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Selective Catalytic Reduction of NO with NH₃ over Ce-W-Ti Oxide Catalysts Prepared by Solvent Combustion Method

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Abstract: In this work, a series of Ce-W-Ti catalysts were synthesized using a solution combustion method for the selective catalytic reduction (SCR) of NO with NH₃ at low temperatures. The reaction performance of NH₃-SCR of NO was significantly improved over the Ce-W-Ti catalysts compared to Ce_{0.4}Ti and W_{0.4}Ti catalysts, while Ce_{0.2}W_{0.2}Ti showed the best activity among all the samples. The Ce_{0.2}W_{0.2}Ti catalyst exhibited over 90% removal of NO and 100% N₂ selectivity in the temperature range of 250–400 °C at a gas hourly space velocity (GHSV) of 120,000 mL·g^{−1}·h^{−1}. The Ce-W-Ti catalysts were characterized using N₂ adsorption-desorption, X-ray diffraction, X-ray photoelectron spectrometry and temperature programmed desorption of NH₃ to establish the structure-activity relationships of the Ce-W-Ti catalysts. The excellent catalytic performance of the Ce_{0.2}W_{0.2}Ti catalyst could be associated with the larger specific surface area, highly dispersed Ce and W species, increased amount of surface adsorbed oxygen (O_{ads}) and enhanced total acidity on the catalyst surfaces.

Keywords: SCR; nitrogen oxides; Ce-W-Ti; solution combustion method

1. Introduction

The emission of nitrogen oxides (NO_x) from stationary sources and lean-burn engines remains one of the major challenges in environmental pollution control due to the negative effect of NO_x on air quality and human health. Selective catalytic reduction (SCR) of NO_x with NH₃ (NH₃-SCR) over TiO₂ supported V₂O₅-WO₃ or V₂O₅-MoO₃ catalysts have been extensively investigated due to the high activity of these catalysts in NO reduction [1–4]. However, the toxicity of active vanadium species and the narrow operation temperature window (300–420 °C) limit the use of these catalysts on a commercial scale to meet the stringent NO_x emission legislations, especially when the boilers are operated at low loads and the temperatures are far below the operation temperature window of the vanadium-based catalysts [5,6].

In recent years, significant efforts have been devoted to the development of an environmentally-benign catalyst with a wide operation temperature window and high deNO_x activity [7,8]. Various types of transition and rare earth metals based catalysts have shown an excellent reactivity in NH₃-SCR reaction over a wide temperature range [9–11]. Among the non-vanadium NH₃-SCR catalysts, cerium-based catalysts have been intensively investigated considering their unique properties of high oxygen-storage capacity and facilitated redox cycles between Ce⁴⁺ and Ce³⁺, e.g., Ce-Ti, Ce-Zr, Ce-Cu-Ti and Ce-Mn, etc. [12–17].

Recently, tungsten, a typical promoter and stabilizer in vanadium-based catalysts, has been used as a dopant to improve the performance of Ce-based catalysts [18–20]. Chen et al. reported that the

doping of W into CeO₂/TiO₂ catalysts significantly enhanced the SCR of NH₃ in the temperature range of 150–300 °C, compared to the catalysts without W doping. The catalyst sample with 6 wt.% W exhibited the best performance [21]. Jiang et al. found Ce₂₀W₁₀Ti catalysts prepared by a single step sol-gel method exhibited a NO conversion of 90% at 275 °C at a gas hourly space velocity (GHSV) of 90,000 h^{−1} [22]. They also developed a Ce-W-Ti catalyst prepared by sol-gel method, which exhibited 95% NO conversion rate (250 °C) at the same GHSV [23]. Shan et al. reported that Ce_{0.2}W_{0.1}Ti catalysts synthesized by a facile homogeneous precipitation method showed 100% NO conversion and N₂ selectivity in a wide temperature range of 250 °C to 400 °C at a high gas hourly space velocity (GHSV) of 250,000 h^{−1}, which was significantly higher than that using Ce-Ti catalysts without W doping [24,25]. Currently, Ce-W-Ti catalysts were assumed to be one of the potential candidates for the commercial vanadium-based catalysts [26]. The performance of the Ce-W-Ti catalysts were closely related to the redox properties between the active metals.

To further improve the activity of the Ce-W-Ti catalysts in low temperature NH₃-SCR, a novel solution combustion method has been used to prepare a series of Ce-W-Ti catalysts with different Ce/W ratios and tested over a wide temperature range. The effect of these catalysts on the conversion of NO and N₂ selectivity has been investigated. A range of catalyst characterization techniques including N₂ adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectrometry (XPS), temperature programmed desorption of NH₃ (NH₃-TPD) has been used to better understand the properties of the Ce-W-Ti catalysts and their effects on the SCR of NO with NH₃.

2. Materials and Methods

2.1. Catalyst Preparation

A series of Ce-W-Ti catalysts with different Ce/W ratios were prepared by a solution combustion method. Tetrabutyl titanate, cerium nitrates and ammonium metatungstate were used as the precursors together with ethanol, nitric acid, ethanedioic acid and glycine for the synthesis of the catalysts. All chemicals were reagent grade from Aladdin Co. Ltd. (Shanghai, China). Typically, tetrabutyl titanate (8.508 g) was firstly dissolved in a 60 mL water-ethanol (*v/v* = 1/1) solution and stirred for 1 h. Stoichiometric amounts of cerium nitrate and ammonium metatungstate were dissolved in deionized water under vigorous stirring. The molar ratio of metal ions to titanium species was kept at 0.4. After mixing the two solutions, glycine was added dropwisely as a fuel and complexant. Note, the molar ratio of glycine to nitrates was 1:1. The obtained mixture was heated in a water bath at 50 °C for 3 h, followed by evaporation at 300 °C in a muffle furnace. The solution was boiled and ignited during the evaporation. In this way, a homogeneous brown powder was obtained. The samples were pelleted and sieved to 40–60 meshes for the test of catalytic activity. In this work, the Ce-W-Ti catalysts were denoted as Ce_xW_{0.4−x}Ti where *x* was the molar ratio of Ce species to Ti species in the catalysts.

2.2. Catalyst Characterizations

N₂ adsorption-desorption isotherms were obtained using a Quantachrome (Boynton Beach, FL, USA) Autosorb-1 apparatus at −196 °C. Prior to N₂ adsorption, the catalysts were degassed under vacuum at 300 °C for 4 h. The specific surface area of the catalysts was determined by the Brunauer-Emmet-Teller (BET) method. Total pore volume and average pore size of the catalysts were evaluated using the Barrett-Joyner-Halenda (BJH) method.

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded using a Rigaku D/Max-2550 instrument (Tokyo, Japan) equipped with a Cu Kα radiation source in the 2θ range of 10–80°.

X-ray photoelectron spectroscopy spectra were measured with a Thermo ESCALAB 250 (Waltham, MA, USA) using Al Kα radiation source (*hν* = 1486.6 eV). The spectra were calibrated with the C 1s binding energy (B. E.) value of 284.6 eV to eliminate the sample charging effects.

Temperature programmed desorption of ammonia (NH₃-TPD) was performed using a Micrometrics AutoChem II 2920 chemisorption analyzer (Ottawa, ON, Canada). Before each test, the samples (100 mg) were purged in a He gas flow at 350 °C for 1 h and then cooled down to 50 °C. Then, the samples were saturated with 2 vol.% NH₃/He gas stream until equilibrium was reached, followed by flushing with He at 100 °C to avoid NH₃ physisorption. Finally, the samples were heated from 100–500 °C at the heating rate of 10 °C·min^{−1}. The signal of NH₃ desorption was recorded using a gas chromatography equipped with a thermal conductivity detector (TCD).

2.3. Catalytic Activity Measurements

The catalytic activity test for all the catalysts was carried out in a fixed-bed reactor packed with 0.4 g catalyst (40–60 meshes). The feed gas contained 500 ppm NO, 500 ppm NH₃, 5% O₂ and balanced N₂. The total flow rate of the feed gas was fixed at 800 mL·min^{−1}, corresponding to a gas hourly space velocity (GHSV) of 120,000 mL·g^{−1}·h^{−1}. The inlet and outlet gas compositions were monitored on-line by a Gasmet Dx-4000 Fourier transform infrared (FTIR) gas analyzer (Helsinki, Finland). The gas analyzer was calibrated with standard gas cylinders of NO, NO₂, N₂O, SO₂ and NH₃ before the experiments. All the measurements were recorded when the reaction reached a steady-state at each temperature. NO conversion and N₂ selectivity was defined as follows:

$$\text{NO conversion (\%)} = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}\right) \times 100\%$$

$$\text{N}_2 \text{ selectivity (\%)} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}}\right) \times 100\%$$

where [NO]_{in} and [NH₃]_{in} are the inlet concentrations of NO and NH₃, respectively. [NO]_{out}, [NO₂]_{out} and [N₂O]_{out} are the outlet concentrations of NO, NO₂ and N₂O, respectively.

3. Results and Discussions

3.1. Catalytic Performance Test

Figure 1 shows the influence of different Ce/W molar ratios of the Ce-W-Ti catalysts on the conversion of NO in the temperature range of 150–450 °C. Almost no catalytic activity was found for W_{0.4}Ti at a temperature below 250 °C, while the conversion of NO increased quasi-linearly from 4.6% to 64.7% when increasing the temperature from 250 to 450 °C. As for the Ce_{0.4}Ti catalyst, the NO conversion increased from 5.8% to 85.0% in the tested temperature range (150–450 °C). The addition of Ce into the W-Ti catalyst dramatically improved NO conversion and shifted the operation temperature of the catalysts to a lower temperature. A maximum NO conversion of 90.1% to 100% was obtained between 250 °C and 450 °C over the Ce_{0.2}W_{0.2}Ti catalysts. However, further increasing the doping amount of Ce or W decreased the NO conversion as the value was in the range of 74.8% to 98.8% for Ce_{0.3}W_{0.1}Ti and 57.5% to 93.2% for Ce_{0.1}W_{0.3}Ti, respectively. The selectivity of N₂ showed a similar trend. As for W_{0.4}Ti, the N₂ selectivity decreased from 98.0% at 300 °C to 83.8% at 450 °C, while this value decreased from 99.7% to 90.4% for Ce_{0.4}Ti. The N₂ selectivity was significantly enhanced when using the Ce-W-Ti catalysts, 100% N₂ selectivity was achieved over Ce_{0.2}W_{0.2}Ti catalyst between 150 °C and 350 °C and further increasing the temperature to 450 °C slightly decreased the N₂ selectivity to 98.5%. The results of NO conversion and N₂ selectivity indicate that strong interactions exist between Ce and W species in the Ce-W-Ti catalysts, which could contribute to the reaction performance of NH₃-SCR process. A series of characterizations were carried out to analyze the physico-chemical properties of the Ce-W-Ti catalysts and the relationships between the catalyst structure and the reaction performance.

Figure 1. NO conversion (a) and N₂ selectivity (b) as a function of reaction temperature over the Ce-W-Ti catalysts. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5%, balanced N₂, GHSV = 120,000 mL·g⁻¹·h⁻¹.

Figure 2 shows the effect of SO₂ on the NH₃-SCR activity over the best-performed Ce_{0.2}W_{0.2}Ti catalyst at 300 °C with and without H₂O over 10 h. Before introducing SO₂ and H₂O into the catalyst layer, the NO conversion rate is 100% at a steady state. When 500 ppm SO₂ was added, the catalytic activity of Ce_{0.2}W_{0.2}Ti dramatically decreases to around 60% in 8 h [22]. Previous work confirmed that the SO₂ could react with NH₃ and form the NH₄HSO₄, which may block the active sites on the surface of Ce_{0.2}W_{0.2}Ti catalyst [26]. On the other hand, the formation of highly thermal stable sulfate species of Ce(SO₄)₂ and Ce₂(SO₄)₃ was also expected on the catalyst surfaces, which would reduce the relative concentration of Ce³⁺/Ce⁴⁺ redox pair on the catalyst surface, and consequently impose a negative effect on the catalytic activity [27,28]. The co-introduction of 500 ppm SO₂ and 5% H₂O significantly affects the catalytic activity of Ce_{0.2}W_{0.2}Ti. The catalytic activity is reduced more quickly compared to the case of introducing SO₂ alone with only 65% after 8 h. After cutting off SO₂ and H₂O from the feeding gas, the activity slightly recovers to around 70%. It is obvious that the addition of W species into the original Ce-Ti catalyst remarkably enhances the resistance of catalysts towards SO₂ and H₂O. Similar observations were also reported in previous work of cerium-based catalysts [27,29].

Figure 2. Effect of SO₂ and/or H₂O on the NH₃-SCR activity of Ce_{0.2}W_{0.2}Ti at 300 °C. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5%, [SO₂] = 500 ppm, [H₂O] = 5%, balanced N₂, GHSV = 120,000 mL·g⁻¹·h⁻¹.

3.2. N₂ Adsorption and Desorption

N₂ adsorption and desorption experiments were performed to analyze the structure of the Ce_xW_{0.4-x}Ti catalysts. All catalysts exhibited typical type III isotherms, indicating the formation

of multilayers in the catalysts and relative weak interactions between N_2 and the catalysts [30]. The hysteresis loop was demonstrated to be H3 type for the catalysts, which is associated with the existence of slit-shaped pores formed from the aggregation of plate-like particles [31]. Table 1 gives the information of the specific surface area (S_{BET}), the pore volume and the average pore diameter of the catalysts based on the calculations from the isotherms. Compared with $Ce_{0.4}Ti$ and $W_{0.4}Ti$, the $Ce_xW_{0.4-x}Ti$ catalysts possessed larger S_{BET} and pore volume, indicating more surface active sites formed on the $Ce_xW_{0.4-x}Ti$ catalysts for the SCR reaction. The highest S_{BET} ($108.1 \text{ m}^2 \cdot \text{g}^{-1}$) and pore volume ($0.121 \text{ cm}^3 \cdot \text{g}^{-1}$) was observed for the $Ce_{0.2}W_{0.2}Ti$ catalyst, while further increasing of the loading amount of Ce or W resulted in decreased S_{BET} and pore volume. It is well recognized that larger specific surface area was beneficial for offering more active sites for the NH_3 -SCR reaction [23,25]. Moreover, $Ce_{0.2}W_{0.2}Ti$ showed the smallest average pore diameter of 3.9 nm compared to the other samples. Zhao et al. also reported that the decrease of average pore diameter and pore volume could improve the performance of the NH_3 -SCR process [32].

Table 1. Textural properties of the Ce-W-Ti catalysts.

Samples	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Average Pore Diameter (nm)	$O_{ads}/$ ($O_{ads} + O_{lat}$) (%)	NH_3 Uptake ($\mu\text{mol} \cdot \text{g}^{-1}$)
$Ce_{0.4}Ti$	26.6	0.076	9.9	17.4	7.8
$Ce_{0.3}W_{0.1}Ti$	46.8	0.086	7.7	27.6	64.7
$Ce_{0.2}W_{0.2}Ti$	108.1	0.121	3.9	33.8	193.9
$Ce_{0.1}W_{0.3}Ti$	68.4	0.085	4.6	21.0	62.3
$W_{0.4}Ti$	16.8	0.069	16.2	16.0	20.0

3.3. XRD Analysis

The XRD patterns of the catalysts are presented in Figure 3. All the catalysts presented the typical diffraction peaks of anatase TiO_2 (JCPDS 21-1272). The characteristic diffraction peaks of Ce and W species were not observed for all catalysts even the loading amount of Ce and W may exceed the limit of monolayer dispersion. This indicated that the active Ce and W species were in amorphous phase or well dispersed on the TiO_2 surfaces. Similar observations were reported in a previous study [22]. The crystallization degrees of the TiO_2 support were smaller in the $Ce_xW_{0.4-x}Ti$ catalysts compared to the $Ce_{0.4}Ti$ and $W_{0.4}Ti$ indicating the smaller crystalline sizes of the $Ce_xW_{0.4-x}Ti$ catalysts, considering the lower peak intensities of the major typical diffraction peaks of TiO_2 (1 0 1) at $2\theta = 25.3^\circ$. This phenomenon indicated a smaller crystalline size of the Ce-W-Ti catalysts compared to the $Ce_{0.4}Ti$ and $W_{0.4}Ti$ catalysts, which was beneficial for the NH_3 -SCR of NO and could be confirmed by the broadening of the characteristic peaks in the Ce-W-Ti catalysts [33,34].

Figure 3. X-ray diffraction (XRD) patterns of the Ce-W-Ti catalysts.

3.4. XPS Analysis

Figure 4 shows the XPS spectra of O 1s for the Ce-W-Ti catalysts. Two major peaks of different surface oxygen species could be obtained by fitting the curves. The peaks located between 529.6 eV and 530.1 eV could be ascribed to the lattice oxygen (O_{lat}), while the peaks at 531.2 eV to 531.6 eV belonged to the surface-adsorbed oxygen (O_{ads}) [22]. The relative concentrations of $O_{ads}/(O_{ads} + O_{lat})$ are calculated and presented in Table 1. The Ce-W-Ti catalysts possessed higher relative concentrations of $O_{ads}/(O_{ads} + O_{lat})$ in the range of 21.0% to 33.8% compared to the $Ce_{0.4}Ti$ (17.4%) and $W_{0.4}Ti$ (16.0%) catalysts, while the highest O_{ads} ratio was observed over the $Ce_{0.2}W_{0.2}Ti$ catalyst. The conventional SCR reaction cycles indicated that redox properties were crucial for the reaction performance at low temperatures. Shan et al. reported that the interactions between Ce and W species could enrich the amount of Ce^{3+} and surface oxygen vacancies, and that these two species were directly correlated with the surface oxygen species [35]. Surface-adsorbed oxygen (O_{ads}) is more chemically reactive due to their higher mobility on the catalyst surfaces compared to the lattice oxygen (O_{lat}) species, which was beneficial for the oxidation of NO to NO_2 , one of the initial steps of NH_3 -SCR [24,36]. The order of O_{ads} was in good agreement with the sequence of the NH_3 -SCR performance.

Figure 4. X-ray photoelectron spectrometry (XPS) spectra of O 1s for the Ce-W-Ti catalyst.

3.5. NH_3 -TPD Analysis

Acidity of the catalysts is crucial for efficiency NH_3 adsorption during the SCR process. The acidity and the relative strength of all the acid sites on the surfaces of the Ce-W-Ti catalysts were analyzed using NH_3 -TPD measurement. A broad desorption peak spanned between 100 °C and 400 °C for all samples in Figure 5, which could be attributed to the desorption of NH_3 molecules on the weak and medium acid sites [3,37]. It is reported that the thermal stability of restrained NH_4^+ ions on the Lewis acid sites were stronger than those on the Brønsted acid sites. The NH_3 desorption peaks below 200 °C belonged to the Brønsted acid sites, while the desorption peaks at higher temperatures were attributed to the Lewis acid sites [35]. For $Ce_{0.4}Ti$ and $W_{0.4}Ti$, the strong desorption peaks at 150 °C and 181 °C belonged to the NH_4^+ ions adsorbed on the Brønsted acid sites, while the peaks located

at 295 °C and 311 °C could be ascribed to the desorption of NH_3 species adsorbed on the Lewis acid sites. For the Ce-W-Ti catalysts, the NH_3 desorption peaks shifted to higher temperatures (between 158 °C and 167 °C) compared to the $\text{Ce}_{0.4}\text{Ti}$ catalyst, while the intensities of the desorption peaks were significantly increased. Moreover, the intensities of the desorption peaks above 200 °C were also enhanced over the Ce-W-Ti catalysts, indicating the existence of stronger Lewis acid sites [38]. This phenomenon could be attributed to the synergistic effect between the cerium and tungsten species. The amounts of NH_3 uptake of all the catalysts were given in Table 1 as evidence for the total acidity on the catalysts. The Ce-W-Ti catalysts show stronger acidity compared to the $\text{Ce}_{0.4}\text{Ti}$ and $\text{W}_{0.4}\text{Ti}$ catalysts, while the $\text{Ce}_{0.2}\text{W}_{0.2}\text{Ti}$ catalyst possessed the largest NH_3 uptake of $193.9 \mu\text{mol}\cdot\text{g}^{-1}$. Further increases or decreases in the Ce/W molar ratio decreases the acidity on the catalysts. It was well acknowledged that the acidity of the catalysts played a significant role in the process of NH_3 -SCR, and more acid sites on the surface $\text{Ce}_{0.2}\text{W}_{0.2}\text{Ti}$ catalysts could be favorable for the conversion of NO in the low temperature range [3].

Figure 5. NH_3 -TPD profiles of the Ce-W-Ti catalysts.

4. Conclusions

In this work, a series of Ce-W-Ti catalysts were synthesized using a solution combustion method for selective catalytic reduction (SCR) of NO with NH_3 at low temperatures. The removal of NO was significantly improved over the Ce-W-Ti catalysts compared to $\text{Ce}_{0.4}\text{Ti}$ and $\text{W}_{0.4}\text{Ti}$ catalyst. Among all the catalysts, $\text{Ce}_{0.2}\text{W}_{0.2}\text{Ti}$ exhibited over 90% NO removal efficiency and 100% N_2 selectivity in the temperature range of 250 °C and 400 °C at the GHSV of $120,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. A series of catalyst characterizations including N_2 adsorption-desorption, XRD, XPS and NH_3 -TPD were performed to establish the structure-activity relationships of the Ce-W-Ti catalysts. The interactions between Ce and W species significantly affected the physic-chemical properties of the catalysts. The Ce-W-Ti catalysts exhibited larger specific surface areas compared to the $\text{Ce}_{0.4}\text{Ti}$ and $\text{W}_{0.4}\text{Ti}$ catalysts, while the Ce and W species were highly dispersed on the surfaces of the catalysts. The interactions between Ce and W species also increased the amount of surface adsorbed oxygen (O_{ads}) and the total acidity of the catalysts, which were beneficial for the adsorption of the reactants and oxidation of the intermediates during the NH_3 -SCR process. To sum up, the catalytic performance of the NH_3 -SCR was improved over the $\text{Ce}_{0.2}\text{W}_{0.2}\text{Ti}$ catalysts.

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