

# Effect of promoters including tungsten and barium on the thermal stability of V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst for NO reduction by NH<sub>3</sub>

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## Abstract

The effect of tungsten and barium on the thermal stability of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst for NO reduction by NH<sub>3</sub> was examined over a fixed bed flow reactor system. The activity of V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst gradually decreased with respect to the thermal aging time at 600 °C. The addition of tungsten to the catalyst surface significantly enhanced the thermal stability of V<sub>2</sub>O<sub>5</sub> catalyst supported on sulfated TiO<sub>2</sub>. On the basis of Raman and XRD measurements, the tungsten on the catalyst surface was identified as suppressing the progressive transformation of monomeric vanadyl species into crystalline V<sub>2</sub>O<sub>5</sub> and of anatase into rutile phase of TiO<sub>2</sub>. However, the NO removal activity of V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst including barium markedly decreased after a short aging time, 6 h at 600 °C. This may be due to the transformation of vanadium species to inactive V–O–Ba compound by the interaction with BaO which was formed by the decomposition of BaSO<sub>4</sub> on the catalyst surface at high reaction temperature of 600 °C. The addition of SO<sub>2</sub> to the feed gas stream could partly restore the NO removal activity of thermally aged V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst containing barium.

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**Keywords:** SCR; Sulfated TiO<sub>2</sub>; Tungsten; Barium; Thermal stability; Vanadyl phase; Titania phase

## 1. Introduction

A vanadia–titania catalyst has been widely employed for selective catalytic reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> due to its high catalytic activity and sulfur tolerance in actual flue gas conditions [1–3]. V<sub>2</sub>O<sub>5</sub> is the active reaction site not only for the reduction of NO<sub>x</sub>, but for the oxidation of SO<sub>2</sub> to SO<sub>3</sub>, which can cause catalyst deactivation and operational problems in an SCR reactor system. Promoters, including tungsten and barium, have been added to the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst to improve the thermal stability due to the retardation of anatase-to-rutile phase transition and reduce the activity of SO<sub>2</sub> oxidation to SO<sub>3</sub>, respectively. The NO removal activity of V<sub>2</sub>O<sub>5</sub> catalyst supported on sulfur-free TiO<sub>2</sub> was significantly enhanced by the addition of tungsten oxide to the surface of the catalyst, while that of V<sub>2</sub>O<sub>5</sub> catalyst supported on sulfated TiO<sub>2</sub> hardly improved [4,5].

Also, the tungsten oxide enhances the activity for SO<sub>2</sub> oxidation, regardless of the presence of sulfur species on the catalyst surface. But the addition of barium oxide on V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst exhibits no change of NO removal activity and the suppression of the activity for SO<sub>2</sub> oxidation [4]. Recently, SCR of NO<sub>x</sub> by urea has been intensively investigated for automotive applications due to the high activity of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst for NO<sub>x</sub> reduction in lean condition such as diesel exhaust gas [6]. However, one of the critical problems, which should be resolved, may be the thermal stability of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst for the commercial application of urea-SCR technology to automotive engine.

In the present study, V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalysts promoted with tungsten and barium oxides were examined to investigate their roles for improving the NO removal activity and thermal stability of the catalyst. The structure of vanadate, titania, and promoters including tungsten and barium on the catalyst surface upon the sintering with and without SO<sub>2</sub> in the feed gas stream were examined by a variety of surface techniques including Raman, XPS and XRD to elucidate the effect of promoters on the catalyst deactivation.

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## 2. Experimental

### 2.1. Catalyst preparation and reaction system

Sulfated titania (ST) and P25 provided from ISK Ltd. and Degussa, respectively, were employed as a support for SCR catalyst [3].  $V_2O_5/TiO_2$  catalysts were prepared by impregnating ammonium metavanadate ( $NH_4VO_3$ ) dissolved in oxalic acid on  $TiO_2$ . The promoters, tungsten or barium, were also loaded on the  $V_2O_5/TiO_2$  catalyst by impregnating the solution of corresponding precursors, ammonium metatungstate ( $NH_4WO_3$ ) and barium perchlorate ( $Ba(ClO_4)_2 \cdot 3H_2O$ ). BET surface area and chemical composition of the catalysts prepared in the present study are summarized in Table 1. The number in the designation of the catalysts denotes the weight percentage of the corresponding metal oxides.

The selective catalytic reduction of NO by  $NH_3$  was carried out in a fixed-bed flow reactor system containing 1 g of 20/30 mesh size catalyst. The details of reactor system and reaction conditions were described in the previous studies [4,7]. A gas mixture typically containing  $NH_3$  (500 ppm), NO (500 ppm),  $O_2$  (5%),  $H_2O$  (5%), and  $N_2$  (balance) was fed to the reactor through mass flow controllers (Brooks 5850). The concentration of NO was analyzed by on-line chemiluminescence NO- $NO_2$  analyzer (Thermo Electron Co., Model 42C). The thermal stability of  $V_2O_5/TiO_2$  catalysts was examined with respect to the thermal aging time at 600 °C, the temperature of interest in the present study and the reactor space velocity of 100,000  $h^{-1}$ . The alteration of the surface characteristics of the catalyst sintered at 600 °C was also examined after being treated with a feed gas stream containing 1000 ppm  $SO_2$ .

### 2.2. Catalyst characterization

The surface area of catalysts prepared in the present study was measured by BET method with Micromeritics ASAP 2010 apparatus using liquid  $N_2$  at 77 K. The sulfur contents of the catalysts were measured with LECO SC-32 analyzer. X-ray powder diffraction (XRD) of the catalysts was examined by X-

ray diffractometer (M18XHF, MAC Science Co.). Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5415 \text{ \AA}$ ) was used as an X-ray gun operated at 40 kV and 200 mA. Diffraction patterns were obtained within the range of  $2\theta = 10\text{--}60^\circ$  at the scanning rate of  $4^\circ \text{ min}^{-1}$ .

Raman spectra were obtained to examine the structure of  $V_2O_5$  and promoters present on the catalyst surface by Renshaw Raman microscope (Model 3000) using He-Ne laser at 632.8 nm. The details of in situ cell systems and the pretreatment conditions have been described elsewhere [3].

The X-ray photoelectron spectra were examined to identify the state of barium species on the promoted catalyst by a Perkin-Elmer PHI 5400 XPS spectrometer with Mg  $K\alpha$  as a radiation source. The charging effect of XPS spectra was calibrated with a carbon peak at 284.6 eV as a standard.

## 3. Results

### 3.1. NO removal activity

The influence of thermal aging on NO removal activity of  $V_2O_5$ /sulfated  $TiO_2$  catalysts has been examined with respect to the thermal aging time at 600 °C and the reactor space velocity of 100,000  $h^{-1}$ . Fig. 1 shows the effect of promoters including barium and tungsten on the thermal stability of  $V_2O_5$  catalysts supported on sulfated  $TiO_2$  for NO reduction by  $NH_3$ . The activity of V2ST catalyst gradually decreased with respect to the thermal aging time. The NO removal activity of V2Ba2ST catalyst containing barium drastically decreased after a short period of the thermal aging time, 6 h at 600 °C. However, the activity loss of the catalyst containing tungsten was not pronounced with respect to the aging time. It indicates that tungsten significantly enhances the thermal stability of  $V_2O_5$ /sulfated  $TiO_2$  catalyst for NO reduction by  $NH_3$  as commonly understood [8].

### 3.2. X-ray diffraction

The structures of surface vanadium and barium species and  $TiO_2$  before and after thermal aging were examined by XRD as

Table 1  
Physicochemical properties of the catalysts employed in the present study

Catalysts	V content (wt.%)	W or Ba content (wt.%)	Sulfur (wt.%)	BET surface area ( $m^2/g$ )
ST <sup>a</sup>	–	–	0.79	88.13
V2STF <sup>b</sup>	2.29	–	0.49	47.26
V2STA24 <sup>c</sup>	2.32	–	0.016	8.84
V2Ba2STF	2.32	1.87	0.81	45.09
V2Ba2STA24	2.42	1.94	0.21	6.14
V2Ba2STA24S <sup>d</sup>	2.38	1.90	0.42	5.54
V2W6STF	2.31	4.60	0.35	53.26
V2W6STA24	2.39	4.80	0.081	18.88
V2Ba2P25 <sup>e</sup>	1.90	1.40	0.20	43.00

<sup>a</sup> ST: sulfated  $TiO_2$ .

<sup>b</sup> F: fresh catalyst.

<sup>c</sup> A24: catalyst aged at 600 °C for 24 h.

<sup>d</sup> A24S: catalyst aged at 600 °C for 24 h and followed by exposing to the feed gas stream containing  $SO_2$  at 500 °C for 3 h.

<sup>e</sup> P25: sulfur-free  $TiO_2$ .

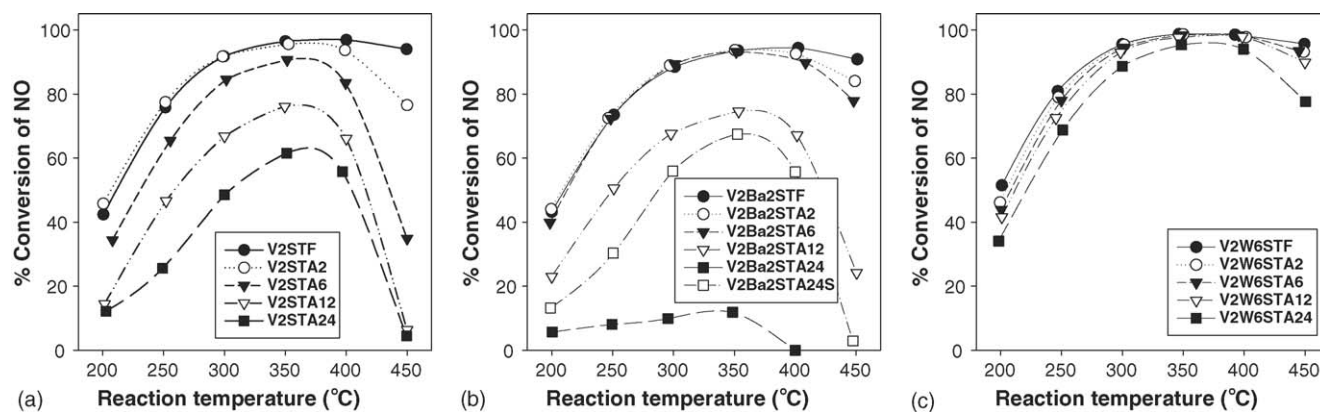


Fig. 1. NO removal activity of  $V_2O_5$ /sulfated  $TiO_2$  catalysts with respect to the thermal aging time at 600 °C: (a) V2ST, (b) V2Ba2ST, and (c) V2W6ST catalysts.

shown in Fig. 2. The XRD peaks of  $TiO_2$  for all the fresh catalysts appear at  $2\theta = 25, 37.5, 47.7, 53.6,$  and  $54.8$ , which are characteristic peaks for the anatase phase of  $TiO_2$ . The crystallinity of  $TiO_2$  becomes obvious after thermal aging for 24 h, indicating that the sintering of  $TiO_2$  takes place by thermal treatment. This may be the reason for the loss of BET surface area as observed in Table 1. For V2STA24 catalyst, especially, strong diffraction peaks for the rutile phase of  $TiO_2$

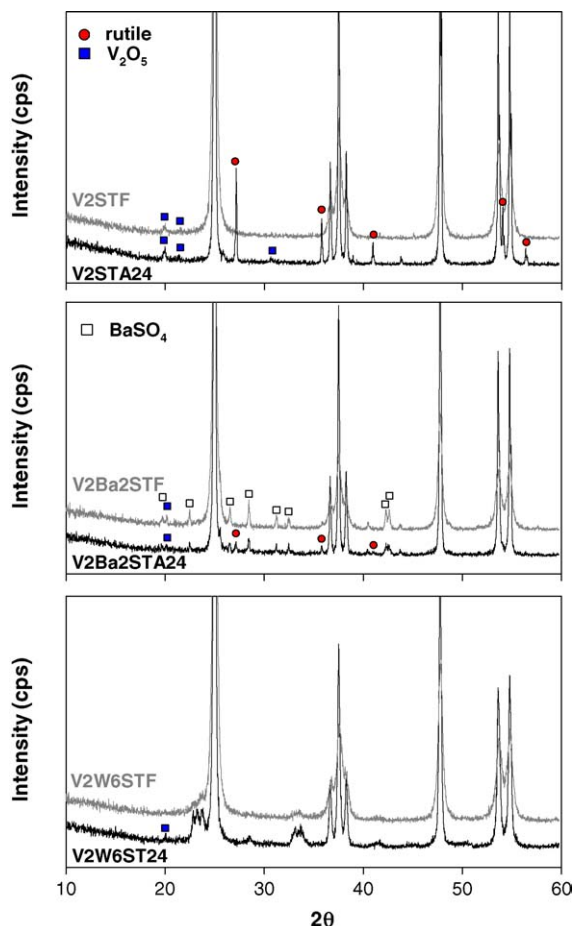


Fig. 2. X-ray diffraction patterns of V2ST, V2Ba2ST, and V2W6ST catalysts before and after thermal aging at 600 °C for 24 h.

are observed at  $2\theta = 27, 35.8, 41, 54.1,$  and  $56.3$ , and a peak for crystalline  $V_2O_5$  on the catalyst surface appears. For V2Ba2STA24 catalyst, the rutile phase of  $TiO_2$  is weakly observed, but the crystalline  $V_2O_5$  is hardly detected by XRD. The peak for  $BaSO_4$  becomes weaker on V2Ba2STA24 than that on V2Ba2STF catalyst. However, for V2W6ST catalysts containing tungsten, the formation of the crystalline  $V_2O_5$  on the catalyst surface and rutile  $TiO_2$  was not observed by XRD even after thermal aging at 600 °C for 24 h. It also reveals that the thermal stability of  $V_2O_5$  catalyst supported on sulfated  $TiO_2$  is significantly enhanced by the addition of tungsten to the catalyst surface.

### 3.3. Effect of $SO_2$ on the thermal stability of V2Ba2STA24 catalyst

As already observed in Fig. 1(b), the NO removal activity of V2Ba2ST catalyst including barium significantly decreased after thermal aging at 600 °C for 24 h. The loss of activity of thermally aged V2Ba2STA24 catalyst seems to be related to the disappearance of  $BaSO_4$  on the catalyst surface, since the amount of  $BaSO_4$  was greatly reduced by thermal aging as shown in Fig. 2. It is well known that the sulfate forms on the catalyst surface by exposing it to a feed gas stream containing  $SO_2$  [9–11]. Therefore, the alteration of NO removal activity of V2Ba2STA24 catalyst was reexamined by treating it with a feed gas stream containing  $SO_2$ . As shown in Fig. 1(b), the NO removal activity of V2Ba2STA24 catalyst was partly regenerated when it was treated with a feed gas stream containing  $SO_2$  at 500 °C for 3 h.

## 4. Discussion

### 4.1. Role of tungsten for the thermal stability of $V_2O_5$ /sulfated $TiO_2$ catalyst

The Raman spectra of vanadium species on the surface of  $V_2O_5$ /sulfated  $TiO_2$  catalysts with respect to the thermal aging time at 600 °C are presented in Fig. 3. It has been generally recognized that the bands at the Raman shifts of 1030 and 900–1000  $cm^{-1}$  represent the terminal  $V=O$  bond

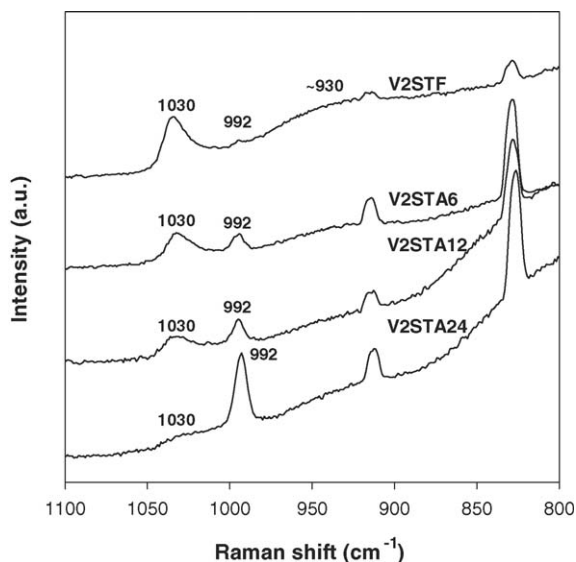


Fig. 3. Raman spectra of V2ST catalysts with respect to the thermal aging time at 600 °C.

of monomeric vanadyl and polymeric vanadyl species, respectively [12–16]. The fresh V2ST catalyst, V2STF, reveals the main peaks at both 1030 and 900–980  $\text{cm}^{-1}$  and a small peak at 992  $\text{cm}^{-1}$ . The sharp spikes at 828 and 912  $\text{cm}^{-1}$  are a laser plasma line. A Raman band at 1030  $\text{cm}^{-1}$  assigned to monomeric vanadyl species gradually decreases with the increase of the thermal aging time and nearly disappears after 24 h of thermal aging at 600 °C; whereas, the intensity of crystalline  $\text{V}_2\text{O}_5$ , which mainly contributes to the oxidation of  $\text{NH}_3$  at high temperature [3], becomes strong as shown in Fig. 3. This reveals that the gradual decrease of NO removal activity of  $\text{V}_2\text{O}_5/\text{sulfated TiO}_2$  catalysts with the increase of the thermal aging time at 600 °C is due to the progressive transformation of monomeric vanadyl species into crystalline  $\text{V}_2\text{O}_5$  of vanadia on the catalyst surface. The formation of crystalline  $\text{V}_2\text{O}_5$  is mainly attributed to the loss of surface area by the sintering of  $\text{TiO}_2$  [3].

To understand the effect of tungsten oxide on the structure of vanadium species upon thermal aging, V2W6ST catalysts were also examined by Raman spectroscopy with respect to the thermal aging time, as shown in Fig. 4. The Raman spectra for vanadium species on sulfated  $\text{TiO}_2$  containing 6 wt.% of  $\text{WO}_3$  also appear at around 1030 and 900–980  $\text{cm}^{-1}$  of Raman shift. In addition, a shoulder peak corresponding to the symmetric stretching of the terminal  $\text{W}=\text{O}$  bond of tungsten oxide appears at around 1010  $\text{cm}^{-1}$  [17–19]. The intensity of the Raman band at around 1030  $\text{cm}^{-1}$  corresponding to the monomeric vanadyl species does not change. However, the intensity of the band at 992  $\text{cm}^{-1}$  assigned to crystalline  $\text{V}_2\text{O}_5$  slightly increases as the sintering reaction proceeds at high reaction temperature of 600 °C. Therefore, one of the main roles of  $\text{WO}_3$  for the thermal stability of  $\text{V}_2\text{O}_5/\text{sulfated TiO}_2$  catalyst may be the reduction of the transformation of vanadium species into crystalline  $\text{V}_2\text{O}_5$ . Furthermore, the loss

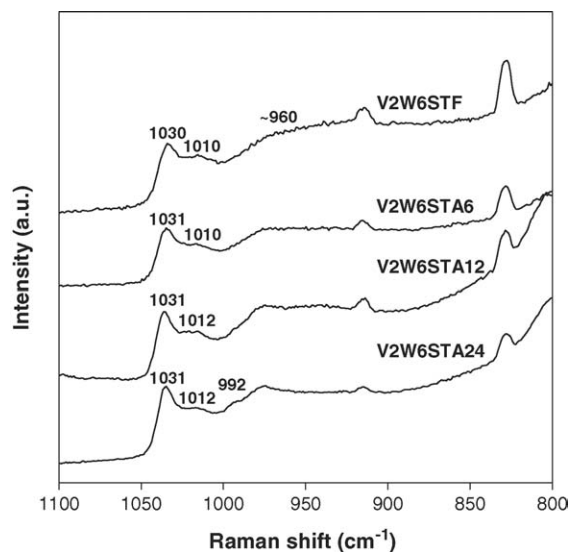


Fig. 4. Raman spectra of V2W6ST catalysts with respect to the thermal aging time at 600 °C.

of BET surface area for V2W6ST catalyst by thermal aging is less than that of V2ST and V2Ba2ST catalysts, as listed in Table 1, and the rutile phase of  $\text{TiO}_2$  is not detected by XRD observation in Fig. 2.

#### 4.2. Role of barium for the thermal stability of $\text{V}_2\text{O}_5/\text{sulfated TiO}_2$ catalyst

Fig. 5 exhibits the Raman spectra of vanadium species on the surface of V2Ba2ST catalysts with respect to the thermal aging time at 600 °C. The Raman spectra for the fresh V2Ba2ST catalyst, V2Ba2STF, reveal the peaks at both 1030 and 900–980  $\text{cm}^{-1}$ . The intensity of a band at 1030  $\text{cm}^{-1}$  gradually decreases, while that at 982  $\text{cm}^{-1}$  slightly increases as the

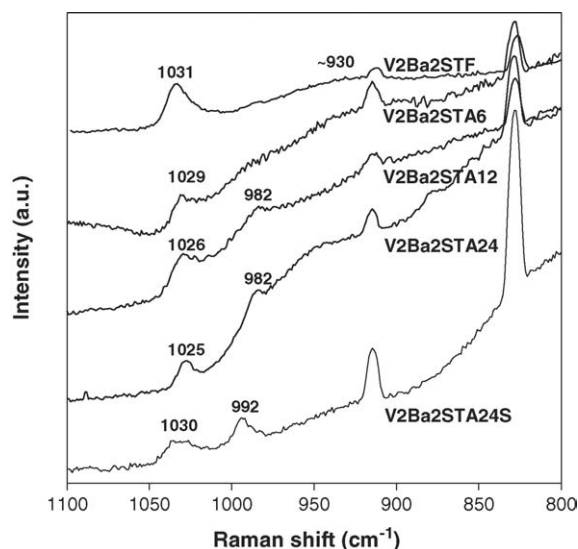


Fig. 5. Raman spectra of V2Ba2ST catalysts with respect to the thermal aging time at 600 °C.

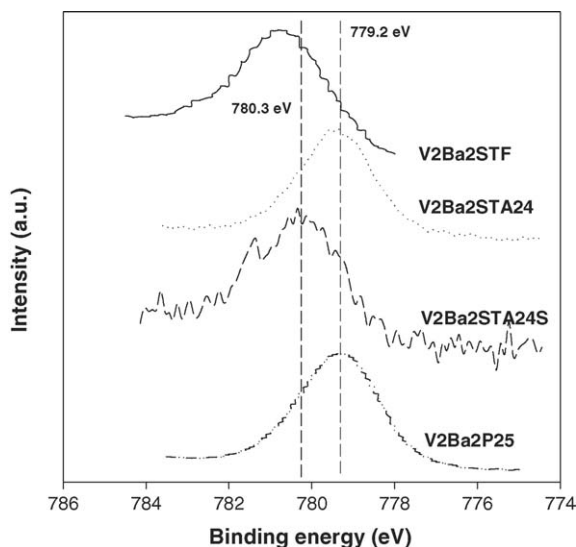


Fig. 6. Ba 3d<sub>5/2</sub>XPS spectra of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts containing barium.

thermal aging time increases. The Raman peaks which are assigned to monomeric vanadyl species and crystalline V<sub>2</sub>O<sub>5</sub> shift to the lower region of Raman bands from 1031 and 992 cm<sup>-1</sup> to 1025 and 982 cm<sup>-1</sup>, respectively. The shift of the Raman band to lower region means a strong interaction between V<sub>2</sub>O<sub>5</sub> on the catalyst surface and barium species formed by thermal aging at a high reaction temperature of 600 °C [4,17].

XPS analysis was conducted to identify the phase of barium species on the surface of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst, as shown in Fig. 6. The binding energy for barium species on sulfated TiO<sub>2</sub>, V2Ba2STF, appears at a higher region of 780–781 eV, which commonly represents barium sulfate [20]. The barium species exist in the form of barium sulfate on the sulfated TiO<sub>2</sub> by the strong interaction of basic barium with acidic sulfate [4]. However, the binding energy of barium species on V<sub>2</sub>O<sub>5</sub>/sulfur-free TiO<sub>2</sub>, V2Ba2P25, appears at around 779.2 eV, which is assigned to barium oxide species [21]. The barium may exist in the form of V–O–Ba compound by a strong interaction of BaO with V<sub>2</sub>O<sub>5</sub> species on the surface of sulfur-free TiO<sub>2</sub> [4].

For V2Ba2STA24 catalyst, an XPS spectrum for the barium species shifts to around 779.2 eV. It indicates that barium sulfate on the catalyst surface transforms into barium oxide through thermal aging at 600 °C. The NO removal activity of V2Ba2ST catalyst was significantly decreased by thermal aging, as observed in Fig. 1. Therefore, it suggests that the reduction of NO removal activity of V2Ba2ST catalyst by thermal aging is mainly due to the alteration of vanadium species into the inactive species on the catalyst surface. For V2Ba2STA24S catalyst treated with the feed gas stream containing SO<sub>2</sub>, however, an XPS spectrum for the barium species shifts to around 780.3 eV again. In addition, the Raman band of vanadia species on V2Ba2A24S shifts to the original region of 1030 and 992 cm<sup>-1</sup>, which is similar to that of fresh V2Ba2ST catalyst, as shown in Fig. 5. The vanadyl species, which is active for NO reduction, are regenerated by treating thermally aged

V2Ba2STA24 catalyst with a feed gas containing SO<sub>2</sub>. This is mainly caused by the strong interaction of barium species in V–O–Ba compounds with SO<sub>2</sub> forming barium sulfate. It may be the reason why NO removal activity of thermally aged V2Ba2STA24 catalyst is partly recovered by SO<sub>2</sub> in the feed gas stream.

## 5. Conclusions

V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalysts promoted with tungsten or barium species were examined to elucidate the alteration of the catalyst characteristics upon sintering. The activity of V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst gradually decreased with respect to the thermal aging time at 600 °C due to the progressive transformation of monomeric vanadyl species into crystalline V<sub>2</sub>O<sub>5</sub> and of anatase into rutile phase of TiO<sub>2</sub>. NO removal activity of V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst including barium drastically decreased after a short period of the thermal aging time, 6 h at 600 °C. This is due to the interaction between V<sub>2</sub>O<sub>5</sub> and BaO on the catalyst surface at high reaction temperature of 600 °C. The addition of SO<sub>2</sub> to the feed gas stream could partly restore the NO removal activity of V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst including barium which was thermally aged. The amount of V–O–Ba compound formed on the sintered V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> was decreased by exposing it to SO<sub>2</sub> in the feed gas as observed by Raman and XPS. It may be the reason for restoring NO removal activity of the catalyst by SO<sub>2</sub>. The thermal stability of V<sub>2</sub>O<sub>5</sub> catalyst supported on sulfated TiO<sub>2</sub>, however, was significantly improved by the addition of tungsten to the catalyst. The main role of tungsten on V<sub>2</sub>O<sub>5</sub>/sulfated TiO<sub>2</sub> catalyst for thermal aging was the suppression of the transformation of monomeric vanadyl species into crystalline V<sub>2</sub>O<sub>5</sub> on the catalyst surface as well as of the phase of TiO<sub>2</sub> from anatase to rutile, as confirmed by the catalyst characterization including BET, XRD, and Raman.

## References

- [1] H. Bosch, F.J.J.G. Janssen, Catal. Today 2 (1988) 369.
- [2] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B 18 (1998) 1.
- [3] S.T. Choo, Y.G. Lee, I.-S. Nam, S.-W. Ham, J.-B. Lee, Appl. Catal. A 200 (2000) 177.
- [4] S.T. Choo, S.D. Yim, I.-S. Nam, S.-W. Ham, J.-B. Lee, Appl. Catal. B 44 (2003) 237.
- [5] S.T. Choo, S.-W. Ham, I.-S. Nam, I.Y. Lee, D.W. Kim, J.B. Lee, H.M. Uhm, P.S. Gi, US Patent 6,380,128 B1 (2002).
- [6] M. Koebel, M. Elsener, M. Kleemann, Catal. Today 59 (2000) 335.
- [7] S.-W. Ham, H. Choi, I.-S. Nam, Y.G. Kim, Catal. Today 11 (1992) 611.
- [8] G. Oliveri, G. Ramis, G. Busca, V.S. Escribano, J. Mater. Chem. 3 (1993) 1239.
- [9] P. Engström, A. Amberntsson, M. Skoglundh, E. Fridell, G. Smedler, Appl. Catal. B 22 (1999) L241.
- [10] A. Amberntsson, M. Skoglundh, S. Ljungström, E. Fridell, J. Catal. 217 (2003) 253.
- [11] F. Rohr, S.D. Peter, E. Lox, M. Kögel, A. Sassi, L. Juste, C. Rigaudeau, G. Belot, P. Gilin, M. Primet, Appl. Catal. B 56 (2005) 201.
- [12] M.A. Vuurman, I.E. Wachs, A.M. Hirt, J. Phys. Chem. 95 (1991) 9928.

- [13] G.T. Went, L.J. Leu, A.T. Bell, *J. Catal.* 134 (1992) 479.
- [14] M.D. Amiridis, I.E. Wachs, G. Deo, J.M. Jehng, D.S. Kim, *J. Catal.* 161 (1996) 247.
- [15] S.T. Oyama, G.T. Went, K.B. Lewis, A.T. Bell, G. Somorjai, *J. Phys. Chem.* 93 (1983) 6786.
- [16] G.T. Went, S.T. Oyama, A.T. Bell, *J. Phys. Chem.* 94 (1990) 4240.
- [17] G. Deo, I.E. Wachs, *J. Catal.* 146 (1994) 335.
- [18] J.P. Dunn, H.G. Stenger, I.E. Wachs, *Catal. Today* 53 (1999) 543.
- [19] I.E. Wachs, *Catal. Today* 27 (1996) 437.
- [20] J. Beyer, T. Schurig, S. Menkel, Z. Quan, H. Koch, *Physica C* 246 (1995) 156.
- [21] N. Ikeo, Y. Iijima, N. Niimura, M. Sigematsu, T. Tazawa, S. Matsumoto, K. Kojima, Y. Nagasawa, *Handbook of X-ray Photoelectron Spectroscopy, Serving Advanced Technology*, JEOL, 1991, p. 194.