Mn/CeO$_2$와 Mn/ZrO$_2$ 촉매 상에서 NH$_3$를 사용한 NO의 선택적 촉매 산화 반응

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Low Temperature Selective Catalytic Reduction of NO with NH$_3$ over Mn/CeO$_2$ and Mn/ZrO$_2$

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(Received October 25, 2011; Revised November 10, 2011; Accepted November 29, 2011)

본 연구에서는 저온에서 질소산화물 저감효율이 뛰어난 것으로 알려진 망간전구체의 종류에 따른 영향을 고찰하기 위해 초임계수열법으로 합성한 세리아(CeO$_2$)와 지르코니아(ZrO$_2$)를 담체로 하여 저온 SCR 공정에서의 온도에 따른 활성변화를 비교 분석하였다. Manganese acetate (MA)와 manganese nitrate (MN), 두 종류 망간전구체의 농도를 영향인 자로 고려하여 촉매의 활성변화를 고찰하였다. 활성화된 시료의 특성은 N$_2$ adsorption-desorption, TGA, XRD, XPS을 통해 분석하였고 질소산화물 저감효율을 측정하기 위해 NOx 분석기를 이용하여 De-NOx 실험을 수행하였다. 제조방법에 따라 합성한 촉매의 질소산화물 저감 효율을 분석한 결과 Manganese acetate (MA)를 활성물질로 사용한 촉매가 Manganese nitrate (MN)을 사용한 촉매에 비해 우수한 질소산화물 저감효율을 보였다. 이는 특성분석 결과를 통해 알 수 있듯이 Manganese acetate (MA)의 주성분인 Mn$_2$O$_3$가 Manganese nitrate (MN)의 주성분인 MnO$_2$에 비해 높은 산소 이동도를 갖고 담체와의 강한 상호작용을 형성하는 것에 기인한 것으로 보인다.

Manganese (Mn) catalysts were generated using CeO$_2$ and ZrO$_2$ supports synthesized by the supercritical hydrothermal method and two different Mn precursors, aimed at an application for a low-temperature selective catalytic reduction process. Manganese acetate (MA) and manganese nitrate (MN) were used as Mn precursors. Effects of the kind and the concentration of the Mn precursor used for catalyst generation on the NOx removal efficiency were investigated. The characteristics of the generated catalysts were analyzed using N$_2$ adsorption-desorption, thermo-gravimetric analysis, X-ray diffraction, and X-ray photoelectron spectroscopy. De-NOx experiments were carried out to measure NOx removal efficiencies of the catalysts. NOx removal efficiencies of the catalysts generated using MA were superior to those of the catalysts generated using MN at every temperature tested. Analyses of the catalyst characteristics indicated that the higher NOx removal efficiencies of the MA-derived catalysts stemmed from the higher oxygen mobility and the stronger interaction with support material of Mn$_2$O$_3$ produced from MA than those of MnO$_2$ produced from MN.

Keywords: De-NOx, SCR, Mn/CeO$_2$, Mn/ZrO$_2$, hydrothermal synthesis in supercritical water

1. Introduction

Stringent regulations are implemented all over the world to reduce NO$_x$ emissions from vehicles, power generation facilities, industrial facilities, and incinerators, fostering extensive research and development for treatment and reduction of NO$_x$. Among a number of available technologies to reduce NO$_x$, contained in exhaust gas from stationary emission sources such as incinerators and thermal power stations, selective catalytic reduction (SCR) is known to be the best technology in the technical and economical aspects, being used extensively all over the world. In SCR processes, NO$_x$ is reduced into non-toxic gases, N$_2$ and H$_2$O, by using reducing agents such as NH$_3$, urea, and hydrocarbons[1-3].

Various metal oxides (Mn, Ni, Cu, Cr, V and Fe) have been applied as the catalytic material for development of low-temperature SCR catalysts[4,5]. In particular, manganese is known to be superior to
The supercritical hydrothermal synthesis process is a method for fast and continuous generation of metal oxide nanoparticles. Homogeneous mixed metal oxide with high crystallinity can be easily generated by the supercritical hydrothermal method and the produced oxides usually have improved oxygen storage characteristics and thermal stability. Therefore, it is expected that a high-efficiency catalyst applicable for low-temperature SCR process can be developed if a support material generated by the supercritical hydrothermal method is impregnated by manganese that is known to have high catalytic activity at low temperature[1]. The coherence between impregnated manganese and the support material and formation of active sites, which are closely related to NO removal efficiency, depend on the manganese precursor used and the synthesis method.

In this study, manganese oxide-based catalysts were prepared by using CeO$_2$ and ZrO$_2$ support produced with supercritical method and two kinds of manganese precursors, Mn(CH$_3$COO)$_2$ (manganese acetate) and Mn(NO$_3$)$_2$ (manganese nitrate). The characteristics of these catalysts were investigated using N$_2$ adsorption-desorption, thermogravimetric analysis (TGA), and X-ray diffraction (XRD). SCR experiments were carried out using NH$_3$ as the reducing agent to measure the NO removal efficiency of the prepared catalysts.

### 2. Experimental

In this study, two kinds of MnO$_x$ were impregnated using the incipient wetness impregnation method on a CeO$_2$ and ZrO$_2$ support produced with supercritical method[6]. Mn(CH$_3$COO)$_2$ (Aldrich, 99%+) and Mn(NO$_3$)$_2$ (Aldrich, 98%) were used as the manganese precursors. Three different concentrations (5, 10, and 15 wt%) of Mn precursors were added to the support and the produced catalysts were calcined for 3 h at 550 °C in the air. The MnO$_x$/CeO$_2$ or ZrO$_2$ catalysts generated using manganese acetate (MA) and manganese nitrate (MN) will be referred to as MA-MnO$_x$ (concentration)/CeO$_2$ or ZrO$_2$ and MN-MnO$_x$ (concentration)/CeO$_2$ or ZrO$_2$, respectively, hereafter corresponding to the kind and the concentration of the manganese precursor used and the calcination temperature.

Specific surface areas of the generated catalysts were analyzed by measuring the N$_2$ adsorption-desorption at -196 °C with Sorptomatic 1990 (Thermo) after pretreating the catalysts at 150 °C under the vacuum condition. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area from the adsorption-desorption isotherms. X-ray photoelectron spectroscopy (XPS) measurements were performed using a AXIS-NOVA (Kratos. Inc). A monochromatic Al Kα (1486.6 eV) of X-ray source and 40 eV of analyzer pass energy were used in ultra high vacuum condition (5.2 × 10$^{-9}$ Torr). An XRD analyzer (Rigaku D/MAX-III) was used to investigate the crystalline phase of MnO$_x$ impregnated on the catalysts. Cu Kα X-ray source was used with the scan range of 0° ~ 90° and the step size of 0.02°. TGA was carried out to measure the reduction of mass of manganese impregnated on the catalyst depending on temperature and to identify the kind of the impregnated manganese oxide. Pyris 1 thermo-gravimetric analyzer (PerkinElmer) was used for the analysis increasing the temperature from room temperature to 700 °C with the rising rate of 5 °C/min under a N$_2$ flow rate of 50 mL/min.

In order to measure the NO removal efficiency of the prepared catalysts, a stainless steel reactor with an inner diameter of 260 mm and a height of 1500 mm was fabricated. The upper and lower spaces of the catalyst layer in the reactor were filled with quartz wool to minimize the channeling phenomenon and to fasten the catalyst layer. The inlet gas was composed of NO, N$_2$, O$_2$, and NH$_3$ with its flow rate controlled by a mass flow controller (Sierra Instruments, Inc, & Hi-Tec co.). The inlet concentrations of NO, NH$_3$, and O$_2$ were controlled at 1000, 1000 ppm, and 5 vol.% respectively. The ratio of the amount of catalyst sample and the inlet gas flow rate (W/F) was set at 5 g min/L (SV ≈ 12000 hr$^{-1}$). A bypass line was added to measure the NO concentration of the inlet gas. The inlet and outlet NO concentrations were measured by a NO$_x$ analyzer (42i-HL, Thermo Ins). The NO$_x$ removal efficiency was calculated by the following equation:

$$\text{NO}_x \text{Removal Efficiency} (\%) = 100 \times \frac{C_{NO_x}^p - C_{NO_x}^c}{C_{NO_x}^p}$$

where $C_{NO_x}^p$ and $C_{NO_x}^c$ are the inlet and the outlet NO concentrations, respectively.

### 3. Results and Discussion

Table 1 shows the specific surface areas and compositions of the catalysts used in this study. The specific surface area of the pure CeO$_2$ others in terms of their activity and cost-effectiveness at lower temperature[1-3].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Atomic surface concentration obtained by XPS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CeO$_2$</td>
<td>52.3</td>
<td>-</td>
</tr>
<tr>
<td>MA-MnO$_x$(0.05)/CeO$_2$ (550)</td>
<td>43.2</td>
<td>54.11</td>
</tr>
<tr>
<td>MA-MnO$_x$(0.10)/CeO$_2$ (550)</td>
<td>39.5</td>
<td>52.98</td>
</tr>
<tr>
<td>MA-MnO$_x$(0.15)/CeO$_2$ (550)</td>
<td>37.8</td>
<td>54.53</td>
</tr>
<tr>
<td>MN-MnO$_x$(0.05)/CeO$_2$ (550)</td>
<td>46.7</td>
<td>53.11</td>
</tr>
<tr>
<td>MN-MnO$_x$(0.10)/CeO$_2$ (550)</td>
<td>40.2</td>
<td>54.73</td>
</tr>
<tr>
<td>MN-MnO$_x$(0.15)/CeO$_2$ (550)</td>
<td>39.6</td>
<td>57.45</td>
</tr>
<tr>
<td>Pure ZrO$_2$</td>
<td>89.3</td>
<td>-</td>
</tr>
<tr>
<td>MA-MnO$_x$(0.05)/ZrO$_2$ (550)</td>
<td>86.4</td>
<td>55.14</td>
</tr>
<tr>
<td>MA-MnO$_x$(0.10)/ZrO$_2$ (550)</td>
<td>79.8</td>
<td>53.13</td>
</tr>
<tr>
<td>MA-MnO$_x$(0.15)/ZrO$_2$ (550)</td>
<td>75.3</td>
<td>52.00</td>
</tr>
<tr>
<td>MN-MnO$_x$(0.05)/ZrO$_2$ (550)</td>
<td>84.1</td>
<td>54.76</td>
</tr>
<tr>
<td>MN-MnO$_x$(0.10)/ZrO$_2$ (550)</td>
<td>78.6</td>
<td>54.34</td>
</tr>
<tr>
<td>MN-MnO$_x$(0.15)/ZrO$_2$ (550)</td>
<td>72.8</td>
<td>52.65</td>
</tr>
</tbody>
</table>
support was 52.3 m$^2$/g. When 5, 10, and 15% of MA precursor was impregnated, its specific surface area decreased to 43.2, 39.5, and 37.8 m$^2$/g, respectively. Similarly, when 5, 10, and 15% of MN precursor was impregnated on the CeO$_2$ support, the specific surface area decreased to 46.7, 40.2, and 39.6 m$^2$/g, respectively. Similar trend was observed when ZrO$_2$ was used as the support material. The specific surface area of the pure ZrO$_2$ support was 89.3 m$^2$/g. When 5, 10, and 15% of MA precursor was impregnated, its specific surface area decreased to 86.4, 79.8, and 75.3 m$^2$/g, respectively, whereas it decreased to 84.1, 78.6, and 72.8 m$^2$/g when 5, 10, and 15%, respectively, of MN precursor was used. These results indicate that impregnation of MnO$_x$ on the support clogged the pores of the support reducing the surface area.

The quantitative analysis of catalyst surface composition using XPS showed that the Mn content of MA-MnO$_x$/CeO$_2$ increased with the precursor concentration. Similar trend was shown for the case of MN-MnO$_x$/CeO$_2$ except that the Mn content obtained with 10% precursor concentration was a little lower than that obtained with 5% precursor concentration. The Mn content of MA-MnO$_x$/ZrO$_2$ was consistently higher than that of MN-MnO$_x$/CeO$_2$. When ZrO$_2$ was used as the support material, the Mn contents of both MA-MnO$_x$/ZrO$_2$ and MN-MnO$_x$/ZrO$_2$ increased with the precursor concentration. Similar to the case of CeO$_2$, the Mn content of MA-MnO$_x$/ZrO$_2$ was generally higher than that of MN-MnO$_x$/ZrO$_2$. The higher Mn content obtained with MA precursor can be attributed to better dispersion of MnO$_x$.

Figure 1 shows the results of XRD analyses conducted to investigate
Figure 3. TG curve profiles of MnO\textsubscript{x}/CeO\textsubscript{2} catalysts.

Figure 4. TG curve profiles of MnO\textsubscript{x}/ZrO\textsubscript{2} catalysts.

the crystalline phase of MnO\textsubscript{x} impregnated on CeO\textsubscript{2} surface. As is shown in this figure, MA-MnO\textsubscript{x}/CeO\textsubscript{2} exhibited peaks at $2\theta = 28.7^\circ$, 47.8°, and 56.6°, which is ascribed to the effect of the support. As the concentration of the Mn precursor increased, the intensity of the peak appearing at 36.2°, which represents Mn\textsubscript{2}O\textsubscript{3}, increased[7,8]. For the case of MN-MnO\textsubscript{x}/CeO\textsubscript{2}, the intensity of the peak appearing at $2\theta = 37.8^\circ$, which represents MnO\textsubscript{2}, increased with the concentration of the precursor[9-11]. Figure 2 shows the XRD analysis results for MnO\textsubscript{x}/ZrO\textsubscript{2}. Both ZrO\textsubscript{2}-based catalysts exhibited peaks at $2\theta = 28.1^\circ$, 31.5°, and 50°, which is attributed to the effect of the support material. Similar to the case of MnO\textsubscript{x}/CeO\textsubscript{2}, when MA was used as the precursor, a Mn\textsubscript{2}O\textsubscript{3} peak appeared at 36.2°, whereas in the case of MN-MnO\textsubscript{x}/ZrO\textsubscript{2}, a MnO\textsubscript{2} peak appeared at $2\theta = 37.8^\circ$.

The MnO\textsubscript{x} can also be identified indirectly by observing the mass
Mn/CeO\(_2\) and Mn/ZrO\(_2\) catalysts showed peaks appearing at four different binding energy levels. Identification and quantification of MnO\(_x\) formed on the surface of MN-MnO\(_x\) catalysts could be done using deconvolution technique. Although the intensity varied with the precursor concentration, the two peaks appearing at 641.1 eV (±0.2 eV) and at 642.3 eV (±0.2 eV) are believed to be due to the effect of MnO\(_2\) as shown in the XRD result\[11-14\]. The third peak appearing at 643.7 eV (±0.2 eV) represents Mn-nitrate\[11,12\], which is due to the nitrate species that were not decomposed during the calcination process. The last peak of MN-MnO\(_x\) catalysts is the MnO\(_3\) peak appearing at 641.5 eV (±0.2 eV), which is believed to be due to conversion of MnO\(_2\), the main crystal phase of MN, into MnO\(_3\) during the calcination process.

Figure 7 compares the NO\(_x\) removal efficiencies obtained using MA-MnO\(_x\)/CeO\(_2\) and MN-MnO\(_x\)/CeO\(_2\) at different temperatures. MA-MnO\(_x\)/CeO\(_2\) exhibited a higher NO\(_x\) removal efficiency than MN-MnO\(_x\)/CeO\(_2\) at every temperature tested regardless of the precursor concentration\[12,15\]. The efficiency of MA-MnO\(_x\)/CeO\(_2\) increased with the precursor concentration at every temperature. As the temperature increased, the efficiency of MA-MnO\(_x\)/CeO\(_2\) increased rapidly until the rate of

\[2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \text{O}^{2-}\]
increased considerably from 125 °C. The NO\textsubscript{x} removal efficiency of MA-MnO\textsubscript{x}(15)/CeO\textsubscript{2}(550), which showed the best performance among the CeO\textsubscript{2}-based catalysts tested in this study, was 20% at 50 °C, increased rapidly reaching 81% at 125 °C, and continued to increase slowly to reach 91% at 200 °C. MN-MnO\textsubscript{x}/CeO\textsubscript{2} also showed increasing NO\textsubscript{x} removal efficiency with precursor concentration at every temperature. However, the temperature dependency of the efficiency of MnO\textsubscript{x} was a little different from that of MA-MnO\textsubscript{x}/CeO\textsubscript{2}; the rapidst increase of the efficiency appeared within the temperature range of 100 ∼ 150 °C. The NO\textsubscript{x} removal efficiency of MN-MnO\textsubscript{x}(15)/CeO\textsubscript{2}(550), which showed the best performance among the MN-MnO\textsubscript{x}/CeO\textsubscript{2} catalysts, was 16, 57, and 80% at 50, 125, and 200 °C.

Figure 8 compares the NO\textsubscript{x} removal efficiencies obtained using MA-MnO\textsubscript{x}/ZrO\textsubscript{2} and MN-MnO\textsubscript{x}/ZrO\textsubscript{2}. Similar to the case of CeO\textsubscript{2}-based catalysts, MA-MnO\textsubscript{x}/ZrO\textsubscript{2} showed a higher NO\textsubscript{x} removal efficiency than MN-MnO\textsubscript{x}/ZrO\textsubscript{2} at every temperature tested. The NO\textsubscript{x} removal efficiency of MA-MnO\textsubscript{x}(15)/ZrO\textsubscript{2}(550), which showed the best performance among all the catalysts tested in this study, was 26% at 50 °C, increased rapidly reaching 88% at 125 °C, and continued to increase slowly to reach 91% at 200 °C. MN-MnO\textsubscript{x}/ZrO\textsubscript{2} also showed increasing NO\textsubscript{x} removal efficiency with precursor concentration over the whole temperature range. The NO\textsubscript{x} removal efficiency of MN-MnO\textsubscript{x}(15)/ZrO\textsubscript{2}(550), which showed the best performance among the MN-MnO\textsubscript{x}/ZrO\textsubscript{2} catalysts, was 21, 54, and 80% at 50, 125, and 200 °C.

4. Conclusions

In this study, the NO\textsubscript{x} removal efficiencies of MnO\textsubscript{x} catalysts generated by using CeO\textsubscript{2} and ZrO\textsubscript{2} supports and two kinds of Mn precursors for low-temperature SCR process were measured at various temperatures. The effects of the kind and concentration of Mn precursors were investigated. XRD analysis showed that the major crystalline phase of MN-MnO\textsubscript{x} catalysts generated by using Mn(NO\textsubscript{3})\textsubscript{2} as the precursor was MnO\textsubscript{x} mixed with small amounts of Mn(NO\textsubscript{3})\textsubscript{2} and Mn\textsubscript{3}O\textsubscript{4}. When Mn(CH\textsubscript{3}COO)\textsubscript{2}\textsubscript{2} was used as the precursor, the major crystalline phase of the resulting MA-MnO\textsubscript{x} catalysts was Mn\textsubscript{6}O\textsubscript{13}. It was shown by XPS analysis that the surface Mn contents and binding energies of MA-MnO\textsubscript{x} catalysts were higher than those of MN-MnO\textsubscript{x} catalysts. Correspondingly, the NO\textsubscript{x} removal efficiencies of MA-MnO\textsubscript{x} catalysts were higher than those of MN-MnO\textsubscript{x} catalysts at every temperature tested in this study. Both kinds of catalysts showed increasing trend of NO\textsubscript{x} removal efficiency with increasing precursor concentration. The results of this study indicate that the NO\textsubscript{x} removal efficiency is dependent on the major crystalline phase and the amount of MnO\textsubscript{x} formed on the support as well as on the interaction between the support material and precursor.

Acknowledgement

This work was supported by Korea Sanhak Foundation.

References

Mn/CeO$_2$와 Mn/ZrO$_2$ 촉매 상에서 NH$_3$를 사용한 NO의 선택적 촉매 산화 반응

855 (2000).


