Catalytic Activity and Surface Characteristics of WO3-doped MnOx-TiO2 Catalysts for Low-temperature Selective Catalytic Reduction of NOx with NH3

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Abstract: The effect of added WO3 on the catalytic activity and surface characteristics of the MnOx-TiO2 system was investigated for the low-temperature selective catalytic reduction of NOx with NH3. Based on physio-chemical characterizations, the specific surface areas of the WO3-MnOx-TiO2 catalysts increased from 76.12 m²/g to 90.29 m²/g as the WO3 content increased, and the crystallinity of the anatase TiO2 phase decreased. The NOx conversion efficiency of the WO3-MnOx-TiO2 catalysts with WO3 content was over 70% at 200 °C, and their efficiency was over 90% at 300 °C. The results of Fourier transform infrared spectroscopy indicated that the 1438 and 1632 cm⁻¹ values, which were assigned to Lewis and Brønsted acid sites, increased with the increase in WO3 content. The enhanced catalytic acidity originated from changes to the physical and chemical structures on the surface. MnOx formed on the TiO2 surface of the 15 wt% WO3-doped MnOx-TiO2, and amorphous state Mn2O3 (Mn3+) and WO3 (W6+) existed on the surface, which led to the improved Lewis and Brønsted acid sites, respectively.

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1. INTRODUCTION

Selective catalytic reduction (SCR) using an ammonia/urea reductant is the most promising technology for controlling NOx (NO + NO2) emissions from automobiles and stationary sources, due to its low cost and high efficiency [1-3]. To avoid additional expense and the reheating of flue gases after desulfurization and electrostatic precipitation in an SCR system, highly active catalysts for low-temperature SCR applications need to be developed [4,5]. Although conventional V2O5-based catalysts have superior catalytic activity and are SO2-resistant, their narrow temperature window of 300-400 °C, and the toxicity of vanadium pentoxide, are significant obstacles to the adoption of low-temperature SCR in a variety of applications [6-8].

Manganese oxide-based catalysts, including Mn-TiO2, Mn-Fe-TiO2, and Mn-Al2O3, have attracted considerable interest for a number of catalytic applications, due to their unique redox properties at low temperatures [7-9]. These catalysts have high activity and selectivity for NO and NO2 reduction, as well as low SO2 poisoning resistance in the presence of small amounts of SO2. Mn-based catalysts with a transition metal (Fe, Cu, Zr, and W) and rare-earth (Pr, Ce) oxides have been widely studied to improve catalytic activity and durability [10-12].

WO3 is among the relatively low cost and high acid intensity transition metal oxides used as a promoter [13-15], and it exhibits superior thermal stability and N2 selectivity compared to V2O5-based catalysts, and also extends the temperature window of the SCR reaction [16,17]. However, it is not well understood how WO3 affects MnOx-based catalysts at low-temperatures, and thus research on the composition and structure of the catalyst surface is needed. In the current study, WO3-MnOx-TiO2 catalysts were synthesized by the sol-gel method to confirm their catalytic activity and surface characteristics, based on their WO3 content. The catalysts were characterized by physio-chemical and spectroscopy analysis, and the catalytic acid sites and physical and chemical states on their surface were investigated to determine the effect of WO3 additives on SCR catalysts.
Table 1. Physical characteristics of MnOx-TiO2 catalysts with various WO3 content.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>75.1</td>
<td>0.21</td>
<td>10.7</td>
</tr>
<tr>
<td>MnOx-TiO2</td>
<td>47.2</td>
<td>0.08</td>
<td>7.5</td>
</tr>
<tr>
<td>5 wt% WO3-MnOx-TiO2</td>
<td>76.1</td>
<td>0.19</td>
<td>10.7</td>
</tr>
<tr>
<td>10 wt% WO3-MnOx-TiO2</td>
<td>81.3</td>
<td>0.19</td>
<td>9.5</td>
</tr>
<tr>
<td>15 wt% WO3-MnOx-TiO2</td>
<td>90.3</td>
<td>0.18</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of WO3-MnOx-TiO2 catalysts calcined at 500 °C.

3. RESULTS AND DISCUSSION

3.1. Catalysts characterization

Table 1 presents the data for the Brunauer-Emmett-Teller (BET) specific surface area, pore volumes, and average pore sizes of the WO3-MnOx-TiO2 catalysts that contained WO3. The specific surface areas of the TiO2 and MnOx-TiO2 catalysts were 75.14 and 47.26 m²/g, and that of the 15 wt% WO3-doped catalyst was increased to 90.29 m²/g. The pore volume and the average pore size of the catalysts were measured to be 0.18-0.19 cm³/g and 9.09-10.70 nm, respectively. Generally, MnOx improves sinterability, and decreases specific surface area, by promoting the mass transport process. However, the addition of WO3 resulted in an enhancement of the specific surface area because it improved the dispersion of MnOx and inhibited the growth of TiO2 particles in the sol-gel reaction.

Based on the XRD characterization, as shown in Fig. 1, the broad diffraction lines of anatase phase TiO2 were dominantly present in all catalysts. The XRD profile of the MnOx-TiO2 catalysts showed that they existed in two crystalline/amorphous states, and that the main peaks at 2θ = 25.3°, 48.1°, 54.5° of TiO2 (anatase) decreased with WO3 content, which indicates a decrease in the crystallinity of these catalysts. This observation suggests that both the crystallinity and the phase transformation of TiO2 were suppressed by the addition of absorption spectra of the WO3-MnOx-TiO2 catalysts were determined through Fourier transform infrared spectroscopy (FT-IR) analysis (NH3 atmosphere, wave number 2000-1000 cm⁻¹, Nicolet 6700, Thermo Scientific, USA). The de-NOx efficiency measurements over synthesized catalysts were carried out using a quartz tubular fixed bed reactor, over a temperature range of 100-400 °C. A simulated reaction stream, consisting of 1000 ppm NO, 1000 ppm NH3, 5 vol% O2, and an N2 balance, was fed into the reactor system through mass flow controllers at a gas hourly space velocity of 10,000 h⁻¹. Raman spectroscopy (Ar-Ion laser-514nm, Raman System 2000, Renishaw, UK) and XPS analysis (VG scientific ESCALAB250 XPS system, UK) were used to identify the structure and valence state of the catalysts.

2. EXPERIMENTAL PROCEDURE

MnOx-TiO2 catalysts with 5-15 wt% WO3 contents were prepared by a sol-gel method, using manganese (II) nitrate hydrate (Mn(NO3)2·xH2O, 99.98%, Alfa Aesar, 20 wt% MnOx); ammonium metatungstate ((NH4)10(W12O41)·xH2O); and titanium tetra-isopropoxide (TTIP, 96%, Aldrich). The slurries were dried in an oven at 70 °C for 24 h to obtain catalysts with WO3 contents of 5, 10, and 15 wt%. The calcination for the catalysts was carried out using a muffle furnace that maintained a constant temperature of 500 °C for 3 h. The Brunauer-Emmett-Teller (BET) surface area of the WO3-MnOx-TiO2 catalysts with different WO3 contents was determined through N2 adsorption (ASAP2010, Micromeritics, USA). X-ray diffraction (XRD) patterns were measured on an X-ray diffractometer (M18XHF, MAC Science, Netherlands) using Cu Kα radiation. The IR
Fig. 2. SEM images of MnO<sub>x</sub>-TiO<sub>2</sub> catalysts with (a) 5 wt%, (b) 10 wt%, (c) 15 wt% WO<sub>3</sub> content calcined at 500 °C.

Fig. 3. Comparison of NO<sub>x</sub> conversion efficiency with NH<sub>3</sub> over MnO<sub>x</sub>-TiO<sub>2</sub> and WO<sub>3</sub>-MnO<sub>x</sub>-TiO<sub>2</sub> with WO<sub>3</sub> content.

WO<sub>3</sub> as a structure promoter [18-20].

The XRD patterns also revealed that the characteristic diffraction lines of WO<sub>3</sub> and MnO<sub>x</sub> were not detected in any of the catalysts up to 15 wt% WO<sub>3</sub> loading. This indicates that the tungsten and manganese oxides were highly dispersed on the surface of the TiO<sub>2</sub>, and that they were either in an amorphous state or were poorly crystalline at the calcination temperature of 500 °C. Considering the existence of the amorphous phase, the adsorbed oxygen on these manganese and tungsten oxides would be expected to participate in the SCR reaction.

Fig. 2 shows the surface morphology of the catalysts, with increasingly suppressed grain growth and agglomeration as the WO<sub>3</sub> contents were increased. The MnO<sub>x</sub>-TiO<sub>2</sub> catalysts with 5 wt% WO<sub>3</sub> had abnormal grain growth (Fig. 2(a)). No visible tungsten oxides phase could be observed at low loadings. This may be due to the low crystallinity of the metal oxides. The crystal phase of the catalysts became apparent as the WO<sub>3</sub> loading was increased. It has been considered that the WO<sub>3</sub> catalyst increased well-ordered crystalline planes by concentrating manganese loading on the surface of the MnO<sub>x</sub>-TiO<sub>2</sub> catalysts, and suppressed grain growth.

### 3.2. Catalytic activity

To apply the low-temperature NH<sub>3</sub>-SCR catalysts, the NO<sub>x</sub> conversion efficiencies of the promising MnO<sub>x</sub>-TiO<sub>2</sub> and WO<sub>3</sub>-MnO<sub>x</sub>-TiO<sub>2</sub> catalysts were evaluated in the temperature range from 100-400 °C under the condition of GHSV = 10,000 h<sup>-1</sup>, and the results are illustrated in Fig. 3. The catalytic activity of the MnO<sub>x</sub>-TiO<sub>2</sub> catalyst showed 88% efficiency at 300 °C, and activity of the WO<sub>3</sub>-MnO<sub>x</sub>-TiO<sub>2</sub> catalysts showed over 90% efficiency at 300-400 °C. The de-NO<sub>x</sub> efficiency of MnO<sub>x</sub>-TiO<sub>2</sub> at 400 °C was 3-5% lower than its efficiency at 300 °C, whereas the efficiency of the WO<sub>3</sub>-doped catalyst increased by 2% under identical temperatures. Among all the catalysts tested, the addition of 15 wt% WO<sub>3</sub> to the MnO<sub>x</sub>-TiO<sub>2</sub> catalyst produced a promoting effect over the whole temperature range, and the NO<sub>x</sub>
conversion was nearly 10% higher than that of the MnOx-TiO2 catalyst at 200 °C. It was previously reported that MnOx species are available to the SCR reaction in the low-temperature range of 150-250 °C, but they had lower thermal stability against phase transition and salts formation [6,16]. Therefore, it is expected that WO3 affects the catalytic activity and thermal stability of the MnOx species on the TiO2 surface by suppressing phase transition and grain growth at low-temperatures.

These results demonstrated that the designed catalyst exhibits better catalytic activity and thermal stability than previously reported catalysts [18,21] in the low-temperature region (100-400 °C) because the tungsten oxide species are structural and chemical promoters for the SCR reaction [12]. Furthermore, they are cost competitive with the NH3-SCR catalysts [13]. In a previous study [21], the WO3 species did not significantly improve the catalytic activity of SCR catalysts at low-temperature for the NOx reduction by NH3. However, the WO3-doped MnOx-TiO2 catalysts in this study exhibited higher NOx conversion efficiency than the MnOx-TiO2 and WO3-TiO2 catalysts. The combination of WO3 and MnOx can lead to the surface characteristics and redox properties of a MnOx-TiO2 matrix in the SCR reaction, as can be observed in Figs. 4, 5, and 6. As a co-catalyst the WO3 species can enhance the de-NOx efficiency and the temperature window of MnOx due to its high acid sites [22,23]. As a result, the MnO2-TiO2 catalysts containing more than 10 wt% tungsten oxides had improved thermal stability and catalytic activity in low-temperature SCR reaction conditions.

To identify the synergistic effects between WO3 and MnOx on redox behaviors, the surface characteristics and physico-chemical properties of the SCR catalysts were investigated over a wide temperature window.

3.3. Spectroscopic analyses

The FT-IR spectra in Fig. 4 show a band at around 1632 cm⁻¹, which was ascribed to (-NH2) species bound to Lewis acid sites, and a band at around 1438 cm⁻¹ which was assigned to the asymmetric and symmetric bending vibrations of NH4+ species that are bound to Brønsted acid sites. As the WO3 loading percentage increased to 5 and 15 wt%, the intensity of the bands assigned to the Lewis and Brønsted acid sites were increased by the enhancement of NH3 adsorption. Moreover, the catalytic acid sites of the 15 wt% WO3-doped catalysts possess abundant catalytic acid sites, in comparison with those of the 5, 10 wt% MnOx-TiO2 catalysts. This fact suggests that the addition of WO3 affects the composition and structure of the catalysts on the surface.

The surface characteristics of the WO3-MnOx-TiO2 catalysts with WO3 content were estimated by Raman measurement. The peaks of the anatase TiO2 located around
Fig. 6. XPS spectra of WO₃-MnOₓ-TiO₂ with various WO₃ content: (a) Mn2p (b) W4f.

636, 512, and 400 cm⁻¹ are shown in Fig. 5. The broad bands which range from 590 to 700 cm⁻¹ were ascribed to the existence of polymeric manganese oxide species, which were tetrahedrally and octahedrally coordinated [8]; their intensity increased with the increase in WO₃ content. The Raman spectra show that the formation and growth of grains was considerably suppressed in the MnOₓ-TiO₂ catalysts with 15 wt% WO₃ content, as compared to the catalysts with 5 wt% WO₃ content. The WO₃ peaks on the TiO₂ surface appeared as surface types of octahedral (polytungstate species, 965 cm⁻¹) and tetrahedral (WO₄²⁻, 935 cm⁻¹) sites, but their peaks were not identified up to 15 wt% WO₃ content as shown in Fig. 4. This may be attributed to their high degree of dispersion in the TiO₂ catalyst, and they were either in an amorphous state or were poorly crystalline.

The WO₃-MnOₓ-TiO₂ catalysts were investigated by X-ray photoelectron spectroscopy to identify the chemical composition of their surface and the valence states of the manganese and tungsten oxides. Two main peaks of Mn 2p３/２ and Mn 2p₁/２ were observed, which ranged from 628 eV to 663 eV. It was found that the 2p３/２ binding energies of metallic Mn (Mn⁰) and MnO₂ (Mn⁴⁺) were 641.2 eV and 642.2 eV, respectively [9]. As shown in Fig. 6, the catalysts with 15wt% WO₃ content showed a peak-shift, which indicates the existence of Mn₂O₃. It is well known that Mn₂O₃ is more amorphous than MnO₂ [24-26], which implies a reason for the difficulty of its detection by XRD. The amorphous Mn₂O₃ was determined to be mainly present on the catalyst surface, which can be attributed to the oxygen-rich concentration. Therefore, the addition of WO₃ could affect the thermal stability of the MnOₓ-TiO₂ catalysts, which leads to their enhanced catalytic activity.

Fig. 6(b) shows the binding energy of the W4f electron from 31-38 eV, which indicates that the binding energies of W⁶⁺, W⁴⁺, and W(0) were 36.6, 34, and 32.4 eV, respectively [27]. The intensities of the catalysts with 5 and 10 wt% WO₃ were similar, but those of the catalyst with 15 wt% WO₃ showed a peak-shift to 36.6 eV, which suggests the existence of WO₃. Consequently, with the addition of 15 wt% WO₃, MnOₓ exists on the catalyst surface, according to the Raman spectroscopy, and the amorphous state Mn₂O₃ (Mn³⁺) and WO₃ (W⁶⁺) were more abundant than the others, which indicates an increase in the Lewis and Brønsted acid sites.

4. CONCLUSIONS

The physico-chemical properties of selected catalysts were investigated to determine the effects of added WO₃ on the catalytic activity and surface characteristics of the MnOₓ-TiO₂ system for low-temperature NH₃-SCR. The specific surface areas of the WO₃-MnOₓ-TiO₂ catalysts were 17% and 48% greater than those of the TiO₂ and MnOₓ-TiO₂ catalysts, respectively. The de-NOₓ efficiency of a WO₃-MnOₓ-TiO₂ catalyst was improved by the increase in WO₃ content: it showed over 90% efficiency in the
temperature range of 300-400 °C. The 15 wt% WO3-doped MnOx-TiO2 catalyst exhibited higher activity than the others over the whole temperature range of 100-400 °C, due to the enhancement of Lewis and Brønsted acid sites, which were measured by FT-IR spectroscopy. The Raman and XPS results indicated that MnOx formed on the surface of the TiO2, and its enhanced surface coverage can account for the high catalytic acidity. The 15 wt% WO3-MnOx-TiO2 catalyst had well-dispersed amorphous state Mn2O3 (Mn3+) and WO3 (W6+) on the catalyst surface, which resulted in the high catalytic activity observed for these NH3-SCR catalysts.

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