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Article

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Research paper

Comparative study of low temperature denitration performance of Mn-Ce/ACFA-TiO₂ catalysts under oxy-fuel and air-fuel combustion flue gases



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ABSTRACT

Low temperature selective catalytic reduction (SCR) catalysts were prepared by using acetic acid modified fly ash (ACFA) and TiO₂ with the loading of Mn-Ce. The powder catalysts were characterized by BET, XRD and SEM. The effects of Mn-Ce molar ratio on the NO conversion of SCR catalyst were investigated under different atmospheres of N₂ and CO₂, respectively. The 8% Mn-Ce/ACFA-TiO₂ catalyst with Mn-Ce molar ratio of 1:1 showed good performance of NO conversion at 300 °C, 84.28% in N₂ atmosphere and 74.29% in CO₂ atmosphere. N₂O was observed in the experiments of 8% Mn/ACFA-TiO₂, 95.3 ppm in N₂ atmosphere and 103.6 ppm in CO₂ atmosphere, respectively.

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1. Introduction

Nitrogen oxides (NO_x) are oxides of nitrogen such as NO, NO₂, N₂O, N₂O₅, N₂O₄ and N₂O₃. The nitrogen oxides are toxic gases and contribute to photochemical smog and acid rain. The NO can also cause neurological disorders in humans. Moreover, the N₂O may destroy the ozone layer, and its contribution of the greenhouse effect is 2.5 times more than methane (Yang and Wang, 2010; Yoshitaka, 2019; Dong, 2010). Oxygen-enriched combustion technology can reduce carbon and NO_x emissions. However, the recirculation of flue gas will increase the concentration of NO_x in flue gas (Zheng et al., 2014). If the flue gas is discharged directly, the NO_x pollution will aggravate.

Selective catalytic reduction (SCR) of NO_x with NH₃ is considered as the most promising technology to meet the standards of NO_x emissions (Metkar et al., 2013; Yang et al., 2018). In NH₃-SCR of the NO reaction, there are both the Langmuir–Hinshelwood (L–H) mechanism and the Eley–Rideal (E–R) mechanism. NH₃ and NO are adsorbed on the surface of catalyst by the L–H mechanism, but adsorbed NH₃ reacts with NO by the E–R mechanism. NH₃ could be adsorbed on both Lewis acid sites and Brønsted acid sites, but NO is adsorbed mainly by physical adsorption (Zhang et al., 2017). At present, most commercial SCR catalysts use TiO₂ as the carriers (Sang et al., 2012). TiO₂ has relatively large specific

surface area, porosity, and good sulfur resistance. The surface acidification of catalyst and high-energy crystal surface of TiO₂ are beneficial to improve the reactivity of NO_x intermediate and the denitration performance (Aguilar-Romero et al., 2017). The acidification can provide abundant acidic sites which enhance the adsorption performance of ammonia. The high surface area can support more active component, and contribute homogeneous dispersion of active components, which makes positive effects on preventing active components from agglomeration. The high energy crystal can promote the formation of the strong acid and chemical adsorption oxygen, which improve the activity of SCR catalysts (Wen et al., 2018). The crystal type and grain size of TiO₂ support have an impact on the denitrification activity of the catalyst (Yu et al., 2020). And the experimental results (Ma et al., 2017) show that in low temperature, the denitrification activities of the catalysts prepared with anatase and rutile TiO₂ as the carriers are not significantly different. Meanwhile the denitrification activity of the catalysts prepared by TiO₂ carrier with different grain sizes varies greatly. The denitrification activity of the catalyst with smaller grain size is lower than that with larger one. Yan et al. (2015) investigated the influence of loading sequence of active components Mn and Ce on catalyst structure. The results show that the crystal phase of the catalyst is anatase type structure. Mn and Ce active components are highly dispersed on the surface of the carrier and form amorphous structure. When Mn and Ce are loaded at the same time, the surface-active components of the catalyst are distributed evenly with the maximum specific surface area.

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Table 1
The ash content analysis.

Component	Content(%)	Component	Content(%)
SiO ₂	37.22	Na ₂ O	3.37
Al ₂ O ₃	17.27	K ₂ O	0.96
Fe ₂ O ₃	7.35	TiO ₂	0.7
CaO	16.11	SO ₃	9.92
MgO	6.66	MnO ₂	0.058

Fly ash (FA) is a solid waste discharged by boilers in coal-fired power plants and main components are SiO₂, Fe₂O₃, Al₂O₃, and MgO. The mineral phases are mainly composed of quartz and mullite (Yan et al., 2016b). The emission of FA increases year by year, but its utilization rate is less than the half (Cao et al., 2012). The common cyclic utilizations of FA include cement manufacture, road construction and brick production. As FA, a porous material with high specific surface area, has good adsorption property, it is commonly used as an adsorbent or the support of catalyst in the field of chemistry and environmental protection. After acid modification, the adsorption effect and surface activity potential of the ash are enhanced. The results of Shi et al. (2015) indicate that the modification effect of acetic acid to FA is better than that of nitric acid and hydrochloric acid. The specific surface area and weak acid level of the catalyst are increased after modification of acetic acid. The catalysts supported by iron and manganese have higher denitration activity and wider reaction temperature range (Shi et al., 2012). Our previous work studied the Mn-Ce/FA and Mn-Ce/FA-30%TiO₂ catalysts and found that with the increase of TiO₂ content, the rates of NO conversion rose (Gou et al., 2017).

The activity temperature of the commercial SCR is commonly in 300–400 °C (Xu et al., 2018). Boiler flue gas in this temperature range contains a large amount of FA, SO₂ and other substances that may deactivate catalysts. In addition, the oxy-fuel combustion technology is an effective method to the recovery of CO₂. A large amount of CO₂ is in the flue gas under the condition of oxy-fuel combustion (Jin et al., 2016). Therefore, it is of great significance to further study the low-temperature SCR and NO conversion under the conditions of CO₂.

2. Experimental

2.1. Catalyst preparation

In this experiment, the fly ash used for the catalysts preparation with ash content analysis shown in Table 1 was taken from Shenhua Coal to Oil Chemical Co., Ltd. China. All the catalysts were prepared by impregnation method. Acid modified FA was prepared by acetic acid (AR). The acetic acid modified fly ash (ACFA) and TiO₂(Nano), used as catalysts supports, were mixed in the ratio of 8:2 and after stirring for 30 min, and they were bagged and sealed for storage. Then, Mn(NO₃)₂ (AR) and Ce(NO₃)₃(AR), used as precursors, were dissolved in deionized water. After adding the precursors (active components mass fraction 8%), the mixture was stirred for 3 h by the magnetic force then resting for 12 h. The solution was dried by water bath heating. The precursor calcined in muffle furnace for 3 h at 350 °C, then heat up to 500 °C for 3 h. After they are grounded into 40–200 mesh, and calcined for 2 h at 500 °C in tube furnace under N₂ atmosphere, the powder catalysts can be prepared. The main catalysts prepared in the experiment are shown in Table 2.

Table 2
The catalyst prepared in this experiment.

Number	Catalyst	Number	Catalyst
1	FA	7	8% Mn- Ce (1:3)/ACFA-TiO ₂
2	ACFA	8	8% Mn- Ce (1:5)/ACFA-TiO ₂
3	FA-TiO ₂	9	8% Mn- Ce (3:1)/ACFA-TiO ₂
4	8%Mn/FA	10	8% Mn- Ce (5:1)/ACFA-TiO ₂
5	8%Ce /FA	11	8% Mn- Ce 1:1 /ACFA-TiO ₂
6	ACFA-TiO ₂	12	8% Mn- Ce (1:1)/ACFA-TiO ₂

Table 3
Parameters of each reaction gas in the experiment.

Number	Name	Unit	Parameters
1	NO	ppm	700
2	NH ₃	ppm	700
3	O ₂	%	6
4	Space velocity	h ⁻¹	4200
5	Flow rate	ml/min	1400

2.2. Catalyst characterization

The Brunauer–Emmett–Teller (BET) was used to analyze the surface area of the catalysts. X-ray diffraction (XRD, Bruker D8 DISCOVER, Germany) with monochromatic Cu K α radiation was used to obtain the crystal structure of the fresh catalysts with power 3kW, scan range from 10° to 90°, and step length 0.02°/0.1 s. The surface morphology of the catalysts was characterized by SEM (S-3500N HITACHI).

2.3. Experimental system

The experiment was carried out in the fixed bed reactor, as shown in Fig. 1. The flue gas including NH₃, NO and O₂ balanced with N₂ or CO₂ was supplied by cylinders. The parameters of flue gas in the experiment are shown in Table 3. The components of flue gas were analyzed and recorded by the flue gas analyzer (Ecom-J2KN^{PRO} and Signal 7710FM for N₂O). The evaluation of NO conversion rate is calculated by Eq. (1).

$$\text{NO conversion rate (\%)} = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100\% \quad (1)$$

where NO_{inlet} and NO_{outlet} represent inlet and outlet NO concentrations (ppm), respectively.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. BET analysis

As shown in Table 4, the minimum specific surface area is ACFA-TiO₂ without loading. The specific area of each catalyst increases after loading the active components. Generally speaking, the larger the specific surface area of the catalysts is, the better the conversion performance to the reaction gas, and the better the denitration effect of the catalyst (Wang et al., 2013; Li et al., 2016; Wan et al., 2011a). However, studies (Wan et al., 2011b; Mhamdi et al., 2009) have shown that the specific surface area has no obvious linear correlation with the NO conversion performance of the catalyst. The appropriate specific surface area with size of the reaction molecules are required for optimum rate of specific reaction.

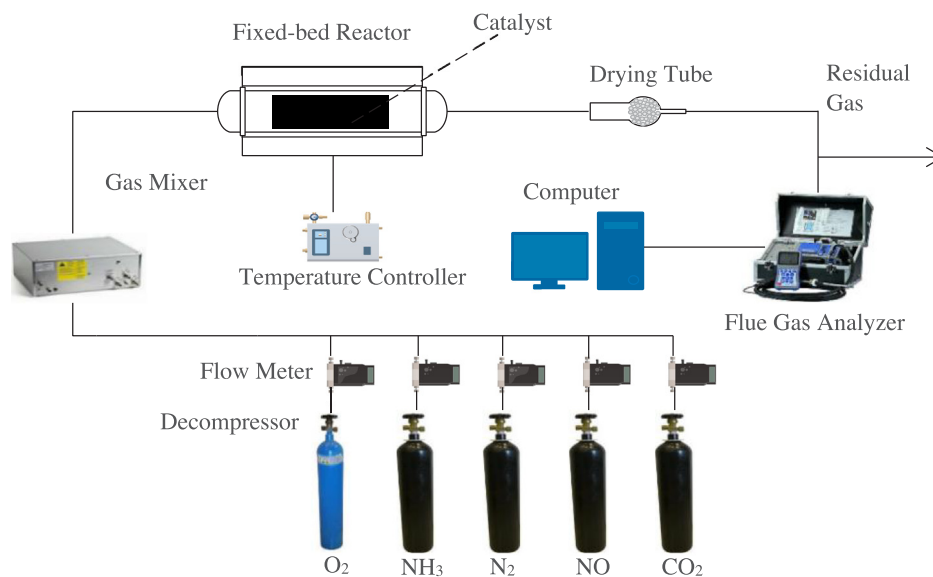


Fig. 1. Schematic diagram of the reaction system.

Table 4
BET analyses of the prepared catalysts.

Catalyst sample	Specific area m ² /g
8%Mn-Ce (5:1)/ACFA-TiO ₂	33.9566
8%Mn-Ce (3:1)/ACFA-TiO ₂	29.5927
8%Mn-Ce (1:1)/ACFA-TiO ₂	26.9623
8%Mn-Ce (1:3)/ACFA-TiO ₂	22.8215
8%Mn-Ce (1:5)/ACFA-TiO ₂	23.9383
ACFA-TiO ₂	19.9091

3.1.2. XRD analysis

It can be seen from the Fig. 2a that FA appears the diffraction peak of SiO₂ in 26.5°, and no other materials diffraction peak is clearly observed. And both SiO₂ and TiO₂ diffraction peaks appear in ACFA-TiO₂. In Fig. 2b the characteristic peaks of TiO₂ and SiO₂ are observed in all five catalysts. In summary, the original crystal structure of FA and titanium dioxide is not changed by composite and all the catalysts do not show MnO_x or CeO_x diffraction characteristic peak. It might be that the active components, MnO_x and CeO_x, are highly dispersed on the carriers, and the basic structure of the carrier is not changed (Liu et al., 2018; Li et al., 2018). By comparing the characteristic peaks, with the addition of Mn and Ce elements, the anatase TiO₂ and SiO₂ diffraction peaks become lower, and the width of the peaks turns into narrower ones. The reason might be that after loading the active component, the active component interacts with the anatase TiO₂ and SiO₂, which reduces the crystallinity of carriers. In addition, a small peak of Fe₂O₃ was observed in some catalysts with Ce, which may be that the small amount of Fe₂O₃ in the ash content of fly ash crystallized with certain mass Ce. Wu et al. (2013) found that, anatase TiO₂ can promote the denitration reaction, and the highly dispersed active components can improve the activity of the catalyst.

3.1.3. SEM Analysis

The five catalysts were characterized by SEM. The original FA is composed of irregular microbeads (Fig. 3a). Fig. 3b shows that the structure of FA microbeads modified by acetic acid is damaged and a large number of pore structures form on the surface of FA. In Fig. 3c and d, the FA compounded TiO₂, forms TiO₂ clusters on the FA surface. Fig. 3e shows that active components directly load on the surface of FA. Meanwhile, they are combined with TiO₂ and filled in the pore structure of FA.

3.2. Effect of Mn-Ce molar ratio on NO conversion

In Fig. 4a, the NO conversion rates of the seven catalysts increase with the temperature rising under the N₂ atmosphere. When the mole ratio of Mn-Ce is 1:1, the NO conversion rate reaches 84.28%, at 300 °C. The NO conversion rate has a great relationship with Mn-Ce molar ratio. The trend, however, is not simply that the NO conversion rate increases as the Mn load increases. It can be explained that at above 150 °C, the ratio 1:1 is the most proper combination of Mn-Ce catalysts for SCR (Gou et al., 2015). Under CO₂ atmosphere, the NO conversion curve of catalysts with temperature is shown in Fig. 4b. The 8% Mn-Ce (1:1)/ACFA - TiO₂ has the highest NO conversion rate, reaching 74.29% at 300 °C. It may be that under both N₂ and CO₂ atmospheres, adsorption can occur on both Lewis acid sites and Brønsted acid sites, but under N₂ atmosphere, the adsorption energy is greater and the adsorption is more stable.

Gou et al. (2015), found that the maximum NO conversion rate of Mn-Ce catalyst is higher than that of Mn or Ce catalyst alone. This shows that the proper combination of Mn-Ce as combined active components can optimize and improve the denitration effect of catalysts.

3.3. Research on sulfur and water resistance of catalysts

3.3.1. Sulfur resistance

Under the conditions of 200 ppm SO₂, 700 ppm NH₃, 700 ppm NO, 6% O₂ and 4200 h⁻¹, the sulfur resistance experiment was performed by using the Mn-Ce (1:1)/ACFA-TiO₂. Without SO₂, the NO conversion rate is 84.29% at 300 °C under N₂ atmosphere. However, with the presence of SO₂, the rate reduces by 8.6% (Fig. 5a). In the sulfur tolerance experiment, after the reaction was carried out at 250 °C for 1 h, 200 ppm SO₂ was added and the sulfur tolerance test was carried out for 6 h. Then the addition of SO₂ stopped and the reaction was carried out for 2 h to test the stability of the catalyst. Without SO₂ in the flue gas, the NO conversion rate is 80.57% and almost unchanged. After SO₂ addition, the NO conversion rate decreases to 70.43%. Then, SO₂ absence for 2 h, the NO conversion rate recovers to 77.05%. The NO conversion decreases by 6.62% after 6 h. Moreover, as shown in Fig. 5b, the NO conversion rate does not return to its original state after it stops flowing into SO₂, and still decreases by 2.53%.

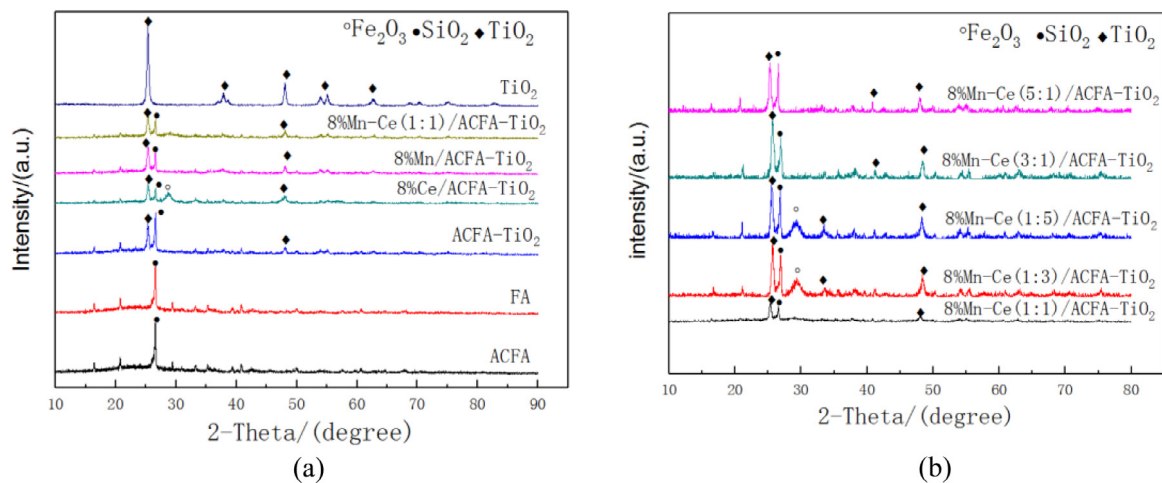


Fig. 2. XRD analyses of the prepared catalysts.

Under CO_2 atmosphere, as shown in Fig. 5c, the NO conversion rate decreases from 74.29% to 66.02% with SO_2 accompanying at 300 °C. In the sulfur tolerance experiment, the NO conversion reduces by nearly 8%. After SO_2 stopping, the NO conversion rate does not return to the original state, and decreased by nearly 4% (Fig. 5d).

Kijlstra et al. (1998) found that the introduction of SO_2 in low temperature SCR reaction will passivate the SCR catalyst and reduce the NO conversion rate. SO_2 reacts with H_2O in flue gas to form H_2SO_3 . The H_2SO_3 will react with the MnO_x in the catalyst and generates compounds with very high decomposition temperature up to 1293 °C. SO_2 reacts with MnO_x to form sulfate. The sulfate generation will consume the active component of the catalysts, and deposit on the surface of the catalysts. Therefore, the adsorption and desorption of reactive gases are hampered, and the NO removal process is inhibited. Moreover, SO_2 will be oxidized into a reaction of SO_3 with NH_3 and H_2O . The reaction will generate $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , which can block the pore channel of the catalyst and cover the active center of the catalyst (Wei et al., 2016; Yan et al., 2016a).

3.3.2. Water resistance

Under the same condition as the resistance experiment of SO_2 , the NO conversion rate of the catalyst decreases due to the addition of H_2O in the N_2 atmosphere, as shown in Fig. 6a. NO conversion rate of catalysts drops by 12.2% at 300 °C. H_2O has less inhibition on the catalyst at lower temperature. After the reaction was carried out for 1 h at 250 °C, H_2O was added and the water resistance test was carried out for 6 h. Then the addition of H_2O stopped and the reaction lasted for 2 h to test the stability of the catalyst. As shown in Fig. 6b, the NO conversion rate of the catalyst decreases from 80.57% to 63.38%, down by 17.19%. The NO conversion rate of the catalyst recovers after H_2O absenting, but it is still lower than the original one, indicating that H_2O passivation is slightly irreversible.

In the CO_2 atmosphere, without H_2O , the NO conversion rate is 74.29% at 300 °C. Then after addition with 6% H_2O , the NO conversion rate drops by 6.49%. Compared with N_2 atmosphere, H_2O with the same volume fraction in CO_2 atmosphere has less passivation effect on the catalyst (Fig. 6c). With the absence of H_2O , the NO conversion rate of the catalyst is 70.57% at 300 °C. The catalyst NO conversion rate reduces by nearly 10% after adding H_2O . As H_2O stops, the catalyst does not restore to the original NO conversion rate. And the conversion is still a slight decline (Fig. 6d). H_2O inhibits the catalyst mainly in two aspects (Niu et al., 2016; Cortés-Reyes et al., 2019): H_2O competes with

NH_3 for the active level, weakening the adsorption effect of the catalyst on NH_3 , and this effect disappears after the stop of H_2O . Furthermore, H_2O adsorbs on the surface of the catalyst to produce hydroxyl, reducing the active level of the catalyst, which is irreversible.

3.3.3. Sulfur and water resistance simultaneous

Fig. 7a exhibits the NO conversion curve of the catalyst with the change of temperature under the N_2 atmosphere, when introducing SO_2 and H_2O . At 300 °C, when the simulated flue gas has 200 ppm SO_2 and 6% H_2O , the NO conversion greatly reduces to 53.10%, down by 31.18%. In Fig. 7b with SO_2 and H_2O existing in the CO_2 atmosphere, the NO conversion curves of the catalyst with the change of temperature show that the NO conversion greatly reduced from 74.29% to 49.52%, at 300 °C

By comparison, when SO_2 and H_2O exist simultaneously, the inhibiting effect of the catalyst on the NO conversion is more obvious. The presence of H_2O will aggravate the SO_2 passivation. Due to the presence of large amounts of H_2O , the production of ammonium sulfate on the surface will increase. In the atmosphere containing SO_2 and H_2O , the Lewis acid level on the catalyst surface is weakened, while NH_3 is mainly adsorbed at the Lewis acid level at low temperature. Therefore, H_2O and NH_3 will compete for adsorption, leading to the reduction of NH_3 adsorption (Shu et al., 2014).

3.4. N_2O Formation

3.4.1. N_2O Formation without catalyst

In the two atmospheres of N_2 and CO_2 , without catalyst, the formation of N_2O in the reaction process is shown in Table 5. The experiments were performed under the conditions at 200–300 °C, 700 ppm ammonia, 700 ppm NO, and 6% O_2 . Without catalysts in the reaction system, in both kinds of atmospheres, large N_2O was produced when the NH_3 , NO and O_2 were presented at higher temperature. Experimental data of Wang et al. (2019) demonstrated the promotion influence of O_2 on NH_3 oxidation and on the formation of NO and N_2O . N_2O derived from the direct reaction between NH_3 and O_2 or the two-step pathway of the pre-requisite formation of NO and then the following non-selective catalytic reduction of NO.

3.4.2. N_2O Formation in the low temperature SCR reaction

Fig. 8 shows the N_2O production of different catalysts, where ACFA-TiO₂ is abbreviated as ACFA and the active component load is 8%. The conditions are: 700 ppm NH_3 , 700 ppm NO, 6% O_2 ,

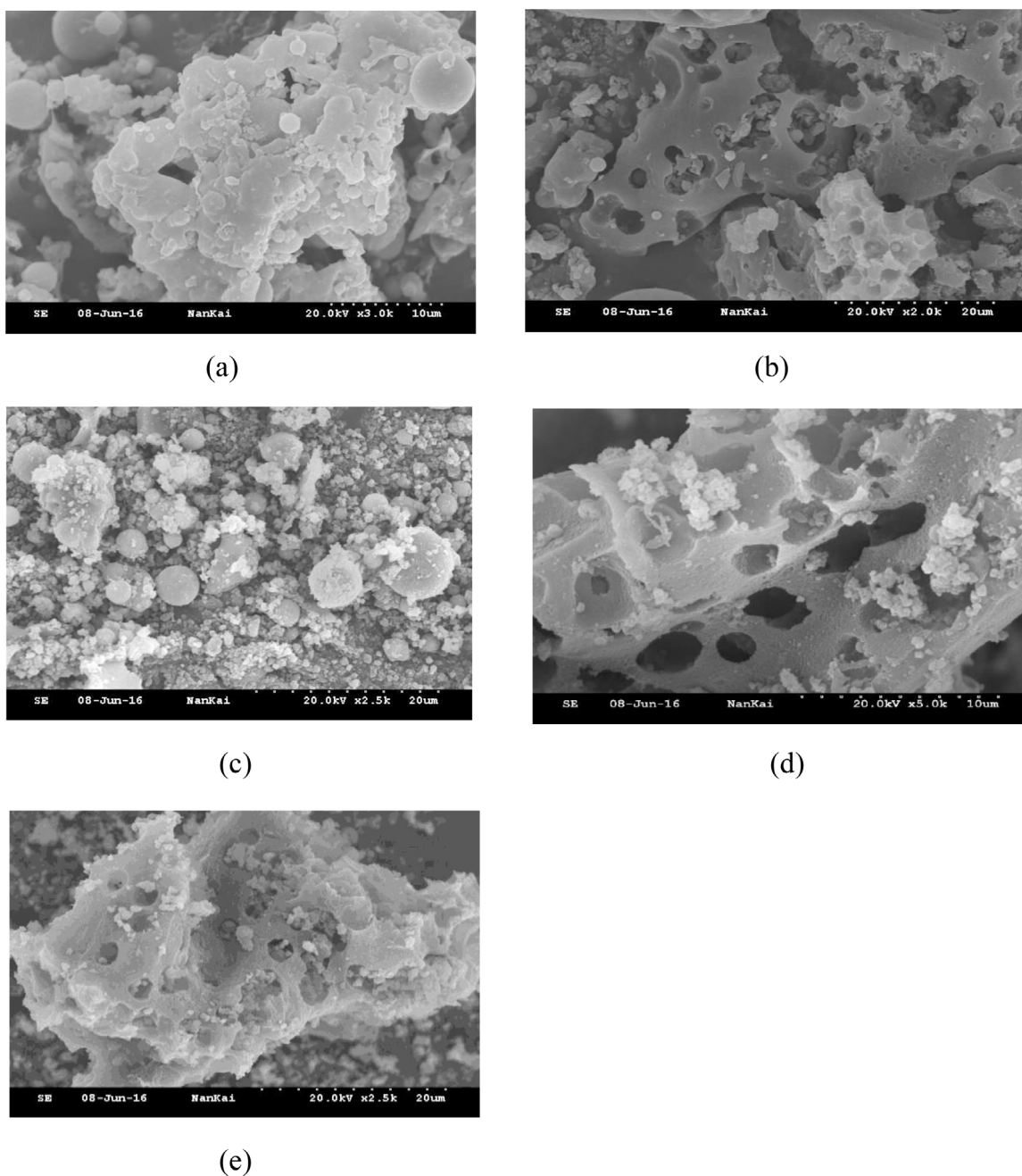


Fig. 3. SEM micrographs of the prepared catalysts. (a) FA; (b) ACFA; (c) FA-TiO₂; (d) ACFA-TiO₂; (e) 8%Mn-Ce(1:1)/ACFA-TiO₂.

Table 5
N₂O production without catalysis in N₂/CO₂ atmosphere (ppm).

Condition	200 ° C		250 ° C		300 ° C	
	N ₂	CO ₂	N ₂	CO ₂	N ₂	CO ₂
NH ₃ +NO+O ₂	3.5	2.1	18.7	19.5	35.8	31.6
NH ₃ +O ₂	0	0	0	0	7.2	6
NO+O ₂	1.6	1	2.6	3	3.8	4.6

250 °C and space velocity 4200 h⁻¹. Under the N₂ atmosphere, the N₂O production of Ce/ACFA catalysts is the least, while the N₂O production of Mn/ACFA is the most, so the addition of Mn element in the catalyst application needs to consider its promotion effect on the production of N₂O. Zou et al. (2015) studied the generation of N₂O and found that the element Mn in SCR catalysts

generates a relatively large amount of N₂O in the process of low-temperature SCR reaction, and the introduction of Ce element can inhibit the generation of N₂O.

In the CO₂ atmosphere, similarly to the N₂ atmosphere, the least and the most N₂O production are Ce/ACFA and Mn/ACFA, respectively. Moreover, the N₂O production in the CO₂ atmosphere is slightly higher than that in the N₂ atmosphere.

4. Conclusions

In this work, a variety of low temperature SCR catalysts were prepared by using FA modified by acetic acid and composite of TiO₂ as the carrier, and their low temperature denitration performances were investigated and tested in fixed bed reactor under the atmospheres of N₂ and CO₂, respectively. The main conclusions are shown below.

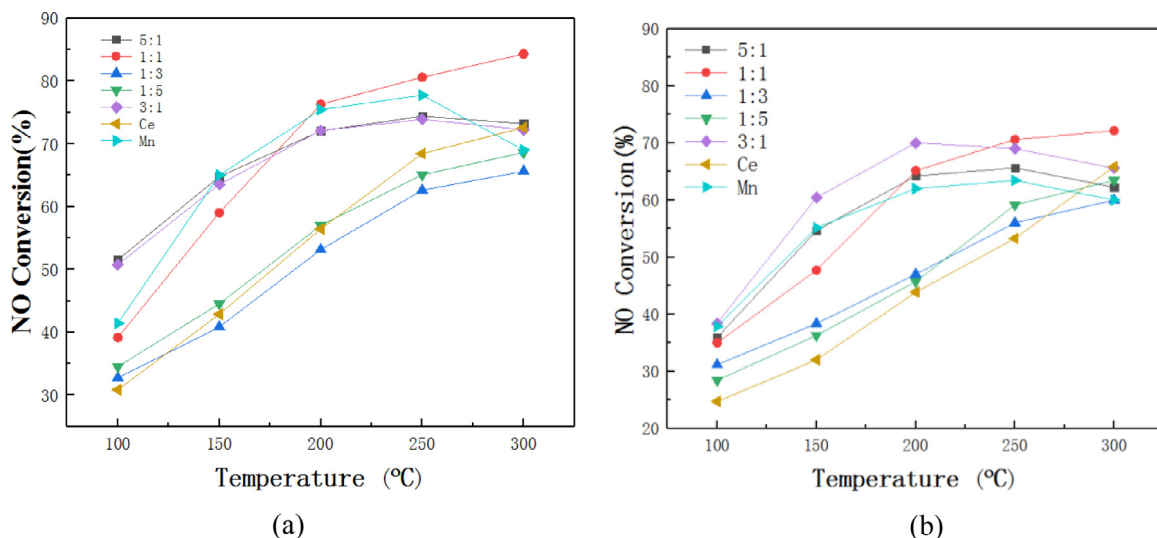


Fig. 4. NO conversion of different catalysts. (a) N₂ atmosphere; (b) CO₂ atmosphere.

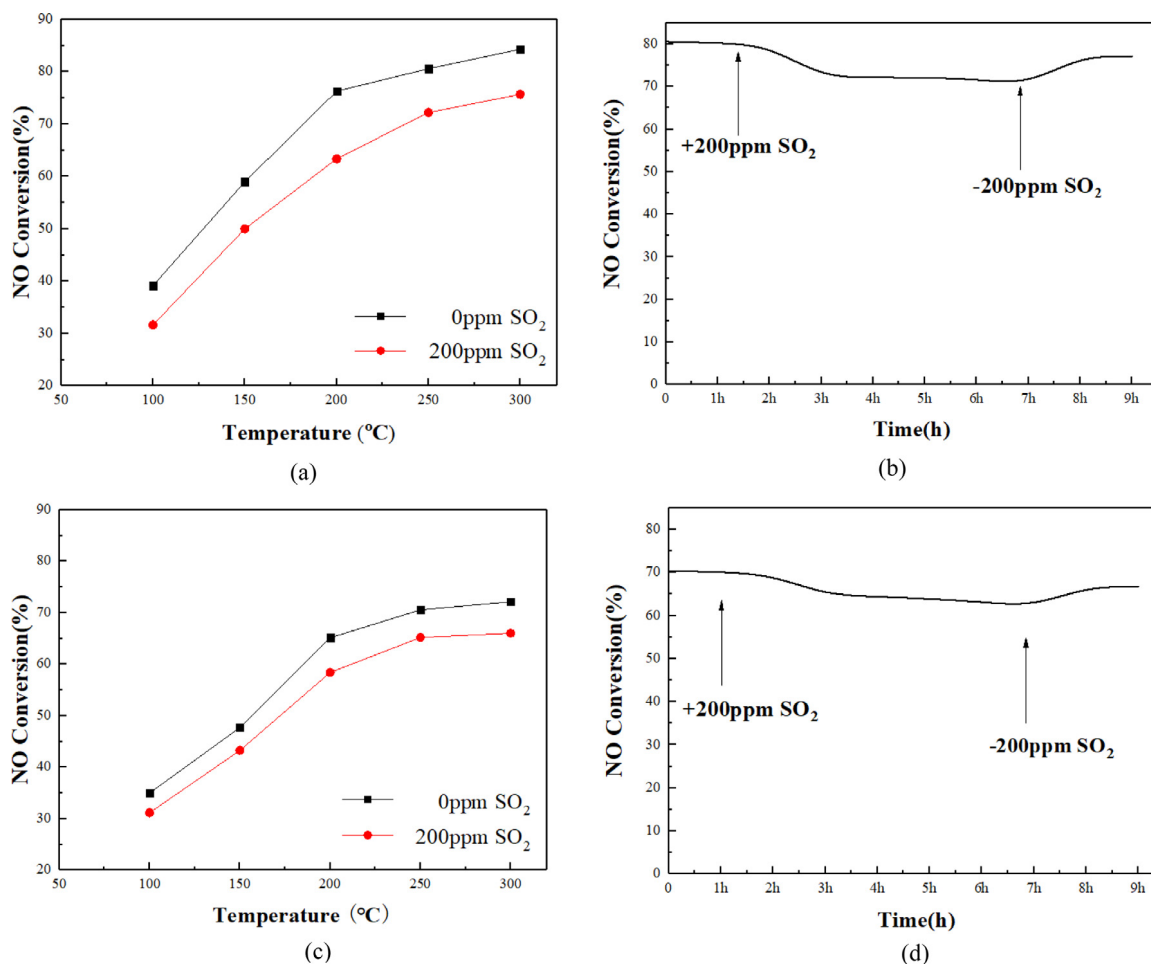


Fig. 5. SO₂ durability of Mn-Ce (1:1)/ACFA-TiO₂. (a) NO conversion (N₂ atmosphere); (b) Stability (N₂ atmosphere); (c) NO conversion (CO₂ atmosphere); (d) Stability (CO₂ atmosphere).

(1) When the mole ratio of Mn-Ce is 1:1, the NO conversion performance of the catalysts is the best in the prepared catalysts, and it reaches 86.28% and 74.29% in N₂ and CO₂ atmospheres, respectively.

(2) BET results show that the specific surface area can determine the denitration performance of the catalyst to a certain

extent, but it is not the only factor affecting the denitration effect of the catalyst. The characteristics of the active substance and the carrier are the main factors affecting the catalytic effect. XRD results show that the crystal structure of FA and TiO₂ has not been changed. MnO_x and CeO_x are loaded on the carrier in a

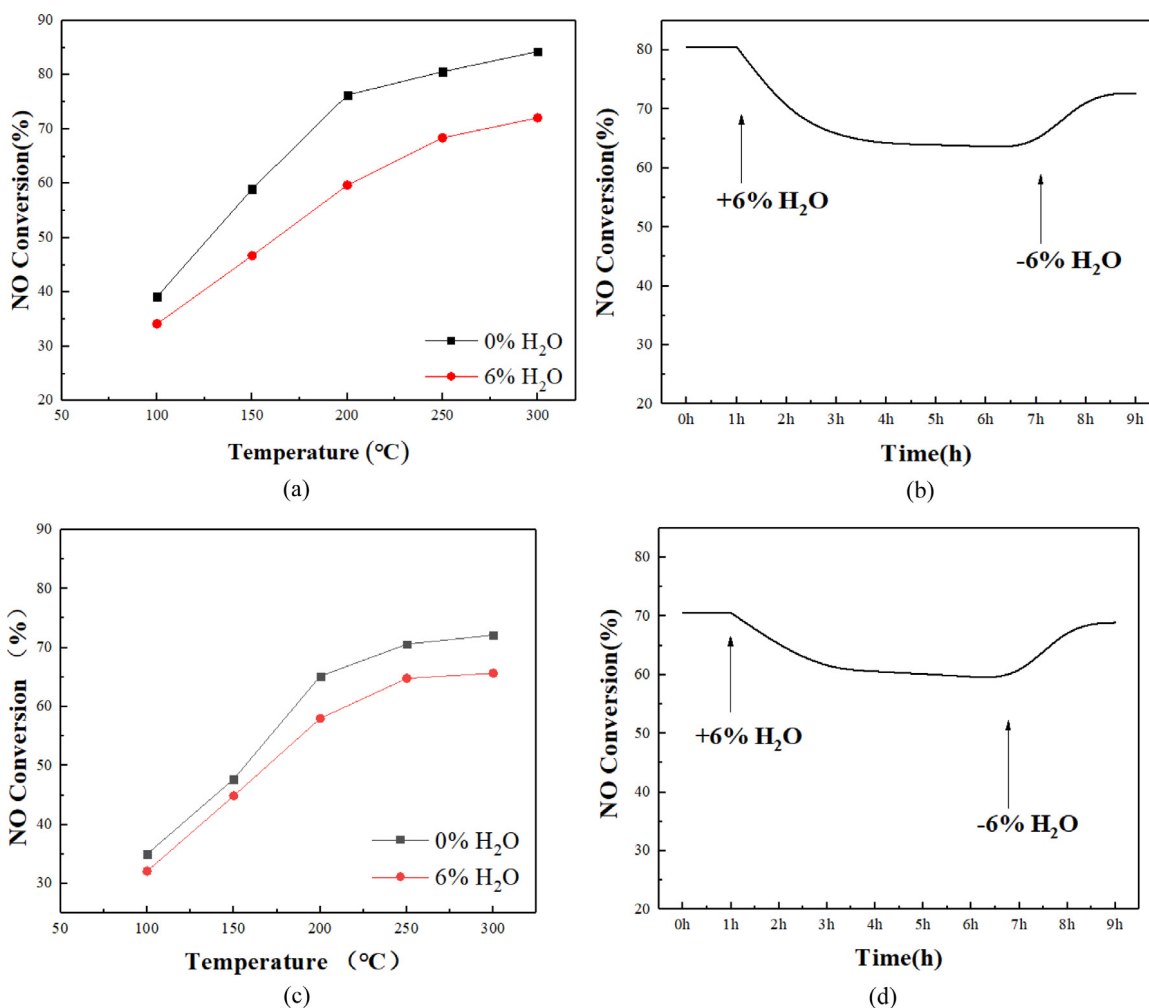


Fig. 6. H₂O durability of Mn-Ce (1:1)/ACFA-TiO₂. (a) NO conversion (N₂ atmosphere); (b) Stability (N₂ atmosphere); (c) NO conversion (CO₂ atmosphere); (d) Stability (CO₂ atmosphere).

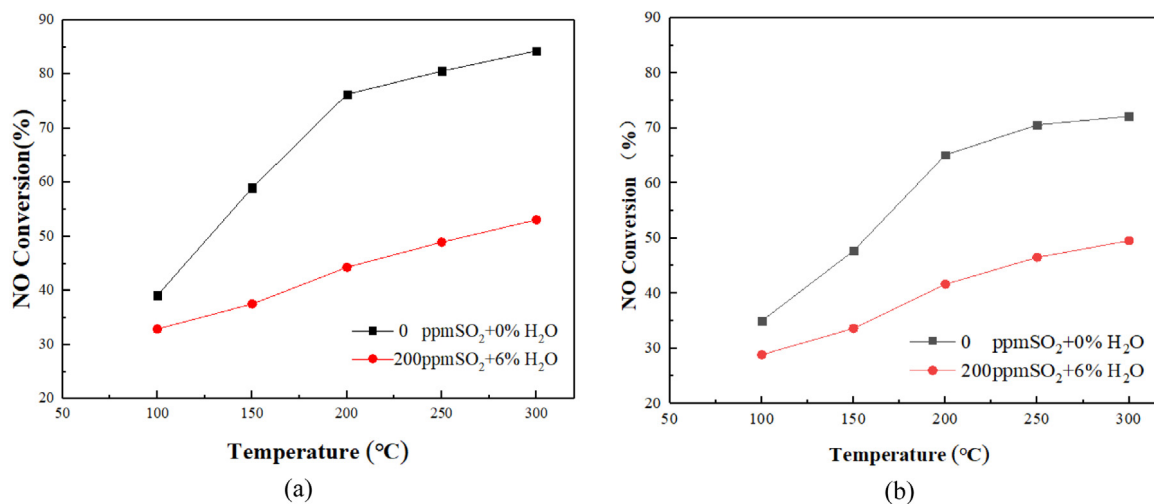


Fig. 7. SO₂ and H₂O durability of Mn-Ce (1:1)/ACFA-TiO₂ (a) N₂ atmosphere; (b) CO₂ atmosphere.

highly decentralized and undefined form. SEM results show that the microbeads structure of FA is damaged after modification by acetic acid, therefore, a large number of pores and TiO₂ clusters are formed on the surface of FA-TiO₂.

(3) SO₂ and H₂O will exert an inhibitory effect on the NO removal performance of the catalyst, which will be intensified as SO₂ and H₂O exist simultaneously.

(4) The amount of N₂O generated in the low-temperature SCR reaction process is large, while the introduction of Ce element can

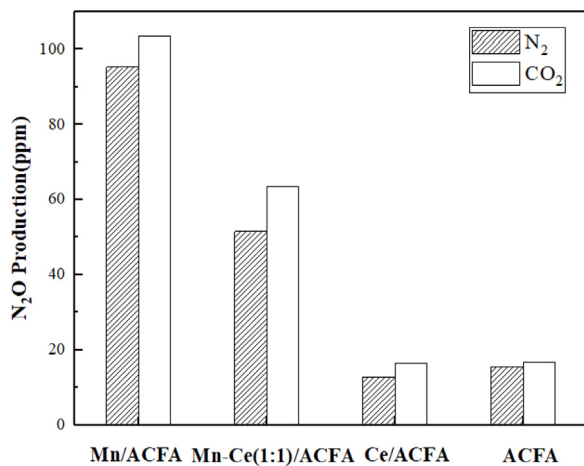


Fig. 8. N₂O production of different catalysts.

inhibit the generation of N₂O. In both atmospheres, 8% Ce/ ACFA-TiO₂ catalyst has the least N₂O production and 8% Mn/ ACFA-TiO₂ has the most N₂O production.

CRedit authorship contribution statement

Xiang Gou: Conceptualization, Methodology, Investigation, Formal analysis, Writing - review & editing, Supervision. **Ruiping Zhang:** Investigation, Formal analysis, Visualization, Writing - original draft. **Guoyou Xu:** Investigation, Validation, Writing - original draft. **Dong Zhao:** Resources, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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