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A study on the selective catalytic reduction of NO_x by ammonia on sulphated iron-based catalysts

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A series of sulphated iron-based catalysts was prepared via an impregnation method by changing the loading content of Fe^{3+} and SO_4^{2-} on ZrO_2 , and their performance in the selective catalytic reduction (SCR) of NO_x by ammonia was investigated. The NO_x conversion exhibited large differences among the sulphated iron-based catalysts. To explore the synergistic mechanism of iron and sulphates, XRD, BET, H_2 -TPR, XPS, TPD and *in situ* DRIFTS were used to characterize the catalysts, and it was found that among all the catalysts, the NO_x conversion by Fe_2SZr was greater than 90% at 350–450 °C. The results indicated that the interaction between Fe^{3+} and SO_4^{2-} can have an effect on the redox ability, acid sites, and adsorption of NO_x and NH_3 . With an increase in the content of Fe^{3+} , the redox activity of the catalyst and the adsorption of ammonia improved at medium and low temperatures. However, at higher temperatures, an increase in Fe^{3+} led to a decrease in the conversion of NO_x due to the enhanced oxidation of NH_3 . At medium and low temperatures, an increase in the content of SO_4^{2-} decreased the concentration of Fe^{3+} on the surface of the catalyst and inhibited the adsorption of NO_x and NH_3 . The addition of SO_4^{2-} reduced the redox activity of the catalyst and inhibited the oxidation reaction of NH_3 , which follows the Eley-Rideal mechanism at high temperatures, further enhancing the SCR activity of the Fe_xS_yZr catalyst.

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1. Introduction

The temperature of the waste gas of a bituminous coal-fired power plant is generally 300–450 °C. 1,2 In particular, the temperature after burning lignite reaches up to 420 °C. Also, under conditions with a high sulphur content, the commercially available catalysts (vanadium-based catalysts) show low denitrification activity and poor N_2 selectivity, which make them easily poisoned and secondary pollution being released into the environment. Therefore, it is urgent to develop environment-friendly catalysts with sulphur resistance, high activity, and high N_2 selectivity at high temperature.

Iron-based catalysts exhibit a good NO_x conversion rate and N_2 selectivity, and thus, have been favored by many researchers. $^{10-17}$ However, the selective catalytic reduction (SCR) activity of α -Fe $_2O_3$ catalysts at temperatures above 300 °C significantly decreases, and thus they cannot be applied in the denitrification of waste gas after burning coal. In recent years, some researchers attempted to improve the performance of catalysts by sulphating them. Gu *et al.* 18 carried out the sulphation of CeO $_2$ via a gas phase method, achieving a reaction activity of up to 99% in the temperature range of 300–500 °C. Ma

et al. 19 prepared Fe₂(SO₄)₃/TiO₂ via impregnation, exhibiting a conversion rate of 97% and N2O selectivity lower than 5% at 350-450 °C. Therefore, the sulphation of catalysts is a very effective way to improve their reactivity and N₂ selectivity at high temperature. According the literature, 20-25 the high catalytic efficiency and good sulfur resistance of catalysts upon acidification treatment can be mainly ascribed to the following reasons: (1) the reaction with the active material improves the transformation between the active material ion, increasing the reaction rate. (2) The number of Brönsted acid sites on the surface of the catalyst increases, increasing the strength of the acid sites, which is the main reason for the increase in catalytic activity. (3) Reaction with other substances on the catalyst to form sulfates, which enclose the active substances and reduce the sulphation of the active substances or act as active substances. Importantly, the NO_x conversion efficiency and N₂ selectivity of the sulphated catalysts improved.

To date, the synergistic mechanism between the active components and sulphates has not been reported. Therefore, we used Fe as an active component, which was sulphated and loaded onto a ZrO_2 carrier, to prepare a catalyst with a high NO_x conversion rate and high NO_x selectivity at high temperature. In this study, we loaded Fe^{3+} and SO_4^{2-} in different amounts on the ZrO_2 carrier via the impregnation method. The impact of Fe^{3+} and SO_4^{2-} loading on the performance of the NH_3 -SCR catalyst was investigated using different characterization methods, and the synergistic mechanism of Fe^{3+} and SO_4^{2-} in the SCR reaction was discussed.

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2. **Experimental**

2.1 Catalyst preparation

Paper

All catalysts were prepared *via* the incipient wetness method. ZrO₂ power was weighed and dissolved in deionized water. Subsequently, Fe(NO₃)₃·9H₂O and (NH₄)₂SO₄ were added to the solution dropwise, and then heated to 70 °C and stirred to form a paste. The resulting mixture was dried at 120 °C overnight and calcined in air at 500 °C for 4 h. Finally, a series of iron-based catalysts was obtained, denoted as Fe_xS_yZr (y = 5, x = 0, 2, 3.5, 7 is denoted as Fe_xSZr and x = 3.5, y = 0, 5, 10, 15 is denoted as $FeS_{\nu}Zr$; where x represents the weight percentage of Fe^{3+} and y represents the weight percentage of SO_4^{2-}).

2.2 Catalyst characterization

The gas concentration was detected using a Gasmet Dx-4000 FT-IR gas analyser, which can monitor NH3, NO2, NO, N2O and water vapour. The reactant gas was 500 ppm NH₃, 500 ppm NO, 3% O2 and N2 balanced.

X-ray diffraction (XRD) measurements were performed on a D/MAX-RB system with Cu Ka radiation. The diffraction curves were measured in the 2θ range 10° to 90° with a step size of 0.018 at a rate of 1 s per step.

BET measurements were performed using a Quantachrome Autosorb AS-1 System using N2 adsorption at 77 K.

X-ray photoelectron spectroscopy (XPS) was performed using an ESCALab220i-XL electron spectrometer with 300 W Mg Ka radiation under 3×10^{-9} mbar. The binding energies were calibrated using adventitious carbon with C 1s at 284.8 eV.

Temperature-programmed reduction (TPR) curves were measured using a Micromeritics ChemiSorb 2720. Firstly, the samples were preheated to 300 °C and maintained at a constant temperature for 1 h under N₂ purging and then cooled to 30 °C. The catalysts were reduced in a flow of N₂-based gas containing 10% H₂/Ar (50 cm³ min⁻¹), and the temperature was programmed from 30 °C to 1000 °C at a heating rate of 10 °C min⁻¹.

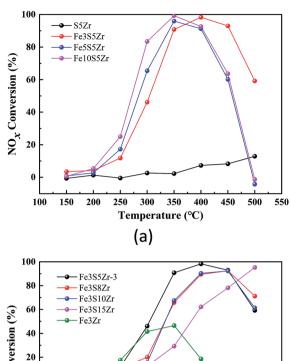
Temperature programmed desorption (NH3-TPD) experiments were conducted in an N2-based mixture gas containing 500 ppm NH₃ (300 mL min⁻¹). The sample was preheated at 500 °C constantly for 1 h, then cooled to 30 °C, and NH₃ was introduced continuously for 1 h. Thirdly, the catalyst was blown with N₂ until to no NH₃ was detected. Finally, the catalyst was heated from 30 °C to 500 °C at a heating rate of 10 °C min⁻¹.

In situ DRIFTS spectra were characterized using a Nicolet NEXUS 870 FT-IR spectrometer. The sample was pre-treated at 300 °C for 1 h under a flow of N_2 (100 cm³ min⁻¹).

3. Results and discussion

3.1 The effects on SCR activity with different loadings of Fe³⁺ and SO₄²⁻

Fig. 1(a) shows the SCR activities of the SZr, Fe₂SZr, Fe_{3.5}SZr and Fe₇SZr catalysts. According to this figure, the NO_x conversions of S₅Zr catalyst were very low in the temperature range of 150-500 °C and it reached the highest of 12% at 500 °C. Upon the addition of 2% Fe³⁺, the NO_x conversions improved



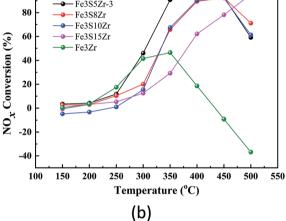


Fig. 1 (a) NO_x conversion of catalysts containing 5% SO_4^{2-} and x% Fe^{3+} (x = 0, 2, 3.5, 7). (b) NO_x conversion of catalysts containing 3.5% Fe³⁺ and y% SO_4^{2-} (y = 0, 5, 10, 15).

significantly, climbing rapidly from 10% at 250 °C to 90% at 350 °C, and reached the highest of 98% at 400 °C. Subsequently, with a further increase in the temperature to 500 $^{\circ}$ C, the NO_x conversion decreased to 57%. With a continuous increase in the loading of Fe^{3+} , the NO_x conversions were slightly higher than that of the Fe₂SZr catalyst in the temperature range of 250-350 °C, but they dropped significantly in the temperature range of 400-500 °C, which was negative at 500 °C.

Fig. 1(b) shows the NO_x conversions by the FeZr, FeS₅Zr, FeS₁₀Zr and FeS₁₅Zr catalysts in the temperature range of 150-500 °C. According to this figure, the NO_x conversions of the FeZr, FeS₅Zr and FeS₁₀Zr catalysts increased initially and then declined in the temperature range of 150-500 °C. The NO_r conversions of the FeZr catalyst were very close to that of the FeS₅Zr catalyst in the temperature range of 150-300 °C, which reached the peak of 46% at 350 °C, and then dropped sharply to a negative value from 400 °C to 500 °C. Upon the loading of SO_4^{2-} , the NO_x conversions improved in the high temperature range. When 10% SO_4^{2-} was added to the catalyst, the NO_x conversions were reduced in the temperature range of 250-450 °C compared with that of the FeS₅Zr catalyst. With the further addition of ${\rm SO_4}^{2-}$ to 15%, the ${\rm NO_x}$ conversion exhibited an increasing trend from 150 °C to 500 °C, which was much lower than that of the FeS₅Zr catalyst in the range of 150–450 °C but it reached close to 100% at 500 °C.

3.2 Impact of Fe³⁺ and SO₄²⁻ loading on ammonia oxidation

Fig. 2(a) shows the curve of ammonia oxidation using a series of acidified catalysts in the temperature range of 150–500 °C. Accordingly, the SZr catalyst without Fe³⁺ loading started to oxidize NH₃ beginning at 400 °C and reached an NH₃ oxidation rate of 40% at 500 °C. However, it was reported that the self-oxidation reaction of NH₃ occurs when the temperature is higher than 400 °C, and thus, we speculated that a self-oxidation reaction mainly occurred on the SZr catalyst. With an increase in the loading amount of Fe³⁺, the conversion of NH₃ oxidation shifted to a lower temperature, that is, the greater the loading amount of Fe³⁺, the more the starting temperature of NH₃ oxidation was shifted to a lower temperature and the higher the corresponding oxidation rate of NH₃ in

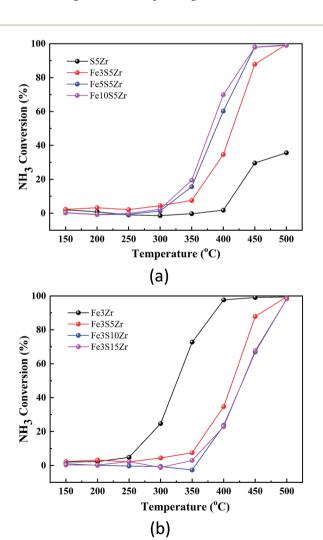
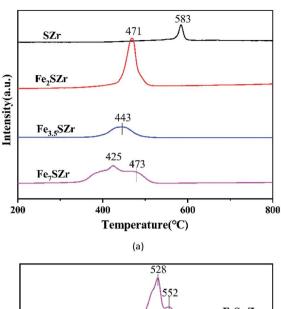


Fig. 2 (a) NH₃ oxidation efficiency of catalysts containing 5% ${\rm SO_4}^{2-}$ and x% Fe³⁺ (x=0, 2, 3.5, 7). (b) The NH₃ oxidation efficiency of catalysts containing 3.5% Fe³⁺ and y% SO₄²⁻ (y=0, 5, 10, 15).

the temperature range of 300-450 °C. However, the NH₃ oxidation rates of the Fe_{3.5}SZr and Fe₇SZr catalysts were close, indicating that although the higher the loading amount of Fe³⁺, the higher the NH₃ oxidation rate, the NH₃ oxidation rate approached a constant at a certain temperature with a continuous increase in Fe3+. In general, an increase in the amount of Fe³⁺ will promote the oxidation of NH₃ at high temperature. Combining the activities of the catalysts with varying amounts of Fe³⁺, the NH₃ self-oxidation reaction mainly occurred on the Fe₂SZr, Fe_{3.5}SZr and Fe₇SZr catalysts at 450-500 °C, which affected the efficiency of the catalytic reduction of the nitrogen oxides. Fig. 2(b) shows the changes in the curves of the NH₃ oxidation rate with the catalysts prepared by changing the content of sulphates. Accordingly, for the FeZr catalyst in the absence of sulphates, the oxidation reaction of NH₃ started from 250 °C, and the NH₃ oxidation rate reached 80% at 350 °C, while it reached 100% at 400 °C. Thus, based on the curve of the NH₃ oxidation rate for the FeZr catalyst, it can be concluded that in the temperature range of 350-500 °C, the NH₃ oxidation reaction mainly occurred on the FeZr catalyst, thus affecting the SCR reaction. With an increase in the sulphate content, the most efficient ammonia oxidation shifted to a higher temperature, that is, the addition of sulphates inhibited the oxidation reaction of NH3 on the catalyst.

3.3 H₂-temperature programmed reduction (TPR) analysis

The redox ability of catalysts is of great importance for the SCR reaction, which can be well characterized by H2-temperature programmed reduction (TPR). Actually, the lower the temperature, the better the redox ability of the catalyst at low or medium temperatures.26 The amount of hydrogen consumption is also an important indicator of the catalytic activity. The greater the hydrogen consumption, the stronger the redox capacity of the catalyst. 26-28 As shown in Fig. 3(a), there is only one H2 reduction peak for the SZr catalyst at 583 °C, which is mainly attributed to the reduction peak of the sulphate species. According to the H₂-TPR curves of the series of Fe₂SZr catalysts, the reduction temperatures of the catalysts after the addition of Fe3+ were lower than that of SZr. The Fe_{3.5}SZr and Fe₂SZr catalysts each showed only one redox peak, and these peaks were close to each other at 471 °C and 443 °C. These two reduction peaks are considered to be the completely overlapping reduction peaks of the iron oxide and the sulphates. The H2-TPR redox curve of the Fe₇SZr catalyst has two reduction peaks at 425 °C and 473 °C. The former reduction peak can be attributed to the reduction peak of the iron oxide, while the peak at 473 °C is considered to be the overlapping reduction peaks of the iron oxide and the sulphates. As shown in Fig. 3(b), the H₂-TPR curve of the FeZr catalyst mainly has three reduction peaks at 330 °C and 410 °C, which can be attributed to the reduction peaks of Fe₂O₃-Fe₃O₄-Fe. 19 After the addition of SO_4^{2-} , the reduction temperatures of the catalysts are higher than that of FeZr. The FeS₁₀Zr catalyst has only one reduction peak at 519 °C, which is close to the reduction peak of the SZr catalyst, and it is also considered to be the overlapping reduction peaks of the iron oxide and sulphates. The H2-TPR redox curve of the FeS15Zr catalyst has



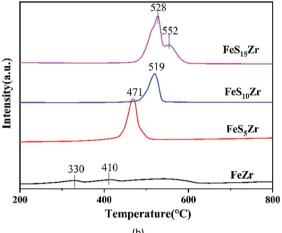


Fig. 3 (a) H_2 -TPR of catalysts containing 5% SO_4^{2-} and x% Fe^{3+} (x=0, 2, 3.5, 7). (b) H_2 -TPR of catalysts containing 3.5% Fe^{3+} and $y\% SO_4^{2-}$ (y = 0, 5, 10, 15).

two reduction peaks at 528 °C and 552 °C. The former reduction peak can be attributed to the reduction peak of the iron oxide, while that at 552 °C is considered to be the overlapping reduction peaks of iron oxide and sulphates. According to Fig. 3, it can be concluded that the increase in the Fe3+ content in the catalyst caused a shift in the starting reduction temperature of the catalyst to a lower temperature, indicating that an increase in the content of Fe³⁺ increased the redox activity of the catalyst, and the addition of SO_4^{2-} caused the starting reduction temperature of the catalyst to shift to a higher temperature, indicating that the addition of $SO_4^{\ 2-}$ significantly reduced the redox activity of the catalyst.

3.4 XPS

Table 1 shows the atomic concentrations of S, O, Fe and Zr on the surfaces of the different catalysts. Accordingly, when the content of Fe³⁺ was constant, with an increase in SO₄²⁻, the concentration of Fe atoms on the surface showed a decreasing trend. This is mainly due to the formation of $Fe_2(SO_4)_3$. When the content of $SO_4^{\ 2-}$ was constant, with an increase in Fe_2O_3 , the concentration of S atoms on the surface of the catalyst

Table 1 The surface element content in the different catalysts (%)

	FeZr	$\mathrm{FeS}_{5}\mathrm{Zr}$	$FeS_{10}Zr$	$FeS_{15}Zr$	SZr	$Fe_{3.5}SZr$	Fe ₇ SZr
S 2p	0.000	0.077	0.076	0.091	0.062	0.080	0.066
Zr 3d	0.217	0.161	0.184	0.164	0.212	0.132	0.131
O 1s	0.698	0.719	0.722	0.723	0.726	0.695	0.690
Fe 2p	0.074	0.045	0.018	0.021	0.000	0.093	0.113

increased initially, and then decreased. Similarly, we concluded that more Fe₂(SO₄)₃ was produced so that the Fe and S atoms were enriched on the surface. However, when the content of Fe³⁺ increased to a certain level, the SO₄²⁻ on the surface was covered by Fe³⁺, and thus, the concentration of S atoms on the surface of the catalyst showed the tendency to increase initially, and then decrease with an increase in Fe³⁺.

The oxidation states of Fe and S on the different catalysts were characterized using XPS, and the results are shown in Fig. 4. The Fe 2p and S bands in Fig. 4 were deconvoluted by searching for the optimal combination with correlation coefficients (R^2) above 0.99 (Origin Pro 8.0). From the curves of Fe 2p, as shown in Fig. 4(a and b), the bonding energies of Fe 2p_{3/2} (710-711.5 eV) and Fe $2p_{1/2}$ (724.3-725.5 eV) corresponded well to the references,29 and the bonding energies of 718.1-719.2 eV corresponded well to the fingerprint peak of Fe³⁺. Specially, when the content of SO_4^{2-} was 5%, with an increase in Fe³⁺, the peak with a binding energy at 718.1-719.2 eV became strong, and when the Fe³⁺ content was 3.5%, with an increase in SO₄²⁻, the peak at 718.1-719.2 eV became weak.

The S 2p XPS spectra for the different catalysts are shown in Fig. 4(c and d). The S 2p XPS spectra of the sulfated catalysts exhibited a main peak at 168.8-170 eV, as shown in Fig. 4. This value is consistent with S⁶⁺ such as sulfur in SO₄²⁻, ¹⁹ indicating that S is in the S⁶⁺ oxidation state on the catalyst.

3.5 NH₃-temperature programmed desorption (TPD) analysis

The acidity of catalysts plays a very important role in the SCR reaction, and Fe³⁺ and sulphates can provide acidic sites, which can improve the acidity of the catalyst. Therefore, the characteristics of NH3-TPD were analysed for a series of acidified catalysts, as shown in Fig. 5. Fig. 5(a) shows the NH₃-TPD curves for the catalysts with different Fe3+ loadings. The SZr catalyst has two desorption peaks at 410 °C and 120 °C. The desorption amount of ammonia at high temperature was much larger than that at low temperature. It has been reported that the desorption at low temperature is mainly physical adsorption or weak chemical adsorption, while the desorption at high temperature is mainly the strong chemical adsorption of NH3.30-32 On the Fe₂SZr catalyst, there was a wide NH₃ desorption peak in the range of 80 °C to 500 °C. With the addition of Fe³⁺, the desorption capacity of Fe_{3.5}SZr at low temperature (90–180 °C) was slightly higher than the desorption at high temperature (>180 °C). Compared to SZr, the desorption peak of the Fe₇SZr catalyst at high temperature (240 °C) shifted to a lower temperature at nearly 170 °C. Thus, it can be concluded that the

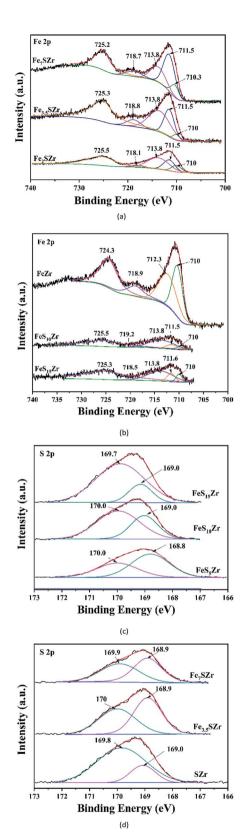
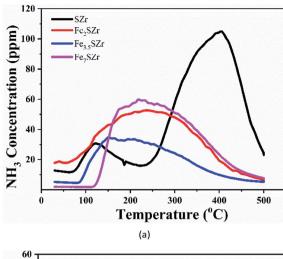


Fig. 4 XPS spectra of different catalysts: (a) XPS-Fe 2p spectra of catalysts containing 5% ${\rm SO_4}^{2-}$ and x% ${\rm Fe}^{3+}$ (x=0,2,3.5,7). (b) XPS-Fe 2p spectra of catalysts containing 3.5% ${\rm Fe}^{3+}$ and y% ${\rm SO_4}^{2-}$ (y=0,5,10,15). (c) XPS-S 2p spectra of catalysts containing 5% ${\rm SO_4}^{2-}$ and x% ${\rm Fe}^{3+}$ (x=0,2,3.5,7). (d) XPS-S 2p spectra of catalysts containing 3.5% ${\rm Fe}^{3+}$ and y% ${\rm SO_4}^{2-}$ (y=0,5,10,15).



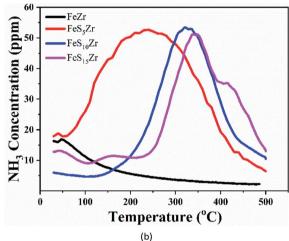
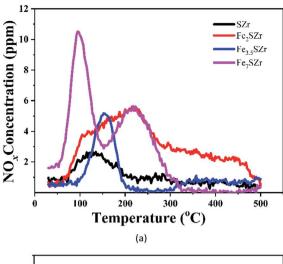


Fig. 5 (a) NH₃-TPD of catalysts containing 5% ${\rm SO_4}^{2-}$ and x% ${\rm Fe}^{3+}$ (x=0,2,3.5,7). (b) NH₃-TPD of catalysts containing 3.5% ${\rm Fe}^{3+}$ and y% ${\rm SO_4}^{2-}$ (y=0,5,10,15).

addition of Fe₂O₃ reduced the ability of the catalyst to adsorb ammonia at high temperatures and improved the ability of the catalyst to adsorb ammonia at moderate and low temperatures. Fig. 5(b) shows the NH₃-TPD curves for the catalysts with different amounts of sulphates. As shown, only a small amount of physically adsorbed ammonia was released on the FeZr catalyst. The addition of 5% sulphate greatly increased the adsorption amount of NH3. With an increase in the amount of sulphate, the desorption peak of ammonia obviously shifted towards a higher temperature, and the FeS₁₅Zr catalyst showed a desorption peak at 410 °C, which is consistent with the desorption peak of the SZr catalyst, but the desorption amount of ammonia was much less than that of the SZr catalyst. Thus, the addition of $SO_4^{\ 2-}$ increased the adsorption of ammonia on the catalyst at high temperatures and reduced the amount of ammonia adsorbed by the catalyst at moderate or low temperatures.

3.6 NO + O_2 -TPD

Fig. 6 shows the NO_x -TPD curve for a series of acidified catalysts. As shown in Fig. 6(a), the SZr catalyst mainly has a nitrogen



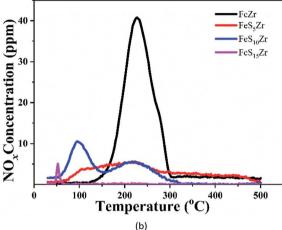


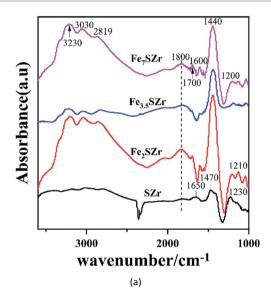
Fig. 6 (a) NO + O₂-TPD of catalysts containing 5% SO₄²⁻ and x% Fe³⁺ (x = 0, 2, 3.5, 7). (b) The NO + O₂-TPD of catalysts containing 3.5% Fe³⁺ and y% SO₄²⁻ (y = 0, 5, 10, 15).

oxide desorption peak at 120 °C with a low desorption amount. After the addition of 2% Fe³⁺, nitrogen oxides were desorbed from 100 °C to 500 °C, and the amount of nitrogen oxides desorbed was greatly enhanced. When the addition of Fe³⁺ reached 3.5%, the desorption peak shifted to a higher temperature by approximately 40 °C, but the desorption amount was significantly reduced. When the addition of Fe³⁺ reached 7%, two desorption peaks at 90 °C and 230 °C existed, and the desorption amount was greater than that of the Fe₂SZr catalyst. As shown in Fig. 6(b), the FeZr catalyst has a nitrogen oxide desorption peak at 240 °C with the highest amount of desorption. The addition of 5% $SO_4^{\ 2-}$ to the catalyst significantly decreased the desorption of nitrogen oxides, indicating that SO₄²⁻ had an inhibitory effect on the adsorption of nitrogen oxides. The further addition of $SO_4^{\ 2-}$ to the $FeS_{10}Zr$ catalyst significantly increased the adsorption of nitrogen oxides at low temperature, but decreased the adsorption of nitrogen oxides at high temperature. When the addition of SO_4^{2-} reached 15%, the adsorption of nitrogen oxides was basically completely suppressed. Because NO can be easily oxidized into NO2 in the presence of O2, and NO together with NO2 are both acidic gases,

the addition of ${\rm Fe^{3^+}}$ to the catalyst enhanced its adsorption capacity of nitrogen oxides, while the addition of ${\rm SO_4}^{2^-}$ to the catalyst will inhibited the adsorption capacity of nitrogen oxides. However, due to the synergistic effect between ${\rm Fe^{3^+}}$ and ${\rm SO_4}^{2^-}$, the desorption amount of nitrogen oxides of the ${\rm Fe_{3.5}SZr}$ catalyst was much less than that of the ${\rm Fe_2SZr}$ catalyst.

3.7 *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

3.7.1 NH₃ species adsorbed on the different catalysts. Fig. 7(a) shows the infrared spectra of a series of catalysts containing 5% SO_4^{2-} and different amounts of Fe^{3+} with the saturated adsorption of NH₃ at 30 °C and after purging with N₂. According to the different reports in the literature and the comparative analysis, ²⁶ the region of 3400–2800 cm⁻¹ should be



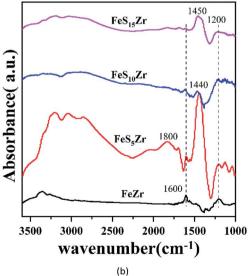
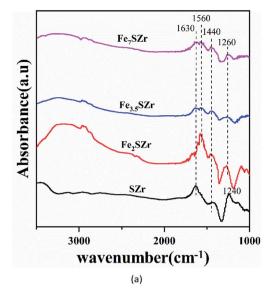


Fig. 7 Infrared spectra of a series of catalysts with the saturated adsorption of NH $_3$ at 30 °C and after purging with N $_2$: (a) catalysts containing 5% SO $_4$ ²⁻ and x% Fe $^{3+}$ (x=0,2,3.5,7) and (b) catalysts containing 3.5% Fe $^{3+}$ and y% SO $_4$ ²⁻ (y=0,5,10,15).

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responsible for the NH stretching vibration, which can be considered as the coordination adsorption formed between NH₃ and the oxygen atoms of the metal oxide on the catalyst surface by hydrogen bonding. The absorption at 1600 cm⁻¹ is the antisymmetric stretching vibration absorption peak of the NH₃ species adsorbed at the Lewis acid sites, while the peaks at 1230, 1210 and 1200 cm⁻¹ are attributed to the symmetric stretching vibration absorption peaks of the NH3 species adsorbed at the Lewis acid sites. The peaks at 1440, 1470, 1650, and 1700 cm⁻¹ are attributed to the anti-symmetric and symmetric stretching vibration absorption peaks of the NH₄⁺ species adsorbed at the Brönsted acid sites.³³ It is worth noting that the absorption peak at 1800 cm⁻¹ is not attributed to the absorption of NH₃ or NH₄⁺ with an increase in the amount of Fe³⁺. The increase in the amount of Fe³⁺ led to the anti-symmetric stretching vibration absorption peak of the NH3 species adsorbed at the Lewis acid sites. Simultaneously, we found that with a further increase in the amount of Fe³⁺, the amount of NH₄⁺ species adsorbed at the Brönsted acid sites first increased and then decreased. As shown in Fig. 7(b), the increase in the amount of SO₄²⁻ significantly increased the anti-symmetric and symmetric stretching vibration absorption peaks of the NH₄⁺ species adsorbed at the Brönsted acid sites, but a further increase in the amount of SO_4^{2-} did not continue to increase the NH_4^+ species adsorbed at the Brönsted acid sites, which decreased instead, and this may be due to the synergistic effect of iron and SO_4^{2-} .

3.7.2 The NO_x species adsorbed on the surfaces of the different catalysts. Fig. 8(a) shows the infrared spectra of a series of catalysts containing 5% $SO_4^{\ 2-}$ and different amounts of $\mathrm{Fe^{3+}}$ with the saturated adsorption of NO + $\mathrm{O_2}$ at 30 °C and after purging with N2. At 30 °C, the nitrogen oxide vibration absorption peaks appeared at 1630, 1560, 1440, 1280, 1260 and 1240 cm⁻¹. According to the literature, 34-37 the vibration absorption peaks at 1630 and 1560 cm⁻¹ are attributed to the vibration absorption of the bridged and bidentate nitrate species adsorbed on the catalyst, respectively, and the vibration absorption peaks at 1440, 1280, 1260 and 1240 cm⁻¹ are attributed to the linear nitrate species adsorbed on the catalyst. With the addition of Fe³⁺, the vibration absorption peak of the linear nitrate species at 1440 cm⁻¹ increased, and the antisymmetric and symmetric vibration absorption peaks of nitrogen oxides at 1230 cm⁻¹ disappeared, showing that the linear nitrate species adsorbed at 1260 cm⁻¹. Combined with the NO-TPD results, with the addition of Fe³⁺, the catalyst could readily adsorb the unstable nitrate species (e.g., linear nitrates), and the desorption temperatures of all the adsorbed nitrates shifted towards a lower temperature. Fig. 8(b) shows the infrared spectra of a series of catalysts containing 3.5% Fe³⁺ and different amounts of ${\rm SO_4}^{2-}$ with the saturated adsorption of NO + O₂ at 30 °C and after purging with N₂. With the addition of SO_4^{2-} to the catalyst, the NO_2 species (1620 cm⁻¹) and the linear nitrate species (1280 cm⁻¹) on the catalyst surface were reduced, and the vibration absorption peak of the nitrate species showed a red-shift (from 1520 cm⁻¹ to 1580 cm⁻¹), with a stable nitrate species appearing at 1440 cm⁻¹. The addition of SO₄²⁻ inhibited the adsorption of nitrogen oxides on the catalyst, which is consistent with the NO_r-TPD results.



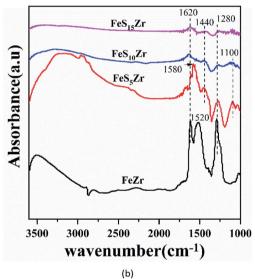
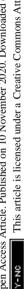


Fig. 8 Infrared spectra of a series of catalysts with the saturated adsorption of NO + O_2 at 30 °C and after purging with N_2 : (a) shows catalysts containing 5% SO_4^{2-} and x% Fe^{3+} (x=0, 2, 3.5, 7) and (b) catalysts containing 3.5% Fe^{3+} and y% SO_4^{2-} (y=0, 5, 10, 15).

3.7.3 Transient DRIFTS for the Fe_7S_5Zr and $Fe_2S_{15}Zr$ catalysts. To better understand the SCR reaction on the sulphated catalysts at high temperature and comparatively analyse the effects of additional Fe^{3+} and $SO_4^{\ 2-}$ on the mechanism of the NH₃-SCR catalytic reaction, we investigated the transient DRIFTS for the Fe_7SZr and $FeS_{15}Zr$ catalysts.

3.7.3.1 Transient DRIFTS of the surface of the Fe₇SZr catalyst at 300 °C. Fig. 9(a) shows the profile of the time-dependent changes of the adsorbed species on the surface of the Fe₇SZr catalyst at 300 °C after introducing NH₃ with the saturated adsorption of NO + O₂. Accordingly, after the adsorption of NO + O₂ on the catalyst surface was saturated, the adsorption peaks appeared at 1620, 1370 and 1140 cm⁻¹. The surface of the catalyst was mainly covered by NO₂ species (1620 cm⁻¹) and nitrate species (1370 and 1140 cm⁻¹). After NH₃ was

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(a)1430 (b) 1420 3260 3260 1600 3050 2830 30min 3050 1600 1280 2830 20min absorbance(a.u.) absorbance(a.u.) 30min 10min 20min 1620 5min 10min 14003min 5min 3min introduce NH₃ 1min 1370 1620 NO+O₂ 30min introduce NH₃ 1min NO+O, 30min 3500 3000 2500 2000 1500 1000 3500 3000 2500 2000 1500 1000 wavenumber(cm⁻¹) wavenumber(cm⁻¹)

Fig. 9 Profile of the time-dependent changes of the adsorbed species on the surface of different catalysts at 300 °C after introducing NH₃ with the saturated adsorption of NO + O_2 on the (a) Fe_7SZr catalyst and (b) $FeS_{15}Zr$ catalyst

introduced for 1 min, the adsorbed nitrogen oxide species began to decrease. After 3 min, the absorption peaks of the adsorbed nitrogen oxide species disappeared, and the adsorption peak attributed to the NH₄⁺ species at 1430 cm⁻¹ appeared, together with the absorption peaks for NH3 (1280 and 1600 cm⁻¹) and NH₄⁺ (1410 and 1690 cm⁻¹) species. After 10 min, the absorption peak of NH₄⁺ on the surface of the catalyst gradually increased. These results indicate that the nitrogen oxide species adsorbed on the Fe₇SZr catalyst surface can react rapidly with NH₃ in the gas phase.

Fig. 10(a) shows the profile of the time-dependent changes of the adsorbed species on the surface of the Fe₇SZr catalyst at 300 °C after introducing NO + O2 with the saturated adsorption of NH₃. When the NH₃ adsorption was saturated, the vibration absorption peaks of NH₃ (1280 cm⁻¹) and NH₄⁺ (1680 and 1430 cm^{-1}) on the surface of the catalyst appeared. When NO + O₂ was introduced onto the catalyst surface, the absorption peak of the ammonia species on the surface of the catalyst did not change significantly. After 5 min, the intensities of all the absorption peaks of the adsorbed NH3 species began to weaken, and even after 30 min, the adsorbed NH₃ species had not reacted completely, and the absorption peak of nitrogen oxide did not appear. This demonstrated that the introduction of NO + O2 caused a weak reaction with various types of adsorbed NH₃ species on the surface of the catalyst. Thus, combined with Fig. 10(a) and 9(a), at 300 °C the nitrogen oxides adsorbed on the surface of the Fe₇SZr catalyst were the main components that reacted very rapidly with NH3 in the gaseous state, and the various NH3 species adsorbed on the surface could also slowly participate in the reaction.

3.7.3.2 Transient DRIFTS of the surface of the FeS₁₅Zr catalyst at 300 °C. Fig. 9(b) shows the profile of the time-dependent changes of the adsorbed species on the surface of the FeS₁₅Zr catalyst at 300 °C after introducing NH3 with the saturated

adsorption of NO + O2. Accordingly, after the adsorption of NO + O2 on the catalyst surface was saturated, the adsorption peaks appeared at 1620, 1340 and 1150 cm⁻¹. The surface of the catalyst was mainly covered by NO₂ species (1620 cm⁻¹) and nitrate species (1340 and 1150 cm⁻¹).39 After NH₃ was introduced, the adsorbed nitrogen oxides species were gradually weakened in 5 min. At the beginning of the 5th minute, the adsorption peak attributed to the NH₄⁺ species appeared at 1400 cm⁻¹. At the 10th minute, the absorption peaks of the nitrogen oxide species basically disappeared, and the absorption peaks of NH₃ (1270 and 1600 cm⁻¹) and NH₄ (1410 and 1700 cm⁻¹) species appeared. After 10 min, the catalyst surface was covered by various ammonia species, and they gradually increased. These results indicate that the nitrogen oxide species adsorbed on the surface of the FeS₁₅Zr catalyst can react with NH3 in the gas phase.

Fig. 10(b) shows the profile of the time-dependent changes of the adsorbed species on the surface of the FeS₁₅Zr catalyst at 300 °C after introducing NO + O2 with the saturated adsorption of NH₃. After NO + O₂ was introduced on the catalyst surface for 5 min, all the adsorbed NH₃ species disappeared. Starting from the 10th minute, the surface was gradually occupied by nitrate. This indicates that NO + O₂ can react with the various NH₃ species adsorbed on the surface. Thus, combined with Fig. 10(b) and 9(b), at 300 °C the NH₃ species adsorbed on the surface of the FeS₁₅Zr catalyst can rapidly react with NO_x in the gas phase, while the nitrogen oxide species adsorbed on the surface can also rapidly react with NH3 in the gas phase.

Combined with the results of the DRIFTs study of the transient reactions of the Fe₇SZr and FeS₁₅Zr catalysts at 300 °C, it can be concluded that there are two NH₃-SCR reaction paths on the surface of the sulphated iron-based catalyst at 300 °C, namely a Langmuir-Hinshelwood15 reaction mechanism and an Eley-Rideal^{27,33} reaction mechanism, that is,

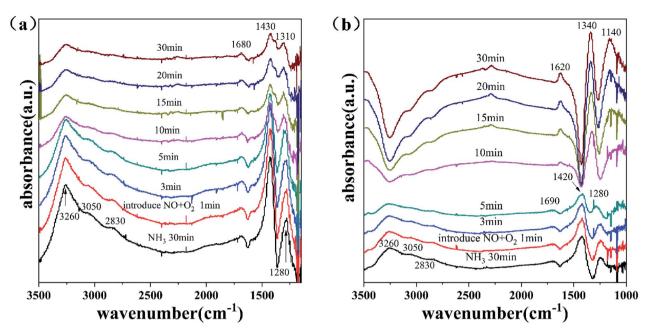


Fig. 10 Profile of the time-dependent changes of the adsorbed species on the surface of different catalysts at 300 °C after introducing NO + O_2 with the saturated adsorption of NH₃ on the (a) Fe₇SZr catalyst and (b) FeS₁₅Zr catalyst.

NH₃ adsorption on the catalyst surface. NO is first oxidized into NO2 to be adsorbed on the surface of the catalyst to produce nitrates or nitrite species, and the NH3 species adsorbed on the surface can react with both gaseous NOx and the adsorbed NO_x species to produce N_2 and H_2O . The nitrogen oxide species adsorbed on the surface of the Fe₇SZr catalyst can react very rapidly with the gaseous NH3, while various NH₃ species adsorbed on the surface can also slowly participate in the reaction, indicating that when the amount of Fe₂O₃ in the catalyst increases, the SCR reaction occurring on the catalyst obviously follows the Langmuir-Hinshelwood reaction path, with a small portion of the reaction following the Eley-Rideal reaction mechanism simultaneously. The NH₃ species adsorbed on the surface of the FeS₁₅Zr catalyst at 300 °C can rapidly react with the NO_r in the gas phase, and the nitrogen oxides species adsorbed on the surface can also rapidly react with the NH3 in the gas phase. This indicates that when the amount of $SO_4^{\ 2-}$ in the catalyst increases, the SCR reaction on the surface of the catalyst obviously follows the Eley-Rideal reaction mechanism, mainly because the increase in the amount of SO_4^{2-} significantly enhances the ammonia adsorption capacity of the catalyst at a high temperature, while reducing the adsorption of nitrogen oxides, which is conducive to enhancing the NH₃ adsorption by the catalyst, thereby promoting the SCR reaction at high temperature. This is consistent with the results of the activity test for the catalyst with varying amounts of SO_4^{2-} .

4. The synergistic mechanism of Fe^{3+} and sulphates for NH_3 -SCR

The roles of Fe³⁺ and sulphates were very different at low temperature and high temperature. When the SO_4^{2-} content is

constant, the addition of Fe³⁺ to the catalyst will enhance its adsorption capacity of nitrogen oxides and NH3 species at moderate and low temperatures. According to the references, 27,33,40,41 the mechanism of the SCR generally follows the Langmuir-Hinshelwood reaction path at moderate and low temperatures, and thus the Fe3+ obviously adsorbed NH3 and oxidized it to -NH2, which is the important intermediate species for the SCR reaction42-46 and can react with the NO oxidation species (NO2 and NO3) to form the intermediate species, and then decompose to N₂ and H₂O. Thus, the addition of Fe³⁺ improved the redox ability, which affected the activity for the SCR at moderate and low temperatures. However, at high temperature, an increase in the amount of Fe³⁺ will promote the oxidation of NH₃ because it can increase the redox activity of the catalyst, which results in a decrease in the efficiency of the catalytic reduction of nitrogen oxides. When the content of Fe³⁺ is constant, with an increase in the content of SO_4^{2-} , the concentration of Fe3+ on the surface showed a decreasing trend because of the formation of Fe₂(SO₄)₃, which leads to the complete inhibition of the adsorption of NO_x and NH₃ to reduce the conversion of NO_r in NH₃-SCR at moderate and low temperature. At high temperature, the redox activity of the catalyst is reduced with the addition of ${\rm SO_4}^{2-}$, which restrains the oxidation reaction of NH₃ on the catalyst. Meanwhile, the significant increase in NH4+ species adsorbed at the Brönsted acid sites improves the activity for the SCR, which follows the Eley-Rideal reaction path. Overall, the effect on the SCR for Fe³⁺ and SO_4^{2-} was restrained by each of them, and thus only the appropriate contents of Fe3+ and SO42- could result in high activity in the temperature range of 300-450 °C. Similar to oxide catalysts such as Mo-Fe,47 W-Fe,48 W-Ce,49 and Mo-Fe50 oxides, the sulphated iron-based catalysts possess acid-redox dinuclear sites, where Fe^{3+} is the redox site and SO_4^{2-} is the acid site. The

interfaces of the acid-redox sites are key to the SCR reaction activities. Thus, designing catalysts to optimize the interaction between the acid-redox sites is an effective measure to control NO emissions.

5. Conclusions

Different sulphated iron-based catalysts with various loadings of Fe³⁺ and SO₄²⁻ on ZrO₂ were prepared via the incipient wetness method, and investigated for the selective catalytic reduction (SCR) of NO_r by ammonia. Compared to all the catalysts, the Fe₂SZr catalyst could achieve above 90% NO_x removal efficiency at 350-450 °C, and the main reactions on its surface were the NH₃-SCR reaction and the oxidation of NH₃. Meanwhile, the interaction between Fe³⁺ and SO₄²⁻ was found to affect the redox ability, acid sites, adsorption of NOx and NH3, and play a role in the SCR activity. Specifically, increasing the content of Fe³⁺ improved the redox activity of the catalyst and enhanced the adsorption of ammonia at medium and low temperatures. In addition, increasing the amount of Fe³⁺ promoted the oxidation of NH₃ at high temperatures, which led to a reduction in the efficiency of NO_x conversion. With an increase in SO_4^{2-} , the concentration of Fe^{3+} on the surface of the catalyst showed a decreasing trend because of the formation of Fe₂(SO₄)₃, which inhibited the adsorption of NO_r and NH₃ and reduced the NO_x conversion of the NH₃-SCR at medium and low temperatures. At high temperatures, the addition of SO_4^{2-} reduced the redox activity of the catalyst and inhibited the oxidation reaction of NH₃. Meanwhile, the significant increase in NH₄⁺ species adsorbed on the Brönsted acid sites improved the SCR activity because the main reaction pathway over the Fe_xS_yZr catalyst follows the Eley-Rideal mechanism at high temperatures.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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