Mechanisms and Kinetics of MnO_x-Based Catalysts at Low-Temperature Selective Catalytic Reduction of NO_x

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Abstract. MnO_x has become a focus in the research of low-temperature SCR De-NO_x catalysts for its good catalytic activity. Many MnO_x-based catalysts have been researched which all have a high selectivity low-temperature N_2 and good anti-poisoning, but most of them lack enough clear reaction mechanism and kinetic. In this paper, the research progress of SCR mechanisms and kinetics were summarized. The mechanisms are for the NH_3 as the reducing agents and MnO_x as the active centres. The overall reaction mechanism can be explained by L-H, E-R and Mars-van Krevelen mechanisms. H_2O and SO_2 deactivation mechanism are also mentioned. The kinetics of SCR reaction of MnO_x at low-temperature are studied based on power function, mechanism derivation and the combination of them.

Introduction

Selective catalytic reduction (SCR) denitration technology is widely used in the industry, which basic principle is: $NH_3+NO+O_2 \rightarrow N_2+H_2O$, the denitration catalyst is the core of SCR. At present, the denitrification catalyst must be arranged before the flue gas dust removal system, because of the reaction temperature must be higher than 350° C. In the high concentration of dust laden gas, the catalyst poisoning is easily caused by heavy metals and SO_2, the life of the catalyst is short and the operating cost is great. Therefore, the research and development of low temperature denitrification catalyst has important environmental and economic value, which is arranged after the dust removal and desulfurization process.

The MnO_x is a focus in the research of low temperature denitration catalysts. As the active component, Mn can provide more free electrons and oxygen vacancies, MnO_x-based catalysts showed good low-temperature denitration activity. According to the study by Peña et al.[1], the result showed that at 393K removal denitrification activity sequence is: Mn>Cu>Cr>Co>Fe>V>Ni, which also showed that Mn has higher catalytic activity in the presence of water vapor (H_2O). Kapteijn et al.[2] made a systematic study on single component MnO_x of different valence states at 385K-575K, the result showed that the removal denitrification activity sequence of different valence state of MnO_x is: $MnO_2>Mn_5O_8>Mn_2O_3>Mn_3O_4>MnO$, Mn_2O_3 showed the highest N_2 selectivity, and the denitrification efficiency of MnO_2 was 100% at 450K.

SCR Mechanism

At present, many low-temperature catalysts have been studied, but most of them lack enough clear reaction mechanism. On the other hand, the SCR mechanism is very important for the research of low-temperature catalysts. It can help us to understand why the activity of catalysts high or low. In this paper, the research progress of SCR mechanisms was summarized, which mains on the removing NO_x by NH_3 as the reducing agent as well as the H_2O and SO_2 deactivation mechanism.

Mechanisms of NH_3 as the reducing agent. According to the current research, there are Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) mechanisms for NH_3-SCR. Many researchers have found that the mechanism of Mars-van Krevelen may be in presence for the MnO_x based low-temperature

catalysts. E-R refers to the mechanism between NO_x of gas phase and the adsorbed NH_3 reacts to form intermediates, and then decomposed into N_2 and H_2O; L-H mechanism refers to the reactants (NO_x and NH_3) first adsorbed on the active site of the catalyst to form an intermediate, and then decomposed into N_2 and H_2O. The E-R and L-H reaction mechanism shows that NH_3 is involved in the reaction of adsorption state, but the adsorption effect of NH_3 for different acid sites (Brønsted acid and Lewis acid sites) is no unified understanding. Most of studies proved that the reaction temperature had a significant effect on the two kinds of acid sites, which shows that Lewis acid at low temperature on adsorption of NH_3 is significant, high temperature Brønsted acid adsorption of NH_3 plays a main role.

The mechanisms and kinetics of Mn-Fe catalyst were studied by Yang et al.[3], the results shows that the reaction of $(Fe_{2.8}Mn_{0.2})_{1-\delta}O_4$ catalyst surface was followed by L-H mechanism, and the mechanism of E-R was dominant at 200°C. For $(Fe_{2.8}Mn_{0.2})_{1-\delta}O_4$ catalyst, the E-R and L-H mechanism from 80°C-200°C to coexist, when temperatures above 100°C E-R play main role. Marban et al.[4] discussed the E-R mechanism of the low-temperature (125°C) selective catalytic reduction of NO with NH_3 over carbon-supported Mn_3O_4, who also shows two different SCR mechanisms (see Fig.1).

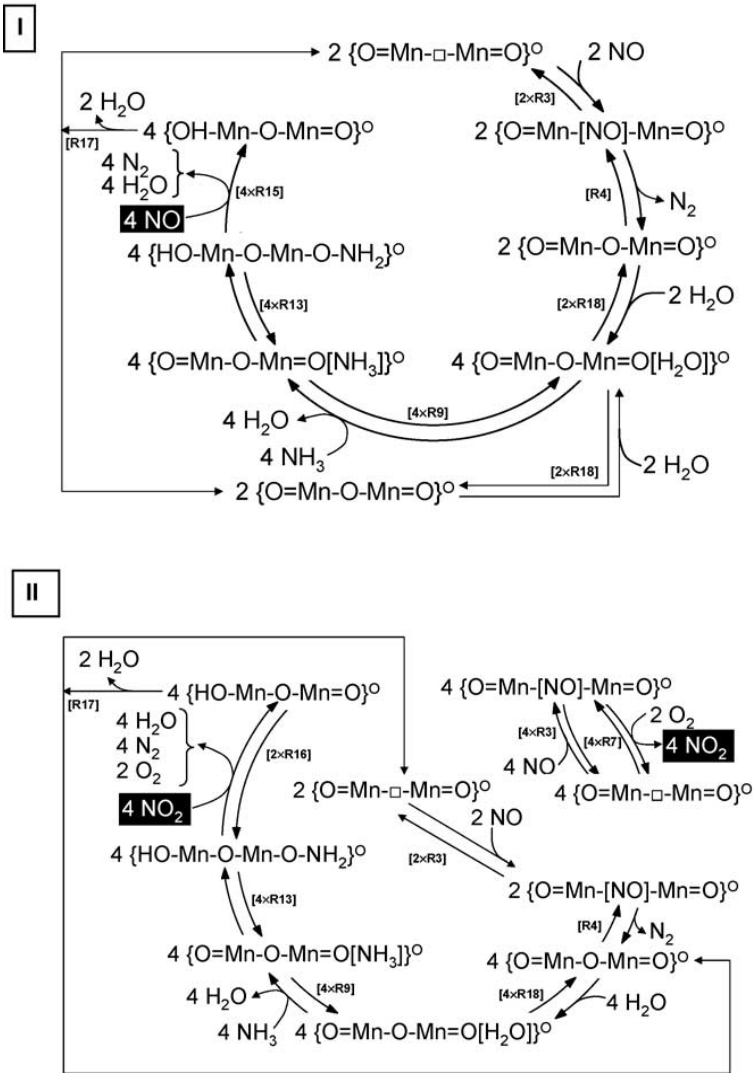
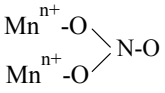
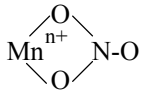
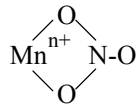
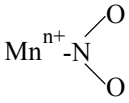
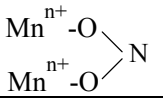


Fig.1. Mechanism of the steady-state SCR reaction: (I) in the absence of oxygen; (II) in the presence of oxygen.

Kijlstra et al.[5] studied the adsorption of NO and NH_3 on MnO_x/Al_2O_3 catalysts, separately by use of TPD and FTIR, also investigated the influence of O_2 on the adsorption of the reactants. At 423 K, the following compounds can be present, in increasing order of thermodynamic stability: linear nitrites, bridged nitrites, monodentate nitrites<bridged nitrates<bidentate nitrates. The formation of

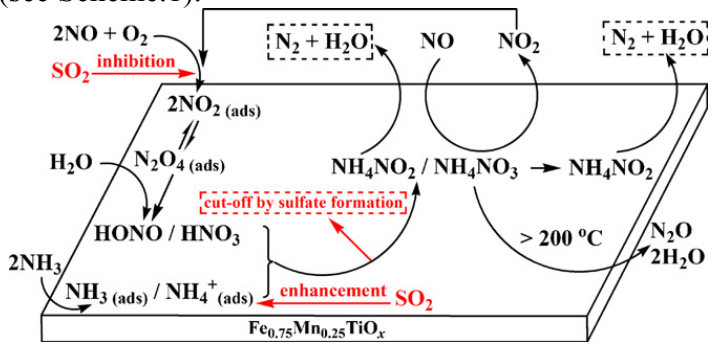
these five species is strongly enhanced in the presence of O_2, and probably proceeds by NO oxidation(see Table 1).

Table 1 Thermal Stabilities Adsorbed NO Complexes

Species	υ_3/m^{-3}	υ_3/m^{-3}		Desorption/ decomposition
Nitrosyl	1835		Mn^{n+}-N=$O^{\delta-}$	323 K
Bridged nitrate	1620	1220		423–573 K
Bidentate nitrate'type II'	1290	1555		573–698 K
Bridged nitrate'type I'	1580	1220		473–573 K
Linear nitrite	1466	1075 (υ_3)	Mn^{n+}-O-N=O	323–473 K
Monodentate Nitrite	1415	1322 (υ_3)		323–473 K
Bridged nitrite		1230		323–523 K

H_2O and SO_2 deactivation mechanism. Low temperature NH_3-SCR denitration device layout after the dust removal and desulfurization process, and the temperature of the flue gas after the desulfurization was generally lower than 200°C, so the catalysts are easily to be poisoned by SO_2 and H_2O(g). Whether the catalyst has excellent anti H_2O and anti SO_2 performance is the key to its ability of industrial application. In recent years, many researchers have carried out a lot of study on the anti H_2O and anti SO_2 performance of MnO_x-based low-temperature NH_3-SCR denitrification catalyst.

Kijlstra et al.[6] studied the influence of H_2O and SO_2 on MnO_x/Al_2O_3 catalyst. The results showed that the influence of water vapor (H_2O) on the catalyst is mainly shown in two aspects: physical competition adsorption and chemical adsorption; SO_2 reacted with MnO_x to produce Mn sulfate, which easily deposited on the pore of the catalyst and reducing catalytic activity. Liu et al.[7] studied the inhibition of SO_2 and H_2O on $Fe_{0.75}Mn_{0.25}TiO_x$ catalyst. The results showed that the effect of H_2O on the activity of SCR catalyst was mild and reversible, and the inhibition effect of SO_2 was more intense and irreversible, because of nitrate deposition on the surface of the catalyst had been cut off the way of SCR reaction(see Scheme.1).



Scheme.1. Proposed mechanism of the NH_3-SCR reaction over Mn substituted irontitanate catalyst at low temperatures and the influence of SO_2 on the reaction pathway.

Jin et al[8]. studied the relationship between reaction of SO_2 in inhibitory action and reaction temperature over Mn-Ce/TiO_2 catalyst. The results showed that the higher reaction temperature, the faster catalyst activity decreased, at 200°C the catalyst active site of sulfation serious resulting in

irreversible deactivation, but at 100°C generated $(NH_4)_2SO_3$ and NH_4HSO_4 leads to catalyst deactivation, which catalytic activity can be recovered by washing with water.

Kinetics

The kinetics of SCR reaction of MnO_x at low temperature was studied based on power function, Mechanism derivation and the combination of them. Qi et al.[9] studied the kinetics of MnO_x-CeO_2 catalyst which based on the power function equation ($r_{NO} = k[NO]^x[NH_3]^y[O_2]^z$) at 120°C, the reaction order was calculated, the NH_3, O_2 and NO of the reaction series were 1, 0 and 0.5. Yang et al.[10] deduced the NO conversion rate of dynamics equation on Mn-Fe catalysts, which based on L-H and E-R mechanisms(see equations.1).

$$X = k_1k_6k_7\mathrm{BET}c_{acid}\int_0^{t'}\exp(-k_1k_6k_7c_{acid}l)dl + k_1k_2k_3\mathrm{BET}[Mn^{4+}] \times c_{acid}t'\frac{[NO(ad)]}{[NO(g)]_0} \quad (1)$$

Conclusions and perspective

The adsorption of NO and NH_3 at the surface of catalysts is very important for low-temperature selective catalystic reduction of NO_x. Through various characterization techniques, we have a preliminary understanding of the mechanism of NH_3-SCR reaction at low temperature. But at present, the MnO_x-based catalyst is not good enough for the SO_2 and H_2O poisoning resistance, the H_2O and SO_2 inhibition mechanism is not yet fully mastered.

In future research, we need to deeply explore the adsorption and activation mechanism of NH_3 and NO in MnO_x catalysts, research clearly H_2O and SO_2 inhibition mechanism of MnO_x catalysts, for high H_2O and SO_2 resistance of MnO_x catalysts research and development to lay the theoretical foundation.

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