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Catalysis Today 63 (2000) 405–411

CATALYSIS TODAY

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# Vanadium-containing catalysts for the selective oxidation of $H_2S$ to elemental sulfur in the presence of excess water

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## Abstract

Various vanadium-containing catalysts were searched for the commercial application in the selective oxidation of $H_2S$ to elemental sulfur at low temperatures (less than 250°C) in the presence of excess (more than 35 vol.%) water. In the test of binary oxides, it was found that $TiVO_x$ was the only catalyst that could sustain its activity without deactivation at 230°C. The best catalytic activity (85–90% sulfur yield) was obtained when $VO_x/TiO_2$ was incorporated with other metals such as Fe, Cr and Mo. Reaction occurred via redox mechanism and the reoxidation of reduced vanadium was the rate-limiting step. A long-term deactivation observed during the reaction was due to slower reoxidation of reduced vanadium by oxygen than the reduction by $H_2S$. Catalytic activities of $VO_x/SiO_2$, $VO_x/TiO_2$ and V–Fe–Cr–Mo–$O_x/TiO_2$ were well correlated with their redox properties that were observed by TPR/TPO and XPS measurements. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* $H_2S$ selective oxidation; Sulfur; Binary oxides; $VTiO_x$; Redox

## 1. Introduction

For treating a low concentration of $H_2S$ in the tail gas from the Claus plant or in other emission sources, various commercial processes that are based on adsorption, absorption and wet oxidation have been used [1,2]. Recently developed were dry catalytic processes that were based on the selective catalytic oxidation of $H_2S$ to elemental sulfur. Commercially developed are titanium-based catalysts in MODOP process [3,4], and iron-based catalysts in SuperClaus process [5–16]. These processes are based on the following irreversible selective oxidation of $H_2S$ to S (1) as a main reaction, and other oxidation reactions ((2) and (3)) and the reversible Claus reaction (4) as side reactions.

$$H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{n}S_n + H_2O \tag{1}$$

$$\frac{1}{n}S_n + O_2 \rightarrow SO_2 \tag{2}$$

$$H_2S + \tfrac{3}{2}O_2 \rightarrow SO_2 + H_2O \tag{3}$$

$$2H_2S + SO_2 \leftrightarrow \frac{3}{n}S_n + 2H_2O \tag{4}$$

It is known that $TiO_2$-based catalyst is easily poisoned by the presence of water vapor. The iron-based catalyst is resistant against water, but requires an excess amount of oxygen (10 times the stoichiometric amount).

Catalyst containing vanadium oxide has also been reported to be active for the reaction both with a stoichiometric and an excess amount of oxygen [17–30]. Bulk $V_2O_5$ was most active over other bulk metal oxides [17]. $VBiO_x/SiO_2$ was used to remove a

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PII: S0920-5861(00)00485-5

long-term deactivation shown with $V/SiO_2$ [18–24]. But the catalyst still needed a dehydration step before catalytic reactor to increase the conversion (BSR Selectox Process) [18–24]. It was suggested that the cause of deactivation was formation of less active forms of vanadium, such as vanadyl sulfate ($VOSO_4$). Various binary oxides such as V–Mg, V–Bi, V–Mo, V–Sb, Fe–Sn, Bi–Mo were also tested in excess oxygen without feeding water [25–28]. Solid solutions of vanadium, $A_{4\pm y}V_{2\pm x}O_9$ (A $=$ Mg, Ca or Zn; $0 \le x \le 0.2$, $0 \le y \le 0.5$) [29,30] were active even in the presence of 30 vol.% of water. However, the catalysts have not been commercialized yet probably because of uncertainty in the water poisoning effect and long-term stability of the catalyst.

We investigated vanadium-containing catalysts for the selective oxidation of $H_2S$ to elemental sulfur in order to understand reaction mechanism and the cause of deactivation. Based on the understanding, we can formulate new types of vanadium-containing multi-component catalysts that do not exhibit deactivation and have a strong resistance against water.

## 2. Experimental

### 2.1. Catalyst preparation

$VO_x/TiO_2$ and $VO_x/SiO_2$ were prepared by dissolving an ammonium metavanadate ($NH_4VO_3$, Junsei, Japan) in 5 wt.% of oxalic acid solution containing the support material. After evaporation, samples were dried at 110°C overnight and calcined at 450°C for 5 h. $SiO_2$ was purchased from Aldrich (Davisil; $300\,m^2\,g^{-1}$, 60–100 mesh, pore volume $1.15\,cm^3\,g^{-1}$) and $TiO_2$ was from Degussa (P-25; $50\,m^2\,g^{-1}$). $TiO_2$ was also made by drying metatitanic acid, $TiO(OH)_2$, a solid suspension of $40\,g\,l^{-1}$, at 120°C overnight and calcining the dried sample at 700°C for 6 h with air. After calcination, manufactured $TiO_2$ has anatase structure and $40\,m^2\,g^{-1}$ of surface area. The manufactured $TiO_2$ are expressed hereafter as m-$TiO_2$, where m is the abbreviation of manufactured. All the supported catalysts are expressed as A($x$)/B, where A, B and $x$ represent metal, support and metal loading, respectively.

For the preparation of vanadium-containing binary oxides, metal salts were dissolved in 5 wt.% of nitric acid solution. A solid precursor that was obtained either by evaporation or by precipitation with aqueous ammonia solution was dried at 110°C overnight, and calcined at 450°C for 5 h. Exception to this procedure was binary oxide with zirconium, which was calcined at 700°C for 5 h to make a known structure of vanadium zirconate, $ZrV_2O_7$. For the preparation of multi-component catalysts containing Fe, Cr, Mo and/or Bi, precursors were dissolved in 5 wt.% of nitric acid solution and precipitated with 28 wt.% of drop wise aqueous ammonia solution. This was followed by drying at 110°C overnight and calcination at 450°C for 5 h.

Chemicals used for the catalyst preparation were manganese sulfate ($MnSO_4{\cdot}H_2O$, Junsei, Japan), tatanium(IV) butoxide ($Ti[O(CH_2)_3CH_3]_4$, Aldrich), cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, Aldrich), ammonium hepta molybdate ($(NH_4)_6Mo_7O_2{\cdot}4H_2O$, Aldrich), ammonium dichromate ($(NH_4)_2Cr_2O_7$, Alfa), iron(III) nitrate enneahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, Kokusan, Japan).

### 2.2. Reaction test

The reaction test was carried out using a vertical packed-bed reactor made of 1-in. Pyrex tube at atmospheric pressure. The feed stream for the reaction contained 5 vol.% hydrogen, a stoichiometric amount (2.5 vol.%) of oxygen and 30 vol.% of water in balance helium. Hydrogen sulfide (Solkatronic Chemical) and air were mixed and diluted in He using mass flow controllers. Water was injected using a syringe pump to a vaporizer that was located before the reactor. Sulfur in the product was separated using a sulfur condenser that was located at the effluent side of the reactor. The temperature of the sulfur condenser was maintained constant at 110°C. A line filter was also installed after the sulfur condenser to trap any sulfur mist that was not collected by the condenser. From the line filter up to the gas chromatograph, all the lines and fittings were heated above 150°C to prevent condensation of sulfur and water vapor. The gaseous products $H_2S$ and $SO_2$ were analyzed by a gas chromatograph (Hewlett Packard 5890) with a Porapak T-column (80/100 mesh, 1.5 m) and a thermal conductivity detector. The exit gas from the analyzer was passed through a trap containing a concentrated NaOH solution and vented out to a hood. The conversion of hydrogen sulfide, the selectivity to sulfur and the yield of sulfur were defined as follows:

$$\text{Conversion of } H_2S\ (\%) = \frac{[H_2S]_{\text{inlet}} - [H_2S]_{\text{outlet}}}{[H_2S]_{\text{inlet}}} \times 100$$

$$\text{Selectivity to sulfur } (\%) = \frac{[H_2S]_{\text{inlet}} - [H_2S]_{\text{outlet}} - [SO_2]_{\text{outlet}}}{[H_2S]_{\text{inlet}} - [H_2S]_{\text{outlet}}} \times 100$$

$$\text{Yield of sulfur } (\%) = \frac{\text{conversion of } H_2S \times \text{selectivity of sulfur}}{100}$$

### 2.3. Characterization

X-ray photoelectron spectra (XPS) were obtained using an ESCALAB 220i (VG Scientific), equipped with Al Kα monochromatic X-ray (1487.0 eV) radiation at 10 kV and 15 mA. Catalysts were uniformly ground into powder and then pressed into self-supporting wafers without any binder. The catalysts were pretreated at an ultrahigh vacuum of 10–12 mm Hg for 10 h. A charging effect of XPS spectra was carefully corrected with the standard carbon peak at 284.6 eV. Temperature-programmed reduction and oxidation (TPR and TPO) were carried out using a packed-bed reactor containing 0.15 g of sample that was pretreated with He at 400°C for 1 h. Gas mixtures of $H_2$(5 vol.%)/$N_2$ and $O_2$(1 vol.%)/He were used for TPR and TPO, respectively. Flow rate of gas and heating rate of temperature were kept at 30 ml min$^{-1}$ and 5°C min$^{-1}$, respectively. The amount of oxygen loss and gain was measured by a thermal conductivity detector (TCD).

## 3. Results and discussion

### 3.1. Reaction over $VO_x/SiO_2$

Conversion of $H_2S$ and selectivity to sulfur were measured over $VO_x/SiO_2$ at 230°C and the results are shown in Fig. 1. The selectivity to sulfur stays more or less constant during the reaction time for more than 70 h, whereas the conversion of $H_2S$ shows a continuous decrease with the reaction time. Lower vanadium content in the catalyst exhibits faster deactivation. Fig. 2 shows the effect of oxygen in the feed on the conversion and selectivity. When a feed containing $H_2S$ only (without oxygen) is passed over fresh catalyst, the complete conversion that is achieved initially shows a dramatic decrease to almost zero value

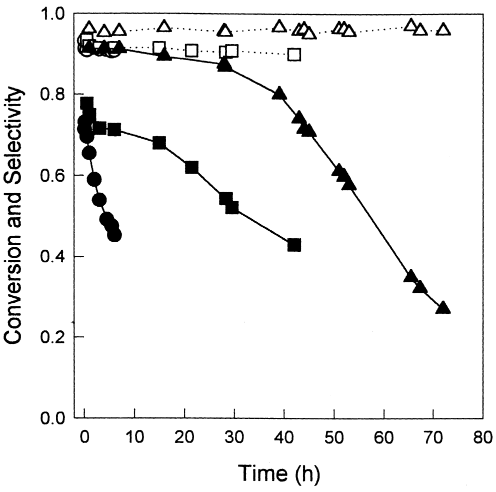

Fig. 1. The conversion of $H_2S$ (filled symbol with solid line) and selectivity to sulfur (open symbol with dotted line) of $VO_x/SiO_2$ following vanadium loading: (●) V(10)/$SiO_2$; (■) V(20)/$SiO_2$; (▲) $V_2O_5$. Reaction condition: $H_2S$ 5 vol.%, $O_2$ 2.5 vol.%, $H_2O$ 30 vol.%, 230°C, GHSV 94 000 h$^{-1}$.

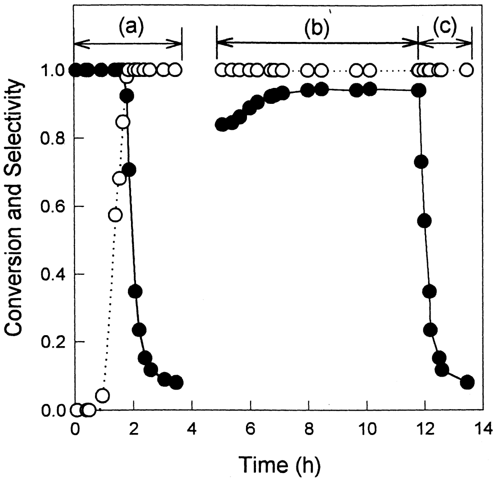

Fig. 2. Conversion of $H_2S$ and selectivity to sulfur of $V_2O_5$ with or without oxygen supply, (● with solid line) conversion; (○ with dotted line) selectivity: (a) feeding $H_2S$ 1 vol.% only; (b) supplying $H_2S$ 1 vol.% and $O_2$ 0.5 vol.%. Reaction condition: 240°C, GHSV 3000 h$^{-1}$.

in about 2 h. The fresh $V_2O_5$ catalyst produces only the complete oxidation product $SO_2$. As the reaction proceeds, the sulfur production increases and 100% selectivity to sulfur can be achieved in 2 h. The results clearly show that an oxidized form of vanadium having very active surface oxygen produces $SO_2$. The complete oxidation period of the initial 0.5 h as shown in Fig. 2 corresponds to the consumption of four times of monolayer oxygen in the fresh $V_2O_5$ (with the assumption that one $VO_4$ occupies 0.1 $nm^2$ at the surface [31]). When $V_2O_5$ is reduced to a suboxide having $V : O = 1 : 1.94$ after the reaction for 2 h, the complete conversion begins to decrease and only sulfur is produced probably due to the depletion of labile oxygen in vanadium. We therefore suggest that only less labile lattice oxygen in reduced vanadium oxides can produce sulfur via redox mechanism. After the reaction without oxygen for 4 h, the reactor was purged with helium for 1 h and the feed was switched to 1 vol.% of $H_2S$ and a stoichiometric amount of $O_2$ (the region (b) in Fig. 2). The conversion increases quickly and reaches a steady state. When the feed is switched again to $H_2S$ without oxygen (the region (c) in Fig. 2), an immediate decreasing pattern of the conversion that has been observed in the region (a) is observed. It is interesting to note that the selectivity does not show any change during the change of the feed composition between regions (b) and (c). A reproducible performance in the conversion and selectivity was observed during repeated switch between regions (b) and (c). When oxygen is added in the feed, the conversion and selectivity seems to attain steady values after filling up the lattice oxygen from gas phase molecular oxygen. From the results, it can be suggested that the steady decrease in the conversion shown in Fig. 1 with a long time of the reaction must be caused by a slow reduction of vanadium. This agrees with the conclusion that sulfation is not a main cause of deactivation [32] as suggested by others [18–24]. We therefore conclude that the slow deactivation is caused by the steady reduction of $V_2O_5$, originated from the relatively slow rate of reoxidation of $V_2O_5$ by gas phase oxygen.

### 3.2. Screen test of vanadium-containing binary and multi-metallic oxides

Fig. 3 shows the conversion and selectivity observed in various vanadium-containing binary oxides at 230°C. $TiO_2$, $Cr_2O_3$, $Fe_2O_3$ and $Zr_2O_3$ were chosen for their known activities for this reaction based on others' works [4–25] and our previous screen test results [33]. $Ce_2O_3$ and $MnO_2$, well-known oxygen donors, were chosen to facilitate the oxygen transfer to reduced $VO_x$. Among tested binary oxides, $TiVO_x$ is the only catalyst that sustains a stable conversion and the others are deactivated eventually.

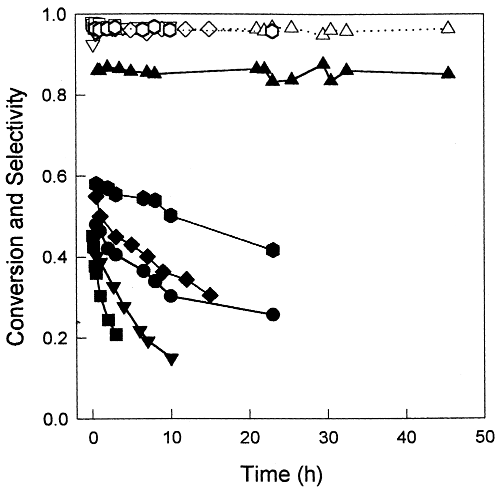

Fig. 3. Conversion of $H_2S$ (filled symbol with solid line) and selectivity to sulfur (open symbol with dotted line) for various vanadium-containing binary oxides: (●) $FeVO_x$; (■) $CrVO_x$; (▲) $TiVO_x$; (▼) $CeVO_x$; (◆) $MnVO_x$; (⬢) $ZrV_2O_7$. Reaction condition: $H_2S$ 5 vol.%, $O_2$ 2.5 vol.%, $H_2O$ 30 vol.%, 230°C, GHSV 94 000 $h^{-1}$.

Fig. 4 shows the conversion of $H_2S$ and selectivity to sulfur for various supported type of $V_2O_5$ containing $TiO_2$. $TiO_2$ alone shows a low conversion of ca. 10% and a fast deactivation. A superior activity and no deactivation is observed for V(10)/$TiO_2$ and V(10)–Ti(10)/$SiO_2$. V(10)/m-$TiO_2$ shows somewhat lower activity than that of V(10)/$TiO_2$. m-$TiO_2$ contains about 1.5 wt.% of sulfate from its source metatitanic acid, $TiO(OH)_2$, which is the middle product of sulfate process for manufacturing pigment type $TiO_2$, supplied from Hankook Titanium, Korea. This implies that the presence of sulfate may be the reason for lower conversion.

In order to improve the redox properties of $VO_x/TiO_2$, multi-metallic oxides containing iron, chromium, molybdenum and/or bismuth were prepared and the conversion and selectivity were

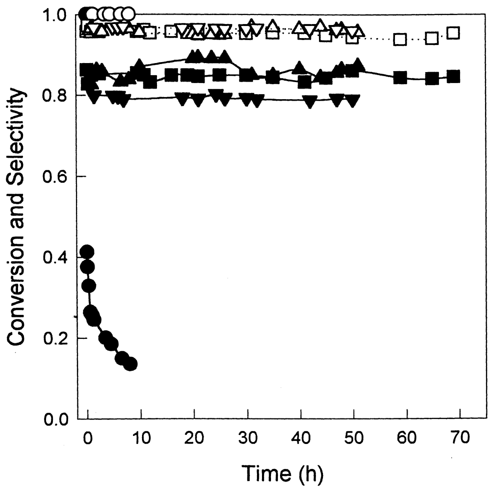

Fig. 4. Conversion of $H_2S$ (filled symbol with solid line) and selectivity to sulfur (open symbol with dotted line) for various $TiO_2$-containing catalysts: (●) $TiO_2$; (■) V(10)/$TiO_2$ (Degussa, P-25); (▲) V(10)–Ti(10)/$SiO_2$; (▼) V(10)/m-$TiO_2$. Reaction condition: 230°C, GHSV 94 000 $h^{-1}$.

compared at 230°C as shown in Fig. 5. The multi-metallic oxide, V–Fe–Cr–Mo–$O_x$/$TiO_2$, exhibits superior performance (90% conversion) to other vanadium-containing binary or multi-component catalysts (84% of $VO_x$/$TiO_2$ or V–Bi–Cr–Mo–$O_x$/$TiO_2$). The catalyst was tested in a pilot scale (with a 100 $nm^3\,h^{-1}$ process gas having 2 vol.% $H_2S$) using a packed-bed reactor for 6 months. A good performance (80–90% sulfur yield) was achieved without showing any deactivation even in the presence of an excess water (30–40 vol.%) in the feed.

### 3.3. Redox property

In Fig. 6, the redox properties were investigated using the TPR–TPO measurements for various vanadium-containing catalysts of $VO_x$/$SiO_2$, $VO_x$/$TiO_2$ and V–Fe–Cr–Mo–$O_x$/$TiO_2$. To avoid the structural change of $TiO_2$, from anatase to rutile, in the presence of $V_2O_5$ [34], catalyst was heated up to 520°C and stayed 1 h at the same temperature. It is evident that, both in TPR and TPO, the location of peak maximum is lower in the order of $V–Fe–Cr–Mo–O_x/TiO_2 < VO_x/TiO_2 < VO_x/SiO_2$. The results agreed with the observation of the color change of catalyst during the TPR/TPO experiments. The dark brown color of V(10)/$TiO_2$ observed during the TPR recovered the initial yellow color during the TPO, which is a characteristic of $V_2O_5$. The reduced V(10)/$SiO_2$ could not recover the initial yellow color but showed dark brown color which is a characteristic

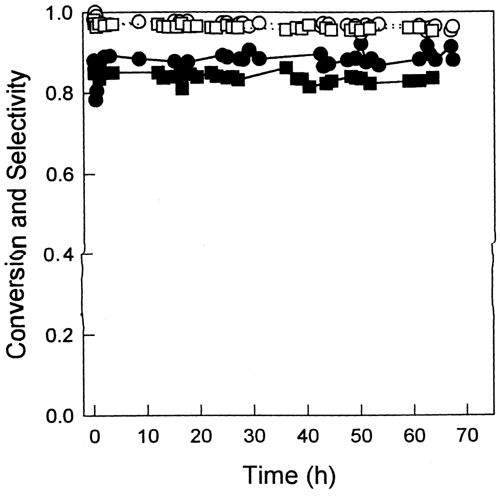

Fig. 5. Conversion of $H_2S$ (filled symbol with solid line) and selectivity to sulfur (open symbol with dotted line) for vanadium-containing multi-metallic oxides: (●) V(10)–Fe(5)–Cr(2.5)–Mo(2.5)–$O_x$/$TiO_2$; (■) V(10)–Bi(5)–Cr(2.5)–Mo(2.5)–$O_x$/$TiO_2$. Reaction condition: 230°C, GHSV 94 000 $h^{-1}$.

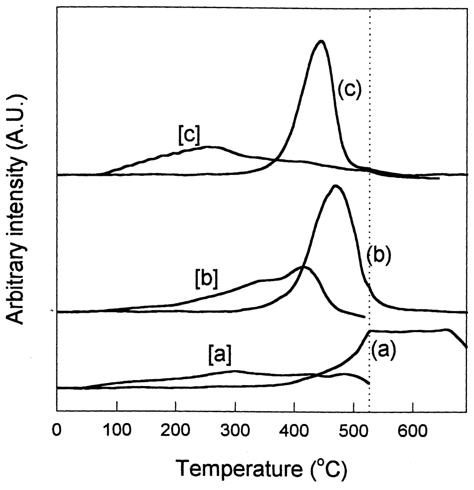

Fig. 6. Temperature-programmed reduction and oxidation (TPR, TPO) for various vanadium-containing catalysts (0.15 g): (a) V(10)/$SiO_2$ TPR, [a] V(10)/$SiO_2$ TPO; (b) V(10)/$TiO_2$ TPR, [b] V(10)/$TiO_2$ TPO; (c) V(10)–Fe(5)–Cr(2.5)–Mo(2.5)–$O_x$/$TiO_2$ TPR, [c] V(10)–Fe(5)–Cr(2.5)–Mo(2.5)–$O_x$/$TiO_2$ TPO.

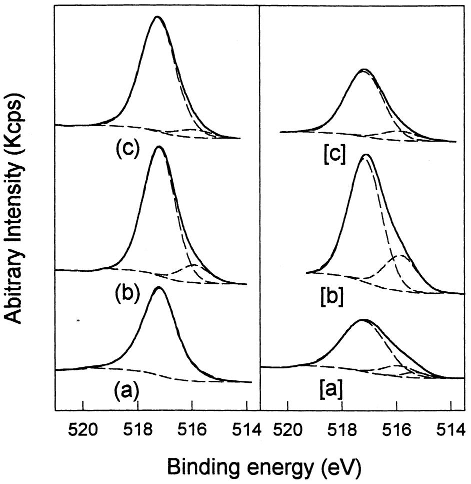

Fig. 7. XPS analyses for various vanadium-containing catalysts: (a) V(10)/$SiO_2$ fresh, [a] V(10)/$SiO_2$ reacted; (b) V(10)/$TiO_2$ fresh, [b] V(10)/$TiO_2$ reacted; (c) V(10)–Fe(5)–Cr(2.5)–Mo(2.5)–$O_x$/$TiO_2$ fresh, [c] V(10)–Fe(5)–Cr(2.5)–Mo(2.5)–$O_x$/$TiO_2$ reacted. Reaction condition: 230°C, GHSV 94 000 $h^{-1}$.

of reduced $V_2O_5$, such as $V_2O_4$ and $V_2O_3$. The ignition temperatures of both reduction and oxidation are the lowest in the multi-metallic oxide. The oxidation of V–Fe–Cr–Mo–$O_x$/$TiO_2$ occurs over a broad range of temperatures with a peak maximum around 250°C, which is much lower (by 150°C) than that of $VO_x$/$TiO_2$.

To compare the oxidation state of vanadium in various catalysts, XPS was carried out before and after the reaction and the results are shown in Fig. 7. Fresh V/$SiO_2$ that has only V(+5) balance state is reduced down to V(+3) balance state after the reaction. V/$TiO_2$ catalysts that contains initially a small portion of V(+4) balance state is not reduced to V(+3) balance state after the reaction. V–Fe–Cr–Mo–$O_x$/$TiO_2$ contains much smaller portion of V(+4) state than that of V(10)/$TiO_2$ after the reaction.

We have suggested that, from the results of Figs. 1 and 2, the deactivation of $VO_x$/$SiO_2$ is caused by the relatively slow rate of reoxidation. Therefore, higher activities of $VO_x$/$TiO_2$ (Fig. 4) and V–Fe–Cr–Mo–$O_x$/$TiO_2$ (Fig. 5) must result from their improved redox properties, especially the improvement of the reoxidation properties that are confirmed by TPR–TPO (Fig. 6) and XPS (Fig. 7) results.

## 4. Conclusion

Various vanadium-containing catalysts were studied for the selective oxidation of $H_2S$ to elemental sulfur in order to find a catalyst that did not show deactivation during the reaction at low temperatures even in the presence of water. In the screen test of binary oxides, $TiVO_x$ was the only catalyst that could sustain its activity without deactivation at 230°C. Much higher activity was observed when the binary oxide containing $VO_x$ and $TiO_2$ became multi-metallic by incorporation with Fe, Cr and Mo. Reaction proceeds via redox mechanism. High activities and stability of $VO_x$/$TiO_2$ and V–Fe–Cr–Mo–$O_x$/$TiO_2$ were well correlated with their redox properties, measured by TPR–TPO and XPS experiment.

## References

[1] J.E. Naber, J.A. Wesselingh, Chem. Eng. Prog. 69 (12) (1973) 29.
[2] B.G. Goar, Oil Gas J. 25 (1975) 96.
[3] R. Kettner, N. Liermann, Oil Gas J. 11 (1983) 63.
[4] R. Kettner, T. Lubcke, N. Liermann, Europe Patent 0 078 690 (1983), to Mobil Oil Corporation.
[5] P.J. Brink, J.W. Geus, Europe Patent 0 409 353 (1991), to VEG-Gasinstituut N.V. and Comprimo B.V.
[6] P.H. Berban, J.W. Geus, US Patent 4 818 740 (1989), to VEG-Gasinstituut N.V. and Comprimo B.V.
[7] P.H. Berban, J.W. Geus, US Patent 5 037 629 (1991), to VEG-Gasinstituut N.V. and Comprimo B.V.
[8] P.J. van den Brink, J.W. Geus, US Patent 5 352 422 (1994), to VEG-Gasinstituut N.V. and Comprimo B.V.
[9] P.J. van den Brink, R.J.A.M. Terorde, J.H. Moors, A.J. van Dillen, J.W. Geus, in: P. Ruiz, B. Delmon (Eds.), New Developments in Selective Oxidation by Heterogeneous Catalysis, Elsevier, Amsterdam, 1991, p. 123.
[10] R.J.A.M. Terorde, P.J. van den Brink, L.M. Visser, A.J. van Dillen, Catal. Today 17 (1993) 217.
[11] J.A. Lagas, J. Borsboom, P.H. Berben, Oil Gas J. 86 (1988) 68.
[12] P.J. van den Brink, A. Scholten, A.J. van Dillen, J.W. Geus, in: C.H. Bartholomew, J.B. Butt (Eds.), Catalyst Deactivation, Elsevier, Amsterdam, 1991, p. 515.
[13] P.J. van den Brink, A. Scholten, A. van Wagenningen, M.D.A. Lamers, A.J. van Dillen, J.W. Geus, in: G. Poncelet, P.A. Jacobs, P. Grange, B. Delmon (Eds.), Preparation of Catalysts V, Elsevier, Amsterdam, 1991, p. 527.
[14] P.F.M.T. van Nisselrooy, J.A. Lagas, Catal. Today 16 (1993) 263.
[15] E. Nasato, R.S. MacDougall, J.A. Lagas, Oil Gas J. 28 (1994) 45.

[16] R.J.A.M. Terorde, M.C. de Jong, M.J.D. Crombag, P.J. Van den Brink, A.J. Van Dillen, J.W. Geus, Stud. Surf. Sci. Catal. 82 (1994) 861.

[17] V.I. Marshneva, V.V. Mokrinskii, Kinet. Catal. 29 (4) (1988) 989.

[18] R.H. Hass, R.C. Hansford, H. Henning, US Patent 4 088 743 (1978), to Union Oil Company.

[19] R.H. Hass, R.C. Hansford, US Patent 4 169 136 (1979), to Union Oil Company.

[20] R.H. Hass, US Patent 4 171 347 (1979), to Union Oil Company.

[21] R.H. Hass, R.C. Hansford, US Patent 4 311 683 (1982), to Union Oil Company.

[22] R.H. Hass, R.C. Hansford, US Patent 4 314 983 (1982), to Union Oil Company.

[23] R.H. Hass, J.W. Ward, US Patent 4 444 741 (1984), to Union Oil Company.

[24] R.H. Hass, J.W. Ward, US Patent 4 528 277 (1985), to Union Oil Company.

[25] K.T. Li, M.Y. Hyang, W.-D. Cheng, Ind. Eng. Chem. Res. 35 (1996) 621.

[26] K.T. Li, C.S. Yen, N.S. Shyu, Appl. Catal. A 156 (1997) 117.

[27] K.T. Li, N.S. Shyu, Ind. Eng. Chem. Res. 36 (1997) 1480.

[28] K.T. Li, M.Y. Hyang, W.D. Cheng, US Patent 5 653 953 (1997), to Tunghai University, Taiwan.

[29] R.A. Bouyanov, A.M. Tsyboulesky, B.P. Zolotovsky, D.P. Klevtsov, V.I. Mourine, US Patent 5 369 076 (1994), to Institut de Rcherches de Gas Naturels, USSR.

[30] R.A. Bouyanov, A.M. Tsyboulesky, B.P. Zolotovsky, D.P. Klevtsov, V.I. Mourine, US Patent 5 512 258 (1996), to Institut de Rcherches de Gas Naturels, USSR.

[31] J.L. Bars, J.C. Védrine, A. Auroux, S. Trautmann, M. Baerns, Appl. Catal. A 119 (1994) 431.

[32] M.Y. Shin, Selective Oxidation of $H_2S$ to elemental sulfur over vanadium-based oxide catalysts, Ph.D. Thesis, Pohang University of Science and Technology, Pohang, Korea, 2000.

[33] H.S. Kim, Selective oxidation of $H_2S$ to elemental sulfur over vanadium oxides, MS Thesis, Pohang University of Science and Technology, Pohang, South Korea, 1996.

[34] J. Soczynski, Appl. Catal. A 146 (1996) 401.