

The contrastive study of Mn-Ce/clay and Mn-Ce/TiO₂ catalysts in denitration performance

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Abstract. The strip-like Mn-Ce/clay and Mn-Ce/TiO₂ catalysts, which used MnO_x and CeO_x as active components, clay and TiO₂ as supports respectively, were prepared by impregnation method. The as-prepared catalysts were systematically characterized by XRF, BET, XRD, NH₃-TPD and in situ DRIFTS respectively. Meanwhile, their denitration performance was also studied. The experimental results presented that Mn-Ce/clay and Mn-Ce/TiO₂ had little difference in denitration performance, which can be attributed to the amorphous status of their active components. When the loading amount of Mn-Ce was 30%, the as-prepared catalyst showed the highest activity at 150~200°C, and the denitration rate was over 90%.

1. Introduction

NO_x is a major component of air pollution and able to result in acid rain and photochemical smog, which will directly cause damage to human body ^[1]. Therefore, how to control efficiently NO_x has been a significant problem in the world. At present, NH₃-SCR technology is acknowledged as the most effective one to remove NO_x domestic and overseas ^[2], which has been applied widely to coal-fired power. The core section of SCR denitration technology is to prepare high active catalyst. The V₂O₅/TiO₂ catalyst ^[3] is the most widely used SCR catalyst, the denitration rate of which is capable of reaching rather high rate at the temperature of 300~450°C. However, the active temperature window of the catalyst is so high that brings about the short life of catalyst. Hence, development of high active catalysts at low temperature has currently turned into a key point to solve these problems.

It is well-known that the clay mineral has improved performance of surface adsorption, wettability, and plasticity because of its small volume and large specific surface area. In addition, the clay also possesses other advantages such as wide raw material sources, good bonding performance, high temperature resistance, and low cost. Zhang Xiongfei et al^[4] have prepared the honeycomb V₂O₅/TiO₂ catalyst with clay as support, the denitration rate of which reached 90% in the range of 400~500°C. Here, strip-like Mn-Ce catalysts, which have been proved to possess excellent activity at low temperature ^[5], were prepared by impregnation method with clay and TiO₂ as supports respectively. To the best of our knowledge, the utilization of clay in low temperature SCR catalyst has not been reported before as well as the compare of clay and TiO₂.



2. Experimental

2.1. Catalyst preparation

Mn-Ce/TiO₂ and Mn-Ce/clay catalysts were prepared by impregnation method. First, the clay or TiO₂ powder and molding promoter (CMC) were mixed together. Then a certain amount of deionized water was added into the mixture to make a plastic compound, which formed into strip-like shape through an extrusion molding process. After that, the strip-like support precursor was dried at 60°C for 12h and finally calcined at 800°C for 6h.

In a typical impregnation process, a certain amount of Ce(NO₃)₃•6H₂O was first dissolved in deionized water followed by the addition of Mn(NO₃)₂(50wt%) solution. The mole ratio of Mn/Ce in the mixed solution was 85:15. Then the above strip-like support was immersed into the resulting solution for impregnation. When the solution was adsorbed by the support completely, the as-prepared catalyst was dried and calcined at 500°C for 6h. The loading amount of active component was calculated according to the following formula: Load=Mass(Mn+Ce)/Mass(support). All chemicals were analytical grade and used without further purification.

2.2. A subsection Catalytic activity evaluation

Catalytic activity test was carried out at different temperature. A fixed bed evaluation platform was employed to test the activity of catalyst; the reaction of ammonia selective catalytic reduction of NO took place in a quartz tube reactor (8mm inner diameter, 10mm outside diameter, 1000mm long). 5ml catalyst sample was put into the reactor before test; the temperature of catalyst bed was controlled by tubular resistance furnace (SK2-2-10, Beijing enterprise). A simulated exhaust gas mixture(0.06% NO, 0.06% NH₃, 6% O₂ and N₂ for balance) was fed to the catalyst sample through a set of rotameters, the gas hourly space velocity(GHSV) was set to 10000h⁻¹ corresponding to the total flow rate of 833ml/min.

In view of NO molecule could be adsorbed by catalyst in experimental condition, so NO gas was primarily fed into the reactor, while the concentration of NO in outlet and inlet equaled, the other simulated gases just began to be fed into the reactor. Under testing, NO concentration in outlet and inlet was detected by flue gas analyzer for 10 min at different temperature, then the average value of NO concentration was attained, finally the denitration rate of catalyst was calculated according to the following formula: $\varphi = (C_0 - C_1) / C_0$ [C₀: NO concentration of inlet C₁: NO concentration of outlet].

3. Performance characterization

D8 advance X-ray diffractometer(German) was employed to analyze catalyst crystal phase. First, the catalyst sample was grinded before testing, Cu K α served as light source, the scan scope of x-ray diffractometer was between 10°~80° interval, and x-ray wavelength was 0.15406nm.

S4-Ex-plorer (German Bruker company produce) x-ray fluorescence spectrometer (XRF) was introduced to determine chemical composition of the clay.

Autosorb-iQ(America Contador instrument company produce) physical adsorption instrument was brought to determine specific surface area, pore volume, pore diameter of catalyst. N₂ served as adsorbate, and the sample was degassed for 3h under vacuum condition at 300°C.

TPD test was performed in Chem BET Pulsar TPR/TPD (America Contador instrument company produce) chemical adsorption instrument, primarily the sample was retreated for 1h at 550°C under He atmosphere, then cooled to room temperature, finally fed adsorbed gas (NH₃) and maintained flow gas for 1h, after reaching to adsorption saturation, the sample's temperature was raised to 100°C and catalyst sample was purged with He for 1h, following to start temperature program and record TCD signal value.

Type 6700 (American NICOLET company) Fourier transform infrared spectrometer equipped with diffusion reflection optics accessory was utilized to research the reaction behaviour of gas molecule on the surface of catalyst. A proper amount of catalyst powder was placed in the pool of in situ diffusion reflection optics accessory. Prior to acquisition of DRIFTS spectra, the sample was firstly

retreated, and the sample temperature was raised from room temperature to 200°C and kept for 2h, meanwhile the sample was purged in N₂, then the sample temperature was decreased to room temperature, afterwards, pyridine vapour was fed into sample to perform adsorption process for 1h, finally the sample was purged in N₂ again, afterwards, the adsorption of pyridine on catalyst sample surface was determined at different temperature.

4. Results and Discussion

4.1. Analysis of clay component

Table 1. XRF results of clay.

Components content (%)	SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	Na ₂ O	MgO	CaO
	61.88	24.87	5.17	4.79	1.05	0.75	0.64
Components content (%)	TiO ₂	P ₂ O ₅	MnO	Rb ₂ O	ZrO ₂	ZnO	Y ₂ O ₃
	0.57	0.11	0.05	0.04	0.37	0.01	0.01

The XRF result of clay is listed in table 1, the clay mainly consists of SiO₂ and Al₂O₃ as well as slightly contains K₂O and Fe₂O₃ etc. For prepared catalyst, K, Na, Ca, Mg are harmful components but slight on the scale. Therefore, the clay is propitious to be catalyst support.

4.2. XRD analysis of Clay

The XRD pattern of the clay is presented in Figure 1, comparing with SiO₂ standard XRD pattern (JCPDS: 78-2315), the XRD pattern of clay is in agreement with SiO₂ standard one. It is not found the diffraction peaks of Al, Ti, Mn Oxides etc. Perhaps, the crystallinity of SiO₂ is too high, which covers up the tiny diffraction peaks of other oxides.

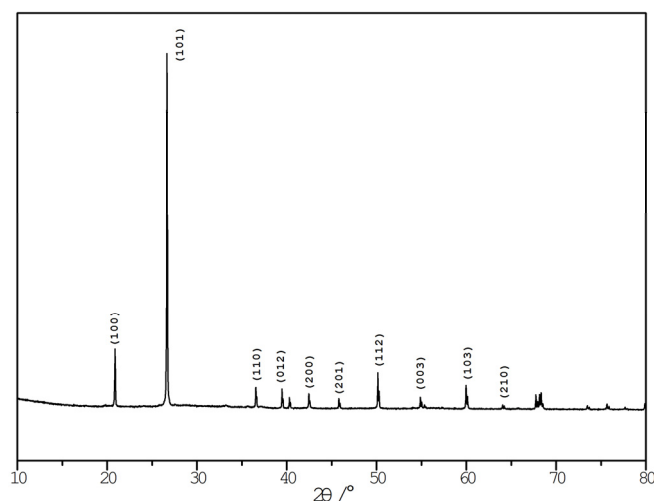


Figure 1. XRD pattern of the clay.

4.3. XRD analysis of Mn-Ce/TiO₂ and Mn-Ce/clay Catalysts

The XRD patterns of Mn-Ce/clay and Mn-Ce/TiO₂ catalyst are shown in figure 2. It reveals that there are just respectively SiO₂ and TiO₂ characteristic peaks. Although the loaded amount of active component on catalyst sample reaches to 30%, the characteristic peaks of Mn and Ce oxides of two

types of catalysts are neither observed in the patterns. Many researches indicate that amorphous MnOx is more conducive to SCR reaction compared to regular crystal MnOx.

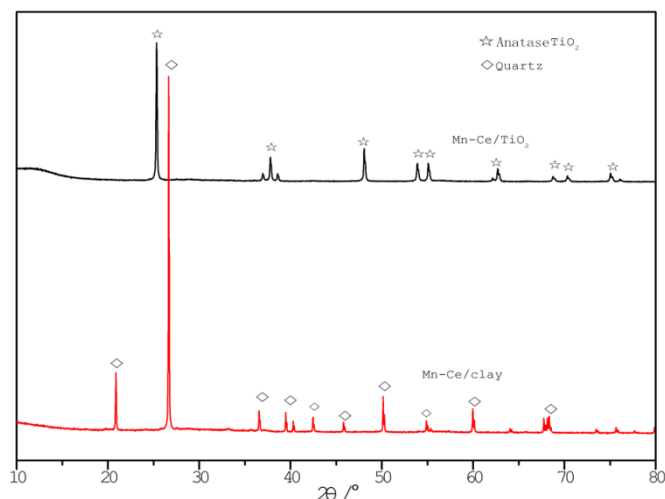


Figure 2. XRD patterns of Mn-Ce/clay and Mn-Ce/TiO₂ catalysts.

4.4. BET analysis of Mn-Ce/TiO₂ and Mn-Ce/clay Catalysts

The BET results of catalyst Mn-Ce/clay and Mn-Ce/TiO₂ are listed in table 2, which show the catalyst based clay has large surface area and pore volume, small pore diameter. These superiorities all contribute to catalytic reaction.

Table 2. BET results of Mn-Ce/clay and Mn-Ce/TiO₂ catalysts.

Catalyst	Surface area/m ² ·g ⁻¹	Pore volume/cm ³ ·g ⁻¹	Pore diameter/nm
Mn-Ce/TiO ₂	10.272	0.05537	21.5603
Mn-Ce/clay	13.884	0.19979	1.12417

4.5. NH₃-TPD analysis of Mn-Ce/TiO₂ and Mn-Ce/clay Catalysts

The NH₃-TPD curves of Mn-Ce/clay and Mn-Ce/TiO₂ catalysts are shown in figure 3. From the graph, it can be observed that the two catalysts both have a weak NH₃-desorption peak around 300°C, moreover Mn-Ce/clay's peak is higher than Mn-Ce/TiO₂'s. Besides, the two type of catalysts also have a NH₃-desorption peak respectively between 600-700°C, the peak of Mn-Ce/clay is still more noticeable compared to Mn-Ce/TiO₂'s, but the NH₃-desorption peak of Mn-Ce/TiO₂ is rather broad. In addition, Mn-Ce/TiO₂ catalyst has a high NH₃-desorption peak between 700-800°C. It can be seen that the NH₃ adsorption around 300°C should belong to weak adsorption and one between 600-700°C be strong adsorption. For the catalyst, moderate adsorption is favourable to catalytic reaction [6], too strong or too weak adsorption is either adverse to continuous reaction. Too weak adsorption makes little reactant molecules be activated, but too strong adsorption does not favour for desorbing product molecules, which also hinders continuous reaction. Comprehensively analyse the two prepared catalysts, the stronger adsorption of Mn-Ce/clay catalyst than Mn-Ce/TiO₂ catalyst is possibly ascribed to its large specific surface area and big capacity at 300-400°C. At high temperature of 600-700°C, Mn-Ce/TiO₂ catalyst owns intense adsorption to NH₃, which may correlate with physical and

chemical nature of TiO_2 , indicates the different type of supports can also impact on NH_3 adsorption intensity.

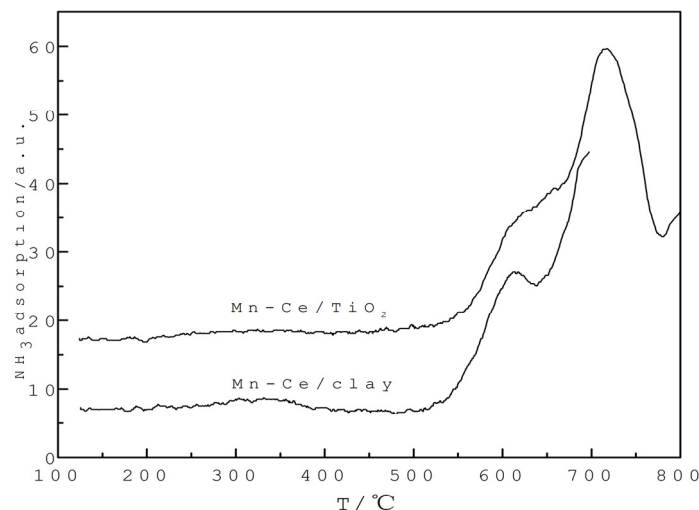


Figure 3. NH_3 -TPD curves of Mn-Ce/clay and Mn-Ce/ TiO_2 catalysts.

4.6. In situ DFIR analysis of Mn-Ce/ TiO_2 and Mn-Ce/clay Catalysts

The DRIF curves of Mn-Ce/ TiO_2 and Mn-Ce/clay catalysts are presented respectively at different temperature in figure 4 and 5. From figure 4(a), it can be seen that the adsorption peak at band 1580 cm^{-1} is assigned to the infrared absorption of the heterocyclic C-H vibration of pyridine, and the IR band observed at 1540 cm^{-1} is attributed to the vibration of pyridine ion on Brönsted acid sites, the weak adsorption peak at 1450 cm^{-1} is formed by coordinated pyridine molecule absorbed on Lewis acid sites, it shows that the activity sites of Mn-Ce/ TiO_2 catalyst is mostly Brönsted acid sites, the Lewis acid sites rarely contribute to the activity sites of Mn-Ce/ TiO_2 catalyst. Moreover, it is found that the IR adsorption peak on Lewis acid sites declines obviously with increasing temperature, but the IR adsorption peak on Brönsted acid sites does not fall down obviously, which indicates that the change of temperature has little influence to the adsorption on Brönsted acid sites.

In figure 4(b), at approximate region of 1500 cm^{-1} , there are mainly two IR adsorption peaks, including 1580 cm^{-1} and 1450 cm^{-1} . The peak at 1580 cm^{-1} is likewise assigned to the infrared absorption of the heterocyclic C-H vibration of pyridine, the other peak at 1450 cm^{-1} is caused by coordinated pyridine molecule absorbed on Lewis acid sites. However, there is hardly the adsorption peak at Brönsted acid sites, which demonstrates Mn-Ce/clay catalyst has few Brönsted acid sites. Meanwhile, it is clearly observed that the amount of pyridine molecule adsorption at Lewis acid sites reduces significantly compared to Mn-Ce/ TiO_2 . From the adsorption change on Lewis acid sites of two types of catalysts, we can reach a conclusion that the pyridine adsorption on Lewis acid sites is declining with increasing temperature (from 50°C to 150°C).

Moreover, according to NH_3 -TPD and in situ DRIF curves of two type of catalysts, we can work out a conclusion which Lewis acid sites is assigned to weak acid sites, because there is an obvious desorption peak on the NH_3 -TPD curve of Mn-Ce/clay catalyst around 350°C . However, this desorption peak is not apparent on NH_3 -TPD curve of Mn-Ce/ TiO_2 catalyst, and refer to the DRIF curves of two type of catalysts, Mn-Ce/ TiO_2 catalyst has few Lewis acid sites between 50 - 150°C , but the activity sites of Mn-Ce/clay catalyst is mostly Lewis acid sites. Besides, In DRIF curves of two types of catalysts. It is found that only the IR adsorption peak of Lewis acid site reduces down obviously as temperature goes up, but Brönsted acid sites not declines apparently. So the desorption of NH_3 -TPD of Mn-Ce/Clay catalyst around 350°C should be the NH_3 desorption on Lewis acid sites. Thus, it is determined that Lewis acid sites are weak acid sites on two type of catalysts.

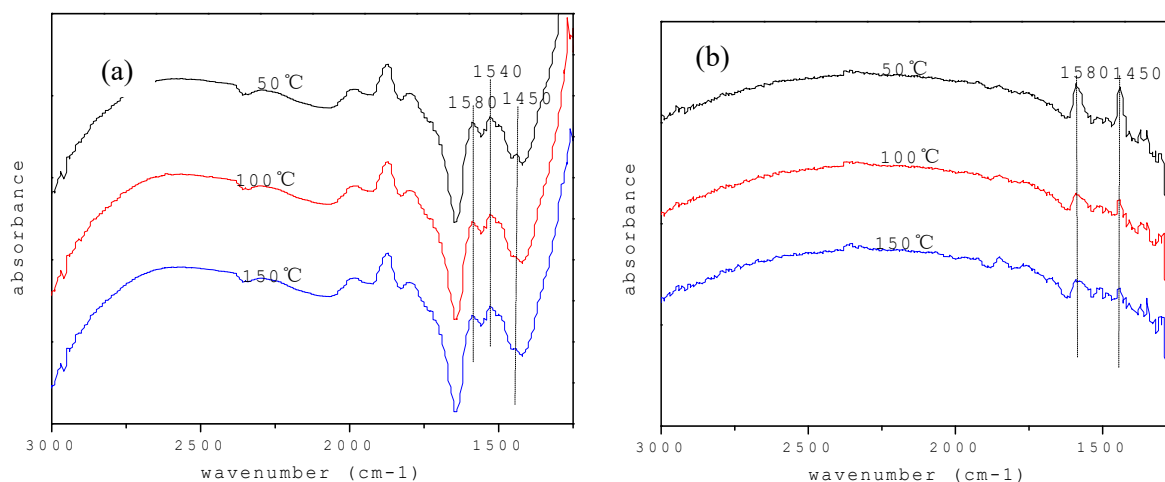


Figure 4. DRIF patterns of Mn-Ce/TiO₂ and Mn-Ce/clay catalysts
(a) Mn-Ce/TiO₂ (b) Mn-Ce/clay.

4.7. Activity evaluation of Mn-Ce/TiO₂ and Mn-Ce/clay Catalysts

The activity of two type of catalysts is tested on catalyst activity test platform, the denitration rate of two type of catalysts are presented in Figure 5, From activity curves, we can see that Mn-Ce/TiO₂ catalyst has higher activity than Mn-Ce/clay between 100-200°C. However, Mn-Ce/clay has higher activity compared to Mn-Ce/TiO₂ above 200°C. for the reason, we can make an analysis from the following ways; firstly, it is seen that the absorbance peak of Lewis acid sites on two kind of catalysts is very weak above 100°C from DRIF curves of two type of catalysts. And the IR adsorption peak of Bronsted acid sites of Mn-Ce/TiO₂ catalyst is pretty obvious, but Mn-Ce/clay catalyst hardly has Bronsted acid sites. Therefore, Mn-Ce/TiO₂ catalyst has higher catalytic activity in the range of 100-200°C

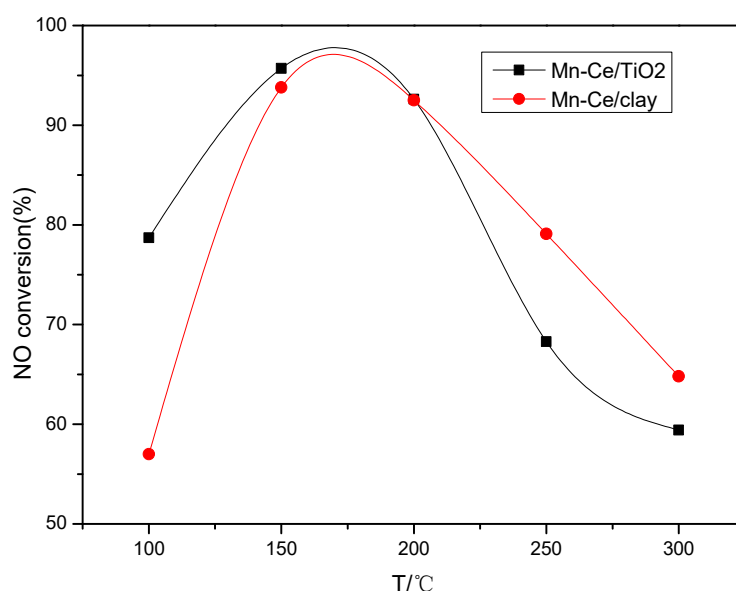


Figure 5. Activity curves of Mn-Ce/clay and Mn-Ce/TiO₂ catalysts.

As for 200-300°C, why the activity of Mn-Ce/clay catalyst is higher than Mn-Ce/TiO₂ catalyst, we can make some analysis from NH₃ adsorption condition on two type of catalysts. From NH₃-TPD curves of two type of catalysts, Mn-Ce/clay catalyst has an intensive desorption peak at 600°C, but the desorption peak of Mn-Ce/TiO₂ is weak and broad at 600°C. Besides, the desorption peak of Mn-Ce/TiO₂ is very intensive at 750°C, it is known that the NH₃ adsorption on catalyst at 600°C is attributed to moderate intensity, which is beneficial to catalytic reaction, but the NH₃ adsorption at 750°C is assigned to strong adsorption, which is not in favour of catalytic reaction. Thus, Mn-Ce/clay catalyst with moderate adsorption is more conducive to catalytic reaction compared to Mn-Ce/TiO₂ with strong adsorption above 200°C, so the activity of Mn-Ce/TiO₂ catalyst is inferior to Mn-Ce/clay catalyst between 200~300°C.

5. Conclusion

Trough researching Mn-Ce/TiO₂ and Mn-Ce/clay catalyst, what is obtained as follow; The active components of two type of catalysts are amorphous status, and the main components of clay are SiO₂ and Al₂O₃. The catalyst which is prepared with clay as support occupies good properties including specific surface area and pore volume, bore diameter is prior to TiO₂-base catalyst. In addition, clay-base catalyst has moderate adsorption with reactant; these are all contributed to catalytic reaction. However, as far as active sites (including L and B acid sites) on catalyst surface is concerned, clay-base catalyst is inferior to TiO₂-base catalyst, particularly the amount of Bronsted acid sites, which influences the activity of clay-base catalyst in low temperature. Comprehensively, the reasons that both catalysts show similar performance in denitration are led by many aspect factors including surface texture and crystallinity of catalyst and so on, and the feasibility using caly as support to prepare Mn serial catalyst is also achieved, which can lay the foundation for further researching and modifying Mn-Ce/clay catalyst.

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References

- [1] Shelef M 1995 Selective catalytic reduction of NO_x with N-Free reductants *Chemical Reviews* **95** 209
- [2] Parvulescu V, Grange P and Delmon B 1998 Catalytic removal of NO *Catalysis Today* **46** 233
- [3] Busca G, Lietti L, Ramis G and Berti F 1998 Chemical and mechanistic aspects of the selective catalytic reduction of NO_x by ammonia over oxide catalysts: A review *Applied Catalysis B: Environmental* **18** 1
- [4] Zhang X F, Xie F H, Wang W, Chen X N and Wang Y X 2012 Molding research of honeycomb clay-base catalyst (in Chinese). *Guangzhou Chemical Industry* **40** 80
- [5] Min K, Park E D, Ji M K and Yie J E 2007 Manganese oxide catalysts for NO_x reduction with NH₃ at low temperatures *Applied Catalysis A: General* **327** 261
- [6] Wang L, Zhang C and Huang H 2016 Catalytic oxidation of toluene over active MnO_x, catalyst prepared via an alkali-promoted redox precipitation method *Reaction Kinetics, Mechanisms and Catalysis* **118** 605