TPR) and temperature-programmed desorption of NH₃ (NH₃-TPD) were tested with a chemisorption analyzer (ChemBET3000 TPR-TPD Quantachrome, USA) connected to on-line mass spectroscopy (MS). Before a TPD or TPR test, the sample was purged in He at 400 °C for 1 h and cooled to room temperature. In the NH₃-TPD test, 150 mg of the sample was exposed to 5% NH₃/He for 1 h followed by purging with He for 45 min at 100 °C to remove weakly adsorbed NH₃ on the surface and then heated up to 600 °C under He flow at a rate of 10 °C min⁻¹. For H₂-TPR, 50 mg of the sample was exposed to 5% H₂/Ar for 30 min at room temperature and then heated to 900 °C at a rate of 10 °C min⁻¹.

Temperature-programmed desorption of NO + O₂ (NO + O₂-TPD) experiments were carried out in the reactor of the NH₃-SCR performance test. The concentrations of NO, NO₂ and NO_x were continually monitored with a Fourier transform infrared (FTIR) gas analyzer (Antaris IGS, Thermo Fisher Scientific). Prior to a TPD experiment, 200 mg samples (40–60 mesh) were pre-treated in N₂ at a flow rate of 200 mL min⁻¹ at 400 °C for 60 min, and then cooled down to room temperature. The samples were then exposed to a flow gas containing 2000 ppm NO, 5 vol% O₂ with the balance N₂ for 60 min, followed by N₂ purging at 60 °C for 60 min. Finally, the temperature was raised to 600 °C in N₂ at a rate of 5 °C min⁻¹.

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) measurements were carried out on a Bruker Vertex 70 infrared spectrometer (Bruker, Germany). Before each test, the sample was heated to 400 °C for 1 h with highly-purified N₂ to remove impurities. Then the sample was cooled to the target temperature in an N₂ atmosphere to collect the background spectrum. Then, the reaction gas was introduced into the reaction chamber and the spectra were recorded at a resolution of 4 cm⁻¹ with 64 scans every minute. The obtained spectra with the background spectrum automatically subtracted were transformed into absorption spectra using the Kubelka-Munk function.

3 Result and discussion

3.1 NH₃-SCR activity

3.1.1 NO_x conversion and N₂ selectivity. Generally, the operating temperature window of a commercial VWTi catalyst reducing NO_x in fixed sources is between 300 and 400 °C. In order to select the optimal molar ratio of Fe and Ce doping, the catalytic test was done in a higher GHSV of 110 000 mL g⁻¹ h⁻¹ and a wider temperature range from 250 to 400 °C. Fig. S1† shows the NO_x conversion and N₂ selectivity of modified VWTi catalysts with different Ce/V and Fe/V molar ratios. In Fig. S1A,† the NH₃-SCR activities of xCeVWTi (*x* representing Ce/V) catalysts followed the sequence VWTi < 1.0CeVWTi < 1.5CeVWTi ≈ 2.0CeVWTi. Considering the activity and cost, 1.5 was the most suitable molar ratio of Ce/V. As shown in Fig. S1B,† the NH₃-SCR activities of yFeCeVWTi (*y* representing Fe/V) catalysts followed the sequence 0.02FeCeVWTi < 0.10 FeCeVWTi < 0.05FeCeVWTi and 0.05 was chosen as the optimal Fe/V molar ratio. As shown in Fig. 1, the NH₃-SCR activities followed the sequence VWTi < CeVWTi < FeCeVWTi. FeCeVWTi exhibited 94.1% NO_x conversion at 250 °C, whereas CeVWTi and VWTi samples displayed 87.3% and 75.1%, respectively. A small amount of Fe doping into the CeVWTi catalyst improved the SCR catalytic activity, especially at a temperature below 350 °C. The FeCeVWTi catalyst modified with a ratio of 0.05 Fe/V and 1.5 Ce/V shows the best catalytic activity among these samples, with NO_x conversion above 94% and N₂ selectivity above 99% (as

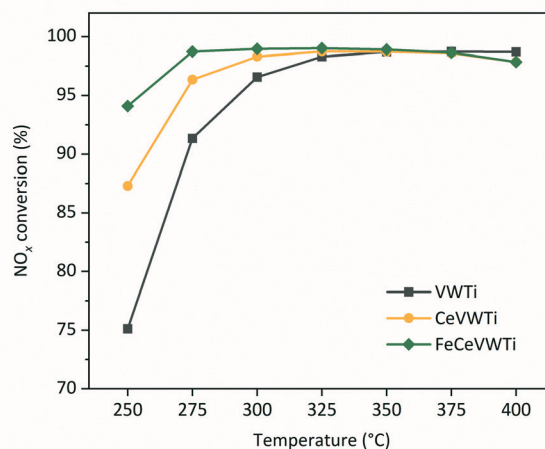


Fig. 1 NO_x conversion of fresh catalysts in GHSV of 110 000 mL g⁻¹ h⁻¹.

shown in Fig. S2†) in the tested temperature range and with GHSV of 110 000 mL g⁻¹ h⁻¹.

The NH₃-SCR activities of K-poisoned catalysts (molar ratio K/V = 1.0) were tested and the results are shown in Fig. S3.† FeCeVWTi-K exhibited 88.6% NO_x conversion, whereas the CeVWTi-K and VWTi-K samples displayed 76.2% and 47.4%, respectively, at 350 °C in GHSV of 60 000 mL g⁻¹ h⁻¹. Fe and Ce doping into the VWTi catalyst significantly enhanced its K resistance. The co-poisoning of K and Pb on these catalysts was further tested. As shown in Fig. 2, FeCeVWTi-K-Pb exhibited 92.7% NO_x conversion at 350 °C, whereas the CeVWTi-K-Pb and VWTi-K-Pb samples displayed 91.1% and 70.6%, respectively. The sequence of these catalysts in resistance to K poisoning and K-Pb co-poisoning was: FeCeVWTi > CeVWTi > VWTi. The above results showed that the cooperation of Fe and Ce effectively enhanced the catalytic activity and the anti-poisoning ability of the VWTi catalyst, and a small amount of Fe doping into CeVWTi played a crucial role in improving the catalytic performance and reducing the economic cost of the catalysts.

3.1.2 Effect of H₂O and SO₂. H₂O and SO₂ generally exist in industrial flue gas, which would have negative effects on the performance of the catalyst. Therefore, it is very necessary for SCR catalysts to have high resistance to H₂O and SO₂. Some research has shown that a commercial V₂O₅-WO₃/TiO₂ SCR catalyst has strong resistance to H₂O and SO₂.^{6,16} Therefore, as shown in Fig. 3, the effect of H₂O and SO₂ with time on the FeCeVWTi sample was tested in GHSV of 60 000 mL g⁻¹ h⁻¹ and at the typical operating temperature (350 °C). Firstly, the SCR reaction was stabilized at 350 °C for 1 h without H₂O or SO₂ and the NO_x conversion of FeCeVWTi was 100%. Then, 5 vol% H₂O was added into the feed gas, and the NO_x conversion of FeCeVWTi slightly decreased by 0.4% and remained stable. Subsequently, after 5 vol% H₂O and 500 ppm SO₂ were both introduced, its NO_x conversion decreased to 98.7% in the first 1 h and then recovered to 99.6% and remained stable over the next 23 h. Finally, after

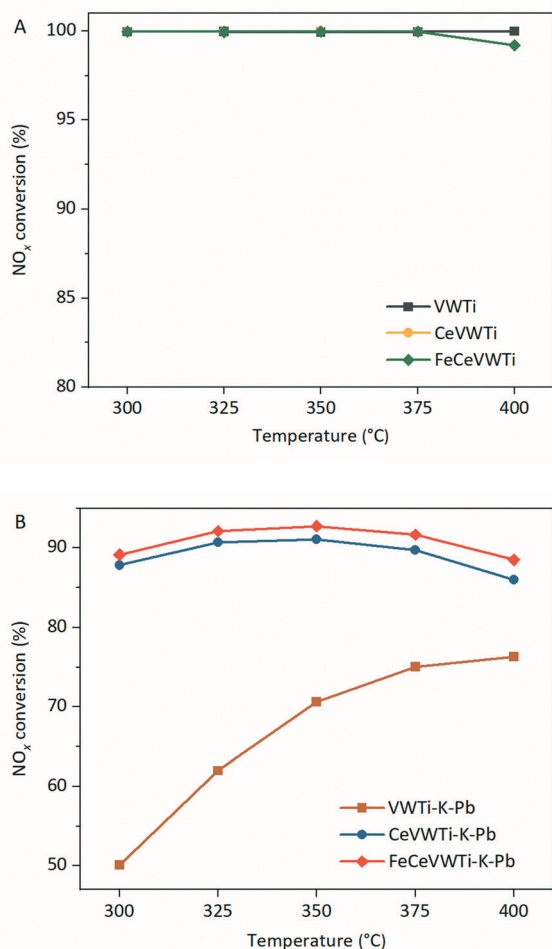


Fig. 2 NO_x conversion of (A) fresh and (B) K-Pb-poisoned catalysts in GHSV of 60 000 mL g⁻¹ h⁻¹.

removing H₂O and SO₂, its NO_x conversion quickly recovered to 100%. The results showed that the NO_x conversion of FeCeVWTi was nearly unaffected by H₂O and SO₂ at 350 °C.

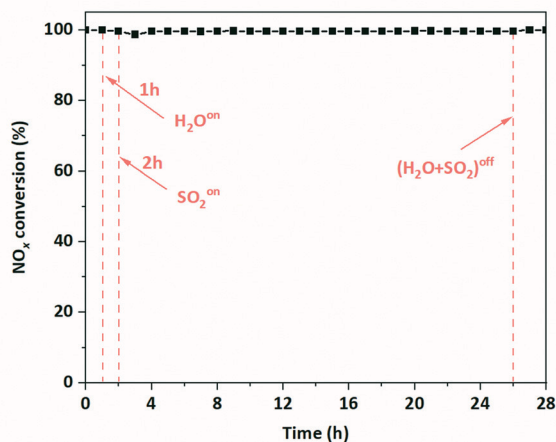


Fig. 3 Effect of H₂O and SO₂ on the NO_x conversion of the FeCeVWTi catalyst at 350 °C.

Moreover, the NO_x conversion of the FeCeVWTi catalyst was stable in the presence of H₂O and SO₂ for 24 h, indicating its good stability. Therefore, the FeCeVWTi catalyst has potential application in practical industry due to its efficient catalytic activity, good stability and high resistance to H₂O and SO₂.

3.2 Composition and structure

As shown in Table S1,[†] the doped Fe/V, Ce/V, K/V and Pb/V molar ratios measured by XRF approached the stoichiometric ratio in preparation. Fig. 4 shows the XRD patterns of the fresh and K-Pb co-poisoned catalysts. As shown in Fig. 4, only the diffraction peaks assigned to anatase-phase TiO₂ (PDF 01-084-1285) are detected on all samples, which may be due to the high dispersion or the low concentration of the other elements. The results of the physical properties of the fresh and poisoned catalysts are summarized in Table S2,[†] including the BET surface area (*S*_{BET}), total pore volume (*V*_P), and average pore radius (*r*_A). The *S*_{BET}, *V*_P and *r*_A changed little for the VWTi catalysts after Fe-Ce doping or K-Pb poisoning, demonstrating that the effects of these dopants on the physical properties were negligible. Considering the obvious difference in activity of the poisoned catalysts, the major factors here were not physical properties but chemical properties of the catalyst.

3.3 Surface chemical properties

3.3.1 Surface chemical state. In order to investigate the surface to study their redox property, known to be an important factor for the NH₃-SCR reaction, XPS analysis was conducted to determine the surface chemical state of the samples. The XPS spectrum of Fe 2p is shown in Fig. S5.[†] Two peaks centered at 718.8 eV and 731.5 eV were observed over FeCeVWTi and FeCeVWTi-K-Pb samples, that were assigned to Fe 2p_{3/2} and Fe 2p_{1/2} for Fe³⁺ species.^{17,18}

The XPS spectra of Ce 3d, V 2p_{3/2} and O 1s of the fresh and poisoned catalysts are shown in Fig. 5. The XPS spectra of Ce 3d in Fig. 5A were fitted into ten peaks.¹⁹ The peaks

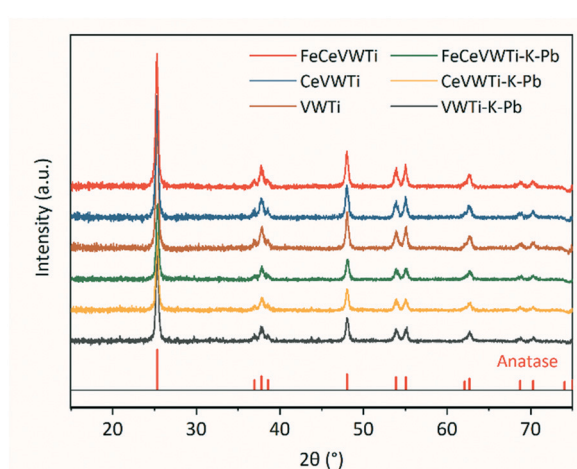


Fig. 4 XRD patterns of fresh and poisoned catalysts.

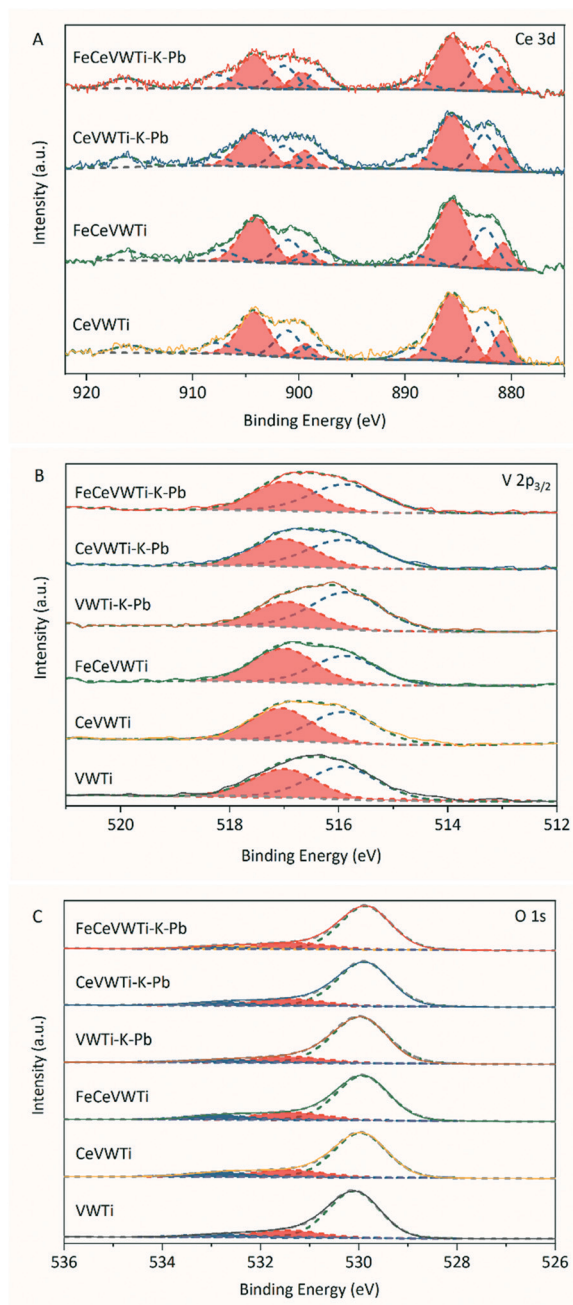


Fig. 5 The XPS spectrum of (A) Ce 3d, (B) V 2p_{3/2}, and (C) O 1s of the fresh and poisoned catalysts.

labeled u''' (916.0 eV), v''' (898.0 eV), u'' (907.7 eV), v'' (888.9 eV), u (901.1 eV) and v (882.5 eV) were assigned to Ce^{4+} . The peaks labeled u_0 (899.4 eV), v_0 (880.8 eV), u' (904.2 eV) and v' (885.6 eV) were associated with Ce^{3+} , suggesting the coexistence of Ce^{3+} and Ce^{4+} on the samples. It has been reported that the Ce^{3+}/Ce^{4+} redox couple is good for the NH_3 -SCR and the presence of Ce^{3+} is accompanied by the generation of oxygen vacancies according to charge compensation, resulting in a higher ratio of surface-active oxygen.²⁰ The atomic ratio of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ was calculated from the area ratio, and the results are listed in Table 1. Ce^{3+}

Table 1 Surface atomic ratios (%) from XPS over samples

Sample	$V^{5+}/(V^{5+} + V^{4+})$	$Ce^{3+}/(Ce^{3+} + Ce^{4+})$	$(O_{\beta} + O_{\gamma})/O_{\alpha}$
VWTi	45.3	—	25.0
CeVWTi	49.8	59.0	29.8
FeCeVWTi	54.0	56.4	31.9
VWTi-K-Pb	38.1	—	21.1
CeVWTi-K-Pb	46.9	55.2	26.1
FeCeVWTi-K-Pb	48.3	53.5	27.4

was the predominant valence state (more than 50%) in these modified catalysts. When Fe was added into the CeVWTi catalyst, the Ce^{3+} ratio dropped from 59.0 to 56.4%, indicating that the addition of Fe may slightly affect the content of Ce^{3+} , because the redox cycles between Fe and Ce ($Fe^{3+} + Ce^{3+} \leftrightarrow Fe^{2+} + Ce^{4+}$) could transfer electrons from Ce^{3+} to Fe^{3+} , thus possibly leading to the slight decrease in the Ce^{3+} ratio. K-Pb poisoning reduced the Ce^{3+} content and thus the reducibility of the CeVWTi and FeCeVWTi catalysts.²¹ According to the literature²² the combination of divalent or trivalent metal cations with a CeO_2 matrix could produce exogenous oxygen vacancies. Ce in the CeO_2 lattice was replaced by Fe, resulting in uneven charge, thus forming oxygen vacancies. Although the $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ ratio was slightly decreased by Fe doping, the addition of Fe contributed to the formation of oxygen vacancies on the catalyst surface.

Fig. 5B shows V 2p_{3/2} spectra of all samples. Each spectrum was fitted into two peaks with binding energies at 515.8–515.9 eV and 516.9–517.1 eV, which were assigned to V^{4+} and V^{5+} of vanadium oxide, respectively.²³ The oxidation of adsorbed ammonia species has been proved to be a key step in the SCR reaction. For commercial VWTi catalysts, oxidation mainly occurs at the vanadium redox site ($V^{5+} = O$).⁶ The V^{5+} ratio was calculated with $V^{5+}/(V^{4+} + V^{5+})$, and the results are shown in Table 1. After introducing Ce into VWTi, the V^{5+} ratio increased from 45.3 to 49.8%. Some studies^{6,24} have demonstrated the existence of the redox cycle $V^{4+} + Ce^{4+} \leftrightarrow V^{5+} + Ce^{3+}$. When Fe was introduced, the V^{5+} ratio of CeVWTi further increased to 54.0%. That may be due to the interaction between V, Fe and Ce through the redox cycles^{25,26} of V^{5+}/V^{4+} , Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} . There was also a similar effect among Fe, Ce and V species in FeCeVWTi catalysts that provided Ce^{3+} and a higher V^{5+} ratio, and increased the redox ability.¹⁹ Topsoe²⁷ *et al.* reported that the decrease in V^{5+} caused a deterioration in the redox properties of the catalyst. Therefore, K-Pb poisoning decreased the V^{5+} ratio and then the redox ability of these catalysts, which may be one of reasons for the decrease in their activity. However, the ratio of V^{5+} was 48.3% for the FeCeVWTi-K-Pb catalyst, which was higher than that of VWTi-K-Pb (38.1%) or CeVWTi-K-Pb (46.9%). Fe and Ce co-doping inhibited the decrease in the V^{5+} ratio resulting from K-Pb poisoning and contributed to the FeCeVWTi-K-Pb catalyst retaining higher redox ability than the VWTi-K-Pb catalyst.

As shown in Fig. 5C, the O 1s peaks could be fitted into three peaks referred to the lattice oxygen species at 530.0 ± 0.1 eV (denoted O_α), the surface OH group at 531.5 ± 0.1 eV (denoted O_β) and the weakly adsorbed oxygen at 532.9 ± 0.1 eV (denoted O_γ).^{28,29} It is universally acknowledged that surface chemisorbed oxygen ($O_\beta + O_\gamma$) is much more reactive in SCR reactions than lattice oxygen species (O_α). The surface chemisorbed oxygen species can effectively oxidize NO to NO_2 , thus improving the catalytic activity *via* a “fast NH_3 -SCR” route.² As listed in Table 1, the ratios of surface chemisorbed oxygen ($O_\beta + O_\gamma$) to lattice oxygen (O_α) over the CeVWTi samples increased compared with VWTi, which further increased after the addition of Fe^{3+} . After K-Pb poisoning, the ($O_\beta + O_\gamma$)/ O_α ratios decreased and their sequence was as follows: FeCeVWTi-K-Pb > CeVWTi-K-Pb > VWTi-K-Pb, consistent with the order in SCR activity of these catalysts. The FeCeVWTi and FeCeVWTi-K-Pb samples possessed the highest surface chemisorbed oxygen ratio and V^{5+} ratio among fresh and poisoned samples, which contributed to its highest activity and K-Pb resistance.

3.3.2 Redox property. The redox property is known to be another important factor for the NH_3 -SCR reaction. Fig. 6 shows the H_2 -TPR profiles for estimating the reducibility of different catalysts. An m/z ratio of 2 in the MS data was selected as the H_2 component. As shown in Fig. 6, the reduction peaks centered at 470 °C and 538 °C^{2,30,31} in the VWTi catalyst could be ascribed to the reduction $V^{5+} \rightarrow V^{4+} \rightarrow V^{3+}$ in the surface region. The peak centered at 645 °C in the VWTi catalyst was attributed to the reduction of WO_x .³⁰ Compared with VWTi, the reduction peaks at 460 °C and 572 °C of the CeVWTi catalyst shown in Fig. S6,[†] could be attributed to the overlapping reduction peaks of nonstoichiometric Ce^{4+} and V^{5+} in the surface region.³² The peak centered at 667 °C on the CeVWTi catalyst was ascribed to the overlapping reduction of CeO_2 and WO_x .^{24,32} With the introduction of Fe, the reduction peak at 460 °C ascribed to

surface Ce^{4+} and V^{5+} on the CeVWTi catalyst shifted to the lower temperature of 451 °C on FeCeVWTi, which may be due to the interaction among Ce, V and Fe oxides. The interaction could effectively improve the redox properties of the FeCeVWTi catalyst, and thus enhance its SCR activity and K-Pb resistance. This was consistent with the conclusion from XPS. Compared with VWTi, the reduction peaks of V species over VWTi-K-Pb shifted to higher temperatures (538 to 582 °C). For FeCeVWTi, the primary reduction peaks also moved to higher temperatures (451 to 465 °C, 570 to 586 °C) after K-Pb poisoning, but the temperature of its first reduction peak was lower than that of VWTi-K-Pb. So, even though K-Pb partially destroyed the redox ability of the catalysts, FeCeVWTi-K-Pb still exhibited higher redox ability than VWTi-K-Pb. In summary, Fe and Ce co-doping enhanced the redox ability of the VWTi catalyst, and effectively inhibited the SCR activity decrease caused by K-Pb poisoning.

3.3.3 Variation in NH_3/NO_x adsorption ability. The adsorption of NH_3 on SCR catalysts is reported to be a crucial step for the NH_3 -SCR reaction.⁴ In order to investigate the change in surface acidity, an NH_3 -TPD test was conducted on fresh and K-Pb-poisoned VWTi and FeCeVWTi catalysts. As shown in Fig. 7, an m/z ratio of 16 in the MS data was selected as an NH_3 indicator, because the signal of $m/z = 17$ may be from ammonia or H_2O and $m/z = 16$ came substantially from ammonia. In order to intuitively reflect the difference in the total acid amount of these samples, the area of the NH_3 -TPD curve for each catalyst was integrated and normalized by the area of the VWTi sample. The results were in the following sequence: VWTi (1.00) > FeCeVWTi (0.94) > VWTi-K-Pb (0.73) > FeCeVWTi-K-Pb (0.60). Compared with the VWTi catalyst, the Fe-Ce doping decreased the acidic sites of the catalysts probably because FeO_x and CeO_x species occupied some acidic sites on VWTi.³³ K-Pb poisoning obviously decreased the acidic sites over the VWTi and FeCeVWTi catalysts.

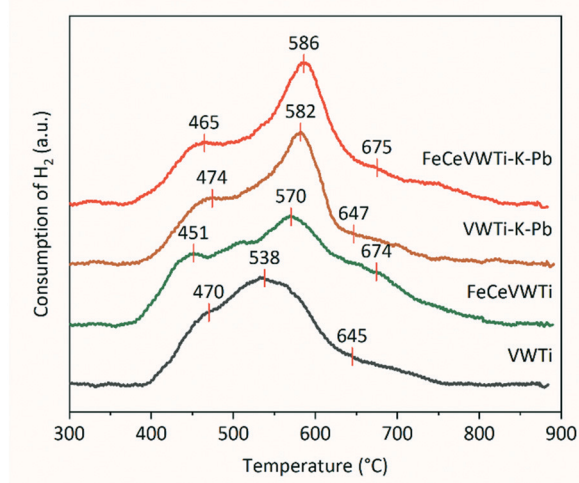


Fig. 6 H_2 -TPR of fresh and K-Pb-poisoned VWTi and FeCeVWTi catalysts.

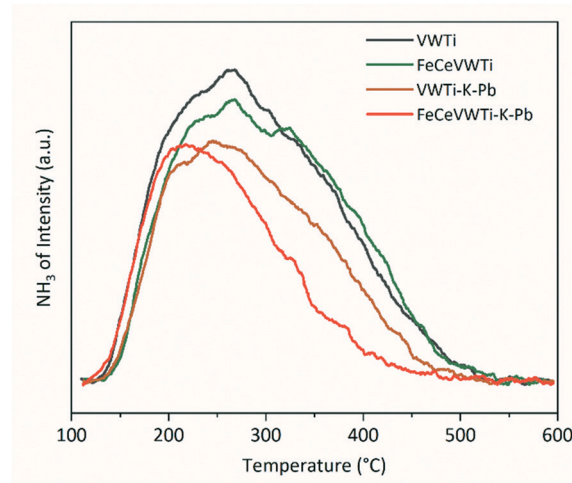


Fig. 7 NH_3 -TPD of fresh and K-Pb-poisoned VWTi and FeCeVWTi catalysts.

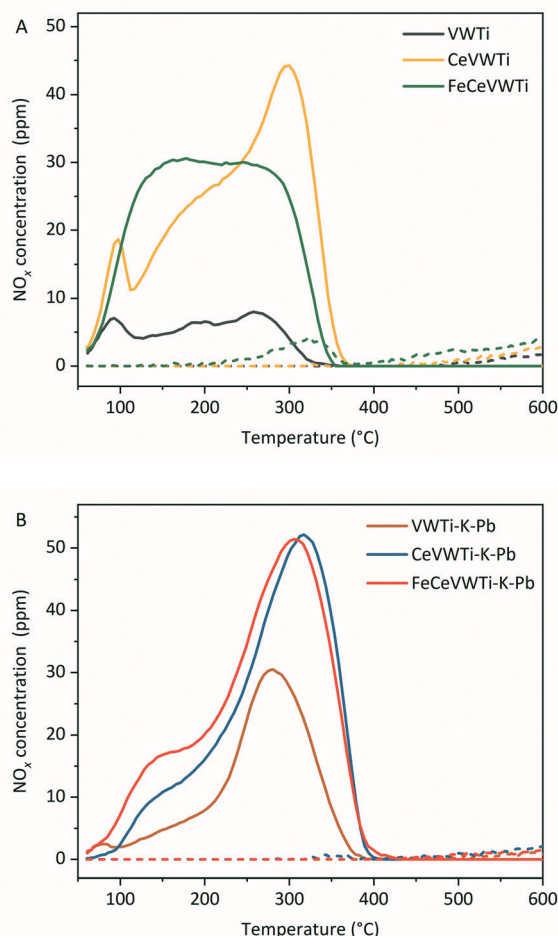


Fig. 8 NO + O₂-TPD results of (A) fresh and (B) K-Pb-poisoned catalysts (solid lines represent NO₂, dotted lines represent NO).

An NO + O₂-TPD test was also performed to investigate the chemical adsorption of NO_x on the catalysts. As shown in Fig. 8, NO_x species were desorbed mainly in the form of NO₂ on the catalysts. NO₂ on fresh and poisoned catalysts were desorbed mainly at temperatures below 400 °C. The NO₂ desorption at 60–225 °C was related to the weakly adsorbed nitrate species and the NO₂ desorption at 225–400 °C was ascribed to the strongly adsorbed ones.³⁴ The desorption peaks over CeVWTi were obviously stronger than those of VWTi and its main peak was at 300 °C, indicating that Ce doping promoted the adsorption of NO_x. As for the FeCeVWTi catalyst, the NO₂ desorption at 60–225 °C obviously increased and the NO₂ desorption at 225–400 °C decreased. Fe doping into the CeVWTi catalyst increased the weak adsorption sites and reduced the strong adsorption sites.

The NO₂ desorption between 225 and 400 °C centered at about 300 °C over the poisoned catalysts was stronger than that of the fresh catalysts, and the NO₂ desorption at 60–225 °C decreased. This indicated that K-Pb increased the strongly adsorbed nitrate species on the catalyst surface. Before and after K-Pb poisoning, FeCeVWTi had the largest amount of

weakly adsorbed nitrate species among VWTi, CeVWTi and FeCeVWTi. It could be deduced that the cooperation of Fe and Ce species on the VWTi catalyst promoted NO_x adsorption, especially of the weakly adsorbed nitrate species, which may more easily react with adsorbed NH₃ and benefit the NO_x conversion of the NH₃-SCR reaction.^{34–36}

After K-Pb poisoning, the FeCeVWTi catalyst maintained higher activity, redox ability and adsorption of NO_x but lower acidity than that of the VWTi catalyst. It seemed like there was a balance between them. In order to further find the reason for the improvement in SCR activity and K-Pb resistance of FeCeVWTi, *in situ* DRIFTS experiments were performed to explore the adsorption and activation characteristics of NH₃ and NO reactants and the NH₃-SCR reaction mechanism on the FeCeVWTi catalyst.

In situ DRIFT spectra of NH₃ adsorption were collected to further investigate the acid sites of fresh and K-Pb co-poisoned catalysts. In each test, the sample pre-adsorbed 2000 ppm NH₃ for 30 min at 300 °C. On the VWTi catalyst, five NH₃ adsorption bands are detected between 1800 and 1000 cm⁻¹ in Fig. 9. The bands centered at 1605 and 1258 cm⁻¹ could be assigned to asymmetric and symmetric bending vibrations of the N-H bonds in NH₃ coordinately linked to Lewis acid sites,³⁷ and the bands at 1666,^{38–40} 1475 and 1440 cm⁻¹ (ref. 39) could be attributed to asymmetric and symmetric bending vibrations of NH₄⁺ species on the Brønsted acid sites.³⁷ Moreover, some other bands also showed up at 1366 and 1331 cm⁻¹, which belonged to the wagging mode of an amide species (–NH₂).^{34,40–43} Similar bands could be observed for the FeCeVWTi sample. The peak intensity ratios of Brønsted acid site/Lewis acid site (B/L ratio) of these catalysts were calculated from the ratio of the peak area at 1666 cm⁻¹ to that at 1605 cm⁻¹, because they were observed on all catalysts. The B/L ratio (0.15) of FeCeVWTi was lower than that of VWTi (0.26). Moreover, the peak area ratio of 1440 cm⁻¹ to 1605 cm⁻¹ of FeCeVWTi was 0.02, which was lower than that of VWTi (0.38). These results

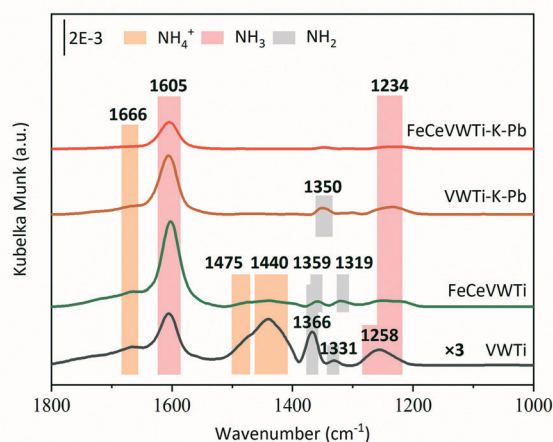


Fig. 9 *In situ* DRIFTS spectra of NH₃ adsorption over fresh and poisoned catalysts at 300 °C.

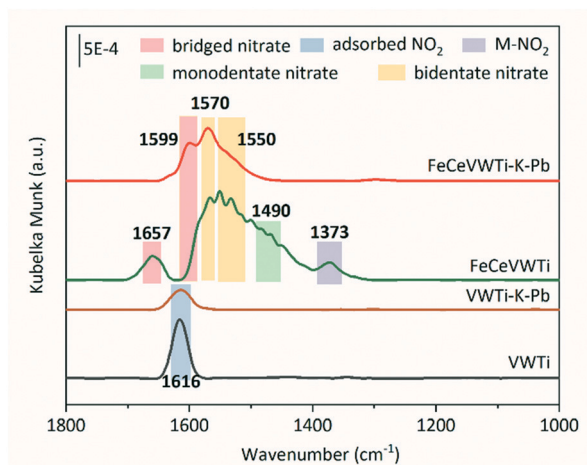


Fig. 10 *In situ* DRIFTS spectra of NO + O₂ co-adsorption over fresh and poisoned catalysts at 300 °C.

suggested that the modification with Fe and Ce oxides slightly decreased the acid sites, and mainly the Brønsted acid sites, but they increased the ratio of Lewis acid sites. After K-Pb poisoning, the bands (1605 and 1234 cm⁻¹)

belonging to Lewis acid sites and the band (1350 cm⁻¹) belonging to -NH₂ could be detected. The band (1666 cm⁻¹) of the Brønsted acid sites became very weak and the bands (1440 and 1475 cm⁻¹) of the Brønsted acid sites could not be detected. The B/L ratios of VWTi-K-Pb and FeCeVWTi-K-Pb decreased to 0.13 and 0.09, respectively. K and Pb poisoning seriously decreased acid sites, especially Brønsted acid sites.

NO adsorption over fresh and K-Pb co-poisoned catalysts was carried out by *in situ* DRIFTS. Each sample was first exposed to 2000 ppm NO + 5% O₂ for 30 min at 300 °C. As displayed in Fig. 10, only a band at 1616 cm⁻¹ attributed to adsorbed NO₂ was recorded over VWTi and VWTi-K-Pb, indicating that NO adsorption was very weak.⁴⁴ Interestingly, over FeCeVWTi, five obvious bands at 1657, 1570, 1550, 1490 and 1373 cm⁻¹ were observed. The peak at 1657 cm⁻¹ was ascribed to bridged nitrate.⁴⁵ The peaks centered at 1570 cm⁻¹ and 1550 cm⁻¹ (ref. 45 and 46) were assigned to asymmetric NO₂ vibration of bidentate nitrate. The peaks at 1490 cm⁻¹ and 1373 cm⁻¹ (ref. 46) were ascribed to monodentate nitrate and metal-NO₂,⁴⁵ respectively. After K-Pb co-poisoning, the adsorbed NO₂ (1657 cm⁻¹), monodentate nitrate (1490 cm⁻¹) and M-NO₂ (1373 cm⁻¹)

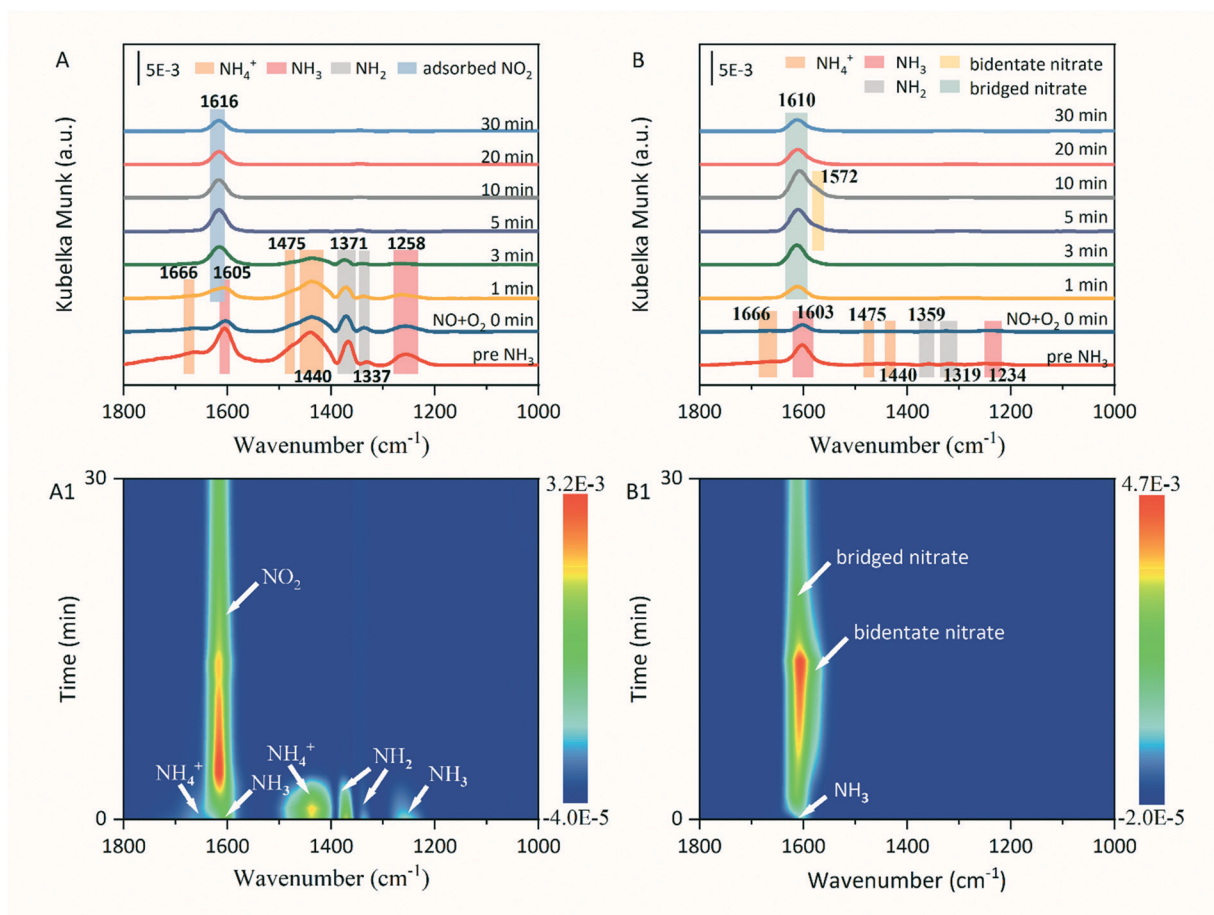


Fig. 11 *In situ* DRIFTS of the transient reactions between NO + O₂ and preadsorbed NH₃ over VWTi (A and A1) and FeCeVWTi (B and B1) at 300 °C with time.

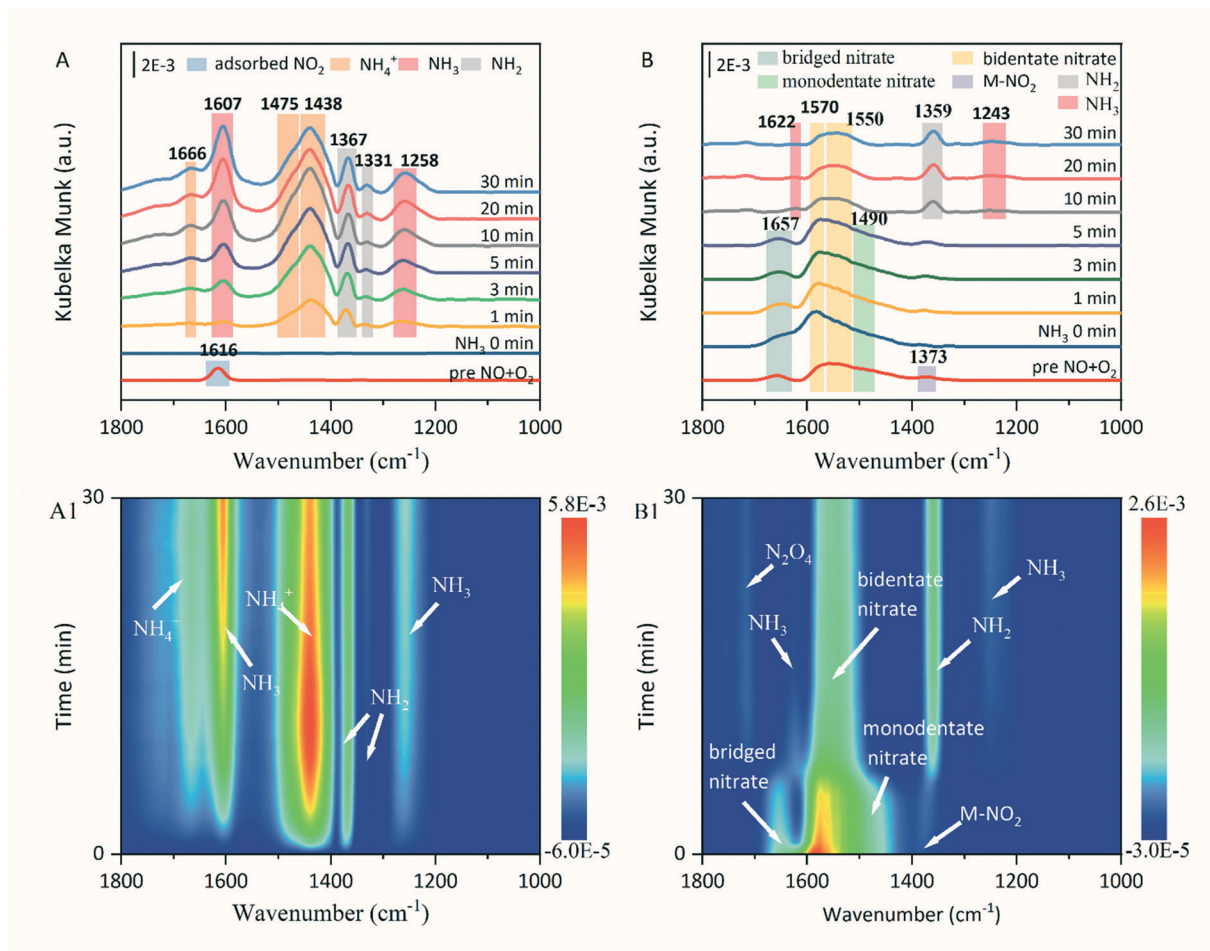


Fig. 12 *In situ* DRIFTS of the transient reactions between NH_3 and preadsorbed $\text{NO} + \text{O}_2$ over VWTi (A and A1) and FeCeVWTi (B and B1) at 300 °C with time.

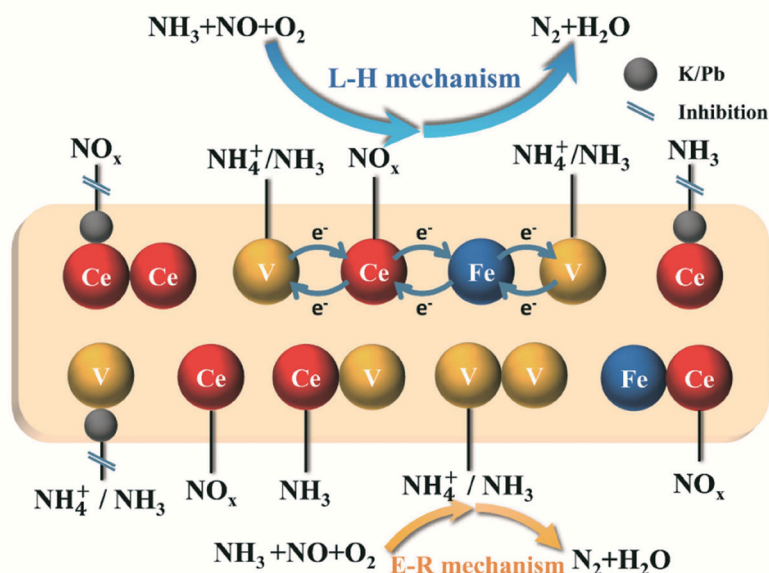
species on FeCeVWTi-K-Pb nearly disappeared. The bridged nitrate (1599 cm^{-1}) and bidentate nitrate (1570 cm^{-1} and 1550 cm^{-1}) remained.⁴⁵ This result suggested that Fe-Ce doping into catalysts could significantly promote the formation of nitrate species which were little destroyed by K-Pb poisoning. Combined with the results of XPS and H_2 -TPR, the increase in NO oxidation and adsorption over Fe-Ce doped catalysts could be attributed to the Fe_2O_3 and CeO_x species and the increased surface adsorbed oxygen, which was beneficial for the oxidation of NO , and then contributed to NO_x adsorption.

3.4 NH_3 -SCR reaction mechanism

3.4.1 Reaction between NO_x and preadsorbed NH_3 . In order to further reveal the changes in the reactivity of adsorbed NH_3 , *in situ* DRIFTS transient reactions of adsorbed species were investigated over VWTi and FeCeVWTi catalysts at 300 °C. The samples were first treated with 2000 ppm NH_3 for 30 min and then purged with pure N_2 at 300 °C for 20 min. Thereafter, 2000 ppm $\text{NO} + 5\% \text{O}_2/\text{N}_2$ was introduced. The coordinated NH_3 species ($1605, 1258\text{ cm}^{-1}$),³⁷ NH_4^+

species ($1666, 1475, 1440\text{ cm}^{-1}$)³⁹ and amide-like species ($1371, 1337\text{ cm}^{-1}$)^{34,40–43} adsorbed on VWTi were all reactive upon introducing $\text{NO} + \text{O}_2$ in Fig. 11A and A1. The intensity of adsorbed NH_3 species on the VWTi catalyst were stronger than that on FeCeVWTi, which were easy to desorb on FeCeVWTi by N_2 purging in Fig. 11B and B1. On VWTi, all the pre-adsorbed NH_3 species were consumed in 5 min after introducing $\text{NO} + \text{O}_2$. On FeCeVWTi, the NH_3 species (1603 cm^{-1}) were consumed in 1 min after the introduction of NO_x , and the band at 1572 cm^{-1} assigned to bridged nitrate emerged after introducing $\text{NO} + \text{O}_2$ for a few minutes. The results indicated that the SCR reaction on the VWTi and FeCeVWTi catalysts probably followed an Eley-Rideal (E-R) mechanism: adsorbed ammonia species react with gas-phase NO .

3.4.2 Reaction between NH_3 and preadsorbed NO_x . It has been demonstrated that NO adsorption over Fe-Ce doped catalysts was improved. Further experiments were conducted to investigate whether these adsorbed NO_x species could participate in the NH_3 -SCR reaction. Fig. 12 presents the DRIFT spectra of VWTi and FeCeVWTi catalysts in a flow of 2000 ppm NH_3 after the catalysts had pre-adsorbed 2000



Scheme 1 Proposed mechanism on the FeCeVWTi catalyst with high K-Pb resistance for the NH_3 -SCR reaction.

ppm $\text{NO} + 5\%\text{O}_2$ for 30 min followed by N_2 purging for 20 min. For the VWTi sample, only the band (1616 cm^{-1}) assigned to adsorbed NO_2 could be detected, and it nearly disappeared after the N_2 purge. The adsorbed NH_4^+ species ($1666, 1607, 1475$ and 1438 cm^{-1}),³⁹ coordinated NH_3 species (1258 cm^{-1})³⁷ and amide-like species ($1367, 1331\text{ cm}^{-1}$)^{34,40–43} could be detected on VWTi after introducing NH_3 , as shown in Fig. 12A and A1. In contrast, the adsorbed bridged nitrate (1657 cm^{-1}), bidentate nitrate (1550 cm^{-1}), monodentate nitrate (1490 cm^{-1}) and metal- NO_2 (1373 cm^{-1}) species on FeCeVWTi were notably reduced with the introduction of NH_3 , and meanwhile the amide-like species (1359 cm^{-1}) and coordinated NH_3 species ($1622, 1243\text{ cm}^{-1}$) emerged (Fig. 12B and B1). The results indicated that the SCR reaction on the FeCeVWTi catalyst followed the Langmuir-Hinshelwood (L-H) mechanism: adsorbed ammonia species react with adsorbed NO_x species. As shown in Fig. S7 and S8,[†] K-Pb poisoning did not change the SCR reaction mechanism on the VWTi and FeCeVWTi catalysts. Overall, the VWTi catalyst followed the E-R mechanism in accordance with previous research on commercial VWTi catalysts. However, FeCeVWTi followed both E-R and L-H mechanisms. According to the above results, FeCeVWTi-K-Pb reserved more reactive adsorbed NO_x species despite having less acidic sites than VWTi-K-Pb, which was an important factor for the strong K-Pb resistance of the FeCeVWTi catalysts.

3.4.3 Proposed promotional mechanism. According to the above results, the SCR reaction on the VWTi catalyst only followed the E-R mechanism. K-Pb poisoning severely destroyed its acid sites and redox sites, which both played crucial roles in the SCR reaction on it. Consequently, the SCR activity of the VWTi catalyst decreased after K-Pb poisoning. According to the DRIFTS studies, FeCeVWTi followed both E-R and L-H mechanisms during the SCR

reaction. As shown in Scheme 1, the adsorbed ammonia species on some of the VO_x active sites of FeCeVWTi catalyst reacted with gas-phase NO and O_2 to form N_2 and H_2O , which followed the E-R mechanism (indicated by the orange arrow). Combined the results of NH_3 -TPD and DRIFTS, although Fe and Ce co-doping decreased Brønsted acid sites due to the combination of FeO_x and CeO_x with VO_x , most of the Lewis acid sites adsorbing NH_3 species were retained on the FeCeVWTi catalyst. Moreover, the results of XPS and H_2 -TPR illuminated that the interaction between Fe, Ce and V through the redox cycles of $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{V}^{5+}/\text{V}^{4+}$ improved the redox ability of the FeCeVWTi catalyst. Thus, they also accelerated the oxidation and adsorption of NO on the FeCeVWTi catalyst, which were very weak on the VWTi catalyst. These changes caused the reaction between adsorbed ammonia species and adsorbed NO_x species to occur on the FeCeVWTi catalyst. So, Fe and Ce co-doping changed the reaction route and made the SCR reaction on FeCeVWTi follow both an L-H mechanism (indicated by the blue arrow) and an E-R mechanism. Although the deposition of K-Pb occupied many acid sites, it only decreased the partial adsorption sites of NO_x species on the FeCeVWTi catalyst, which ensured the higher reaction activity of FeCeVWTi catalyst than that of the VWTi catalyst after K-Pb poisoning.

Conclusions

Fe and Ce co-doping significantly promoted the NO_x conversion and resistance to K and Pb poisoning on a commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst. The optimum doping ratio was a 1.5Ce/V and 0.05Fe/V molar ratio. Fe-Ce co-doping gave the FeCeVWTi catalyst a higher V^{5+} ratio, surface chemisorbed oxygen ratio and redox ability than the VWTi

catalyst due to the interaction between Fe, Ce and V through the redox cycles of $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{V}^{5+}/\text{V}^{4+}$. Fe–Ce co-doping slightly decreased the specific surface area and NH_3 adsorption, but greatly increased the adsorption of NO_x , which induced a change in the SCR reaction mechanism from an E–R mechanism on the VWTi catalyst to both an E–R mechanism and an L–H mechanism on the FeCeVWTi catalyst. Although the deposition of K–Pb occupied some acid sites, it only decreased the partial redox ability and adsorption sites of NO_x species on the FeCeVWTi catalyst, which ensured its higher resistance to K and Pb than that of the VWTi catalyst. With such good SCR activity and K–Pb resistance, the FeCeVWTi catalyst has the potential to be an effective NH_3 -SCR catalyst, especially under complex flue gas conditions containing K–Pb.

Author contributions

Conceptualization: Xianfang Yi, Jinxiu Wang; methodology: Xianfang Yi, Jinxiu Wang; formal analysis and investigation: Xianfang Yi, Jinxiu Wang, Yuqiu Liu, and Yanting Chen; writing – original draft preparation: Xianfang Yi; writing – review and editing: Jinxiu Wang; supervision: Jinxiu Wang and Jinsheng Chen.

Conflicts of interest

There are no conflicts to declare.

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