Insight into the Promoting Role of Er Modification on SO\textsubscript{2} Resistance for NH\textsubscript{3}-SCR at Low Temperature over FeMn/TiO\textsubscript{2} Catalysts

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Abstract: Er-modified FeMn/TiO\textsubscript{2} catalysts were prepared through the wet impregnation method, and their NH\textsubscript{3}-SCR activities were tested. The results showed that Er modification could obviously promote SO\textsubscript{2} resistance of FeMn/TiO\textsubscript{2} catalysts at a low temperature. The promoting effect and mechanism were explored in detail using various techniques, such as BET, XRD, H\textsubscript{2}-TPR, XPS, TG, and in-situ DRIFTS. The characterization results indicated that Er modification on FeMn/TiO\textsubscript{2} catalysts could increase the Mn\textsuperscript{4+} concentration and surface chemisorbed labile oxygen ratio, which was favorable for NO oxidation to NO\textsubscript{2}, further accelerating low-temperature SCR activity through the “fast SCR” reaction. As fast SCR reaction could accelerate the consumption of adsorbed NH\textsubscript{3} species, it would benefit to restrain the competitive adsorption of SO\textsubscript{2} and limit the reaction between adsorbed SO\textsubscript{2} and NH\textsubscript{3} species. XPS results indicated that ammonium sulfates and Mn sulfates formed were found on Er-modified FeMn/TiO\textsubscript{2} catalyst surface seemed much less than those on FeMn/TiO\textsubscript{2} catalyst surface, suggested that Er modification was helpful for reducing the generation or deposition of sulfate salts on the catalyst surface. According to in-situ DRIFTS the results of the, the presence of SO\textsubscript{2} in feeding gas imposed a stronger impact on the NO adsorption than NH\textsubscript{3} adsorption on Lewis acid sites of Er-modified FeMn/TiO\textsubscript{2} catalysts, gradually making NH\textsubscript{3}-SCR reaction to proceed in E-R mechanism rather than L-H mechanism. DRIFTS.

Keywords: FeMn/TiO\textsubscript{2}; Er modification; SCR; SO\textsubscript{2} resistance; low temperature

1. Introduction

Nitrogen oxides (NO\textsubscript{x}) emitted from diesel engines and industrial processes are significant atmospheric pollutants, which can lead to a number of environmental problems, such as acid rain, photochemical smog, ozone depletion, and greenhouse effects [1–4]. During the past decades, a number of NO\textsubscript{x} removal technologies have been developed with the purpose of abating NO\textsubscript{x} emissions. Among them, selective catalytic reduction (SCR) with NH\textsubscript{3} (or urea) as a reductant is an effective and economic NO\textsubscript{x} removal technique. It has been widely used in stationary and mobile sources [5–7]. In SCR systems, catalysts play a critical role in creating an efficient reaction and controlling the construction cost [8]. At present, V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} and V\textsubscript{2}O\textsubscript{5}-MoO\textsubscript{3}/TiO\textsubscript{2} catalysts have been used extensively in commercial projects. However, there are still several disadvantages, such as the narrow catalytic temperature window (300–400 °C) and toxic effect of vanadium species, limiting
their further applications [9,10]. Therefore, it is of great significance to develop vanadium-free SCR catalysts with excellent catalytic activities at low temperatures (<250 °C).

In recent years, more and more researchers around the world are trying to develop high-activity low-temperature SCR catalysts. Several kinds of transition metals, such as Mn, Co, Fe, Cu, and Ni, have been extensively studied and exhibited promising SCR performance [11–15]. It is worthy to point out that FeMn/TiO₂ catalysts have been investigated extensively due to their advantages of excellent low-temperature SCR performance, environmentally friendly nature, and low cost [16–18]. However, there are still some challenging problems for FeMn/TiO₂ catalysts to overcome, including poor N₂ selectivity and weak tolerance to SO₂ and H₂O.

Generally, when a certain concentration of SO₂ gas co-exists in flue gas, ammonium sulfates and/or metal sulfates are unavoidably formed on the SCR catalyst surface. They block and destroy active sites on SCR catalyst surface, causing the deactivation of low-temperature catalysts. To enhance SO₂ resistance of FeMn/TiO₂ catalysts, a promising method is to modify the catalysts with other metal elements, further inducing some synergetic effects between the dopants and Fe-Mn-Ti oxides [19–21]. Jiang et al. demonstrated that doping Zr in FeMn/TiO₂ catalyst could enhance the formation of NO₂ in the SCR reaction, thus improve the tolerance of SO₂ [19]. Hou et al. found that the addition of proper amount of praseodymium (Pr) to FeMn/TiO₂ catalyst could restrain the deposition of ammonium sulfates, thus improve the catalyst stability against SO₂ poisoning [22]. A similar conclusion was drawn from their other work in which SO₂ resistance for NH₃-SCR at low temperature was enhanced by the doping of lanthanum (La) [23]. The adsorption and oxidation of SO₂ on the catalyst were inhibited by La modification.

Erbium (Er) is a kind of rare earth element. It has been applied as a doping additive in various fields due to the incompletely occupied 4f and empty 5d orbitals [24]. For example, Er-doped ZnO (EZO) have been widely studied and expected as one of the promising materials for ZnO based optoelectronic device. The incorporation of Er could affect the band gap and optical constants of ZnO thin films [25]. Er was also used to enhance the sonocatalytic performance of organic dye degradation [26]. The prepared Er³⁺:YAlO₃/TiO₂-Fe₂O₃ composite demonstrated a good sonocatalytic activity. Er³⁺ ion is an attractive optical activator and displays the richest spectra in the UV-vis-IR range due to its rich energy level structure.

The application of Er in the field of NH₃-SCR catalysts is rare. However, it has been used as doping additives to enhance the NH₃-SCR performance of V and Ce based catalysts. Vargas et al. found that Er modification on V₂O₅-WO₃/TiO₂ catalyst could improve the catalytic activity of catalysts after ageing [27], and the addition of Er caused modifications in symmetric deformation modes of ammonia coordinated on Lewis acid sites. Casanova et al. found that Er mixed with FeVO₄ supported on TiO₂-WO₃-SiO₂ could enhance the structural and textural stability of the system by hindering the transformation of anatase to rutile, thus enhance activity after thermal treatment [28]. Kim et al. found that Er doping in CeV₅O₁₈ catalyst could enhance redox features and improve the quantities of acid sites and defects. This led to the high-performance of NH₃-SCR reaction [29]. Jin et al. found that Er doping could increase oxygen storage capacities and oxygen vacancy concentrations of CeZr/TiO₂ catalysts, resulting in excellent SCR activity and SO₂ resistance [30]. It was considered that the introduction of Er into SCR catalysts was in favor of enhancing the structural and textural stability, redox property, improving the mounts of acid sites and oxygen vacancy, and blocking anatase transformation to rutile. It was possible to improve the activity and SO₂ resistance of FeMn/TiO₂ catalysts by doping with Er. However, to the best of our knowledge, the promotional effect of Er incorporation on SO₂ resistance for NH₃-SCR at low temperature over FeMn/TiO₂ catalysts has not been investigated yet.

In the present study, a series of Er-modified FeMn/TiO₂ catalysts with different Er/Mn molar ratios were successfully synthesized via the wet impregnating method. NH₃-SCR activity and SO₂ resistance over the prepared catalysts were tested. The promotional effects of Er modification on SO₂ resistance were studied systematically by various characteriza-
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2. Results

2.1. Low Temperature SCR Activity and SO$_2$ Resistance

Figure 1a and Figure S1a show the activities of Er$_x$FeMn/TiO$_2$ catalysts prepared with different Er/Mn molar ratios across a temperature window of 60–240 °C. Compared to the FeMn/TiO$_2$ catalyst, Er$_{0.01}$FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts exhibited higher NO$_x$ conversion efficiencies over the whole temperature range. But the activity at low temperature (<120 °C) decreased sharply when further increasing Er doping amount. The result indicated that, the low-temperature catalytic performance of FeMn/TiO$_2$ catalyst could be enhanced by doping only a small amount of Er. As shown in Figure 1a, Er$_{0.05}$FeMn/TiO$_2$ catalyst possessed more than 95% NO$_x$ conversion efficiency in the temperature range of 120–240 °C. Since the NO$_x$ conversion performance of Er$_{0.05}$FeMn/TiO$_2$ catalyst was better than those of other catalysts over the whole temperature range, a proper Er doping molar ratio of 0.05 (Er/Mn) was chose for further investigation in this work.

Figure 1. NO$_x$ conversion (a), resistance to sulfur poisoning test (b), resistance to water vapor poisoning test (c), resistance to water vapor and sulfur poisoning test (d) during the NH$_3$-SCR reaction over FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts. (Reaction conditions: 1 mL catalyst, [NO] = [NH$_3$] = 500 ppm, [O$_2$] = 5 vol.%, [SO$_2$] = 100 ppm (when used), 5% H$_2$O (when used), balanced with N$_2$, GSHV = 30,000 h$^{-1}$).

The N$_2$ selectivity of the prepared catalysts in the temperature range of 60–240 °C is illustrated in Figure S1b. It could be seen that the N$_2$ selectivity of FeMn/TiO$_2$ catalyst at 100 °C was 92.4%, but quickly decreased to 18.8% as reaction temperature increased.
to 240 °C. N₂ selectivity of the prepared FeMn/TiO₂ catalyst was not so good, and this result was similar to that of some previous work [31]. The poor N₂ selectivity could be ascribed to the formation of unwanted N₂O through some side reactions [32]. When the Er doping molar ratio was 0.01, the effect of Er doping on N₂ selectivity in the whole temperature range was negligible. However, when further increasing Er doping molar ratio, N₂ selectivity of Er-modified catalysts improved obviously. The higher the Er doping molar ratio was, the better N₂ selectivity was. Here, the enhancement effect on N₂ selectivity was mainly ascribed to the inhibition of N₂O formation by the introduction of Er element.

In order to investigate the SO₂ tolerance of FeMn/TiO₂ and ErₓFeMn/TiO₂ catalysts, the SO₂ resistance of these two catalysts was tested in the presence of 100 ppm SO₂. As shown in Figure 1b, the NOₓ conversion efficiency of FeMn/TiO₂ catalyst decreased quickly from 100% to 56.0% after introducing SO₂ in feeding gas for 6 h, and it could be restored to 61.0% after stopping SO₂ for 2 h. Compared with FeMn/TiO₂ catalyst, Er₀.₅FeMn/TiO₂ catalyst displayed much better SO₂ resistance performance. After the introduction of SO₂ in feeding gas, NOₓ conversion efficiency of Er₀.₅FeMn/TiO₂ catalyst decreased slowly, and it could be maintained at 90.8% after exposure to 100 ppm SO₂ for 6 h. After stopping the injection of SO₂ for 2 h, NOₓ conversion efficiency of Er₀.₅FeMn/TiO₂ catalyst could recover to 95.5%. This result indicated that the introduction of Er element could greatly improve SO₂ resistance performance of FeMn/TiO₂ catalysts.

Generally, a small amount of H₂O vapor will exist in the flue gas of stationary and mobile sources. Here, 5% H₂O was introduced in the feeding gas to test the H₂O resistance of the selected catalysts. As shown in Figure 1c, the NOₓ conversion efficiency of FeMn/TiO₂ catalyst decreased gradually from 100% to 88.0% after introducing 5% H₂O for 6 h, and it could be recovered to 100% quickly by stopping H₂O injection. This indicated that the deactivation of FeMn/TiO₂ catalyst by H₂O was reversible. By contrast, Er₀.₅FeMn/TiO₂ catalyst exhibited excellent H₂O resistance performance. The introduction of 5% H₂O had little effect on the NOₓ conversion efficiency of Er₀.₅FeMn/TiO₂ catalyst during the whole reaction process.

The effect of coexistence of 100 ppm SO₂ and 5% H₂O in feeding gas on NOₓ conversion performance of FeMn/TiO₂ catalysts with and without Er modification was also evaluated, and the results are illustrated in Figure 1d. It was clear that coexistence of SO₂ and H₂O imposed a much greater impact on FeMn/TiO₂ catalyst than that for Er₀.₅FeMn/TiO₂ catalyst. NOₓ conversion efficiency of FeMn/TiO₂ catalyst decreased quickly from 100% to 18.0% after introducing SO₂ and H₂O for 6 h. As to Er₀.₅FeMn/TiO₂ catalyst, the change trend of NOₓ conversion efficiency was similar to the case exposed to single SO₂. NOₓ conversion efficiency of Er₀.₅FeMn/TiO₂ catalyst decreased slowly from 100% to 84.7% after injection of SO₂ and H₂O for 6 h. Therefore, a conclusion could be drawn that the resistance to SO₂ and H₂O of FeMn/TiO₂ catalyst could be enhanced obviously by Er modification.

Previous studies reported that there were two main reasons for the deactivation of catalysts suffered from SO₂ poisoning [33–35]. On one hand, NH₃ used as NO reductant would react with SO₂ at low temperature, and the generated ammonium sulfates would cover on the catalyst surface which would block the active sites. One the other hand, the active species of the catalysts would also react with SO₂ to form inactive metal sulfates, which were destructive to the NH₃-SCR reaction. According to the SO₂ resistance tests in this work, the introduction of Er element could greatly improve SO₂ resistance performance of FeMn/TiO₂ catalysts at 200 °C. It is known that ammonium sulfates can be decomposed at 230–400 °C [36], while metal sulfates can be decomposed at a much higher temperature [37]. In view of this, it was possible that Er modification restrained the formation of ammonium sulfates and inactive metal sulfates to some extent, thus preventing the active sites being blocked or deactivated. The mechanisms of the enhancement effect of Er modification on SO₂ resistance were further analyzed through the following characterizations.
2.2. BET Results

$N_2$ adsorption-desorption isotherms of FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts are shown in Figure 2. According to IUPAC classification, the adsorption isotherms of all the catalysts were type IV, suggesting that the mesoporous structures of the prepared catalysts were not changed after SO$_2$ resistance tests [38]. The specific surface areas, pore volumes, and pore sizes of these catalysts were shown in Table S1. The specific surface areas of FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts were 58.6 and 59.5 m$^2$/g, respectively. After SO$_2$ resistance tests, the specific surface area of FeMn/TiO$_2$-S catalyst decreased by 10.9%, while that of Er$_{0.05}$FeMn/TiO$_2$-S catalyst decreased by 3.5% only. It implied that a certain amount of ammonium sulfates had been formed on the surface of both kinds of catalysts due to the reaction between NH$_3$ species and SO$_2$ [33]. As the decrease in specific surface area of Er$_{0.05}$FeMn/TiO$_2$ catalyst was much less than that of FeMn/TiO$_2$ catalyst, it demonstrated that Er modification could effectively restrain the formation of ammonium sulfates on the surface of FeMn/TiO$_2$ catalyst.

![Figure 2. $N_2$ adsorption/desorption isotherms of the fresh and used FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts.](image)

2.3. XRD Analysis

Figure 3 presents the XRD patterns of FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts. The diffraction peaks of 20 at 25.3°, 36.9°, 38.6°, 48.0°, 53.9°, 55.1°, and 62.7° could be assigned to anatase TiO$_2$ characteristic peaks (ICCD PDF-2, 21-1272), and the diffraction peaks of 20 at 33.0°, 38.2°, and 55.1° could be assigned to Mn$_2$O$_3$ characteristic peaks (ICCD PDF-2, 65-7467). It could be seen that all catalysts exhibited distinct anatase TiO$_2$ diffraction peaks, and no obvious diffraction peaks of rutile TiO$_2$ were found. The diffraction peaks of MnO$_x$ in the prepared FeMn/TiO$_2$ catalyst matched well with the standard powder diffraction pattern of Mn$_2$O$_3$, implying Mn$_2$O$_3$ was the main crystal phase. The diffraction peaks of Mn$_2$O$_3$ in Er-modified FeMn/TiO$_2$ catalysts were not obvious. This suggests that Er modification promoted the transformation of MnO$_x$ from crystalline state to highly dispersed amorphous state, which was beneficial to enhance the catalytic performance at low temperature [39,40]. After the SO$_2$ resistance test, there were more peaks appeared in the diffraction pattern of the used FeMn/TiO$_2$ catalyst, which could be ascribed to the formation of Ti(SO$_4$)$_2$ on catalyst surface (ICCD PDF-2, 18-1406) [41]. However, the same diffraction peak of Ti(SO$_4$)$_2$ was not observed in the diffraction pattern of Er$_{0.05}$FeMn/TiO$_2$-S catalyst. Since sulfates would cover active sites on the surface of FeMn/TiO$_2$ catalysts, it might be the main reason for the FeMn/TiO$_2$ catalyst’s low SCR activity. This result also agreed well with the aforementioned SO$_2$ resistance test results. Furthermore, it could also demonstrate that Er doping in FeMn/TiO$_2$ catalysts was in favor of inhibiting the
formation of sulfates on the catalyst surface, thus improving SO$_2$ tolerance of Er-modified FeMn/TiO$_2$ catalysts.

**Figure 3.** XRD patterns of the fresh and used FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts.

### 2.4. **H$_2$-TPR Analysis**

The redox properties of FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts were investigated via H$_2$-TPR, and the results are shown in Figure 4. The reduction peak temperatures and H$_2$ consumption values were listed in Table S2. As for the FeMn/TiO$_2$ catalyst, there were three reduction peaks: the low temperature reduction peak centered at 313 °C could be assigned to the reduction of MnO$_2$ to Mn$_2$O$_3$, the peak centered at 389 °C belonged to the reduction of Mn$_3$O$_4$ to MnO or Fe$_2$O$_3$ to Fe, and the peak centered at 582 °C belonged to the reduction of Mn$_3$O$_4$ to MnO [18,42]. Compared to ErFeMn/TiO$_2$ catalyst, all the reduction peaks of Er$_{0.05}$FeMn/TiO$_2$ catalyst were shifted toward low temperature direction, indicating that Er$_{0.05}$FeMn/TiO$_2$ catalyst had a better redox ability at low temperature. As shown in Table S2, the total H$_2$ consumption value of Er$_{0.05}$FeMn/TiO$_2$ catalyst was much more than that of FeMn/TiO$_2$ catalyst, indicating the number of reductive species on the surface of Er$_{0.05}$FeMn/TiO$_2$ catalyst was much more than that of FeMn/TiO$_2$ catalyst. The low reduction temperature and high H$_2$ consumption value demonstrated that Er modification could improve the low-temperature redox ability of FeMn/TiO$_2$ catalysts [33]. This result also agreed well with the improved SCR activity of Er-modified FeMn/TiO$_2$ catalysts at a low temperature.

**Figure 4.** H$_2$-TPR profiles of the fresh (a) and used (b) FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts.

After SO$_2$ resistance tests, the reduction peaks of the used catalysts shifted toward a higher temperature zone. As shown in Figure 4b, there were three reduction peaks in the profiles of these two kinds of catalysts. Their strongest peaks were centered at 457 °C and...
460 °C, respectively, which were related to the reduction of sulfate species (Mn sulfates) [33]. The corresponding H₂ consumption value (151.6 cm³/g STP) for the strongest reduction peak of Er₀.₀₅FeMn/TiO₂-S catalyst was less than that (194.8 cm³/g STP) of FeMn/TiO₂-S catalyst. It suggested that less amount of sulfate species had been formed on the surface of Er₀.₀₅FeMn/TiO₂ catalyst. The peaks centered at 379 and 360 °C could be assigned to the reduction of MnO₂ and Mn₂O₃ [38], and the corresponding H₂ consumption value (39.3 cm³/g STP) for Er₀.₀₅FeMn/TiO₂-S catalyst was much more than that (24.1 cm³/g STP) of FeMn/TiO₂-S catalyst. It indicated that Er modification was favorable to maintain the redox ability of FeMn/TiO₂ catalyst when SO₂ coexisted in feeding gas. It was possible that Er modification on FeMn/TiO₂ catalyst could alleviate the deactivation due to the reaction between active species and SO₂, thus inhibiting the formation of Mn sulfate species on the catalyst surface.

2.5. XPS Analysis

The surface compositions and elementary oxidation states of the fresh and used catalysts (FeMn/TiO₂ and Er₀.₀₅FeMn/TiO₂) were analyzed by X-ray photoelectron spectrometer (XPS). The spectra of Mn 2p, O 1s and S 2p are shown in Figure 5, and the analysis results of surface atomic concentration ratios are presented in Table S3. As shown in Figure 5a, two main peaks assigned to Mn 2p₃/₂ and Mn 2p₁/₂ were observed in the spectra of the catalysts. The overlapping peaks of Mn 2p₃/₂ could be divided into several sub-peaks with Shirley-type background. The obtained peaks could be ascribed to Mn²⁺ (640.9–641.7 eV), Mn³⁺ (642.0–643.0 eV) and Mn⁴⁺ (643.3–644.5 eV), respectively [37]. The atomic ratio of Mn⁴⁺ to Mnⁿ⁺ was decided according to the peak area. As shown in Table S3, the atomic ratios of Mn⁴⁺/Mnⁿ⁺ for FeMn/TiO₂ and Er₀.₀₅FeMn/TiO₂ catalysts were 31.9% and 33.9%, respectively. It suggested that more surface Mn⁴⁺ species were generated with the introduction of Er. This result was in accordance with the result of H₂-TPR, in which the area of the reduction peak ascribed to MnO₂ to Mn₂O₃ in the profile of Er₀.₀₅FeMn/TiO₂ catalyst was larger than that of FeMn/TiO₂ catalyst. Kapteijn et al. found that NO removal efficiency at low temperature for manganese oxides decreased in an order of MnO₂ > Mn₅O₈ > Mn₃O₅ > Mn₃O₄ [43]. The high catalytic activity of MnO₂ (Mn⁴⁺) was ascribed to its lattice defects [44]. Here, it could be inferred that the formation of more surface Mn⁴⁺ species was conducive for achieving a high NOx conversion efficiency over Er₀.₀₅FeMn/TiO₂ catalyst, as shown in Figure 1a. Compared with the fresh FeMn/TiO₂ and Er₀.₀₅FeMn/TiO₂ catalysts, the peaks of Mn 2p₃/₂ for the used catalysts were shifted toward higher binding energy (from 641.8 and 642.1 to 642.3 and 642.5 eV, respectively). It indicated that Mn atoms in the used catalysts were not only bonded to O atoms, but also to the atoms with lower electronegativity [38]. According to S 2p spectra in the XPS and the analysis results of H₂-TPR, it was speculated the atoms with lower electronegativity might be originated from Mn sulfates [37,38]. The shift of binding energy of the used FeMn/TiO₂ catalyst before and after SO₂ resistance test was more obvious than that for Er₀.₀₅FeMn/TiO₂ catalyst. It implied that Er modification inhibited the formation of sulfates to a certain extent. In addition, Mn atomic concentration on the surface of FeMn/TiO₂ catalyst decreased by 4.4% after SO₂ resistant test, while that of Er₀.₀₅FeMn/TiO₂ catalyst decreased by only 0.5%. It demonstrated that Er modification could also inhibit the loss of Mn active species on the surface of catalysts, and thus improving the SO₂ resistance.
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Figure 5. XPS spectra of Mn 2p (a), O 1s (b) and S 2p (c) over FeMn/TiO 2 and Er0.05FeMn/TiO 2 catalysts.

XPS spectra of O 1s over the fresh and used catalysts were divided into two sub-peaks, and the results are presented in Figure 5b. The sub-peaks centered at 529.7–530.3 eV could be assigned to lattice oxygen O 2− (denoted as Oβ). The sub-peaks centered at 530.9–531.9 eV could be assigned to surface chemisorbed labile oxygen (denoted as Oα), including defect oxide (O 22−) and hydroxyl-like group (O −) [45,46]. The surface chemisorbed labile oxygen (Oα) was not only beneficial for oxidizing NO into NO 2, but also contributive to the generation of more active intermediate species such as –NH2 and adsorbed NO 2 during the NH 3-SCR process [31,47]. Thus, the surface chemisorbed labile oxygen could exhibit better catalytic activity than lattice oxygen. The ratio of Oα to (Oβ + Oα) was calculated according to the relative peak areas. As shown in Table S3, Oα/(Oβ + Oα) ratio of Er0.05FeMn/TiO 2 catalyst was 45.7% which was much higher than that of FeMn/TiO 2 catalyst (20.9%). It indicated that Er modification was favorable for forming more surface chemisorbed labile oxygen species on the catalyst surface. This result was in accordance with that of catalytic activity tests in which Er0.05FeMn/TiO 2 catalyst exhibited higher NO 3 conversion efficiency than that of FeMn/TiO 2 catalyst. Here the increase of chemisorbed labile oxygen ratio was ascribed to the interaction between Er and Ti, which could enhance the formation of oxygen vacancies on the catalyst surface [30]. After SO 2 resistance tests, both binding energy peaks of surface chemisorbed labile oxygen (Oα) and lattice oxygen (Oβ) were shifted toward higher values compared to those of the fresh catalysts. It implied that O− and O 2− might be bonded with other substances when the catalysts were poisoned by SO 2. Despite that, the surface chemisorbed labile oxygen (Oα) concentration of Er0.05FeMn/TiO 2-S catalyst was still much higher than that of the FeMn/TiO 2-S catalyst.
The XPS spectra of S 2p for the used catalysts are shown in Figure 5c. The two sub-peaks could be ascribed to S$^{6+}$ in the form of SO$_4^{2-}$ (168.6–168.9 eV) and S$^{4+}$ in the form of SO$_3^{2-}$ (169.7–170.1 eV), respectively [33,48,49]. It demonstrated that sulfate and sulfite salts had been formed on the catalyst surface after SO$_2$ resistance tests, possibly as ammonium or Mn salts. This result could not only explain the shift of binding energy found in XPS, but also confirm Ti(SO$_4$)$_2$ diffraction peak detected in XRD. In addition, as shown in Table S3, the contents of S and N on the surface of Er$_{0.05}$FeMn/TiO$_2$ catalyst were 2.8% and 1.6%, respectively, which were much less than those of FeMn/TiO$_2$ catalyst (5.3% and 2.2%), suggesting that Er modification could inhibit the formation of sulfate and/or sulfite salts on the catalyst surface when SO$_2$ coexisted in feeding gas.

2.6. TG Analysis

In order to further investigate the surface compounds of the catalysts poisoned by SO$_2$, thermogravimetric analysis of FeMn/TiO$_2$-S and Er$_{0.05}$FeMn/TiO$_2$-S catalysts were performed, and the TG-DTG curves are presented in Figure 6. Four temperature steps could be found in the weight loss curves of the catalysts. In the temperature range from room temperature to 200 °C (Step 1), the weight losses were assigned to the evaporation of physically absorbed H$_2$O on the catalysts [50]. As (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$ would be decomposed completely when heating temperatures were above 230 and 350 °C, respectively [51], the weight losses in the temperature range of 200 to 400 °C (Step 2) was mainly ascribed to the decomposition of (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$. In the temperature range of 500–650 °C (Step 3), the weight losses were related to the phase transformation of metal oxides [52]. The weight losses in the temperature range of 650–900 °C (Step 4) were mainly attributed to the decomposition of MnSO$_4$ [37]. The weight loss in the second step for Er$_{0.05}$FeMn/TiO$_2$-S catalyst was 0.281% which was obviously less than that for FeMn/TiO$_2$-S catalyst (0.671%). The intensities of DTG curves (Step 2) for Er$_{0.05}$FeMn/TiO$_2$-S catalyst were lower than those of FeMn/TiO$_2$-S catalyst. It indicated that less (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$ were formed on Er-modified catalyst compared with FeMn/TiO$_2$ catalyst. These results agreed well with the XPS spectra of S 2p. The TG-DTG results further proved that less sulfates formed on the surface of Er-modified FeMn/TiO$_2$ catalysts during SCR reaction in the presence of SO$_2$.

![Figure 6](image_url)

**Figure 6.** TGA-DTG profiles of FeMn/TiO$_2$-S (a) and Er$_{0.05}$FeMn/TiO$_2$-S (b) catalysts.

2.7. In-Situ DRIFTS

Aiming to get further insight into the adsorption behavior and the reaction mechanism during NH$_3$-SCR process in the presence of SO$_2$ at low temperature, in-situ DRIFTS experiments were performed at relatively low temperature (200 °C).

2.7.1. Adsorption of SO$_2$

Figure 7 shows in-situ DRIFTS spectra of SO$_2$ adsorption over FeMn/TiO$_2$ and
Er$_{0.05}$FeMn/TiO$_2$ catalysts. After pretreatment of each catalyst sample, 500 ppm SO$_2$ (50 mL/min) was introduced for 30 min, and then IR spectra were recorded. Several bands were observed in the ranges of 800–2000 cm$^{-1}$. The bands at 1060, 1162, 1284 cm$^{-1}$ were ascribed to the mononuclear bidentate sulfate complex [38]. The band around 1613 cm$^{-1}$ was attributed to the sulfates formed by the weak adsorption of SO$_2$, while the band at 1344 cm$^{-1}$ was ascribed to the asymmetric stretching vibration of O=S=O in sulfates [38]. It could be seen that the intensities of all the bands over Er$_{0.05}$FeMn/TiO$_2$ catalyst were similar with those over FeMn/TiO$_2$ catalyst, implying that Er modification had no obvious effect on the SO$_2$ adsorption over the FeMn/TiO$_2$ catalyst.

2.7.2. Effect of SO$_2$ on NH$_3$ Adsorption on Catalyst Surface

In order to investigate the effect of SO$_2$ on NH$_3$ adsorption on the catalysts, in-situ DRIFTS spectra of the co-adsorption of NH$_3$ + SO$_2$ at 200 °C were analyzed. After pretreatment, the catalysts were pre-adsorbed with 500 ppm NH$_3$ (50 mL/min) for 30 min, then 100 ppm SO$_2$ was introduced, and the IR spectra were measured as a function of time.

As shown in Figure 8a, several bands were found in the spectra of FeMn/TiO$_2$ catalyst after the adsorption of NH$_3$ for 30 min. The strong absorbed bands (1166 and 1605 cm$^{-1}$) were assigned to coordinate NH$_3$ on Lewis acid sites, and the weak band (1450 cm$^{-1}$) was assigned to NH$_4^+$ species on Brønsted acid sites [37,45,53]. After the introduction of SO$_2$, the absorbance intensities of all the adsorbed bands increased obviously. With the introduction of SO$_2$, the absorbance intensity of the band (1166 cm$^{-1}$) assigned to NH$_4^+$ species on Brønsted acid sites was enhanced gradually, and a new band (1678 cm$^{-1}$) assigned to NH$_4^+$ species on Brønsted acid sites appeared in the spectra. Zhang et al. also reported that SO$_2$ could promote the generation of NH$_4^+$ species on Brønsted acid sites [38]. However, the band (1166 cm$^{-1}$) corresponding to NH$_3$ species on Lewis acid sites decreased gradually, and almost disappeared after 5 min of SO$_2$ injection. At the same time, three bands appeared at 1261, 1144 and 1033 cm$^{-1}$ which were ascribed to sulfates, and they were also enhanced with the increase of SO$_2$ injection duration [38]. It indicated that the adsorption of NH$_3$ on Lewis acid sites was inhibited by the introduction of SO$_2$, thus reducing the SCR activity at low temperature. As shown in Figure 8b, the change in absorbed bands of Er$_{0.05}$FeMn/TiO$_2$ catalyst was similar to that of FeMn/TiO$_2$ catalyst. However, the intensity of the band (1169 cm$^{-1}$) corresponding to NH$_3$ species on Lewis acid sites increased gradually with the introduction of SO$_2$ for 30 min. According to the previous study, adsorbed NH$_3$ species on Lewis acid sites played a key role in SCR activity at low temperature [54]. Here it was concluded that the inhibition of competitive adsorption between SO$_2$ and NH$_3$ species on Lewis acid sites was a contributive factor to high SO$_2$ tolerance of Er-modified FeMn/TiO$_2$ catalysts.
2.7.2. Effect of SO2 on NH3 Adsorption on Catalyst Surface

In-situ DRIFTS spectra FeMn/TiO2 (a) and Er0.05FeMn/TiO2 (b) catalysts exposed to 500 ppm NH3 followed by the introduction of 100 ppm SO2 at 200 °C, and in-situ DRIFTS spectra of adsorption 500 ppm NH3 over the fresh and used catalysts at 200 °C (c).

Figure 8c exhibits the in-situ DRIFTS spectra of NH3 adsorption on FeMn/TiO2-S and Er0.05FeMn/TiO2-S catalysts at 200 °C. After adsorption of 500 ppm NH3 for 30 min and N2 purging, several bands ascribed to various NH3 species were found in the spectra of the fresh catalysts. The strong absorbed bands (1166 and 1605 cm\(^{-1}\)) were assigned to asymmetric and symmetric bending vibrations of the N–H bonds in NH3 coordinated to Lewis acid sites, and the weak band (1450 cm\(^{-1}\)) was assigned to the asymmetric bending vibrations of ionic NH\(^4+\) bonded to the Brønsted acid sites \([37,45,53,55]\). The intensities of all of bands over Er0.05FeMn/TiO2 catalyst were higher than those over the FeMn/TiO2 catalyst. It demonstrated that there were more Lewis acid sites and Brønsted acid sites existed on the surface of Er0.05FeMn/TiO2 catalyst. As to the used catalysts, the intensity of the bands (1609 and 1084 cm\(^{-1}\)) ascribed to NH3 species adsorbed on Lewis acid sites decreased obviously due to the formation of new bands (1260 and 1032 cm\(^{-1}\)) ascribed to sulfate species \([37,38]\). However, the intensities of the bands (1684 and 1443 cm\(^{-1}\)) ascribed to NH\(^{4+}\) species adsorbed on Brønsted acid sites increased remarkably due to the formation of sulfate species during the SO2 resistance tests. Some previous studies reported that the formation of sulfates on the catalyst surface could result in an increase in the amount of NH\(^{4+}\) species adsorbed on Brønsted acid sites and a decrease in the amount of NH3 species adsorbed on Lewis acid sites \([17,55,56]\). Here the decrement of adsorbed NH3 species on Lewis acid sites and the increment of adsorbed NH\(^{4+}\) species on Brønsted acid sites over Er0.05FeMn/TiO2-S catalyst were much less compare to FeMn/TiO2-S catalyst. It demonstrated that Er modification improved the NH3 adsorption on Lewis acid sites of Er0.05FeMn/TiO2-S catalyst, and less sulfate species formed on the surface of Er0.05FeMn/TiO2-S catalyst. As a result, Er modification on FeMn/TiO2 catalyst improved the SO2 tolerance during the NH3-SCR process at a low temperature.
2.7.3. Effect of SO\textsubscript{2} on NO \text{+} O\textsubscript{2} Adsorption on Catalyst Surface

To understand the effect of SO\textsubscript{2} on NO\textsubscript{x} adsorption on FeMn/TiO\textsubscript{2} and Er\textsubscript{0.05}FeMn/TiO\textsubscript{2} catalysts, each catalyst was exposed to 500 ppm NO and 5\% O\textsubscript{2} at 200 °C for 30 min, then 100 ppm SO\textsubscript{2} was introduced. As shown in Figure 8a, with the introduction of NO + O\textsubscript{2} for 30 min, several bands of adsorbed NO\textsubscript{x} species appeared at 1575, 1380, 1366, and 1262 cm\textsuperscript{-1} in the spectra of FeMn/TiO\textsubscript{2} catalyst, which were ascribed to bidentate nitrate (1575 cm\textsuperscript{-1}) [53], M-NO\textsubscript{2} nitro compounds (1380 and 1366 cm\textsuperscript{-1}) [53], and monodentate nitrate (1262 cm\textsuperscript{-1}) [53], respectively. With the introduction of SO\textsubscript{2}, all bands in the spectra of FeMn/TiO\textsubscript{2} catalyst exhibited an obvious decrease in intensity. Moreover, several new bands (1602, 1270, 1159 and 1069 cm\textsuperscript{-1}) ascribed to sulfates appeared with the injection of SO\textsubscript{2}, and the absorbance intensities of these bands increased gradually. It indicated that SO\textsubscript{2} could restrain the adsorption of NO\textsubscript{x} species on FeMn/TiO\textsubscript{2} catalysts. In other words, there was obvious competitive adsorption between NO and SO\textsubscript{2} which would inhibit the SCR reaction under L-H mechanism. It might be the reason for the low NO\textsubscript{x} conversion efficiency in the presence of SO\textsubscript{2} for FeMn/TiO\textsubscript{2} catalyst [57]. The inhibiting effect of SO\textsubscript{2} on NO\textsubscript{x} adsorption on Er\textsubscript{0.05}FeMn/TiO\textsubscript{2} catalyst surface was quite similar to that for FeMn/TiO\textsubscript{2} catalyst. But the absorbance intensity of the band (1601 cm\textsuperscript{-1}) assigned to sulfates was obviously lower than that of FeMn/TiO\textsubscript{2} catalyst, indicating that less sulfate species formed on Er\textsubscript{0.05}FeMn/TiO\textsubscript{2} catalyst.

Figure 9c exhibits the in-situ DRIFTS spectra of 500 ppm NO and 5\% O\textsubscript{2} adsorption on FeMn/TiO\textsubscript{2} and Er\textsubscript{0.05}FeMn/TiO\textsubscript{2} catalysts at 200 °C. After adsorption of NO and O\textsubscript{2} for 30 min and purging with N\textsubscript{2}, several bands were found in the spectra of the fresh catalysts, which could be ascribed to bidentate nitrate (1575 cm\textsuperscript{-1}) [53], M-NO\textsubscript{2} nitro compounds (1380 and 1366 cm\textsuperscript{-1}) [53], and monodentate nitrate (1262 cm\textsuperscript{-1}) [53], respectively. After SO\textsubscript{2} resistance tests, the intensities of the bands ascribed to NO\textsubscript{x} species in the spectra of both used catalysts decreased dramatically. It implied that the formation of nitrate species could be inhibited by SO\textsubscript{2} adsorption. In addition, the negative bands (1326 and 1311 cm\textsuperscript{-1}) ascribed to the displacement of the sulfates were found on FeMn/TiO\textsubscript{2}-S and Er\textsubscript{0.05}FeMn/TiO\textsubscript{2}-S catalysts. This indicated that competitive adsorption between NO and SO\textsubscript{2} occurred on the surface of FeMn/TiO\textsubscript{2} and Er\textsubscript{0.05}FeMn/TiO\textsubscript{2} catalysts [58].

According to the in-situ DRIFTS results mentioned above, it can be confirmed that the adsorption of NO on FeMn/TiO\textsubscript{2} and Er\textsubscript{0.05}FeMn/TiO\textsubscript{2} catalysts was deeply inhibited by SO\textsubscript{2}, while the inhibition effect of SO\textsubscript{2} on NH\textsubscript{3} adsorption over the Er\textsubscript{0.05}FeMn/TiO\textsubscript{2} catalyst was much weaker than that over the FeMn/TiO\textsubscript{2} catalyst. As a result, the reaction through the Langmuir–Hinshelwood (L–H) mechanism for these two catalysts was suppressed severely. While the inhibiting effect on the reaction through Eley–Ridel (E–R) mechanisms for Er\textsubscript{0.05}FeMn/TiO\textsubscript{2} catalyst was obviously weaker than that for FeMn/TiO\textsubscript{2} catalyst. Therefore, Er modification promoted SO\textsubscript{2} resistance of the FeMn/TiO\textsubscript{2} catalyst during the NH\textsubscript{3}-SCR process at low temperature.
ally. It indicated that SO$_2$ could restrain the adsorption of NO$_x$ species on FeMn/TiO$_2$ catalysts. In other words, there was obvious competitive adsorption between NO and SO$_2$ which would inhibit the SCR reaction under L-H mechanism. It might be the reason for the low NO$_x$ conversion efficiency in the presence of SO$_2$ for FeMn/TiO$_2$ catalyst [57]. The inhibiting effect of SO$_2$ on NO$_x$ adsorption on Er$_{0.05}$FeMn/TiO$_2$ catalyst surface was quite similar to that for FeMn/TiO$_2$ catalyst. But the absorbance intensity of the band (1601 cm$^{-1}$) assigned to sulfates was obviously lower than that of FeMn/TiO$_2$ catalyst, indicating that less sulfate species formed on Er$_{0.05}$FeMn/TiO$_2$ catalyst.

Figure 9c exhibits the in-situ DRIFTS spectra of 500 ppm NO and 5% O$_2$ adsorption on FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts at 200 °C. After adsorption of NO and O$_2$ for 30 min and purging with N$_2$, several bands were found in the spectra of the fresh catalysts, which could be ascribed to bidentate nitrate (1575 cm$^{-1}$) [53], M-NO$_2$ nitro compounds (1380 and 1366 cm$^{-1}$) [53], and monodentate nitrate (1262 cm$^{-1}$) [53], respectively. After SO$_2$ resistance tests, the intensities of the bands ascribed to NO$_x$ species in the spectra of both used catalysts decreased dramatically. It implied that the formation of nitrate species could be inhibited by SO$_2$ adsorption. In addition, the negative bands (1326 and 1311 cm$^{-1}$) ascribed to the displacement of the sulfates were found on FeMn/TiO$_2$-S and Er$_{0.05}$FeMn/TiO$_2$-S catalysts. This indicated that competitive adsorption between NO and SO$_2$ occurred on the surface of FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts [58].

3. Discussion

In our present work, compared to the FeMn/TiO$_2$ catalyst, Er$_{0.05}$FeMn/TiO$_2$ exhibited better SCR activity and SO$_2$ tolerance at a low temperature. According to the analysis results of H$_2$-TPR, XPS and in-situ DRIFTS, the increased amounts of Mn$^{4+}$ (Equations (5) and (6)), surface chemisorbed labile oxygen (Equation (4)) and Lewis acid sites (Equation (1)) were considered as the dominant factors which were beneficial to achieve high SCR activity at low temperature for Er$_{0.05}$FeMn/TiO$_2$ catalyst. When SO$_2$ was introduced in feeding gas, the adsorbed NH$_3$ species and Mn$^{4+}$ active species could react with the adsorbed SO$_2$ species (Equations (10) and (11)). The generated (NH$_4$)$_2$SO$_4$ and MnSO$_4$ could not only block the active sites, but also suppress the redox cycles and the relevant reactions [59,60]. Based on the analysis results of BET, XRD, H$_2$-TPR, XPS, TG-DTG and in-situ DRIFTS, the amounts of ammonium sulfates and metal sulfates generated on Er$_{0.05}$FeMn/TiO$_2$ catalyst were obviously less than those for FeMn/TiO$_2$ catalyst. Thus, the SO$_2$ tolerance of FeMn/TiO$_2$ catalyst was remarkably enhanced by Er modification.

\[
\begin{align*}
\text{NH}_3 (g) & \rightarrow \text{NH}_3 (ad) \quad \text{(Lewis acid sites)} \\
\text{NO (g)} & \rightarrow \text{NO (ad)} \\
\text{SO}_2 (g) & \rightarrow \text{SO}_2 (ad) \\
\text{O}_2 (g) & \rightarrow 2\text{O}^- (ad)
\end{align*}
\]
\[
\begin{align*}
\text{NH}_3 \text{(ad)} + \text{Mn}^{4+} + \text{O}^- \text{(ad)} &\rightarrow \text{NH}_2 \text{(ad)} + \text{Mn}^{3+} + \text{OH} \quad (5) \\
\text{NO} \text{(ad)} + \text{Mn}^{4+} + \text{O}^- \text{(ad)} &\rightarrow \text{Mn}^{3+} + \text{NO}_2 \text{(ad)} \quad (6) \\
\text{NO} \text{(g)} + \text{NH}_2 \text{(ad)} &\rightarrow \text{NH}_2 \text{NO} \text{(ad)} \quad (7) \\
\text{NH}_2 \text{NO} \text{(ad)} &\rightarrow \text{N}_2 \text{(g)} + \text{H}_2 \text{O} \text{(ad)} \quad (8) \\
2\text{NH}_3 \text{(ad)} + \text{NO}_2 \text{(ad)} + \text{NO} \text{(g)} &\rightarrow 2\text{N}_2 + 3\text{H}_2 \text{O} \quad (9) \\
4\text{NH}_3 \text{(ad)} + 2\text{SO}_2 \text{(ad)} + \text{O}_2 + 2\text{H}_2 \text{O} &\rightarrow 2\text{(NH}_4)_2\text{SO}_4 \quad (10) \\
\text{MnO}_2 + \text{SO}_2 \text{(ad)} &\rightarrow \text{MnSO}_4 \quad (11) \\
2\text{NH}_3 + \text{NO} + \text{NO}_2 &\rightarrow 2\text{N}_2 + 3\text{H}_2 \text{O} \quad (12)
\end{align*}
\]

According to the result of in-situ DRIFTS, competitive adsorptions of SO2 with NO and NH3 would occur after the introduction of SO2. Therefore, the adsorption and activation of NO and NH3 on FeMn/TiO2 catalyst would be inhibited greatly (Equations (1) and (2)), further suppressing the subsequent SCR reactions. However, coexisting SO2 only imposed a slight impact on NH3 adsorption on Lewis acid sites of Er0.05FeMn/TiO2 catalyst, thus NH3-SCR reaction through E-R mechanism could proceed in a normal way. It played a key role for achieving excellent SO2 tolerance over the Er0.05FeMn/TiO2 catalyst. In addition, XPS analysis results indicated that the amounts of Mn4+ and surface chemisorbed labile oxygen on the surface of Er0.05FeMn/TiO2 catalyst were much more than those for FeMn/TiO2 catalyst. It was reported that abundant Mn4+ and surface chemisorbed labile oxygen species were beneficial for fast SCR reaction (Equation (12)) [61,62], which would accelerate the consumption of adsorbed NH3 species on Er0.05FeMn/TiO2 catalyst. Therefore, the competitive adsorption of SO2 and NH3 species could be inhibited by Er modification on FeMn/TiO2 catalyst. The reaction between adsorbed SO2 and NH3 species was limited, resulting in less ammonium sulfates formed on the surface of Er-modified FeMn/TiO2 catalyst. According to the results and discussions mentioned above, the promotional effect and mechanism of Er modification on SO2 resistance for NH3-SCR at low temperature over FeMn/TiO2 catalysts are illustrated in Figure 10.

**Figure 10.** The promotional effect and mechanism of Er modification on SO2 resistance for NH3-SCR at low temperature over FeMn/TiO2 catalysts.

### 4. Materials and Methods

#### 4.1. Catalysts Preparation

A facile wet impregnating method was used to prepare Er-modified FeMn/TiO2 catalysts. The molar ratio of Fe/Mn/Ti was fixed at 2.6:15 while Er/Mn molar ratios varied in the range of 0–0.2. In a typical preparation process, 1.686 g Fe(NO3)3·9H2O, 3.143 Mn(NO3)2·4H2O and a certain amount of Er(NO3)2·6H2O were dissolved in 100 mL deionized water, successively. 2.5 g TiO2 powder (Degussa P25) was added into the mixture...
solution, followed by stirring thoroughly at 80 °C for 2 h. Then, the ammonia solution (28 wt.%) was added dropwise until solution pH reached at 10. Subsequently, the precipitate was collected by vacuum filtration, dried at 120 °C overnight, and calcined at 500 °C for 3 h in air. All the catalysts were crushed and sieved to 40–60 mesh for activity evaluation. Here Er-modified FeMn/TiO$_2$ catalysts were denoted as Er$_x$FeMn/TiO$_2$, where $x$ represented various Er/Mn molar ratios (0.01, 0.05, 0.1 and 0.2). For comparison, FeMn/TiO$_2$ catalyst without Er modification was also prepared by using the same method without the addition of Er salt. The FeMn/TiO$_2$ and Er$_{0.05}$FeMn/TiO$_2$ catalysts after SO$_2$ resistance experiments were denoted as FeMn/TiO$_2$-S and Er$_{0.05}$FeMn/TiO$_2$-S, respectively.

4.2. Catalyst Activity Test

SCR activity measurements were performed using 1 mL (~0.5 g) of catalyst sample in a fixed-bed quartz reactor (i.d. 6 mm). Before each test, the catalyst was pretreated at 240 °C for 1 h in N$_2$ stream, and then cooled down to room temperature. Then, the catalyst was exposed to a reactant gas mixture containing 500 ppm NO, 500 ppm NH$_3$ (Waltham, MA, USA) equipped with a heated low-volume multiple-path gas cell (2 m) (28 wt.%), and 5% O$_2$ (if used), 100 ppm SO$_2$ (if used), and N$_2$ as balance gas. The total flow rate of simulated flue gas was 500 mL/min corresponding to a gas hourly space velocity (GHSV) of 30,000 h$^{-1}$. After purging for 1 h, reactant gases adsorbed on catalyst surface reached an adsorption-desorption equilibrium. The reaction temperature increased from room temperature to 240 °C. The concentrations of NO, NO$_2$, N$_2$O, SO$_2$, NH$_3$, and H$_2$O were monitored continuously by a FTIR spectrometer (Antaris IGS, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a heated low-volume multiple-path gas cell (2 m) and a MCT detector cooled by liquid nitrogen. NO$_x$ conversion and N$_2$ selectivity were calculated as follows:

$$\text{NO}_x \text{ conversion (}) = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\% \quad (13)$$

$$\text{N}_2 \text{ selectivity (}) = (1 - \frac{[\text{NO}_2]_{\text{out}} + 2[N_2]_{\text{out}}}{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \times 100\% \quad (14)$$

4.3. Catalyst Characterization

The textural properties of the prepared catalysts were measured by a physisorption analyzer (ASAP 2020 PLUS, Micromeritics, Norcross, GA, USA). Before each test, the catalyst was degassed under vacuum at 350 °C for 4 h, and the N$_2$ adsorption-desorption data was recorded at liquid nitrogen temperature (~196 °C). The specific surface areas were calculated via the Brunauer–Emmett–Teller (BET) equation. The pore sizes and pore volumes were calculated via the Barrett–Joyner–Halenda (BJH) method.

Powder XRD patterns were carried out using an X-ray diffraction meter (Empyrean, PANalytical, Eindhoven, Noord-Brabant, The Netherlands) using Cu Kα as radiation source ($\lambda = 0.15406$ nm) at 40 kV and 30 mA. The diffractogram was recorded in a 2θ range of 10–80° with a scanning step size of 0.02°.

H$_2$-temperature programmed reduction (H$_2$-TPR) was tested using a chemisorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA). Prior to each test, the sample was pretreated at 350 °C for 1 h in He stream (50 mL/min), and then cooled down to 50 °C. H$_2$ reduction data were recorded by a TCD detector from 50 to 800 °C at a heating rate of 10 °C/min. A mixture gas of 10% H$_2$/Ar was used as reduction gas with a flow rate of 50 mL/min, and H$_2$O produced in the reduction process was removed by a cold trap.

TG analysis was performed on a thermo gravimetric analyzer (TGA-50, Shimadzu, Tokyo, Honshu, Japan). The weight loss curves of the samples were collected over a temperature range of 0–1000 °C in N$_2$ atmosphere with a programmed heating rate of 10 °C/min.

X-ray photoelectron spectroscopy (XPS) profiles were collected using a surface analysis photoelectron spectrometer (AXIS-ULTRA DLD-600W, Shimadzu, Tokyo, Honshu, Japan), with Al Kα as radiation source at 300 W. All binding energies were standardized to
the adventitious C 1s peak at 284.8 eV. The pass energies of survey spectrum and high-resolution spectrum were 100 and 30 eV, respectively. Line shapes with sum of Gaussian and Lorentzian functions and Shirley-type background were applied for fitting XPS spectra.

In-situ DRIFTS measurements were performed on an FTIR spectrometer (Nicolet iS50, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a MCT/A detector cooled by liquid nitrogen and a high-temperature reaction chamber (Praying Mantis, Harrick, Waltham, MA, USA). Prior to each test, the catalyst was pretreated in a N2 flow at 200 °C for 30 min. Then, the background spectra recorded in N2 flow were automatically subtracted from the corresponding spectra. All DRIFTS spectra were collected by accumulating 64 scans with a resolution of 4 cm⁻¹ as a function of time.

5. Conclusions

In this work, the effect and mechanism of Er modification on SO2 resistance over FeMn/TiO2 catalysts were investigated systematically. The results showed that Er modification on FeMn/TiO2 catalysts could effectively improve SO2 tolerance at low temperature. After exposure to 100 ppm SO2 for 6 h, Er0.05FeMn/TiO2 catalyst still exhibited more than 90% NOx conversion efficiency at 200 °C. BET results indicated that Er doping could alleviate the decrease of specific surface area of FeMn/TiO2 catalyst in the presence of SO2. Less sulfates were confirmed on Er0.05FeMn/TiO2-S catalyst compared with those for FeMn/TiO2-S catalyst. The XPS results indicated that Er modification could result in an increase in the concentrations of surface Mn4+ species and chemisorbed liable oxygen on both fresh and used catalyst. In-situ DRIFTS spectra revealed that Er modification could effectively alleviate the inhibiting effect of coexisting SO2 on NH3 adsorption. NH3-SCR reaction for Er-modified FeMn/TiO2 catalysts could proceed through E-R mechanism in almost a normal way rather than L-H mechanism. As a result, superior NOx conversion performance could be achieved on Er-modified FeMn/TiO2 catalyst, even in the presence of SO2.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/103390/catal11050618/s1, Figure S1: (a) NOx conversion, (b) N2 selectivity in the NH3-SCR reaction (Reaction conditions: 1 mL catalyst, [NO] = [NH3] = 500 ppm, [O2] = 5 vol.%, [H2O] = 5 vol.% (when used), [SO2] = 100 ppm (when used), balanced with N2, GHSV = 30,000 h⁻¹). Figure S2: EDS mapping of FeMn/TiO2 and Er0.05FeMn/TiO2 catalysts. Figure S3: XPS survey spectrum of Er0.05FeMn/TiO2 catalyst. Table S1: Textural properties of the fresh and used catalysts. Table S2: H2-TPR results of the fresh and used catalysts. Table S3: Calculation results of surface atomic concentration ratios of Fe, Mn and O in the fresh and used catalysts. Table S4: Surface element contents of FeMn/TiO2 and Er0.05FeMn/TiO2 catalysts.

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