

DOI: 10.1016/S1872-5813(23)60377-9

Effect of Fe₂O₃ on ZrTiO₄ support for NH₃-SCR catalytic performance

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Abstract: The selective catalytic reduction (SCR) NH₃ catalyst is mainly used in industrial production and automobile exhaust cleaning. In this study, a novel $\alpha\%$ Fe₂O₃/ZrTiO₄ ($\alpha=0\%$, 8%, 12%, 15%) catalyst was prepared by the coprecipitation impregnation method. The results show that the NO_x conversion rate of 12% Fe₂O₃/ZrTiO₄ catalyst with the optimal composition is high above 80% at 250–400 °C, close to 100% at 300 °C, and N₂ selectivity is high above 90% at 200–450 °C. The redox properties, surface acidity, and O_β/(O_α + O_β) ratio of ZrTiO₄ catalysts are improved after loading Fe₂O₃ on the ZrTiO₄ surface, which is attributed not only to the porous structure of $\alpha\%$ Fe₂O₃/ZrTiO₄ catalyst but also to the synergistic interaction between the active component Fe₂O₃ and the support ZrTiO₄. In addition, in-situ DRIFT reactions show that the NH₃-SCR reaction of 12% Fe₂O₃/ZrTiO₄ catalyst follows the Eley-Rideal mechanism. A clear reaction mechanism is conducive to a deeper understanding of the reaction process of NO_x conversion during SCR. This work provides a feasible strategy for Fe-based SCR catalysts to replace V-based catalysts in the medium temperature range in the future.

Key words: Fe₂O₃/ZrTiO₄ catalyst; NH₃-SCR; Porous structure; Reaction mechanism.

CLC number: O643.36

Document code: A

In recent years, with the rapid development of science and technology, the smoke pollution produced by industrial power plants and automobile exhaust becomes more serious, and the pollutants emitted mainly include CO, C_xH_y, NO_x, and SO₂^[1,2]. Among them, NO_x, as one of the main sources of air pollution, can cause photochemical smog, acid rain, and the greenhouse effect. At the same time, as a pollution gas, it can damage the human central nervous system and bring great pressure on human health and environmental preservation^[3,4]. Therefore, effectively solving this problem can better balance the development between human beings and environmental protection.

So far, the commonly used flue gas deNO_x technologies include a selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). The catalysts used in selective catalytic reduction mainly include noble metal catalysts, metal oxide catalysts, and molecular sieve catalysts. At present, a more mature metal oxide V₂O₅-WO₃(MoO₃)/TiO₂ catalyst is used commercially with a temperature range between 300 °C and 400 °C, high NO_x conversion rate,

excellent stability, and performance^[5,6]. However, the vanadium system has a narrow operating temperature window, low activity at low temperatures, high operating temperature (350–450 °C), and vanadium toxicity^[7,8]. Therefore, it is important to develop a new catalyst system.

As an eco-friendly oxide, Fe₂O₃ has been widely used in NH₃-SCR reactions due to its low cost and the unsaturated properties of *d* orbitals^[9]. In addition, the coupling between Fe³⁺ and Fe²⁺ also greatly enhanced the SCR activity^[9]. The NO_x conversion rate of the Fe_{1.2}Al_{0.8}O_x catalyst prepared by Bie et al. is greater than 80% between 250 °C and 350 °C^[10]. The 3% Fe/WO₃-ZrO₂ catalyst prepared by the impregnation method of Foo et al. achieved 80–85% NO_x conversion at 400–550 °C^[11]. In addition, Fe₂O₃ as active components, such as Fe₂O₃/ZrO₂^[12] and Fe₁-V₁/TiO₂^[13], showed excellent SCR activity. However, the deNO_x efficiency of pure Fe₂O₃ in practical applications is still challenging.

There have been many studies of ZrO₂ and TiO₂ as catalyst carriers. TiO₂ carriers have good water resistance, trace SO₂ resistance, and high activity in NO

Received: 2023-03-15; Revised: 2023-04-08

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selection reduction in the NO-NH₃-O₂ system^[14]. ZrO₂ carrier has good chemical stability, unique weak acid, and weak base dual function properties^[15]. It is also a p-type semiconductor, and can easily produce oxygen holes, producing strong interactions with active components. However, Liu et al. found that the BET surface area was often too low when ZrO₂ was used as a carrier alone^[16]. Guo et al. found that the electron absorption ability of bulk TiO₂ support was not strong enough^[17]. In addition, ZrO₂ has three kinds of crystal phase structures (tetragonal, monoclinic, and cubic) and TiO₂ has two kinds of crystal phase structures (anatase and rutile). In the process of using the catalyst, ZrO₂ and TiO₂ as the carrier will undergo crystal phase changes, which will affect the reaction performance of the catalyst. Compared to a single oxide, we synthesized two metal oxides to prepare a ZrTiO₄ carrier with a high BET surface area and excellent thermal stability.

In this study, the $\alpha\%$ Fe₂O₃/ZrTiO₄ catalyst was prepared by coprecipitation and impregnation methods, and its deNO_x activity was evaluated in a fixed-bed reactor. The physicochemical properties of the catalyst were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), H₂ temperature-programmed reduction (H₂-TPR), NH₃ temperature-programmed desorption (NH₃-TPD), and N₂ physisorption. The reaction mechanism of the $\alpha\%$ Fe₂O₃/ZrTiO₄ catalyst was further analyzed by in-situ diffuse reflectance infrared Fourier transform (DRIFT).

1 Experimental

1.1 Catalyst preparation

All chemicals used in the experiments, Ti(SO₄)₂ (Sinopharmed Chemical Reagent Co., LTD.) and ZrOCl₂·8H₂O (Shanghai Zhanyun Chemical Co., LTD.), were of analytical grade. During the experiment, 42.6 wt.% Ti(SO₄)₂ and 57.4 wt.% ZrOCl₂·8H₂O were dissolved in 200 mL deionized water and stirred. In the two precursors, ammonia was added to adjust the solution pH to 9 at room temperature, and the impurity ions were removed after filtration by deionized water for 6 times and by alcohol for another 3 times. ZrTiO₄ samples were prepared by drying and grinding at 80 °C and annealing at 500 °C for 80 min in the air atmosphere.

Different amounts of $\alpha\%$ Fe₂O₃ in Fe(NO₃)₃·9H₂O (Macklin) were fully dissolved in deionized water, and

then a certain amount of ZrTiO₄ powder was fully impregnated in Fe(NO₃)₃ aqueous solution, and stirred at room temperature for a period of time. First, the catalyst was dried at 80 °C for 10 h in air, and then dried at 110 °C for 12 h in vacuum. After grinding, the catalyst was annealed at 500 °C for 3 h. After natural cooling to room temperature, the calcined mixture was pressed, grinded and sieved to obtain $\alpha\%$ Fe₂O₃/ZrTiO₄ catalyst, where $\alpha=0\%$, 8%, 12%, and 15%.

1.2 Catalyst characterization

Field emission scanning electron microscopy (FESEM, Gemini SEM 300) was used to observe the morphology of the catalyst and energy dispersive spectroscopy (EDX) was used to observe the distribution of Fe on the surface of ZrTiO₄. The phase composition was measured by powder XRD (Bruker AXS D8). The surface area of the catalyst was measured by the JW-BK222 instrument, and was calculated by the Brunauer-Emmett-Teller (BET) method. XPS characterization was performed using a Thermo ESCALAB 250XI instrument. The voltage was 16 kV, and the charge calibration was performed by using C 1s=284.8 eV as the standard. NH₃-TPD and H₂-TPR were carried out on a chemisorption analyzer US-Micromeritics-AutoChem II 2920 equipped with a thermal conductivity detector (TCD). For the H₂-TPR test, 140 mg samples were pretreated in 50 mL min⁻¹ N₂ atmosphere at 400 °C for 60 min and then the temperature was reduced to 50 °C. Finally, the pretreated samples were analyzed in 5 vol.% H₂/He, 50 mL min⁻¹ at 750 °C with a heating rate of 10 °C min⁻¹. In addition, for NH₃-TPD, 140 mg samples were pretreated in an N₂ atmosphere (30 mL min⁻¹) at 400 °C for 60 min and then the temperature was reduced to 50 °C. The pretreated samples were adsorbed in 1% NH₃/N₂ at 50 °C and then purged with N₂ for 60 min. The samples were heated from 50 °C to 750 °C (10 °C min⁻¹) at 50 mL min⁻¹ in an N₂ atmosphere. The in-situ DRIFT spectra were obtained using a Thermo Scientific Nicolet 6700 spectrometer. The reaction conditions were as follows: 500 ppm NH₃, 500 ppm NO, 3% O₂ balanced by N₂, and the gas flow rate was 100 mL/min.

1.3 Catalytic activity test

The activity test was carried out in a fixed-bed quartz reactor with 0.8 g catalyst, crushed, and sieved to a 40–60 mesh range in a quartz tube. The inner diameter of quartz tube is 4.8 mm, and the length of catalytic bed is 8 cm. The test conditions were 500 ppm

NH₃, 500 ppm NO, 3% O₂ balanced by N₂. The gas flow rate was 500 ml/min, and the weight hourly space velocity (WHSV) was 37,500 mL g⁻¹ h⁻¹. The catalyst was pretreated in N₂ at 200 °C for 60 min. The test temperature was 100–500 °C. The outlet gas concentration of NO, NO₂, NH₃ and N₂O was measured by Thermo Scientific Nicolet 50 with DTGS detector. The NO_x conversion, N₂ selectivity and NH₃ conversion rate were calculated as:

$$\text{NO}_x \text{ conversion}(\%) = \left(\frac{([\text{NO}]_{(\text{in})} + [\text{NO}_2]_{(\text{in})}) - ([\text{NO}]_{(\text{out})} + [\text{NO}_2]_{(\text{out})})}{[\text{NO}]_{(\text{in})} + [\text{NO}_2]_{(\text{in})}} \right) \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity}(\%) = \left(1 - \frac{2\text{N}_2\text{O}_{x(\text{out})}}{\text{NO}_{x(\text{in})} - \text{NO}_{x(\text{out})}} \right) \times 100\% \quad (2)$$

$$\text{NH}_3 \text{ conversion}(\%) = \left(\frac{[\text{NH}_3]_{(\text{in})} - [\text{NH}_3]_{(\text{out})}}{[\text{NH}_3]_{(\text{in})}} \right) \times 100\% \quad (3)$$

2 Results and discussion

2.1 Morphology of $\alpha\%$ Fe₂O₃/ZrTiO₄ catalyst

In order to analyze the surface characteristics of the samples, SEM characterization was carried out. As seen in Figure 1a, the ZrTiO₄ particles exhibit irregular morphology and a fluffy porous structure on the sample surface. This fluffy multi-pore sample can promote the reaction gas to enter the mass transfer channel better, which is conducive to the adsorption and diffusion of the gas, and promote the catalytic performance of the catalyst^[18]. After loading Fe₂O₃ on the surface of the ZrTiO₄ sample, it is found that $\alpha\%$ Fe₂O₃/ZrTiO₄ and ZrTiO₄ samples show the same morphological characteristics, with a large number of pores on the surface, indicating that the loading of Fe₂O₃ does not affect the morphology of pure ZrTiO₄ (Figure 1b). However, with the increase of Fe₂O₃ loading, the surface morphology of the catalyst became slightly rougher, possibly because of the aggregation of Fe₂O₃ on the surface of ZrTiO₄ support (Figure 1c&d).

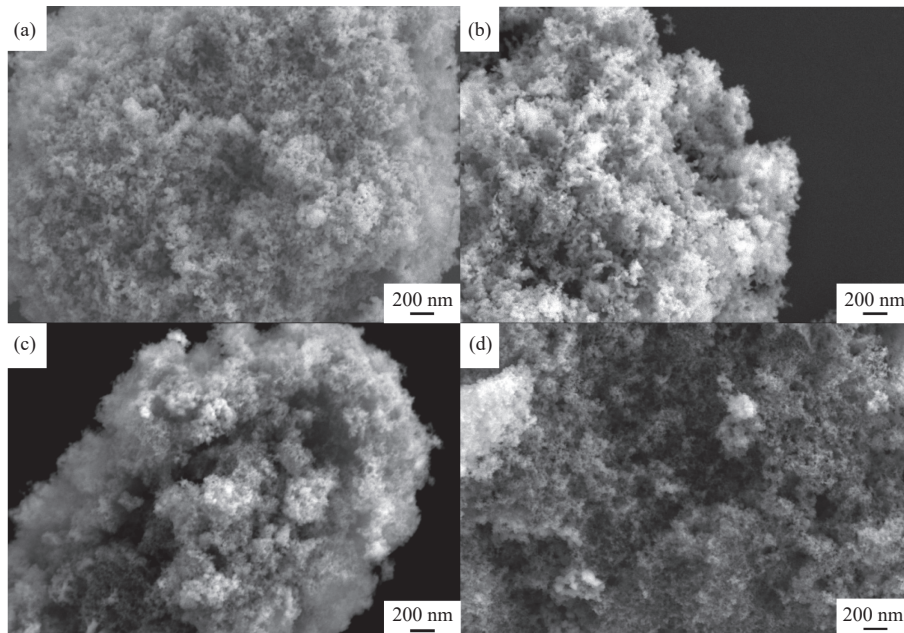


Figure 1 SEM images of ZrTiO₄ and $\alpha\%$ Fe₂O₃/ZrTiO₄ samples: (a) ZrTiO₄; (b) 8% Fe₂O₃/ZrTiO₄; (c) 12% Fe₂O₃/ZrTiO₄; (d) 15% Fe₂O₃/ZrTiO₄

2.2 N₂ physisorption of $\alpha\%$ Fe₂O₃/ZrTiO₄ catalyst

To further characterize the porous properties of the samples, N₂ adsorption-desorption was performed to obtain BET surface area, pore volume and pore size of the ZrTiO₄ and $\alpha\%$ Fe₂O₃/ZrTiO₄ samples. The adsorption isotherms of the four samples are shown in Figure 2. All four curves have similar shapes and a hysteresis loop, which are typical type IV isotherms

belonging to mesoporous structures with 2–50 nm pore sizes^[19]. The BET surface area and pore size were further analyzed. Table 1 shows that the maximum specific surface area and pore volume of pure ZrTiO₄ are 161.3 m²/g and 0.85 cm³/g, and the specific surface area will be reduced to a certain extent after Fe₂O₃ is loaded on the surface. This may be because that Fe₂O₃ deposition blocks the pore channels of some ZrTiO₄

samples. With the increase of Fe_2O_3 loading, the specific surface area of $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst decreases first, then increases, then decreases again, and the pore volume and pore size change correspondingly. This may be attributed to the fact that the deposited Fe_2O_3 will block the pores of ZrTiO_4 , resulting in the decrease of the specific surface area and pore volume of the catalyst. Therefore, an appropriate amount of Fe_2O_3 is conducive to the interaction between the active components and the support. Among the composite catalysts, 12% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst has the largest specific surface area and pore volume, which are $139.6 \text{ m}^2/\text{g}$ and $0.77 \text{ cm}^3/\text{g}$, respectively. Generally speaking, the higher the specific surface area of the catalyst, the more active sites will be provided for the SCR reaction, which in turn facilitates the adsorption of reaction gases such as NH_3 and NO_x ^[20]. Therefore, this is one of the key conditions for the 12% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst to have the highest SCR activity.

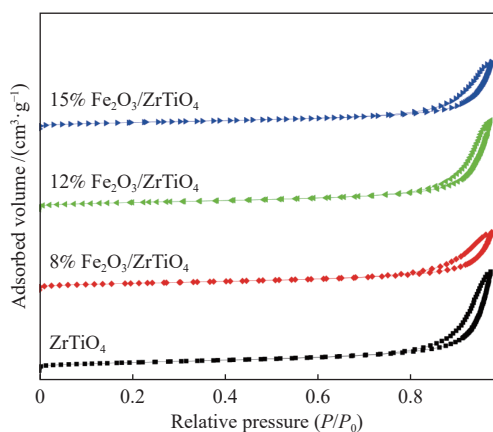


Figure 2 Adsorption isotherms of ZrTiO_4 and $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ samples. The curves are offset for clarity and are plotted with the same y scale

Table 1 S_{BET} surface area, pore volume and pore size of ZrTiO_4 and $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ samples

Sample	Surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore Size (nm)
ZrTiO_4	161.3	0.85	21.19
8% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$	134.3	0.50	14.87
12% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$	139.6	0.77	22.02
15% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$	129.1	0.58	17.92

2.3 Phases and energy spectra of $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst

Figure 3 shows the XRD patterns of the ZrTiO_4 and $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ samples. As seen in Figure 3, the

XRD results of pure ZrTiO_4 samples show only the corresponding ZrTiO_4 reflections, which are in good agreement with the standard PDF card of ZrTiO_4 (PDF#74-1504). After loading Fe_2O_3 on the surface of ZrTiO_4 , only the corresponding ZrTiO_4 XRD reflections are observed in $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst, but no corresponding XRD reflections of Fe_2O_3 are observed, indicating that the doped Fe_2O_3 is highly dispersed on the surface of ZrTiO_4 . Good dispersion can promote the interaction between the active components and the support, and improve the SCR activity of the catalyst^[21]. In addition, the loading of Fe_2O_3 also reduces the reflection intensity of ZrTiO_4 , and the crystallinity decreases significantly. Some diffraction reflections disappear completely because of the loading of Fe_2O_3 , which enhances the amorphous form of ZrTiO_4 . The results show that the doping of Fe_2O_3 promotes the interaction between the active components and the support.

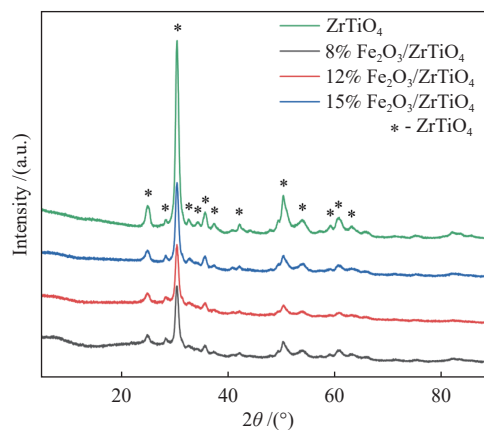


Figure 3 XRD patterns of ZrTiO_4 and $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ samples

In order to further determine the dispersion state of the Fe element, the distribution of the Fe element on the surface of ZrTiO_4 support was characterized by EDX. As seen in Figure 4, there is a homogeneous distribution of Fe on the surface of ZrTiO_4 support, which is conducive to the SCR reaction of the catalyst. From the comparison of intensity, the contrast of Zr and Ti components is strong, while the contrast of Fe components is weak, because the molar percentage of Fe is only 12%, and its content is low.

2.4 Surface acidity of $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst

The concentration of acid sites on the catalyst surface were tested by NH_3 -TPD, and the results are shown in Figure 5. The first peak corresponds to the physically adsorbed NH_3 molecule at the weak acid site, the second peak corresponds to the chemically

adsorbed NH₃ at the weak acid site, and the third peak corresponds to the adsorbed NH₃ site at the strong acid site. Researchers generally believe that the chemically adsorbed NH₃ molecule can better participate in the SCR reaction^[22]. Therefore, although all the samples have similar peaks and curves, it is obvious from Figure 5 that the peak areas of a weak acid, medium acid and strong acid of pure ZrTiO₄ are smaller than those of the composite Fe₂O₃/ZrTiO₄ catalyst, indicating that the Fe₂O₃ loading greatly increases the strength and number of acid sites of the catalyst. In addition to the acidity of Fe₂O₃, the Fe element

enhances the interactions among Fe, Ti and Zr elements, and promotes the acidity of the catalyst surface. The relative curve area of the surface acidity of the four catalysts is 12% Fe₂O₃/ZrTiO₄ (1.41) > 15% Fe₂O₃/ZrTiO₄ (1.36) > 8% Fe₂O₃/ZrTiO₄ (1.28) > ZrTiO₄ (1). The 12% Fe₂O₃/ZrTiO₄ catalyst has the largest peak area and the lowest reduction peak in the medium and low-temperature region, which indicates that it has the highest surface acidity and more medium and weak acid sites, and can effectively adsorb more NH₃ molecules to promote the SCR performance of the catalyst^[23].

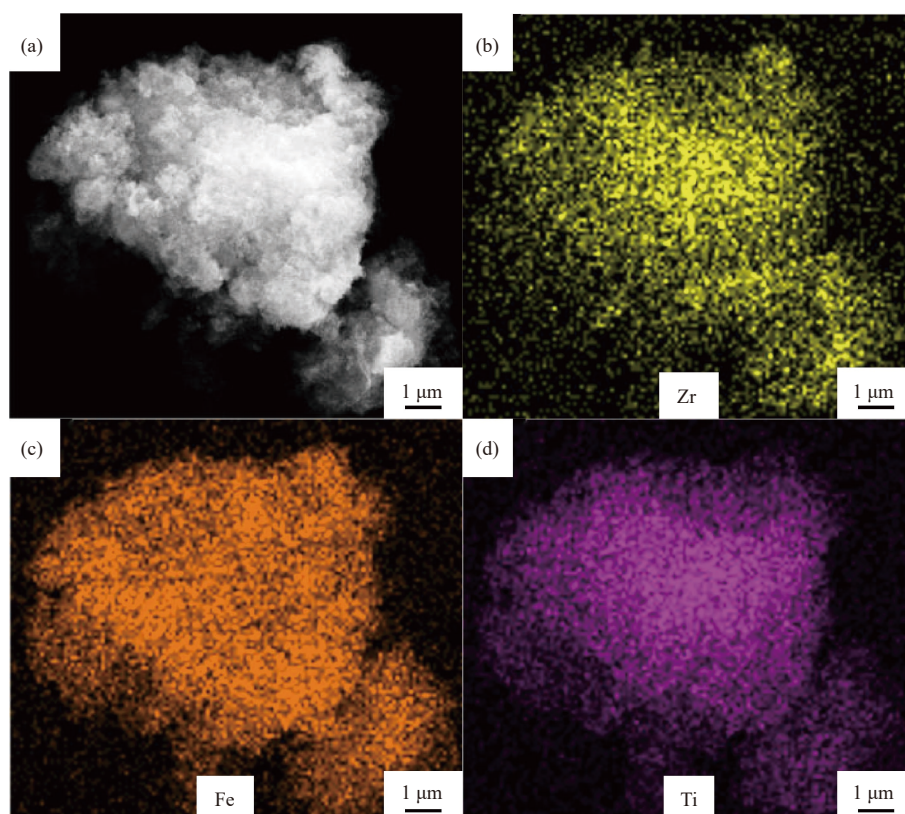


Figure 4 (a) SEM image and EDX elemental maps of the 12% Fe₂O₃/ZrTiO₄ catalyst: (b) Zr, (c) Fe, and (d) Ti

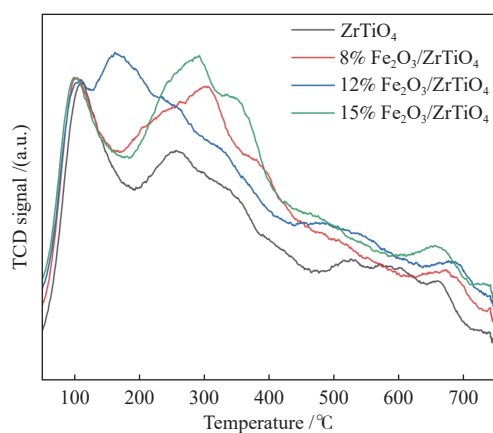


Figure 5 NH₃-TPD profiles of ZrTiO₄ and $\alpha\%$ Fe₂O₃/ZrTiO₄ samples

2.5 Redox properties of $\alpha\%$ Fe₂O₃/ZrTiO₄ catalyst

The redox properties of the catalyst and the interactions between the active components and the support were tested by H₂-TPR, and the results are shown in Figure 6. As can be seen in Figure 6, pure ZrTiO₄ has a single peak. Some studies claim that ZrO₂ has high thermal stability and is not easy to be reduced by H₂ below 900 °C^[24], so this single peak may be attributed to the reduction of TiO₂ to Ti₂O₃. It is worth noting that after loading Fe₂O₃ on ZrTiO₄ support, three peaks can be seen in all $\alpha\%$ Fe₂O₃/ZrTiO₄ catalysts, *i.e.* 342 °C, 410 °C and 629 °C for 8% Fe₂O₃/ZrTiO₄ catalyst, 341 °C, 430 °C and 646 °C for 12%

$\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst, 354 °C, 443 °C and 653 °C for 15% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst. The three peaks are attributed to $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, $\text{TiO}_2 \rightarrow \text{Ti}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, respectively. The relative curve area of the four catalysts consuming H_2 is 12% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ (3.27) > 15% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ (2.77) > 8% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ (1.48) > ZrTiO_4 (1). In $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst, the new peak area increases and the reduction peak temperature decreases greatly, which means that the Fe_2O_3 loading improves the reduction performance of the $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst. Therefore, the presence of Fe atoms affects the reduction performance of the $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst, which may be attributed to the charge transfer between the Fe_2O_3 active component and the ZrTiO_4 support, resulting in a strong synergistic effect, leading to the electron transfer between the active component and the support, and finally promoting the SCR activity of the catalyst^[25]. In addition, the 12% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst has the largest reduction peak area and the lowest reduction peak temperature, which indicate that it has the best reduction properties and thus has the best SCR activity, which is consistent with our test results.

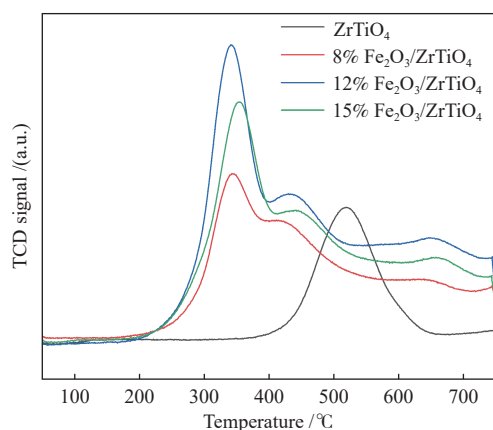
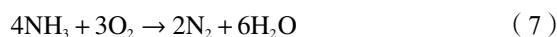
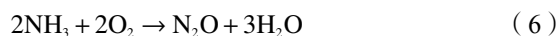
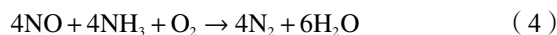


Figure 6 H_2 -TPR profiles of ZrTiO_4 and $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ samples

2.6 SCR activity of $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst

Figure 7(a) shows the NH_3 -SCR activity results of the four samples. It can be seen that the NO_x conversion rate of pure ZrTiO_4 samples increases continuously in the 100–500 °C range, but the maximum NO_x conversion rate is only 38.5% at 100–400 °C, and then the NO_x conversion rate can reach 86.3% at 500 °C because the reducing ability of ZrTiO_4 carrier is not active at low temperature. After loading Fe_2O_3 on the ZrTiO_4 carrier, the NO_x conversion rate is significantly increased. The NO_x

conversion rate of $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ samples is greater than 85% at 300–400 °C and greater than 95% at 300–350 °C. Then, as the temperature continues to rise, the NO_x conversion rate decreases significantly, mainly because the high oxidation ability of Fe_2O_3 makes NH_3 react with O_2 , leading to the reduction of SCR activity. The NO_x conversion of the best 12% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst is greater than 80% at 250–400 °C and close to 100% at 300 °C, which is consistent with the H_2 -TPR test results. The experimental results show that the loading of Fe_2O_3 can effectively improve the NH_3 -SCR activity of the catalyst, which is attributed to the synergistic interaction between Fe, Zr and Ti elements to promote the electron transfer ability of the catalyst, which leads to the improvement of SCR activity. As shown in Figure 7(b), the N_2 selectivity of the four samples was further tested. The N_2 selectivity of pure ZrTiO_4 samples is less than 90% between 100 °C and 400 °C. However, after loading Fe_2O_3 on the surface of ZrTiO_4 , the N_2 selectivity of $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ samples is significantly improved, which is more than 90% at 200–450 °C, and then the N_2 conversion rate decreases slightly at 350 °C, which is similar to the NO_x conversion at high temperature. In addition, the results of NH_3 conversion during SCR reaction were also tested. As shown in Figure 7(c), the NH_3 conversion rate of all samples continuously increases between 150 and 500 °C until it reaches 100%. However, above 300 °C, the NO_x conversion rate significantly decreases, while the NH_3 conversion rate continues to increase. In addition to the SCR reaction between NH_3 and NO in Eq. 4, the direct reaction between NH_3 and O_2 may occur due to the high oxidation capacity of Fe_2O_3 (Eq. 5, Eq. 6 and Eq. 7), as shown in Figure 7(d). This is also confirmed by the decrease in NO conversion rate above 400 °C and the continuous increase of N_2O emission above 400 °C^[26,27].



2.7 Electron transport between Fe_2O_3 and ZrTiO_4 carrier

XPS was used to determine the content of elements on the catalyst surface, the state of metal oxides and the type of adsorbed oxygen, and to explore the interaction between the elements. Figure 8(a) shows

the Zr 3d orbital XPS profiles of ZrTiO₄ and α % Fe₂O₃/ZrTiO₄ catalysts. The four catalysts all contain two typical characteristic peaks. The characteristic peak located at 182.37–182.47 eV is attributed to Zr⁴⁺ species, and the characteristic peak located at 184.67–184.87 eV is attributed to Zr 3d_{3/2}. The Zr⁴⁺ binding energy of the four samples does not change significantly, indicating that the presence of Zr⁴⁺ in the catalyst is very stable, and the loading/calcination of

Fe₂O₃ does not affect the stability of Zr⁴⁺. In addition, the Zr⁴⁺ binding energy of the four catalysts is lower than the ZrO₂ standard of 182.7 eV, which proves the interaction between Zr and Ti⁴⁺. As shown in Table 2, the content of Zr species decreases after loading 8% Fe₂O₃ on ZrTiO₄, but the content of Zr species remains almost unchanged when the loading of Fe₂O₃ is further increased, possibly because some Fe species exist in the bulk of ZrO₂.

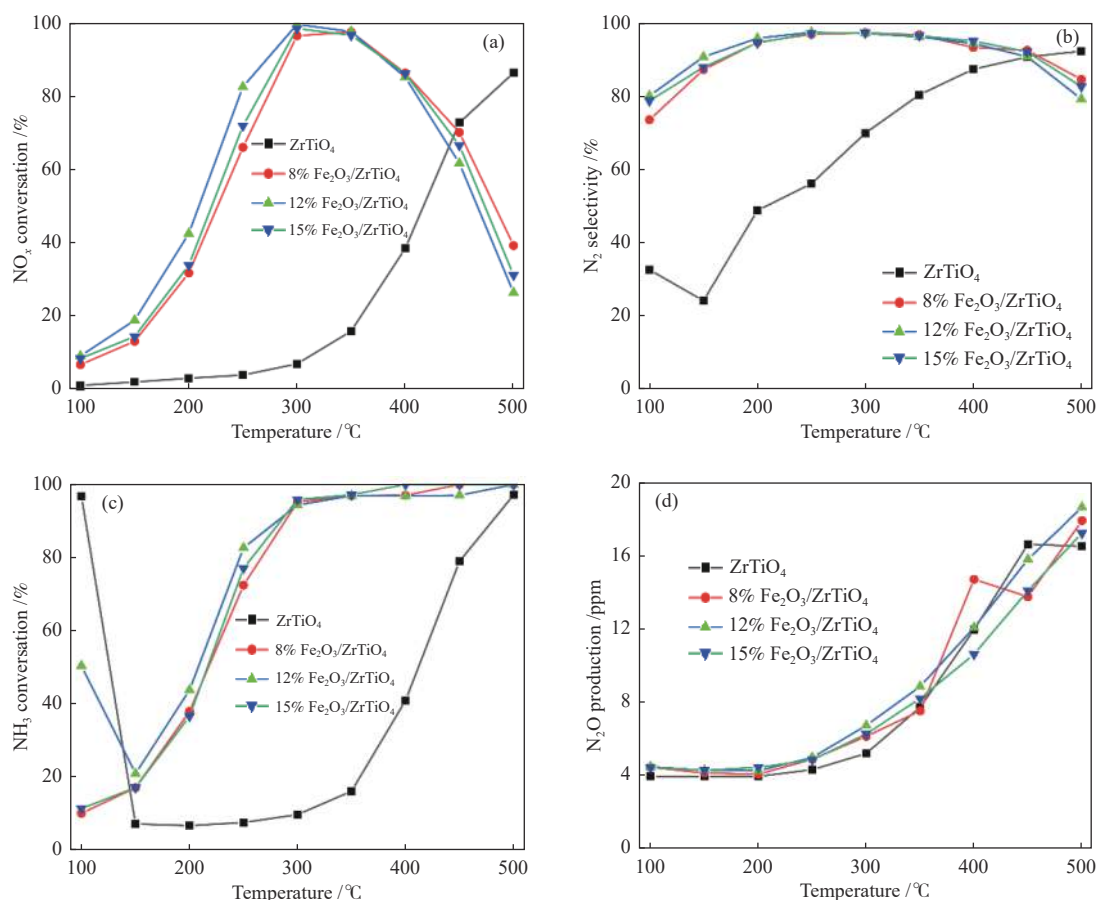


Figure 7 (a) NO_x conversion of ZrTiO₄ and α % Fe₂O₃/ZrTiO₄ samples; (b) N₂ selectivity; (c) NH₃ conversion; (d) N₂O emissions (Reactant feed contains 500 ppm of NO, 600 ppm of NH₃, 3 vol% O₂, balanced with N₂)

Figure 8(b) shows the Ti 2p XPS profiles of ZrTiO₄ and α % Fe₂O₃/ZrTiO₄ catalysts. The characteristic peak at 458.47–458.67 eV belongs to Ti 2p_{3/2}, and the peak at 464.17–464.47 eV belongs to Ti 2p_{1/2}, indicating the existence of Ti⁴⁺. The binding energy of pure ZrTiO₄ catalyst is 458.47 eV. The characteristic peak of α % Fe₂O₃/ZrTiO₄ catalyst after Fe₂O₃ deposition moves to a higher binding energy and increases with the Fe₂O₃ content, indicating that the electron density of the Ti element decreases. In addition, the shift of characteristic peaks indicates the presence of Fe₂O₃, which promotes the strong interaction between Ti and Fe, leading to the migration

of electron clouds^[29].

Figure 8(c) shows the Fe 2p XPS pattern of α % Fe₂O₃/ZrTiO₄ catalyst. The XPS pattern has a larger fold because of less Fe loading. The characteristic peaks located at 711 eV and 725 eV belong to Fe 2p_{3/2} and Fe 2p_{1/2} peaks, respectively^[30]. Fe 2p_{3/2} is divided into Fe³⁺ (711.17–711.87 eV) and Fe²⁺ (709.27–710.67 eV) sub-peaks, respectively^[31]. As shown in Table 2, with the increase of Fe₂O₃ loading, the Fe content on the catalyst surface increases and the Fe³⁺/(Fe³⁺ + Fe²⁺) ratio increases continuously from 43% to 91.7%. This shows that there is electron transfer between Fe₂O₃ and the carrier, and some electrons from

the carrier are transferred to Fe_2O_3 . It can be speculated that there is a strong interaction between Fe, Ti and Zr,

which leads to the coexistence of Fe in different valence states on the surface of the catalyst.

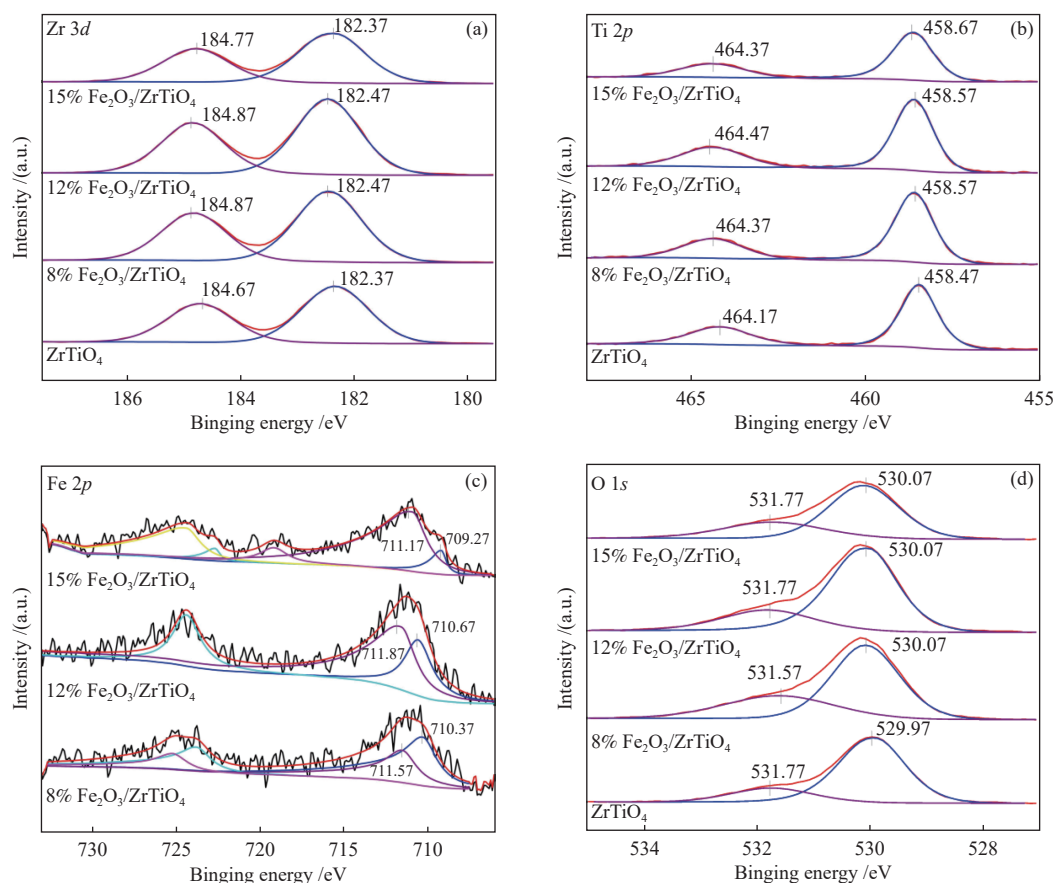


Figure 8 XPS profiles of ZrTiO_4 and $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ samples: (a) Ti 2p; (b) Zr 3d; (c) Fe 2p; (d) O 1s.

Table 2 XPS concentration of ZrTiO_4 and $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$.

Samples	Atomic concentration				Relative concentration	
	Fe	Zr	Ti	O	$\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$	$\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$
ZrTiO_4	—	14.4	15.3	70.3	23.1%	—
8% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$	1.85	13.3	13.2	71.6	34.0%	43%
12% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$	2.21	13.3	12.8	71.6	31.7%	73.4%
15% $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$	2.68	13.2	13.1	71.0	28.7%	91.7%

As shown in Figure 8(d), the two characteristic peaks in the XPS pattern of the O 1s peak of ZrTiO_4 and $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalysts are attributed to the lattice oxygen (O_α) at 530-531 eV, and the other characteristic peak at 531-532 eV is attributed to the surface chemisorbed oxygen (O_β)^[32,33]. Generally, in SCR reaction, since the adsorbed oxygen is more active, it is easy to oxidize NO to NO_2 , so it is easy to participate in the catalytic reaction^[32]. As shown in Table 2, O atom concentration is the highest on the surface of all samples. The relative concentration of

$\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$ in pure ZrTiO_4 catalyst is 23.1%. After Fe_2O_3 is loaded on the ZrTiO_4 catalyst, the relative concentration of oxygen adsorption on the surface of $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst is higher than pure ZrTiO_4 catalyst. These results indicate that Fe loading enhances the chemisorption oxygen concentration of $\alpha\%$ $\text{Fe}_2\text{O}_3/\text{ZrTiO}_4$ catalyst, and promotes the adsorption of oxygen on the surface to participate in SCR reaction. This indicates that the strong interaction between Fe, Ti and Zr can induce surface active sites to activate oxygen. However, with the increase of Fe loading, the

ratio of $O_{\beta}/(O_{\alpha} + O_{\beta})$ decreased, which may be attributed to the formation of aggregates on the surface of ZrTiO₄ by Fe₂O₃ species.

2.8 Adsorption of NH₃(NO_x) species

It is of great significance to determine the reaction mechanism of 12% Fe₂O₃/ZrTiO₄ catalyst by studying the adsorption behavior of NH₃ and NO_x species by in-situ DRIFT. Figure 9(a) shows DRIFT spectra of adsorbed NH₃ species on a 12% Fe₂O₃/ZrTiO₄ catalyst surface. At 50 °C, a series of peaks appear in 12% Fe₂O₃/ZrTiO₄ catalysts stabilized by NH₃ adsorption. The adsorption peak at 984 cm⁻¹ can be attributed to the gas phase or weakly adsorbed NH₃^[34]. The adsorption peak at 1005 cm⁻¹ is attributed to the gas phase or weakly adsorbed NH₃^[34]. The adsorption peak at 1070 cm⁻¹ is attributed to the coordinated NH₃ at the Lewis acid site^[34,35]. The adsorption peak at 1,244 cm⁻¹ is attributed to the coordination of NH₃ at the Lewis acid site^[34,36]. The adsorption peak at 1,362 cm⁻¹ is attributed to the wagging vibration of NH₂ species^[37]. The adsorption peak at 1,440 cm⁻¹ is attributed to NH₄⁺ species at the Brønsted acid site^[38]. The adsorption peak at 1521 cm⁻¹ is attributed to an amide (NH₂)

substance^[37]. The adsorption peaks at 2887 cm⁻¹ and 2951 cm⁻¹ are attributed to NH₄⁺ species at the Brønsted acid site^[38,39]. The adsorption peak at 3,614 cm⁻¹ is attributed to surface O-H/N-H stretching^[40,41]. In addition, with the increase in temperature, the adsorbed NH₃ species on the surface of the catalyst changed, and the adsorption peaks at 984 cm⁻¹ and 1244 cm⁻¹ continuously weakened, indicating that the adsorbed NH₃ species on the surface of 12% Fe₂O₃/ZrTiO₄ catalyst decreased. The above can be attributed to the desorption of adsorbed species at high temperatures. The adsorption peak at 1521 cm⁻¹ constantly shifted to 1491 cm⁻¹ with the increase in temperature, which may be because the unstable adsorption peak at 1521 cm⁻¹ was transformed into more stable species. In addition, the adsorption peaks of 1005 cm⁻¹, 1070 cm⁻¹, 1362 cm⁻¹, 1440 cm⁻¹, 2887 cm⁻¹, 2951 cm⁻¹ and 3614 cm⁻¹ on 12% Fe₂O₃/ZrTiO₄ catalysts do not change significantly with the increase of temperature, indicating that the adsorptions are relatively stable, which may be one of the reasons for the high activity of the 12% Fe₂O₃/ZrTiO₄ catalyst.

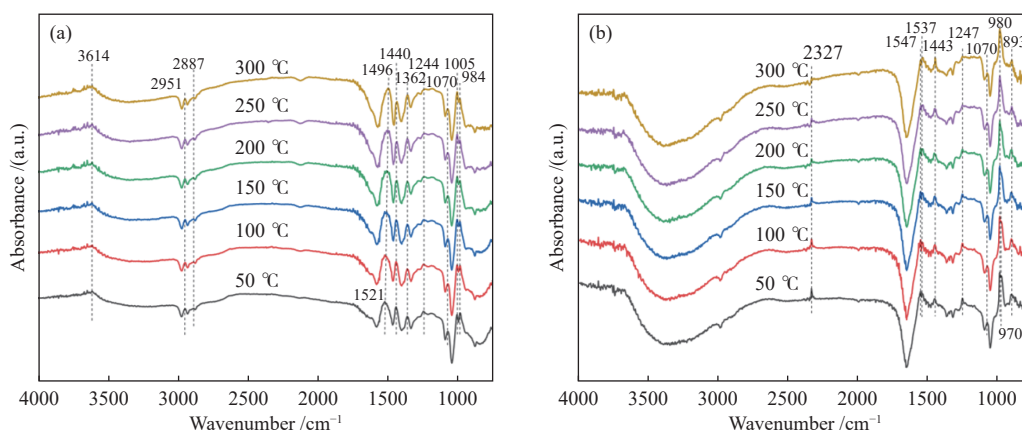


Figure 9 DRIFT spectra of (a) NH₃ adsorption and (b) NO + O₂ adsorption on 12% Fe₂O₃/ZrTiO₄ catalyst at different temperatures

Fig. 9(b), shows DRIFT spectra of adsorbed NO_x species on the surface of a 12% Fe₂O₃/ZrTiO₄ catalyst. At 50 °C, a series of adsorption peaks appear after 12% Fe₂O₃/ZrTiO₄ catalyst adsorbs NO + O₂. The peaks at 970 cm⁻¹ and 980 cm⁻¹ can be attributed to cis-(N₂O₂)²⁻ species^[42]. The adsorption peak at 1,070 cm⁻¹ is attributed to bidentate nitrate^[43]. The adsorption peak at 1247 cm⁻¹ is attributed to bridge nitrate^[44,45]. The adsorption peak at 1443 cm⁻¹ is attributed to nitro compounds^[46]. The adsorption peaks at 1,537 cm⁻¹ and 1547 cm⁻¹ are attributed to bidentate nitrate^[46,47]. The

adsorption peak at 2327 cm⁻¹ belongs to the adsorbed state N₂O^[48]. The miscellaneous peaks above 3600 cm⁻¹ are attributed to the surface basic hydroxyl band^[48]. In addition, with the increase in temperature, some adsorption peaks changed significantly, and the adsorption peak located at 970 cm⁻¹ disappeared when the temperature increased to 150 °C. The intensity of the adsorption peaks at 1247 cm⁻¹, 1547 cm⁻¹ and 2327 cm⁻¹ decreases with temperature, which means that these adsorptions are not stable on the surface of the 12% Fe₂O₃/ZrTiO₄ catalyst.

2.9 Reaction mechanism of the 12% Fe₂O₃/ZrTiO₄ catalyst

Based on the previous conclusions of adsorption peaks of NH₃ species and NO_x species adsorbed by 12% Fe₂O₃/ZrTiO₄ catalyst at different temperatures, we further determined the reaction mechanism on 12% Fe₂O₃/ZrTiO₄ catalyst by pre-adsorbed NH₃ (NO + O₂) and then passing through NO + O₂ (NH₃). Because the 12% Fe₂O₃/ZrTiO₄ catalyst has the highest SCR activity at 300 °C, the SCR reaction mechanism on the surface of 12%Fe₂O₃/ZrTiO₄ catalyst was studied by selecting 300 °C as the in-situ DRIFT test temperature.

Figure 10(a), shows the in-situ DRIFTs spectra of 12% Fe₂O₃/ZrTiO₄ catalyst surface adsorbed NH₃ at 300 °C for 30 min before N₂ scavenging and blowing into NO + O₂. Figure 10(a) shows that a series of adsorption peaks appear on the surface of 12% Fe₂O₃/ZrTiO₄ catalyst after pre-adsorption of NH₃, and both ionic NH₄⁺ species and coordinated NH₃ species appear on the surface of the catalyst. After the introduction of NO + O₂, some characteristic peaks changed significantly. With the increase of NO + O₂ penetration time, the adsorption peak at 950 cm⁻¹ belonging to the gas phase or weakly adsorbed NH₃ began to weaken, and the intensity of the adsorption peak at 1,765 cm⁻¹ (NH₄⁺) began to weaken, and no

new adsorption peak appeared on the catalyst surface. This indicates that the NH₃ species adsorbed on the surface of the catalyst reacted with the NO_x species entering the catalyst. Then, NO + O₂ was pre-adsorbed on the surface of 12% Fe₂O₃/ZrTiO₄ catalyst at 300 °C for 30 min, and NH₃ was introduced after N₂ scavenging. As seen in Figure 10(b), NO adsorbed NO_x species are observed in DRIFT spectra after NO + O₂ gas is pre-adsorbed by the catalyst, which means that 12% Fe₂O₃/ZrTiO₄ catalyst does not adsorb NO_x species at 300 °C, and then after NH₃ is continuously introduced, new adsorption peaks (945 cm⁻¹, 1,167 cm⁻¹, 1,252 cm⁻¹, 1,360 cm⁻¹, 1,425 cm⁻¹, 1,498 cm⁻¹) appeared at 3 min, and the intensity of the new adsorption peak also increased with the introduction of NH₃. The adsorption peaks of Lewis acid sites (1,167, 1,252 cm⁻¹) and Brønsted (1,360, 1,425, 1,498 cm⁻¹) on the catalyst surface reached a stable state after the introduction of NH₃ for 60 min. Therefore, 12% Fe₂O₃/ZrTiO₄ catalyst in NH₃-SCR reaction is mainly through the Eley-Rideal (E-R) reaction mechanism, as shown in Eq. 8, 9 and 10. Gaseous NH₃ molecules adsorbed on the active site on the catalyst surface to form adsorbed NH₃ species, and then reacted directly with gaseous NO_x to generate adsorbed N₂, which is desorbed to produce final product N₂ (Figure 11).

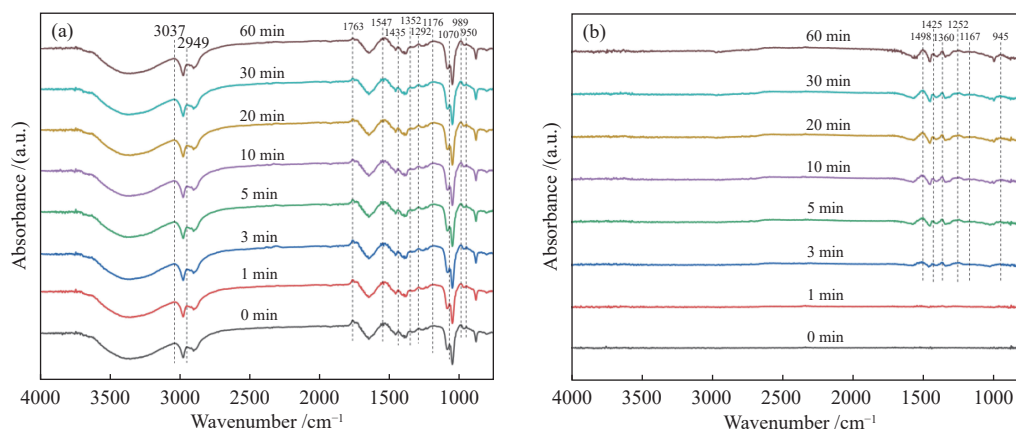


Figure 10 DRIFT spectra of reaction between (a) pre-adsorption of NH₃ and NO + O₂ (b) pre-adsorption of NO + O₂ and NH₃ on 12% Fe₂O₃/ZrTiO₄ catalyst

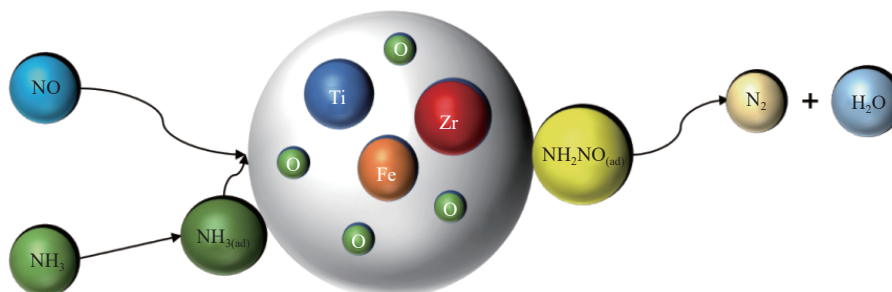


Figure 11 Reaction mechanism of 12% Fe₂O₃/ZrTiO₄ catalyst



Note: * represents the active site on the catalyst; *g* represents the gas phase component; *ads* represents the adsorbed component.

3 Conclusions

(1) Fe₂O₃ modified ZrTiO₄ composite oxide catalyst shows excellent NO_x conversion rate and N₂ selectivity. The best temperature window is between 250 °C and 400 °C, the NO_x conversion rate is greater than 80% and N₂ selectivity is greater than 90% at 200–450 °C.

(2) The excellent SCR activity is mainly due to the synergistic interaction between Fe₂O₃ and ZrTiO₄ support, which leads to the best redox performance and surface acidity of the 12% Fe₂O₃/ZrTiO₄ catalyst. In addition, the presence of high surface area, high

dispersion and the porous structure can also promote the ability of α% Fe₂O₃/ZrTiO₄ catalyst to adsorb NH₃ species, thus promoting the catalytic activity of the catalyst.

(3) In-situ DRIFT shows that the surface of 12% Fe₂O₃/ZrTiO₄ catalyst mainly follows the E-R mechanism at 300 °C.

Acknowledgments

This work was supported by the Scientific and Technological Innovation Team Project of the Shaanxi Innovation Capability Support Plan, China (2022TD-30), the Youth Innovation Team of Shaanxi Universities (2019-2022), the top young talents project of “Special support program for high-level talents” in the Shaanxi Province (2018-2023), and the International Science and Technology Cooperation Program of the Shaanxi Province (2022KW-39), Xi’an Science and Technology Planning Project (2022JH-RYFW-0196).

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Fe₂O₃ 对 ZrTiO₄ 载体 NH₃-SCR 催化性能的影响

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摘要: NH₃-SCR 催化剂主要用于工业生产和汽车尾气清洁, 本研究采用“共沉淀-浸渍法”制备了新型 α Fe₂O₃/ZrTiO₄ ($\alpha=0, 8, 12, 15$) 催化剂。结果表明: α % Fe₂O₃/ZrTiO₄ 催化剂的最佳成分配比的 12% Fe₂O₃/ZrTiO₄ 催化剂在 250–400 °C 之间 NO_x 转化率大于 80%, 在 300 °C 时 NO_x 转化率接近 100%, 并且 N₂ 选择性在 200–450 °C 之间大于 90%。在 ZrTiO₄ 表面负载 Fe₂O₃ 后, 催化剂的氧化还原性能、表面酸度和 O _{β} /(O _{α} + O _{β}) 比例都有所提高, 这不仅归因于 α % Fe₂O₃/ZrTiO₄ 催化剂具有一种多孔结构, 还归因于活性组分 Fe₂O₃ 和载体 ZrTiO₄ 之间的电子相互作用。此外, 原位 DRIFTS 反应表明 12% Fe₂O₃/ZrTiO₄ 催化剂的 NH₃-SCR 反应遵循 Eley-Rideal 机制。明确的反应机制有利于更深入的了解 SCR 过程中 NO_x 转化的反应过程。这项工作为未来 Fe 基 SCR 催化剂在中温范围内替代 V 基催化剂提供了可行的策略。

关键词: Fe₂O₃/ZrTiO₄ 催化剂; NH₃-SCR; 多孔; 反应机制

中图分类号: O643.36

文献标识码: A