CeO\textsubscript{2} $\square$ $\square$ MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} $\square$ $\square$ $\square$ SCR $\square$ $\square$ $\square$ $\square$ $\square$

Research on SCR Denitrification of MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} Modified by CeO\textsubscript{2} and Its Mechanism at Low Temperature

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Abstract: The Al\textsubscript{2}O\textsubscript{3}, which has large specific surface area and is used as carrier, was prepared by sol-gel method in this study. Series catalysts of MnO\textsubscript{x}, CeO\textsubscript{2} plus MnO\textsubscript{x} supported on Al\textsubscript{2}O\textsubscript{3} by isomorphous impregnation method. The SCR denitrification experimental conditions were as follows: NH\textsubscript{3} as reductive agent, certain gas velocity and suitable ratio of gas mixed was setup. Furthermore, the experiments of BET, XRD and SEM were also carried out respectively in order to obtain physicochemical properties of the prepared catalysts. The experimental results showed that the loading of active component and calcination temperature made a big difference to the catalysts’ performance. The experimental addition of CeO\textsubscript{2}, MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}, exhibits better activity and stability. For MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}, the catalytic activity on NO was greatly influenced by its loaded content, and 7% MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} showed superior catalytic activity among the MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}. The addition of CeO\textsubscript{2} could greatly improve the dispersibility of MnO\textsubscript{x}, on the carrier and increase its catalytic activity. The 4% CeO\textsubscript{2} addition was the optimum loaded mass percent. Furthermore, 550°C is the best calcination temperature, as MnO\textsubscript{x} formed different crystalline phases with temperature, at the same time, the addition of CeO\textsubscript{2} could affect MnO\textsubscript{x} crystalline phase. The catalytic mechanism of SCR on NO was also discussed.

Key words: selective catalytic reduction (SCR); NO; MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}; CeO\textsubscript{2}; low temperature denitrification


低胶温脱硝催化剂的制备
各种因素对脱硝性能的影响

减压蒸馏约和关键

材料与方法

在采用等体积浸渍法制备催化剂

称取适量异丙醇铝

配制合适的浓度比

将其浸渍于上述溶

再称取一定量的

异丙醇铝

催化剂在

焙烧

从而制得

载体

其成

速为

空速为

净化效率

的添加量有关

和

随着

负载量的增加

使

催化剂的研究及

内实验气体由钢瓶提供

出在所测试的催化剂中

实验气组配比


do

testo350XL

 Autosorb- IC/TCD Automatic Chemisorption &
 Physisorption Analyper; XRD; BRUKER D- 8 ADVANCE; SEM; HITACHI S-4800.

\[ \eta = \frac{c_{0,0} - c_{0,2}}{c_{0,0}} \times 100\% \] (1)
Table 1  BET results of catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>147.3</td>
</tr>
<tr>
<td>5% MnO₂/Al₂O₃</td>
<td>144.9</td>
</tr>
<tr>
<td>7% MnO₂/Al₂O₃</td>
<td>139.6</td>
</tr>
<tr>
<td>11% MnO₂/Al₂O₃</td>
<td>136.5</td>
</tr>
<tr>
<td>4% CeO₂-7% MnO₂/Al₂O₃</td>
<td>139.1</td>
</tr>
</tbody>
</table>

Catalyst's specific surface area decreases due to two possible reasons: (1) the active component is distributed on the surface or enters the micropores, causing a decrease in the specific surface area; (2) the active component reacts with the carrier to some extent, affecting the specific surface area.

After modifying the catalyst, when the same active component is loaded, its specific surface area is greater than that of the catalyst loaded with the active component alone. This may be due to the formation of a certain reaction between the two components, which maintains the stability of the carrier and plays a role in maintaining the high specific surface area of the catalyst, thus making the specific surface area of the modified catalyst higher than that of the unmodified catalyst. This may be due to the reaction with the carrier.

The XRD pattern of the modified catalyst and after reaction shows differences in the spectra. The specific surface area of MnO₂/Al₂O₃ in Fig. 1 is greater than that of the unmodified catalyst.

2.3 SEM

Fig. 2 (a)  Al₂O₃ SEM; (b)  7% MnO₂/Al₂O₃ SEM; (c)  4% CeO₂-7% MnO₂/Al₂O₃ SEM.

The effect of adding CeO₂ in the carrier can effectively promote the dispersion of MnO₂/Al₂O₃, leading to a significant change in its catalytic performance, which will be discussed in the following sections.

2.4 SCR
2.4.1 MnO<sub>x</sub> / Al<sub>2</sub>O<sub>3</sub>  

<table>
<thead>
<tr>
<th>MnO&lt;sub&gt;x&lt;/sub&gt; / Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>550°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO&lt;sub&gt;x&lt;/sub&gt; / Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NO</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>MnO&lt;sub&gt;x&lt;/sub&gt;</td>
<td></td>
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<td></td>
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</tbody>
</table>

2.4.2 CeO<sub>2</sub> / MnO<sub>x</sub> / Al<sub>2</sub>O<sub>3</sub>  

![Graph showing the effect of CeO<sub>2</sub> addition on NO conversion.](image)
条件下的化学反应式为

2NH_{3} + 4NO + O_{2} \rightarrow 4N_{2} + 6H_{2}O \quad (2)

该反应式表明，NH_{3} 和 NO 在氧气存在下反应生成 N_{2} 和 H_{2}O。该反应在某些酸性或碱性催化剂的作用下可以发生。

脱硝的最佳操作温度为

脱硝性能随着温度的升高而增加，但超过某一温度后，脱硝效率开始下降。脱硝效率递增明显。

催化剂焙烧温度对其脱硝性能的影响

催化剂焙烧温度对脱硝性能的影响比较大，通过催化剂的焙烧温度调整，可以得到最佳的脱硝性能。在不同焙烧温度下所制得的催化剂出现波动，尤其是催化剂表面反应机制分析。

在研究催化剂焙烧温度对其脱硝性能的影响时，也得出相似的结论。一般认为，随着温度的升高，催化剂的活性性会增强，但超过某一温度后，催化剂的活性性会下降，这将在后面进行讨论。

催化剂表面反应机制分析

对于催化剂表面反应机制大部分是在接近酸性或碱性条件下进行的。在这些条件下，NH_{3} 和 NO 反应生成 N_{2} 和 H_{2}O。该反应在某些酸性或碱性催化剂的作用下可以发生。NH_{3} 和 NO 反应的化学反应式为

4NH_{3} + 4NO + O_{2} \rightarrow 4N_{2} + 6H_{2}O \quad (2)

催化剂最大活性在 600°C 左右。对于不同焙烧温度下所制得的催化剂出现波动，究其原因，是反应金属氧化物催化还原过程的催化剂最大活性可达 80% ～ 90%。这将在后面进行讨论。

催化剂表面反应机制分析

催化剂最大活性在 600°C 左右。对于不同焙烧温度下所制得的催化剂出现波动，究其原因，是反应金属氧化物催化还原过程的催化剂最大活性可达 80% ～ 90%。这将在后面进行讨论。
2.85, Mn$_2$O$_3$, MnO$_2$,

MN$_2$O$_3$, MnO$_2$, CeO$_2$,

Mn$_2$O$_3$ + CeO$_2$ → 2MnO$_2$ + Ce$_2$O$_3$ (10)

Ce$_2$O$_3$ + 1/2O$_2$ → 2CeO$_2$ (11)

2MnO$_2$ + O$_2$ → 4MnO$_2$ (12)

NO + 2MnO$_2$ → NO$_2$ + Mn$_2$O$_3$ (13)

NO + 2MnO$_2$ + Mn$_2$O$_3$ → NO$_2$ + Mn$_2$O$_4$ (14)

2NO + 2MnO$_2$ + 3NH$_3$ → 2N$_2$ + 3H$_2$O + 2Mn$_2$O$_4$ (15)

2NO$_2$ + 4MnO$_2$ + 4NH$_3$ → 3N$_2$ + 6H$_2$O + 2Mn$_2$O$_3$ (16)

3

(1) MnO$_2$ + Al$_2$O$_3$, 7% MnO$_2$,

(2) CeO$_2$ + MnO$_2$ + Al$_2$O$_3$, 4% CeO$_2$,

(3) CeO$_2$, 550°C,

(4) CeO$_2$ + SCR,

Mn$_2$O$_3$, MnO$_2$,


[17] Qi G S, Yang R T. Performance and Kinetics study for low-


