

Characterization and De-NO_x activity of binary V₂O₅/TiO₂ and WO₃/TiO₂, and ternary V₂O₅-WO₃/TiO₂ SCR catalysts

Byeong Woo Lee*, Hyun Cho^a and Dong Woo Shin^b

Department of Materials Engineering, Korea Maritime University, Busan 606-791, Korea

^aDepartment of Nanosystem and Nanoprocess Engineering, Pusan National University, Kyungnam 627-706, Korea

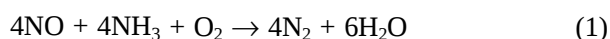
^bSchool of Nano and Advanced Materials Engineering, ERI, Gyeongsang National University, Jinju 660-701, Korea

The influence of tungsten and vanadium oxides on the microstructure, phase formation and De-NO_x activity of selective catalytic reduction (SCR) catalysts has been investigated. Binary (V₂O₅/TiO₂ and WO₃/TiO₂) and ternary (V₂O₅-WO₃/TiO₂) samples with compositions similar to those of commercial SCR catalysts were examined in terms of structural analyses and the reduction of NO_x to N₂ in the presence of NH₃. The TiO₂ supported catalysts with different W- and V-loadings (WO₃: 10 wt%, V₂O₅ <10 wt%), heat-treated in the temperature range of 450 °C to 650 °C, have been characterized. The addition of W to TiO₂ led to lowering the transition temperature of anatase-to-rutile. Upon the phase transition, WO₃ phase segregation was observed. The W-loading in the TiO₂ support did not influence the crystallite dimensions and surface area. In the case of the V-loading, the transition temperature was significantly reduced along with an abruptly decreased surface area due to the crystallite growth with increasing V-content. Ternary V₂O₅-WO₃/TiO₂ catalysts exhibited higher De-NO_x efficiency than binary V₂O₅/TiO₂ and WO₃/TiO₂ samples with the same amount of loading. In V₂O₅(3 wt%)-WO₃(10 wt%)/TiO₂ catalysts, the highest De-NO_x activity was achieved in a wide temperature range. A catalyst heat-treatment at 650 °C showed a relatively high efficiency and wider temperature range, maintaining peak activity in comparison with the catalysts prepared at 450 °C.

Key words: Selective catalytic reduction (SCR), V₂O₅-WO₃/TiO₂, NO_x conversion, anatase TiO₂.

Introduction

The selective catalytic reduction (SCR) of NO_x by ammonia is the most successful method for eliminating NO (x=1) emitted from stationary sources [1]. It is generally accepted that the SCR reaction obeys the following reaction [2]:



Commercially available SCR catalysts are in the form of an TiO₂ (anatase) support with active components, i.e. V₂O₅, MoO, CuO and WO₃. In particular, mixed oxides of V₂O₅ and WO₃ supported on TiO₂ (V₂O₅-WO₃/TiO₂) are the most widely studied and technologically important SCR materials because of their high catalytic activity [2-7]. Although V₂O₅ is the active component, in some operating conditions, it has been reported that undesirable reactions (poisoning effect) were induced such as the oxidation of ammonia and SO₂ [2, 3, 8]. For V-loaded TiO₂ catalysts, a decrease of the catalytic activity could also occur when the temperature of SCR reaction exceeds 400 °C [2, 3, 7]. Therefore, the V₂O₅ content of the catalyst is generally kept as low as possible (< 5 wt%). WO₃ is usually added

to the V₂O₅/TiO₂ as a promoter to improve the catalytic properties [2-7]. WO₃ has been reported to reduce the oxidation of ammonia as well as SO₂ and is usually added to the V₂O₅/TiO₂ in larger amounts (~10 wt%). The WO₃ is also used to provide thermal stability to the catalysts by increasing the transition temperature from anatase to rutile phase of the TiO₂ support [4].

Most research has mainly focused on the chemical activities of the V₂O₅-WO₃/TiO₂ system. Therefore, how V₂O₅ and WO₃ interact with the TiO₂ lattice and affect thermal stability, especially for the binary (V₂O₅/TiO₂ and WO₃/TiO₂) and ternary (V₂O₅-WO₃/TiO₂) catalyst system have not yet been clearly defined.

The objective of the present study is to obtain further understanding of the nature of the V₂O₅-WO₃/TiO₂ catalyst exhibiting a high NO reduction efficiency and a high phase stability using structural and catalytic data obtained from binary V₂O₅/TiO₂ and WO₃/TiO₂ systems. To improve the catalytic properties of the V₂O₅-WO₃/TiO₂ system, thermal, physical and chemical analyses were performed to clarify the powder and catalytic properties of this catalyst system and the properties were compared to those of the corresponding binary V₂O₅/TiO₂ and WO₃/TiO₂ systems.

Experimental

Binary V₂O₅/TiO₂ and WO₃/TiO₂, and ternary V₂O₅-WO₃/TiO₂ catalysts with different WO₃ (10 wt%) and

*Corresponding author:
Tel : +82-51-410-4356
Fax: +82-51-403-3986
E-mail: bwlee@hhu.ac.kr

V_2O_5 (1, 3, 5 and 10 wt%) loadings were prepared by a wet impregnation method. For simplicity, the wt% will be further denoted as %.

Partially sulfated TiO_2 (96%, SO_3 -2%) powder provided from Nano Co. Ltd, Korea was used as the support of the catalysts. The commercial powder had been synthesized from meta-titanic acid and the (anatase) crystallinity was poor. Although, the powder has a high BET surface area of $280\text{ m}^2/\text{g}$, a considerable amount of weight loss of more than 15% was observed during heat treatment up to 650°C . In order to give thermal stability, the powder was heat-treated and stabilized at 650°C before use as the support of the catalysts. Ammonium-metavanadate (NH_4VO_3) and ammonium-metatungstate-hydrate ($(NH_4)_6W_{12}O_{39}\cdot xH_2O$) were used as catalyst precursors for V_2O_5 and WO_3 , respectively. The precursors were dissolved in hot distilled water. To impregnate the catalysts, the raw materials including the solution of catalyst precursors and TiO_2 support powders were mixed and wet ball-milled for 12 h. The resulting slurries were dried at 90°C for 24 h and heated in air from ambient temperature to 1200°C .

The crystalline structure and phase of the synthesized powders were identified by X-ray powder diffractometry (XRD, Cu-K α). The morphologies of prepared powders were characterized using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The surface area of the powders was measured by the BET technique.

Catalytic activities have been measured by reduction of NO in the presence of NH_3 in a fixed bed reactor containing 1 g catalyst. A feed consisting of 500 ppm NO, 600 ppm NH_3 , and 6 vol% O_2 with N_2 being the carrier gas (total space velocity = 100000 h^{-1}) was used. Activity data were collected at different temperatures in the range of 200 to 450°C , each temperature was maintained until steady-state conditions were reached.

Results and Discussion

Structural and morphological properties

The commercial TiO_2 powder exhibited the anatase phase with poor crystallinity [9]. To enhance the crystallinity, the powder was heat-treated at 650°C before use as a support for the catalysts. The BET surface area value (S_{BET}) of the powder heat-treated at 650°C was $81\text{ m}^2/\text{g}$. The particle size ($D_{BET} = 6/\rho S_{BET}$, where ρ is the theoretical density of the powder) calculated from the value of specific surface area (S_{BET}) was $\sim 19\text{ nm}$. This is in good agreement with the results of the TEM morphology showing ultra-fine crystallites sized below 20 nm (Fig. 1). Rutile phase which is the high temperature polymorph of TiO_2 was observed at temperatures above 1000°C and the phase transition was completed at 1200°C .

Figure 2 shows the XRD results of the binary WO_3 (10%)/ TiO_2 composition heat-treated at various temper-

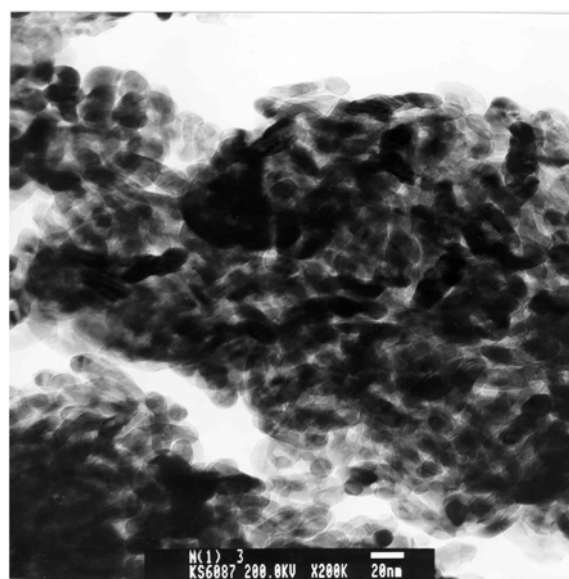


Fig. 1. TEM morphology of TiO_2 (support) powder (bar: 20 nm).

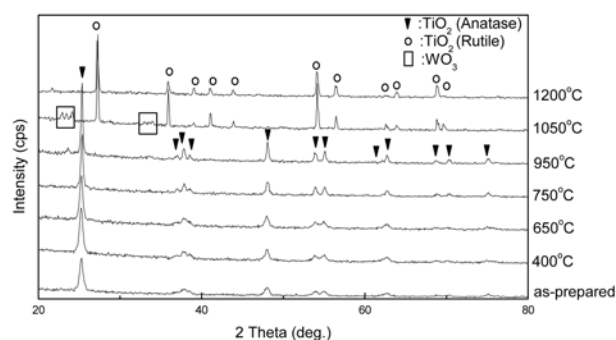


Fig. 2. XRD patterns of the WO_3 (10%)/ TiO_2 catalyst heat-treated at different temperatures (The WO_3 precursor was ammonium-metatungstate-hydrate).

atures. All of the compositions have only the anatase phase up to the heat-treatment temperature of 900°C . Up to 900°C , there was no trace of tungsten precursor or tungsten oxide phase, because the ammonium-metatungstate-hydrate was amorphous and the tungsten oxide that was a dissociated product from the precursor could be easily dissolved in the anatase lattice below 500°C [9]. The W-addition led to lowering the anatase-to-rutile transition temperature from 1200°C to 1050°C . This might be a different result in comparison to that of the research showing the inhibited transition in W-loaded TiO_2 [4]. Upon the anatase-to-rutile transition, the WO_3 phase segregation occurred at 1050°C . This could have originated from the lower solubility of the rutile lattice than that of anatase. Figure 3 shows the results of XRD of 10% WO_3 added rutile- TiO_2 powders heat-treated at different temperatures. There was no noticeable reaction between rutile- TiO_2 and WO_3 , up to 1000°C . This could be explained by the decreased unit cell volume from $34\text{ \AA}^3/\text{atom}$ (anatase) to $31\text{ \AA}^3/\text{atom}$ (rutile), and then the decreased unit cell volume induces the reduced W-solubility in the rutile lattice and it is

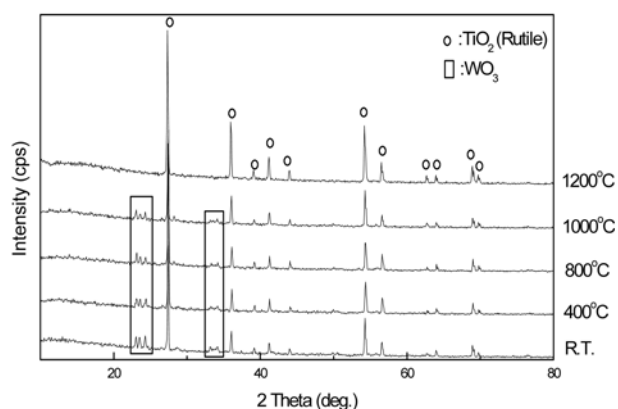


Fig. 3. XRD patterns of 10% WO₃ added rutile-TiO₂ powders heat-treated at different temperatures. The TiO₂ powders were heat-treated and converted to the rutile phase at 1200 °C before use, from the anatase-TiO₂ support.

hard to form a solid solution at low temperatures below 1000 °C.

In the case of the vanadium loading, the anatase-to-rutile transition temperature is considerably reduced with increasing V-content. For 5 and 10% V₂O₅ loaded

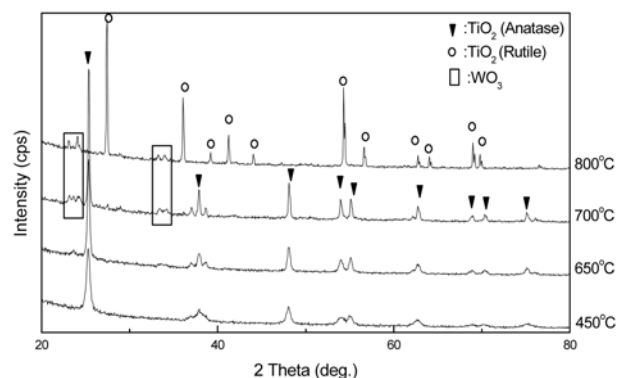


Fig. 4. XRD patterns of V₂O₅(3%)-WO₃(10%)/TiO₂ catalyst heat-treated at different temperatures.

binary compositions, the transition temperature was drastically down to 650 and 600 °C, respectively, and there was no evidence of the phase segregation of V₂O₅, which was shown in the W-loaded composition.

For both the vanadium and tungsten loaded (ternary) catalyst (V₂O₅(5%)-WO₃(10%)/TiO₂), the XRD results are presented in Fig. 4. As expected, the V-loading considerably lowers the anatase-to-rutile transition temper-

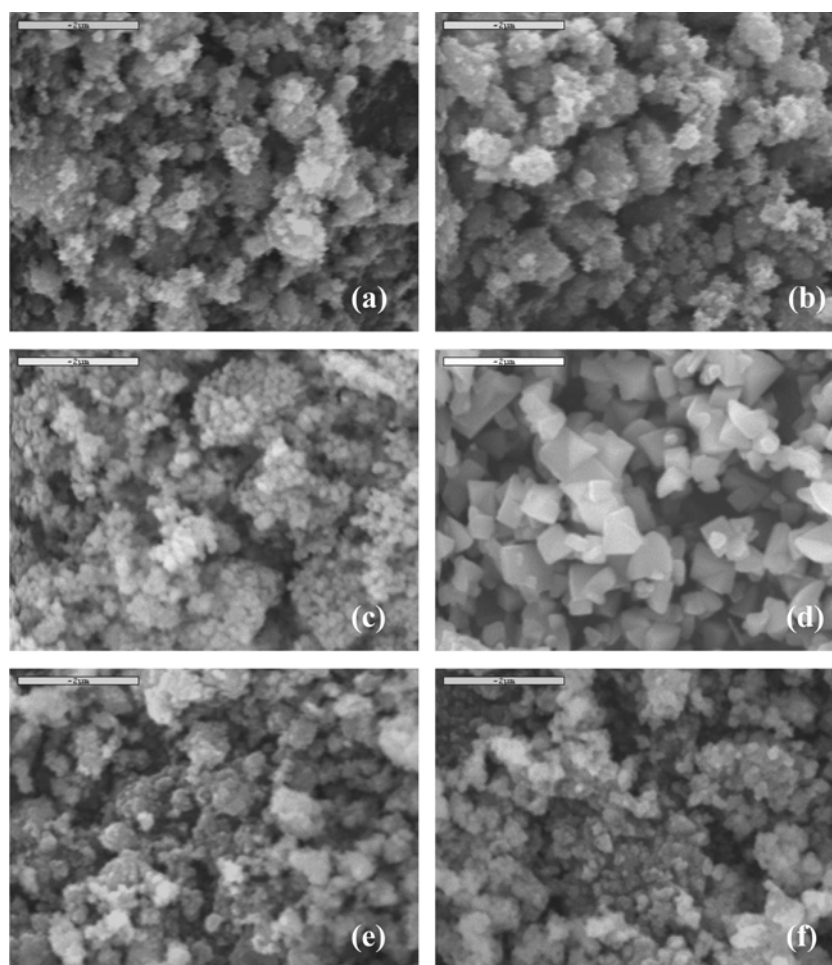


Fig. 5. SEM morphology of prepared samples (bar: 2 μm): (a) TiO₂ support (prepared at 650 °C, S_{BET}: 81 m²/g), (b) WO₃(10%)/TiO₂ (650 °C, 79 m²/g), (c) V₂O₅(5%)/TiO₂ (650 °C, 36 m²/g), (d) V₂O₅(10%)/TiO₂ (650 °C, 3.6 m²/g), (e) V₂O₅(3%)-WO₃(10%)/TiO₂ (450 °C, 62 m²/g), and (f) V₂O₅(3%)-WO₃(10%)/TiO₂ (650 °C, 13 m²/g).

ature down to 800 °C and, upon the transition, the WO₃ segregation was also observed. However, the lowering of the transition temperature is reduced in contrast to that of the V-loaded binary catalyst. It seems that the tungsten plays a complicated role in thermal stability, i.e., speeding up the transition in W-loaded TiO₂ and retarding the transition in both W- and V-loaded TiO₂.

Figure 5 shows the SEM morphology of various samples heat-treated at 450 °C and 650 °C showing the variations of crystallite dimension with tungsten and vanadium additions. Crystallite dimensions increase with increasing heat-treatment temperature and then the surface area decreases with the heat-treatment temperature for all of the samples. The W-loading in the TiO₂ support did not influence the crystallite dimensions and surface area value of the pure TiO₂. The S_{BET} value obtained at 650 °C for the W-loaded catalyst was 79 m²/g and the value was almost identical with that (S_{BET} ~81 m²/g) of the pure TiO₂ support. It was found that, compared to the W-loaded catalyst, the surface area of the V-loaded catalyst significantly decreased with increasing heat-treatment temperature as well as vanadium loading. With an increase of V-content from 5 to 10% of V₂O₅ in the TiO₂ composition heat-treated at 650 °C, S_{BET} values are drastically reduced from 36 to 3.6 m²/g. A considerable amount of crystallite growth was observed in the 10% of V₂O₅ in TiO₂. In the light of the structural and thermal stability, it could be proposed that the V₂O₅ loading for a conventional SCR catalyst should be limited to below 10%.

In the ternary V₂O₅(5%)-WO₃(10%)/TiO₂ composition heat-treated at 650 °C, the S_{BET} value was reduced to 13 m²/g. Since there was no significant difference in S_{BET} values between the pure TiO₂ support and the W-loaded sample, the abruptly decreased S_{BET} values in both the vanadium- and tungsten-loaded sample indicate that TiO₂ interacts more strongly with V than with W.

Catalytic performances

To investigate the effect of preparation temperatures on the catalytic activity, the impregnated powders were heat-treated at 450 °C and 650 °C. At the heat-treatment temperature of 450 °C, all impregnated samples showed an anatase single phase, whereas, for the samples prepared at 650 °C, the anatase or rutile phases were developed as presented in the XRD study.

A high catalytic activity has been observed in a limited temperature range for the catalyst with W- and V-loaded binary compositions. Figure 6 shows the catalytic efficiency measured by NO reduction of the W- and V-loaded binary catalysts. For the WO₃(10%)/TiO₂ (anatase) composition, the SCR prepared at 650 °C showed a higher NO_x conversion efficiency over the whole (reaction) temperature range between 250 and 400 °C than the SCR prepared at 450 °C and a considerably high efficiency near 100% was achieved at high temperatures above 350 °C. The highest NO_x conversion efficiency

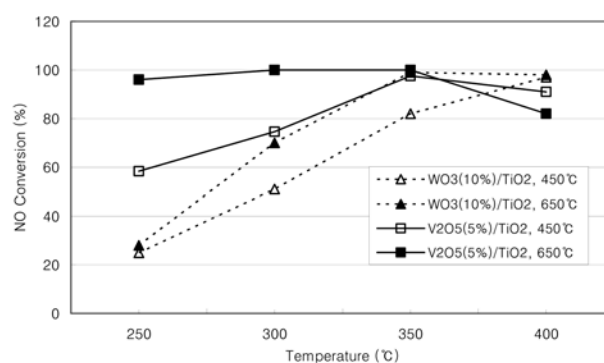


Fig. 6. Conversion of NO versus reaction temperature over WO₃(10%)/TiO₂ and V₂O₅(5%)/TiO₂ catalysts prepared at 450 °C and 650 °C.

of 100% was obtained in the binary V₂O₅(5%)/TiO₂ (rutile) SCR composition heat-treated at 650 °C in the low temperature range of 250–350 °C, while the catalytic efficiency rapidly decreased at 400 °C, which is in agreement with previous observations [2, 3]. For the V₂O₅(10%)/TiO₂ (rutile) catalyst prepared at 650 °C, the catalytic efficiency was significantly reduced in comparison with the 5% V₂O₅ loaded catalyst. Also the reduced efficiency could be attributed to the lowered surface area resulting from the grain growth (Fig. 5(d)) due to the highly reactive vanadium addition. Although the high activity of W-loaded catalysts remained at higher reaction temperatures, the activity at temperatures below 350 °C was lower than that of V-loaded catalysts.

It has been generally observed that binary catalysts prepared at 650 °C showed the higher efficiency and enlarged temperature range where peak activity remained in comparison with the catalysts prepared at 450 °C.

In order to improve the catalytic properties through getting the synergistic effects such as the high catalytic efficiency value in a lower reaction temperature region via V-loading and also a high efficiency value in a higher temperature region via W-loading, ternary V₂O₅-WO₃/TiO₂ catalysts were prepared. Three different loadings of V₂O₅ (1, 3 and 5%) were prepared on WO₃(10%)/TiO₂. All the ternary compositions prepared at 450 °C and 650 °C showed anatase single phase. Figure

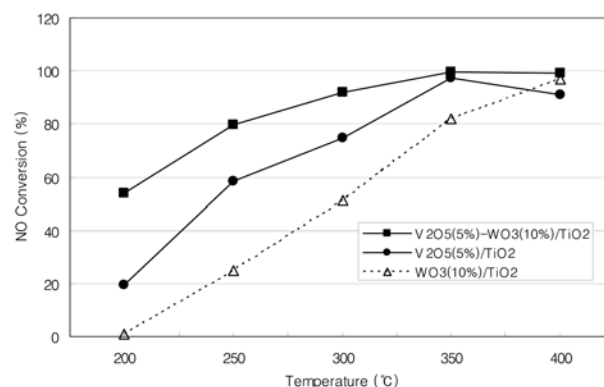


Fig. 7. Comparison of NO conversion efficiency over binary and ternary catalysts with the same catalyst loading prepared at 450 °C.

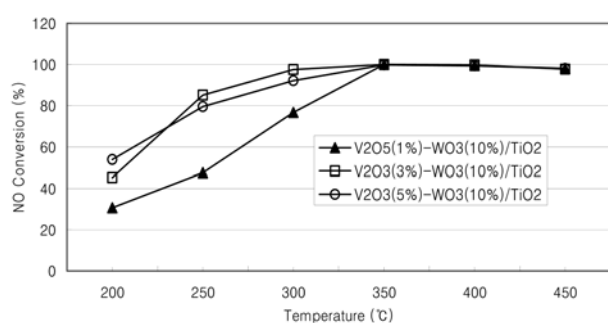


Fig. 8. Comparison of NO conversion efficiency over ternary V₂O₅(1, 3, and 5%)-WO₃(10%)/TiO₂ catalysts prepared at 450 °C.

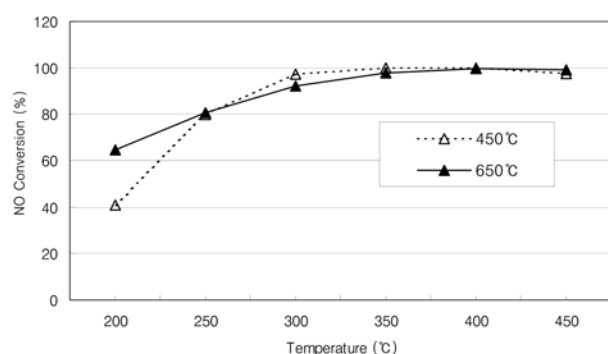


Fig. 9. Conversion of NO versus reaction temperature over V₂O₅(3%)-WO₃(10%)/TiO₂ catalyst prepared at 450 °C and 650 °C.

7 shows the advantageous features of the ternary catalyst system. V₂O₅-WO₃/TiO₂ catalysts exhibited higher efficiency than binary V₂O₅/TiO₂ and WO₃/TiO₂ samples with the same catalyst loading. Among the ternary catalysts, the 3% V₂O₅ loaded WO₃(10%)/TiO₂ sample prepared at 450 °C showed the highest catalytic activity representing the desirable synergistic effects as shown in Fig. 8. Over 80% NO_x conversion efficiency was obtained in the considerably wide temperature range of 250 to 450 °C. The result indicates that more than 3% V₂O₅ addition could be unnecessary in the ternary system.

Figure 9 shows the catalytic efficiency of the V₂O₅(3%)-WO₃(10%)/TiO₂ catalysts prepared at 450 °C and 650 °C. A considerably high activity was observed over a wide temperature range in both cases. For the catalyst prepared at the higher temperature (i.e. 650 °C), the relatively high efficiency at the lowest temperature of 200 °C and the high efficiency value over 98% was retained above 400 °C.

Conclusions

The effects of V- and W-loading on the thermal stability and De-NO_x activity of heat-treated SCR catalysts were investigated for the binary V₂O₅/TiO₂ and WO₃/TiO₂, and ternary V₂O₅-WO₃/TiO₂ catalysts with different

WO₃ (10%) and V₂O₅ (1, 3, 5 and 10%) loadings.

The addition of W promoted the early transition from anatase to the rutile phase at which WO₃ phase segregation was observed. The W loading in the TiO₂ support did not influence the crystallite dimensions and surface area. In the case of the vanadium loading, the transition temperature was considerably reduced with increasing V. A significantly decreased surface area value resulting from a considerable amount of the crystallite growth was observed in V-loaded catalysts. Thus, the V₂O₅ loading for a conventional SCR catalyst could be limited below 10%. For both the V- and W-loaded ternary catalyst, the V-loading considerably lowered the anatase-to-rutile transition temperature and, upon the transition, WO₃ segregation was also observed.

The V and W-loaded binary catalysts showed higher catalytic efficiency in the limited temperature range at low and high reaction temperature regions, respectively. The catalytic activity of all the binary catalysts prepared at 650 °C always showed the higher efficiency and enlarged temperature range where higher efficiency remained in comparison with the catalysts prepared at 450 °C. Ternary V₂O₅-WO₃/TiO₂ catalysts exhibited improved catalytic activity over a wide temperature range taking advantage of the catalytic activity shown in the binary catalysts. This study could contribute to the property design of ternary V₂O₅-WO₃/TiO₂ SCR catalysts.

Acknowledgements

This research was performed under the program of Basic Atomic Energy Research Institute (BAERI), which is a part of the Nuclear R&D Programs funded by the Ministry of Science & Technology (MOST) of Korea.

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