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Article

In situ DRIFTS study of the mechanism of low temperature selective catalytic reduction over manganese-iron oxides

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ABSTRACT

To investigate the mechanism of selective catalytic reduction (SCR) of NO_x with NH_3 , $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst was prepared by self-propagating high-temperature synthesis (SHS) method and evaluated at 25–450 °C. The catalyst was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The possible SCR mechanism over $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ was studied by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ showed both high SCR activity and N_2 selectivity over a broad temperature window of 100–350 °C. The XRD and TEM results indicated that the active components of Mn and Fe were in a highly dispersed state and in an amorphous form on TiO_2 . The DRIFTS results revealed that Brønsted acid sites were the active centers for NO removal and monodentate nitrates were the key intermediate in the SCR reaction. At 150 °C, both Langmuir-Hinshelwood and Eley-Rideal mechanisms are involved in the SCR reaction, while the former one mechanism dominates the catalytic activity of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$. Additionally, the presence of O_2 significantly affects NO oxidation and coordinated NH_3 activation.

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1. Introduction

Nitrogen oxides (NO_x) are a major component of air pollution. Selective catalytic reduction (SCR) of NO_x with NH_3 is a well-known promising technique for removing NO_x [1,2]. The industrial catalysts for NH_3 -SCR usually comprise $\text{V}_2\text{O}_5/\text{TiO}_2$ in combination with either WO_3 or MoO_3 , however, there are also some disadvantages, such as the narrow operating temperature window (300–400 °C) [3,4] and the environmental toxicity of vanadium species at high temperatures [5]. Therefore, novel high performance catalysts with transition metal alternatives to vanadium have been extensively investigated [6–11].

Mn/TiO_2 anatase catalyst reported by Ettireddy et al. [4] shows high activity for low temperature SCR of NO with NH_3

and shows stable NO conversion and N_2 selectivity, even after 10 days of time-on-stream in the presence of 11 vol% water vapor at 175 °C. However, the low temperature SCR performance of Mn-based catalysts is reduced by poisoning from sulfur residuals in fuels and engine oils. A series of catalysts composed of manganese oxide and iron-manganese oxide supported on TiO_2 were studied for low-temperature SCR in the presence of excess oxygen. It was found that the addition of iron oxide not only increased the NO conversion and N_2 selectivity but also increased catalyst resistance to H_2O and SO_2 [12].

Roy et al. [8] have prepared serial $\text{Ti}_{0.9}\text{M}_{0.1}\text{O}_{2-\delta}$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{and Cu}$) catalysts using a self-propagating high-temperature synthesis (SHS) method. It was found that the optimum $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst showed good activity in the

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150–500 °C temperature range and more than 80% N₂ selectivity even at 450 °C. SCR catalysts prepared by the SHS method exhibited reasonably high specific surface areas, appropriate pore volumes, average pore diameters, and typical nanoparticle sizes [10], which significantly enhanced the catalyst performance.

The Mn-Fe based catalysts exhibit high activities at low temperature, which is possibly caused by the strong interactions of Fe and Mn. However, the SCR mechanism for this catalyst is still uncertain. For the Fe-Ce-Mn/ZSM-5 catalyst [13], two possible reaction pathways were proposed. One was that NO₂ could react with NH₄⁺ on Brönsted acid sites and the formed NO₂[NH₄⁺]₂ would react with NO, producing N₂ and H₂O. Another pathway involves NH₃ adsorption and subsequent reaction with NO or HNO₂. Possible intermediates NH₄NO₂ and NH₂NO were unstable and would decompose into N₂ and H₂O. Additionally, the SCR reaction over (Fe_{2.5}Mn_{0.5})_{1-δ}O₄ mainly follows an Eley-Rideal (E-R) mechanism [14]. Adsorbed ammonia species are activated to form amide species (–NH₂) by Mn⁴⁺ and Fe³⁺ on the surface. Then, gaseous NO is reduced by –NH₂ on the surface to form N₂ and H₂O. For the case of the Ti_{0.9}Mn_{0.05}Fe_{0.05}O_{2-δ} prepared by Roy et al. [8], according to a Langmuir-Hinshelwood (L-H) mechanism, the adsorbed NH₃ or NH₄⁺ can react with adsorbed NO to form an NH₂NO adduct, which can then dissociate into N₂ and H₂O. Overall, the process of adsorption and activation of reactant NH₃ or NO is important because it is related to the intermediate species and determines the reaction pathways.

The purpose of this study is to obtain information on the reaction mechanism of manganese and iron oxide catalysts at low temperatures through the respective adsorption of NH₃ and NO, as well as the reaction between NH₃ and NO. SHS is an effective, low-cost method for production of various industrially useful materials [15]. In this paper, an SCR catalyst, Ti_{0.9}Mn_{0.05}Fe_{0.05}O_{2-δ} was also prepared by the SHS method [16]. The catalyst sample was exposed to simulated exhaust gas mixtures (NO/O₂/NH₃/N₂) to evaluate the SCR performance and was characterized by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to investigate the possible mechanism of NH₃-SCR.

2. Experimental

2.1. Catalyst preparation

Catalyst Ti_{0.9}Mn_{0.05}Fe_{0.05}O_{2-δ} was prepared by the SHS method. First, the required amount of absolute alcohol was added dropwise into the precursor tetrabutyl titanate (Ti(OCH₂(CH₂)₃)₄), and deionized water was likewise added to the product of metatitanic acid (TiO(OH)₂). Next, in order to get titanyl nitrate (TiO(NO₃)₂), the right amount of HNO₃ solution was added. At the same time, a solution of metal nitrate (Mn(NO₃)₂·4H₂O and Fe(NO₃)₃·9H₂O) in deionized water was prepared in stoichiometric amounts. Then, the nitrate solution was combined with the titanyl nitrate. Glycine (CH₂NH₂COOH) was sequentially added to fuel the reaction. After stirring at 50 °C for 1 h, the aqueous solution was placed in a muffle furnace

at 350 °C in air. During the first few minutes, the solution boiled with froth and combusted with smoke. The resulting product was finally calcined at the ignition temperature for 1 h. The synthesized catalyst was allowed to cool and was sieved to 40–80 mesh for further analysis.

2.2. Catalytic activity tests

Catalytic activity tests were carried out using the temperature-programmed reaction (TPR) method. The powder sample (0.5 mL) was used in a fixed-bed quartz reactor (i.d. 9 mm), and the reaction temperature was raised from room temperature to 450 °C at a ramp rate of 5 °C/min. A simulated exhaust gas mixture (0.06% NO, 0.06% NH₃, 5% O₂, and N₂ for balance) was fed to the catalyst sample through a set of mass flow controllers. The total flow rate was set to 100 mL/min, corresponding to a gas hourly space velocity (GHSV) of 12000 h⁻¹. The outlet gas composition containing NO, NO₂, N₂O, and NH₃ was measured on-line with an FTIR gas analyzer (Thermo Nicolet 6700). Before the experiment, concentrations of the gases were quantified based on the classic least squares methodology using the Omnic Quantpad software. A calibration run of each gas consisting of four spectral absorption standards was performed and used to generate each standard curve within Quantpad.

2.3. Catalyst characterization

X-ray diffraction (XRD) was used to reveal the catalyst crystal phases. XRD continuous measurements were performed on a Rigaku D/max-2200/PC system. Diffraction patterns were obtained from 20° to 90° (2θ) with a scanning rate of 5°/min, and a step size of 0.02° at ambient temperature.

The microscopic morphology of catalyst was interrogated by transmission electron microscopy (TEM) on a JEOL JEM-2010 analytical electron microscope operating at an accelerating voltage of 200 kV. Before TEM characterization, the catalyst powder was ultrasonically suspended in alcohol for 10 min, after which the obtained suspension was deposited on copper-grid-supported amorphous carbon films. The impregnated mesh was allowed to dry in air for TEM analysis.

2.4. In situ DRIFTS studies

In situ DRIFTS spectra were measured by an FTIR gas analyzer (Thermo Nicolet 6700) equipped with a diffuse reflectance optics accessory (HVC-DRP-4). The inlet gas concentrations were identical to those used in the catalytic activity test (0.06% NO, 0.06% NH₃, 5% O₂, and N₂ for balance). A 60 mg of powder sample was used, and the total flow rate was 50 mL/min. To clean the catalyst surface, the sample was purged in N₂ at 450 °C for 2 h prior to acquisition of DRIFTS spectra. Thereafter, the background spectra were recorded from 50 to 450 °C, with 50 °C increments. In this experiment, the IR range was from 4000 to 650 cm⁻¹, and the resolution was set to 4 cm⁻¹.

3. Results and discussion

3.1. $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst activity

TPR was performed to evaluate the SCR performance of the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst, as shown in Fig. 1. The calculation methods to determine NO_x conversion, N_2O selectivity, and N_2 selectivity were described in our earlier paper [10]. More than 80% of NO is reduced by NH_3 on the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst in a wide temperature window of 100 to 350 °C (Fig. 1(a)). $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ reaches the maximum NO conversion of 100% at an especially low temperature of 120 °C, and this NO conversion rate remains at its peak until 350 °C. NO conversion subsequently decreases sharply above 350 °C. The main reason for this is unselective NH_3 oxidation by O_2 . The N_2 yield initially reaches over 95% at ambient temperature to 100 °C, but then decreases to a lower level of around 70% at 250 °C (Fig. 1(b)). With further rise in temperature, the N_2 yield again increases. From 350 °C, N_2 selectivity decreases monotonically due to oxidation of NH_3 . This can be seen from the NO_2 concentration curve in Fig. 1(b). At the same time, under 250 °C, N_2O selectivity shows the reverse trend as N_2 selectivity. A fast drop in selectivity happens between 250 and 300 °C. N_2O selectivity then decreases slightly with increasing temperature. Overall, in a broad temperature window of 100–350 °C, $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ has high SCR activity, which is comparable to that reported by Roy et al. [8].

3.2. Catalyst characterization

The power XRD pattern of the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst sample is shown in Fig. 2, with peaks indicated as identified in the ICDD (anatase TiO_2 phase: PDF #21-1272). The XRD peaks of the catalyst closely conform to anatase phase TiO_2 , with no evidence for the rutile phase. No diffraction peaks for FeO_x , MnO_x , or any other mixed oxides are seen, which indicates that

Fig. 2. Power XRD pattern of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst.

the Mn and Fe are either in a highly dispersed state and assumes an amorphous form on TiO_2 , or that the formed crystallites cannot be detected by XRD. This is due to strong Fe-Mn interactions, which leads to enhanced dispersion and lower crystallization for both [12].

TEM was used to examine the morphology and size of the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$. As presented in Fig. 3, there are many nanoparticles dispersed on the catalyst, and no obvious particle agglomeration is apparent. The TEM image shows that the typical nanoparticles are well dispersed with sizes on the order of 10 nm. At higher magnification, a crystal plane spacing of 0.346 nm is detected, which is slightly smaller than the spacing of the anatase TiO_2 (101) plane. Any morphology of the manganese and iron oxides are not observed, which is consistent with the XRD result.

Fig. 1. NO conversion (a) and N_2 selectivity, N_2O selectivity, and NO_2 concentration (b) over $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$. Reaction conditions: 0.06% NO , 0.06% NH_3 , 5% O_2 , N_2 as balance gas, total gas flow rate 100 mL/min, and GHSV = 12000 h^{-1} .

Fig. 3. TEM images of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ sample.

3.3. In situ DRIFTS

3.3.1. Adsorption of NH_3

NH_3 adsorption measurements were performed in a feed of 0.06% NH_3 in N_2 at 50 °C for 30 min. Catalyst $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ was then purged with N_2 for 30 min. Surface adsorption species with IR bands at 1188 and 1598 cm^{-1} are formed (Fig. 4), which are assigned to coordinated NH_3 adsorbed on Lewis acid sites [10]. In the NH vibration region, IR bands at 3160, 3253, and 3334 cm^{-1} are seen and are also assigned to coordinated NH_3 bound to Lewis acid sites. The band at 1306 cm^{-1} is probably due to NH_3 adsorbed on different Lewis sites [17]. At the same time, IR bands observed at 1458 and 1680 cm^{-1} are from asymmetric and symmetric deformations of NH_4^+ on Brönsted acid sites. It seems that there are less Brönsted acid sites than Lewis acid sites on the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst. It can also be seen that the intensity of the bands at 1188 and 1598 cm^{-1} are far stronger than those at 1458 and 1680 cm^{-1} . Additionally, the two stronger bands reach their peak intensities after NH_3 is saturated on the catalyst at 50 °C.

All surface-adsorbed NH_3 species are quite stable during subsequent purging with N_2 at 50 °C. The spectra of these surface species at different temperatures are also presented in Fig. 4. With increasing temperature, the intensity of the bands at 1188 and 1598 cm^{-1} drops off gradually. At 450 °C, these bands still obviously exist. The intensities of the bands in the 3400–3100 cm^{-1} region also decrease slightly. Meanwhile, the intensities of the bands at 1458 and 1680 cm^{-1} decline drastically, and the band at 1458 cm^{-1} can no longer be observed above 200 °C. These results demonstrate that NH_3 desorbs at increased temperatures. Moreover, Brönsted acid sites have lower thermal stability than Lewis acid sites.

3.3.2. Co-adsorption of $\text{NH}_3 + \text{O}_2$

In this experiment, the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst is treated with $\text{NH}_3 + \text{O}_2$ in the same way. Both NH_4^+ ions and coordinated

Fig. 4. In situ DRIFTS spectra of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ during NH_3 adsorption at different temperatures. Reaction conditions: 0.06% NH_3 , N_2 as balance, total gas flow rate 50 mL/min.

NH_3 are formed (Fig. 5). The intensities of the coordinated NH_3 bands at 1188 and 1598 cm^{-1} decrease with increasing temperature as NH_3 desorbs. However, when compared to the spectra of NH_3 adsorbed on Lewis acid sites in Fig. 4, the variations between spectra at different temperatures are larger. The intensities of the bands at 1188 and 1598 cm^{-1} initially decrease gradually beginning at 150 °C. When reaching a temperature of 450 °C, the coordinated NH_3 almost vanishes, without any obvious intensity. According to the literature [18], this may be caused by oxidation of NH_3 to NH_2 at a relatively low temperature range and oxidation of NH_3 to N_2 at a relatively high temperature. Additionally, a new band begins to appear at 1245 cm^{-1} at 400 °C, which was attributed to a bridging nitrate. This nitrate could be due to side reactions taking place, yielding a certain amount of NO .

3.3.3. Adsorption of NO

NO adsorption measurements were performed in a feed of 0.06% NO in N_2 for 30 min. The catalyst was then purged with N_2 for 30 min. Surface nitrate species are observed at 1245, 1276, 1470, 1576, and 1612 cm^{-1} (Fig. 6). The IR band at 1245 cm^{-1} can be assigned to a bridging nitrate, and that at 1276 cm^{-1} and 1470 cm^{-1} are assigned to monodentate nitrate, while bands at 1576 cm^{-1} are attributed to bidentate nitrate. According to results of Long et al. [17], the band at 1612 cm^{-1} is not easy to assign. They assigned it to an NO_2 adspecies (nitro or adsorbed NO_2 molecule) on the catalyst, because this species had a different thermal stability from that of other nitrate species. It can be also seen that the species appeared at 1612 cm^{-1} exhibits a similar thermal stability as the bridging nitrate. Thus, we assign it to the bridging nitrate.

IR bands in these regions decrease with increasing temperature (Fig. 6), indicating desorption of NO . IR bands at 1276 and 1470 cm^{-1} show the most rapid disappearance, occurring at 200 °C. The intensities of the bands at 1245 and 1612 cm^{-1}

Fig. 5. In situ DRIFTS spectra of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ during $\text{NH}_3 + \text{O}_2$ adsorption at different temperatures. Reaction conditions: 0.06% NH_3 , 5% O_2 , N_2 as balance, and total gas flow rate 50 mL/min.

Fig. 6. In situ DRIFTS spectra for adsorption of NO over $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ at different temperatures. Reaction conditions: 0.06% NO, N_2 as balance, and total gas flow rate 50 mL/min.

decrease slightly slower, such that they can still be observed at 350 °C. The bidentate nitrate at 1576 cm^{-1} does not disappear until 450 °C. The thermal stability of the nitrate species follows the order: bidentate nitrate > bridging nitrate > monodentate nitrate.

To investigate the influence of gaseous O_2 , we carried out the adsorption of NO and NO + O_2 over $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ at 150 °C. First, the catalyst was treated with NO and NO + O_2 in N_2 for 30 min, and then was purged with N_2 for an extended 90 min. The recorded IR spectra are shown in Fig. 7. It is obvious that NO + O_2 adsorption is much stronger than NO adsorption because gaseous O_2 could enhance the oxidation of NO to NO_2 , leading to the formation of surface nitrate species. In the NO only treatment case, oxidation of NO is simply caused by lattice oxygen. After purging with N_2 for 90 min, only a slight decrease in the intensities of the surface nitrate species bands is seen in the two cases, which implies that surface NO adsorption species are caused by fairly stable chemisorption, regardless of O_2 . This is consistent with results reported by Centi et al. [19], who proposed that chemisorption of NO on the catalyst copper sites was significant and that chemisorption is enhanced by the

Fig. 7. In situ DRIFTS spectra for adsorption of NO over $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ with and without O_2 at 150 °C. Reaction conditions: 0.06% NO, 5% O_2 , N_2 as balance, total gas flow rate 50 mL/min.

presence of oxygen.

3.3.4. Reaction studies under transient conditions

3.3.4.1. Reaction between only NO and adsorbed NH_3

To investigate the reaction mechanism of SCR by NH_3 over the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst, the sample was first exposed to NH_3 at 150 °C until it was saturated. The catalyst was then purged with N_2 and subsequently exposed to NO. IR spectra were recorded as a function of time (Fig. 8). Because of exposure to NH_3 , IR bands assigned to coordinated NH_3 or NH_4^+ appear. However, after 70 min of NO exposure, no apparent decrease in the adsorbed NH_3 is seen, and no surface NO adsorption species are seen to accumulate on the catalyst. At the same time, we could not find evidence for the formation of any new adsorption species. This can be explained from several aspects [17,20,21]. First, the absence of gaseous O_2 inhibits NO oxidation, suppressing the formation of nitrate species. Additionally, our observations are possibly caused by competition between NO and NH_3 for the same adsorption sites on the catalyst surface. Moreover, gaseous NO has a low reaction probability with adsorbed NH_3 , owing to lack of gaseous O_2 in the reaction conditions. The activation of adsorbed NH_3 by gaseous O_2 to form NH_2 is a main step in the catalytic mechanism.

3.3.4.2. Reaction between gas mixtures NO + O_2 and adsorbed NH_3

For the case of reaction between NO + O_2 and adsorbed NH_3 , the catalyst sample was first exposed to NH_3 at 150 °C until it was saturated, then purged with N_2 . After that, NO+ O_2 was introduced into the cell. The results are shown in Fig. 9. IR bands at 1188, 3160, 1598, and 3253 cm^{-1} , assigned to coordinated NH_3 on Lewis acid sites as noted above, decrease gradually with time until they disappear. The vibrational signature of NH_4^+ on Brönsted acid sites at 1680 cm^{-1} vanishes quickly after exposure to NO for about 25 min, indicating that NO rapidly reacts with adjacent adsorbed NH_4^+ 25 min later. Thus, it is suggested that both Brönsted and Lewis acid sites are involved in NO reduction.

Fig. 8. In situ DRIFTS spectra of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ during transient NO exposure after NH_3 adsorption at 150 °C. Reaction conditions: 0.06% NO, N_2 as balance, and total gas flow rate 50 mL/min.

Fig. 9. In situ DRIFTS spectra of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ during transient $\text{NO} + \text{O}_2$ exposure after NH_3 adsorption at $150\text{ }^\circ\text{C}$. Reaction conditions: 0.06% NO , 5% O_2 , N_2 as balance, total gas flow rate 50 mL/min .

Some new species appear after 25 min of reaction. The band at 1245 cm^{-1} is assigned to low-frequency vibrations of a bridging nitrate, and the band at 1576 cm^{-1} is assigned to bidentate nitrate. The intensities of the bands at 1245 and 1576 cm^{-1} increase with time after their initial appearance. However, signals for the monodentate nitrate species at 1276 and 1470 cm^{-1} do not emerge, indicating that the monodentate nitrate on the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ surface reacts with NH_3 immediately preventing detectable concentrations to arise. The bridging nitrate and bidentate nitrate seem to be inactive for the SCR reaction. Hence, the monodentate nitrate is suggested to be a key intermediate.

Furthermore, it can be seen that the rate of SCR reaction becomes faster after 25 min. For the competitive adsorption of NO and NH_3 on the catalyst surface, no nitrate species formation is seen in the first 25 min. Coordinated NH_3 is first activated by active oxygen from the dehydration between manganese oxides, yielding the amide species from H abstraction [21]. At this point, the intermediate species NH_2 further reacts with gaseous NO to form N_2 and H_2O following an E-R mechanism. Then as the adsorbed NH_3 species are consumed, sufficient adsorption sites are available for NO . The SCR process then begins to follow a L-H mechanism, in which adsorbed NH_4^+ and coordinated NH_3 react with nitrate species. Comparing with the results presented in Section 3.3.4.1., it is clear that oxygen plays an important role in the reaction between NO and NH_3 [21], as a result of the oxidation of NH_3 and NO . At a low temperature ($150\text{ }^\circ\text{C}$), it is difficult to form NH_2 species because of the high activation energy [20]. Conversely, NO oxidation occurs a little faster by the high oxidative ability of Mn. As more nitrate species adsorb, the reaction rate is accelerated. This is why the catalysts with Mn have outstanding low-temperature performance. As a result, at $150\text{ }^\circ\text{C}$ both L-H and E-R mechanisms are involved in the SCR reaction, while the L-H mechanism is dominant for the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst.

3.3.4.3. Reaction between NH_3 and adsorbed $\text{NO} + \text{O}_2$

To investigate the reaction between NH_3 and adsorbed gas mixture $\text{NO} + \text{O}_2$, the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst sample was first treated with gas mixtures $\text{NO} + \text{O}_2$ at $150\text{ }^\circ\text{C}$ until it was saturated, followed by N_2 purging. When the treated sample is exposed to NH_3 , the intensities of the bands at 1245 , 1276 , 1576 , and 1612 cm^{-1} , assigned to surface nitrate species, decrease (Fig. 10). The band intensity for the bridging nitrate at 1245 cm^{-1} decreases quickly, disappearing within 15 min, while the band intensity of the monodentate nitrate at 1276 cm^{-1} decreases slightly slower, disappearing after about 35 min of NH_3 exposure. The bridging nitrate band at 1612 cm^{-1} can still be observed after 40 min. Exposure to NH_3 results in little change to the band intensity of the bidentate nitrate at 1576 cm^{-1} . These intensity changes for the nitrate species indicate that monodentate and bridging nitrates have high reactivities with NH_3 , while the bidentate nitrate seems to be little reactive towards NH_3 . This is consistent with the results of reaction between $\text{NO} + \text{O}_2$ and adsorbed NH_3 .

Meanwhile, IR bands at 1188 , 1230 , 1295 , 1458 , 1680 , 3160 , 3253 , and 3334 cm^{-1} emerge, belonging to a group of surface NH_3 adsorption complexes on the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst. The intensity of all these bands increases quickly within about 10 min, because surface acid sites have a strong adsorption capacity of NH_3 due to the effect of the active Fe metal [20]. The intensity of the band at 1188 cm^{-1} remains strong after 10 min exposure to NH_3 , suggesting continuous accumulation of coordinated NH_3 on the catalyst. However, almost no changes are seen in the ionic NH_4^+ bands at 1458 and 1680 cm^{-1} after 10 min. New bands at 1230 and 1295 cm^{-1} are detected, and they increase with time in NH_3 flow. So these bands could not be attributed to surface nitrate species. In contrast to the results of adsorbed NH_3 shown in Fig. 4, no adsorbed species are seen at 1230 and 1295 cm^{-1} when the catalyst is first treated with NH_3 and then purged by N_2 . Therefore, we assigned these bands to

Fig. 10. In situ DRIFTS spectra of NH_3 -SCR reaction over $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ during transient NH_3 exposure after $\text{NO} + \text{O}_2$ co-adsorption at $150\text{ }^\circ\text{C}$. Reaction conditions: 0.06% NH_3 and N_2 as balance, total gas flow rate 50 mL/min .

weak adsorbed NH_3 species.

On the basis of the above analysis, the L-H mechanism is dominant for the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst at 150 °C, and both adsorbed NH_4^+ and coordinated NH_3 participate in the L-H reaction path. During the reaction of NH_3 and adsorbed $\text{NO} + \text{O}_2$, surface NH_4^+ on Brönsted acid sites remain stable, maintaining their intensity, probably because the rate of NH_3 adsorption on Brönsted acid sites is equal to the rate of NH_4^+ reaction with NO . The amount of coordinated NH_3 on Lewis acid sites continues to increase due to the relatively slow rate of reaction between NO and coordinated NH_3 . This suggests that Brönsted acid sites are more active than Lewis acid sites on the $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst.

According to the results of in situ DRIFTS, the reaction mechanism can be deduced as following the reaction scheme depicted in equations (1)–(4):

The formation of monodentate nitrate $\text{M}^{n+}-\text{O}-\text{NO}_2$ ($\text{M} = \text{Fe}$ and Mn) is involved in reaction with adsorbed NH_4^+ or NH_3 on neighboring acid sites, to produce an active intermediate $\text{M}^{n+}-\text{O}-\text{NO}_2[\text{NH}_4^+]_2$ or $\text{M}^{n+}-\text{O}-\text{NO}_2[\text{NH}_3]_2$, which finally reacts with gaseous NO to form N_2 and H_2O [17,20].

4. Conclusions

The $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalyst shows high SCR performance over a broad temperature window of 100–350 °C. The active components of Mn and Fe exist in a highly dispersed state and amorphous form on TiO_2 . In situ DRIFTS measurements suggest that Brönsted and Lewis acid sites both take part

in the SCR reaction, and Brönsted acid sites may play a more important role in determining the activity of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$. The monodentate nitrate species is key active intermediate, in comparison to the less important bridging and bidentate nitrate species. At 150 °C, both L-H mechanism and E-R mechanisms are involved in the SCR reaction, while the L-H mechanism dominates catalytic activity of $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$. The presence of O_2 significantly affects NO oxidation and coordinated NH_3 activation. Hence, at a low temperature, NO oxidation is a main step, which depends on the oxidative ability of the active metal.

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Graphical Abstract

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In situ DRIFTS study of the mechanism of low temperature selective catalytic reduction over manganese-iron oxides

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Selective catalytic reduction reactions over $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ catalysts possibly proceed according to both Langmuir-Hinshelwood and Eley-Rideal mechanisms, but NO more likely reacts as an adsorbed species.

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原位漫反射傅里叶变换红外光谱研究锰铁基催化剂上 低温选择性催化还原反应机理

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摘要: 采用自蔓延燃烧法制备了 $\text{Ti}_{0.9}\text{Mn}_{0.05}\text{Fe}_{0.05}\text{O}_{2-\delta}$ 催化剂, 运用原位漫反射傅里叶变换红外光谱对该催化剂的NO和 NH_3 稳态吸附以及NO和 NH_3 瞬态反应进行了详细地分析与讨论. 结果表明, 相比于Lewis酸性位, 150 °C时Brönsted酸性位吸附的 NH_3 更具有SCR活性; 与双齿硝酸盐和桥式硝酸盐相比, NO吸附产生的单齿硝酸盐是主要的中间物种; 该SCR反应遵循Eley-Rideal和Langmuir-Hinshelwood机理, 但以后者为主. 另外, O_2 的存在有利于NO的氧化和配位态 NH_3 的活化.

关键词: 氮氧化物; 氨; 锰铁基催化剂; 低温选择性催化还原; 原位漫反射傅里叶变换红外光谱

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