Mechanisms and Kinetics of MnO\textsubscript{x}-Based Catalysts at Low-Temperature Selective Catalytic Reduction of NO\textsubscript{x}

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Abstract. MnO\textsubscript{x} has become a focus in the research of low-temperature SCR De-NO\textsubscript{x} catalysts for its good catalytic activity. Many MnO\textsubscript{x}-based catalysts have been researched which all have a high selectivity low-temperature N\textsubscript{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\textsubscript{3} as the reducing agents and MnO\textsubscript{x} as the active centres. The overall reaction mechanism can be explained by L-H, E-R and Mars-van Krevelen mechanisms. H\textsubscript{2}O and SO\textsubscript{2} deactivation mechanism are also mentioned. The kinetics of SCR reaction of MnO\textsubscript{x} at low-temperature are studied based on power function, mechanism derivation and the combination of them.

Introduction

Selective catalytic reduction (SCR) denitrification technology is widely used in the industry, which basic principle is: NH\textsubscript{3}+NO+O\textsubscript{2} \rightarrow N\textsubscript{2}+H\textsubscript{2}O, the denitrification 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\textdegree C. In the high concentration of dust laden gas, the catalyst poisoning is easily caused by heavy metals and SO\textsubscript{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\textsubscript{x} is a focus in the research of low temperature denitrification catalysts. As the active component, Mn can provide more free electrons and oxygen vacancies, MnO\textsubscript{x}-based catalysts showed good low-temperature denitrification activity. According to the study by Peña et al.\textsuperscript{[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\textsubscript{2}O). Kapteijn et al.\textsuperscript{[2]} made a systematic study on single component MnO\textsubscript{x} of different valence states at 385K-575K, the result showed that the removal denitrification activity sequence of different valence state of MnO\textsubscript{x} is: MnO\textsubscript{2}>Mn\textsubscript{3}O\textsubscript{4}>Mn\textsubscript{2}O\textsubscript{3}>Mn\textsubscript{3}O\textsubscript{4}>MnO, Mn\textsubscript{2}O\textsubscript{3} showed the highest N\textsubscript{2} selectivity, and the denitrification efficiency of MnO\textsubscript{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 mainly on the removing NO\textsubscript{x} by NH\textsubscript{3} as the reducing agent as well as the H\textsubscript{2}O and SO\textsubscript{2} deactivation mechanism.

Mechanisms of NH\textsubscript{3} as the reducing agent. According to the current research, there are Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) mechanisms for NH\textsubscript{3}-SCR. Many researchers have found that the mechanism of Mars-van Krevelen may be in presence for the MnO\textsubscript{x} based low-temperature...
catalysts. E-R refers to the mechanism between NO\textsubscript{x} of gas phase and the adsorbed NH\textsubscript{3} reacts to form intermediates, and then decomposed into N\textsubscript{2} and H\textsubscript{2}O; L-H mechanism refers to the reactants (NO\textsubscript{x} and NH\textsubscript{3}) first adsorbed on the active site of the catalyst to form an intermediate, and then decomposed into N\textsubscript{2} and H\textsubscript{2}O. The E-R and L-H reaction mechanism shows that NH\textsubscript{3} is involved in the reaction of adsorption state, but the adsorption effect of NH\textsubscript{3} for different acid sites (Br\text{"{o}}nsted 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\textsubscript{3} is significant, high temperature Br\text{"{o}}nsted acid adsorption of NH\textsubscript{3} plays a main role.

The mechanisms and kinetics of Mn-Fe catalyst were studied by Yang et al.\cite{3}, the results shows that the reaction of (Fe\textsubscript{2.8}Mn\textsubscript{0.2})\textsubscript{1-\delta}O\textsubscript{4} catalyst surface was followed by L-H mechanism, and the mechanism of E-R was dominant at 200°C. For (Fe\textsubscript{2.8}Mn\textsubscript{0.2})\textsubscript{1-\delta}O\textsubscript{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.\cite{4} discussed the E-R mechanism of the low-temperature (125°C) selective catalytic reduction of NO with NH\textsubscript{3} over carbon-supported Mn\textsubscript{3}O\textsubscript{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.](image)

Kijlstra et al.\cite{5} studied the adsorption of NO and NH\textsubscript{3} on MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts, separately by use of TPD and FTIR, also investigated the influence of O\textsubscript{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

<table>
<thead>
<tr>
<th>Species</th>
<th>$v_3$/m$^{-3}$</th>
<th>$v_3'/m$</th>
<th>Desorption/decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrosyl</td>
<td>1835</td>
<td>1220</td>
<td>Mn$^{n+}$-N=O</td>
</tr>
<tr>
<td>Bridged nitrate</td>
<td>1620</td>
<td>1220</td>
<td>Mn$^{n+}$-O-Mn$^{n+}$-O</td>
</tr>
<tr>
<td>Bidentate nitrate type II</td>
<td>1290</td>
<td>1555</td>
<td>Mn$^{n+}$-O-N=O</td>
</tr>
<tr>
<td>Bridged nitrate type I</td>
<td>1580</td>
<td>1220</td>
<td>Mn$^{n+}$-N=O</td>
</tr>
<tr>
<td>Linear nitrite</td>
<td>1466</td>
<td>1075 ($v_3$)</td>
<td>Mn$^{n+}$-O-N=O</td>
</tr>
<tr>
<td>Monodentate Nitrite</td>
<td>1415</td>
<td>1322 ($v_3$)</td>
<td>Mn$^{n+}$-O</td>
</tr>
<tr>
<td>Bridged nitrite</td>
<td>1230</td>
<td></td>
<td>Mn$^{n+}$-O</td>
</tr>
</tbody>
</table>

**H$_2$O 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$_2$O(g). Whether the catalyst has excellent anti H$_2$O 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$_2$O 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$_2$O and SO$_2$ on MnO$_x$/Al$_2$O$_3$ catalyst. The results showed that the influence of water vapor (H$_2$O) 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$_2$O on Fe$_{0.75}$Mn$_{0.25}$TiO$_x$ catalyst. The results showed that the effect of H$_2$O 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](image_url)

Scheme 1. Proposed mechanism of the NH$_3$-SCR reaction over Mn substituted iron titanate 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 (NH4)2SO3 and NH4HSO4 leads to catalyst deactivation, which catalytic activity can be recovered by washing with water.

Kinetics

The kinetics of SCR reaction of MnOx at low temperature was studied based on power function, Mechanism derivation and the combination of them. Qi et al.\cite{9} studied the kinetics of MnOx-CeO2 catalyst which based on the power function equation ($反应速率 = k[N0][NH3][O2]$) at 120°C, the reaction order was calculated, the NH3, O2 and NO of the reaction series were 1, 0 and 0.5. Yang et al.\cite{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).

$$X = k_{calcid}[NO(ad)] \exp(-k_{calcid}t) + k_{calcid}[Mn^{4+}]$$

Conclusions and perspective

The adsorption of NO and NH3 at the surface of catalysts is very important for low-temperature selective catalytic reduction of NOx. Through various characterization techniques, we have a preliminary understanding of the mechanism of NH3-SCR reaction at low temperature. But at present, the MnOx-based catalyst is not good enough for the SO2 and H2O poisoning resistance, the H2O and SO2 inhibition mechanism is not yet fully mastered.

In future research, we need to deeply explore the adsorption and activation mechanism of NH3 and NO in MnOx catalysts, research clearly H2O and SO2 inhibition mechanism of MnOx catalysts, for high H2O and SO2 resistance of MnOx catalysts research and development to lay the theoretical foundation.

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References