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

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Abstract: The effect of added WO₃ on the catalytic activity and surface characteristics of the MnO_x-TiO₂ system was investigated for the low-temperature selective catalytic reduction of NO_x with NH₃. Based on physio-chemical characterizations, the specific surface areas of the WO₃-MnO_x-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 NO_x conversion efficiency of the WO₃-MnO_x-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. MnO_x formed on the TiO₂ surface of the 15 wt% WO₃-doped MnO_x-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 NO_x (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 MnO_x-based catalysts at low-temperatures, and thus research on the composition and structure of the catalyst surface is needed. In the current study, WO₃-MnO_x-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.

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Table 1. Physical characteristics of MnO_x-TiO₂ catalysts with various WO₃ content.

Samples	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
TiO ₂	75.1	0.21	10.7
MnO _x -TiO ₂	47.2	0.08	7.5
5 wt% WO ₃ -MnO _x -TiO ₂	76.1	0.19	10.7
10 wt% WO ₃ -MnO _x -TiO ₂	81.3	0.19	9.5
15 wt% WO ₃ -MnO _x -TiO ₂	90.3	0.18	9.1

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

2. EXPERIMENTAL PROCEDURE

MnO_x-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% MnO_x); 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-MnO_x-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

absorption spectra of the WO₃-MnO_x-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-NO_x 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.

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-MnO_x-TiO₂ catalysts that contained WO₃. The specific surface areas of the TiO₂ and MnO_x-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, MnO_x 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 MnO_x 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 MnO_x-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

Fig. 2. SEM images of $\text{MnO}_x\text{-TiO}_2$ catalysts with (a) 5wt %, (b) 10 wt%, (c) 15 wt% WO_3 content calcined at 500 °C.

WO_3 as a structure promoter [18-20].

The XRD patterns also revealed that the characteristic diffraction lines of WO_3 and MnO_x were not detected in any of the catalysts up to 15 wt% WO_3 loading. This indicates that the tungsten and manganese oxides were highly dispersed on the surface of the TiO_2 , 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

Fig. 3. Comparison of NO_x conversion efficiency with NH_3 over $\text{MnO}_x\text{-TiO}_2$ and $\text{WO}_3\text{-MnO}_x\text{-TiO}_2$ with WO_3 content.

increasingly suppressed grain growth and agglomeration as the WO_3 contents were increased. The $\text{MnO}_x\text{-TiO}_2$ catalysts with 5 wt% WO_3 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_3 loading was increased. It has been considered that the WO_3 catalyst increased well-ordered crystalline planes by concentrating manganese loading on the surface of the $\text{MnO}_x\text{-TiO}_2$ catalysts, and suppressed grain growth.

3.2. Catalytic activity

To apply the low-temperature $\text{NH}_3\text{-SCR}$ catalysts, the NO_x conversion efficiencies of the promising $\text{MnO}_x\text{-TiO}_2$ and $\text{WO}_3\text{-MnO}_x\text{-TiO}_2$ catalysts were evaluated in the temperature range from 100-400 °C under the condition of $\text{GHSV} = 10,000 \text{ h}^{-1}$, and the results are illustrated in Fig. 3. The catalytic activity of the $\text{MnO}_x\text{-TiO}_2$ catalyst showed 88% efficiency at 300 °C, and activity of the $\text{WO}_3\text{-MnO}_x\text{-TiO}_2$ catalysts showed over 90% efficiency at 300-400 °C. The de- NO_x efficiency of $\text{MnO}_x\text{-TiO}_2$ at 400 °C was 3-5% lower than its efficiency at 300 °C, whereas the efficiency of the WO_3 -doped catalyst increased by 2% under identical temperatures. Among all the catalysts tested, the addition of 15 wt% WO_3 to the $\text{MnO}_x\text{-TiO}_2$ catalyst produced a promoting effect over the whole temperature range, and the NO_x

Fig. 4. FT-IR spectra of adsorbed NH₃ for MnO_x-TiO₂ catalysts with different WO₃ content.

conversion was nearly 10% higher than that of the MnO_x-TiO₂ catalyst at 200 °C. It was previously reported that MnO_x 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 MnO_x 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 NO_x reduction by NH₃. However, the WO₃-doped MnO_x-TiO₂ catalysts in this study exhibited higher NO_x conversion efficiency than the MnO_x-TiO₂ and WO₃-TiO₂ catalysts. The combination of WO₃ and MnO_x can lead to the surface characteristics and redox properties of a MnO_x-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-NO_x efficiency and the temperature window of MnO_x due to its high acid sites

Fig. 5. Raman spectra of MnO_x-TiO₂ catalysts as a function of WO₃ content.

[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 MnO_x 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% MnO_x-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-MnO_x-TiO₂ catalysts with WO₃ content were estimated by Raman measurement. The peaks of the anatase TiO₂ located around

Fig. 6. XPS spectra of $\text{WO}_3\text{-MnO}_x\text{-TiO}_2$ with various WO_3 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 WO_3 content. The Raman spectra show that the formation and growth of grains was considerably suppressed in the $\text{MnO}_x\text{-TiO}_2$ catalysts with 15 wt% WO_3 content, as compared to the catalysts with 5 wt% WO_3 content. The WO_3 peaks on the TiO_2 surface appeared as surface types of octahedral (polytungstate species, 965 cm^{-1}) and tetrahedral (WO_4^{2-} , 935 cm^{-1}) sites, but their peaks were not identified up to 15 wt% WO_3 content as shown in Fig. 4. This may be attributed to their high degree of dispersion in the TiO_2 catalyst, and they were either in an

amorphous state or were poorly crystalline.

The $\text{WO}_3\text{-MnO}_x\text{-TiO}_2$ 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 $2p_{3/2}$ and Mn $2p_{1/2}$ were observed, which ranged from 628 eV to 663 eV. It was found that the $2p_{3/2}$ binding energies of metallic Mn (Mn^0) and MnO_2 (Mn^{4+}) were 641.2 eV and 642.2 eV, respectively [9]. As shown in Fig. 6, the catalysts with 15wt% WO_3 content showed a peak-shift, which indicates the existence of Mn_2O_3 . It is well known that Mn_2O_3 is more amorphous than MnO_2 [24-26], which implies a reason for the difficulty of its detection by XRD. The amorphous Mn_2O_3 was determined to be mainly present on the catalyst surface, which can be attributed to the oxygen-rich concentration. Therefore, the addition of WO_3 could affect the thermal stability of the $\text{MnO}_x\text{-TiO}_2$ 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 W^{6+} , W^{4+} , and $\text{W}(0)$ were 36.6, 34, and 32.4 eV, respectively [27]. The intensities of the catalysts with 5 and 10 wt% WO_3 were similar, but those of the catalyst with 15 wt% WO_3 showed a peak-shift to 36.6 eV, which suggests the existence of WO_3 . Consequently, with the addition of 15 wt% WO_3 , MnO_x exists on the catalyst surface, according to the Raman spectroscopy, and the amorphous state Mn_2O_3 (Mn^{3+}) and WO_3 (W^{6+}) 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 WO_3 on the catalytic activity and surface characteristics of the $\text{MnO}_x\text{-TiO}_2$ system for low-temperature $\text{NH}_3\text{-SCR}$. The specific surface areas of the $\text{WO}_3\text{-MnO}_x\text{-TiO}_2$ catalysts were 17% and 48% greater than those of the TiO_2 and $\text{MnO}_x\text{-TiO}_2$ catalysts, respectively. The de- NO_x efficiency of a $\text{WO}_3\text{-MnO}_x\text{-TiO}_2$ catalyst was improved by the increase in WO_3 content: it showed over 90% efficiency in the

temperature range of 300-400 °C. The 15 wt% WO₃-doped MnO_x-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 MnO_x formed on the surface of the TiO₂, and its enhanced surface coverage can account for the high catalytic acidity. The 15 wt% WO₃-MnO_x-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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