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Additional Information

Partial oxidation of H₂S to sulphur on V-Cu-O mixed oxides bronzes

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Abstract

The present paper shows the influence of Cu-content in Cu-promoted V_2O_5 catalysts on both the physicochemical characteristics of catalysts and their catalytic performance in the partial oxidation of hydrogen sulfide. Both the catalytic activity for H_2S conversion and the selectivity to sulphur increases when increasing the Cu/V ratio of catalysts. The best catalyst gives a selectivity to sulphur of ca. 98% at total conversion of H_2S are observed. According to the characterization results (XRD, FTIR), V_2O_5 is partially transformed into vanadium oxide bronze, i.e. $\beta-Cu_{0.261}V_2O_5$, up to Cu/V ratios of 0.25. For higher Cu/V ratios, CuV_2O_6 and $\beta-Cu_{0.261}V_2O_5$ are observed. In the same way, the reducibility of V-species increases when increasing the Cu/V ratio of catalysts. On the other hand, the characterization of used catalysts indicates the transformation of V_2O_5 into V_4O_9 , whereas the vanadium oxide bronze is stable under our reaction. The catalytic results are explained on the basis of the nature of crystalline phases and the presence of V^{5+} -O- V^{4+} pairs in the more selective catalysts.

Keywords: hydrogen sulfide oxidation; Sulphur; vanadium oxide bronze; copper

1. INTRODUCTION

Hydrogen sulfide (H_2S) is one of the most toxic chemical compounds emitted from chemical industries, so sulphur-containing gases must be treated prior to its emission into the atmosphere. The most widely used technology now is the Claus process, which recovers elemental sulphur from sulphur-containing gas. Nevertheless, reasonably efficient removal of H_2S from the gas flow is difficult because of thermodynamic limitations [1]. Partial oxidation of hydrogen sulfide is an interesting alternative for H_2S transformation [1-14], including biogas purification [12-14]. However, the key feature will be the development of effective catalysts preventing the undesired reactions, i.e. the reverse Claus reaction and the deep oxidation of elemental sulphur to SO_2 [1-5].

Vanadium oxide based materials have been extensively studied in the last decades and reported as potential catalysts for the partial oxidation of H_2S to sulphur [8-11, 13-17]. In both unsupported and supported V_2O_5 -containing catalysts, the partially reduced V_4O_9 phase is formed in situ during the catalytic tests as revealed by operando and in-situ Raman and XAS spectroscopies, respectively [10, 11], suggesting that V_4O_9 is stable in reaction conditions. But, in addition, it is also observed that the selectivity to sulphur increases when increasing the formation of V_4O_9 in the catalyst because of the presence of $\text{V}^{5+}\text{-O-V}^{4+}$ pairs [10]. According to these results, the characteristics of vanadium oxide-based catalysts should be tailored in order to improve the catalytic behavior [10, 11, 15]. In this way, alkali metal promoted vanadium oxide catalysts have been found to be active, selective and relatively stable during the partial oxidation of hydrogen sulfide at low reaction temperatures (i.e. 160-200 °C) [16]. The better catalytic performance of Na-promoted catalysts has been related to the presence of a Na-containing vanadium oxide bronzes such as $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ (also named as $\text{NaV}_6\text{O}_{15}$)

as a consequence of the presence of V^{4+} -O- V^{5+} pairs, being V^{4+} species stabilized by the presence of Na^+ cations [17].

The $M_xV_2O_5$ vanadium oxide bronzes (VOB's) represent an interesting family of crystalline compounds presenting different structures and physicochemical properties, strongly related to the stoichiometry and the nature of the M elements (alkali, alkaline earth, but also Ag, Cu, etc.) and as a consequence of the presence of the mixed valence of the vanadium (V^{5+} and V^{4+}) [18,19]. In fact, the incorporation of cations between 2D sheets of the V_2O_5 framework induces partial reduction of the framework vanadium atoms. These materials are attractive for technological applications in areas ranging from photocatalysis to memristors, adsorbents, or for low friction coatings [19-20]. Among these, the copper vanadium bronze family has been studied in the last two decades [20-23]. Although they are usually prepared by solid-state reaction, they can be also obtained from hydrothermal synthesis as reported recently [24].

In this paper, we present the synthesis, characterization and catalytic performance for the H_2S partial oxidation reactions of V-Cu-O mixed oxide catalysts. The materials have been prepared by hydrothermal synthesis (using Cu/V molar ratios in the synthesis gel from 0.09 to 0.33) and finally activated in N_2 at 500 °C for 2h. In addition, they have been tested in the partial oxidation of H_2S and both fresh and used catalysts have been characterized by several techniques, i.e. DRX, UV-Vis, Raman, TPR and XPS, in order to determine the main features of active and selective catalysts.

2. EXPERIMENTAL

2.1. Catalyst preparation

Vanadium oxide bronzes were prepared hydrothermally. V_2O_5 was initially dispersed in aqueous H_2O_2 solution (35 wt%). Then the required amount of Cu(I) acetate salt was added and the mixture kept under magnetic stirring at room temperature for 2h. The suspension was loaded in Teflon-lined stainless-steel autoclaves and heated at 175 °C. After 3 days, the solids obtained were filtered, washed with distilled water and dried overnight at 100 °C. Finally, the samples were heat-treated at 500°C in N_2 flow for 2 h. The resulting catalysts were named CuV-x, where x is Cu/V atomic ratio in the synthesis gel and varies in the range $0 < x < 0.33$. For comparison, pure vanadium oxide V_2O_5 has been also studied. Table 1 shows the main physicochemical characteristics of heat-treated samples.

2.2. Catalyst characterization

X-ray diffraction patterns of catalysts were obtained using a PANalytical X'Pert PRO diffractometer with Cu $K\alpha$ radiation and an X'Celerator detector in Bragg–Brentano geometry operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file in the 2θ range of 5-50°.

Raman spectra were recorded in ambient conditions using a Renishaw system 1000 “in via” attached to a microscope. An argon ion laser (514 nm) was used as the excitation source and was typically operated at a power of 20 mW. Spectra were collected using a backscattering geometry with a 180° angle between the illuminating and the collected radiation.

Diffuse reflectance UV–vis (DR–UV–vis) spectra were recorded on a Cary 5 equipped with a Praying Mantis attachment from Harric.

Temperature-programed reduction with H_2 (H_2 -TPR) experiments were carried out in a Micromeritics Autochem 2910 equipped with a TCD detector, using 0.05 g of freshly

calcined catalyst and increasing the temperature from room temperature to 800 °C with a heating ramp of 10 °C min⁻¹, under 10% H₂/Ar (vol.%) and a constant flow rate of 50 ml min⁻¹.

X-ray photoelectron spectra were collected using a Physical Electronics spectrometer (PHI VersaProbe II Scanning XPS Microprobe) for the analysis of core level signals of C 1s, O 1s, V 2p, Cu 3d and S 2p, with scanning monochromatic X-ray Al K α radiation (100 μ m, 100 W, 20 kV, 1486.6 eV) as the excitation source and a dual beam charge neutralizer. High-resolution spectra were recorded at a take-off angle of 45° using a concentric hemispherical analyzer operating in the constant pass energy mode at 23.5 eV with a 100 μ m diameter of the highly focused X-ray beam. The spectrometer energy scale was calibrated using Cu 2p_{3/2}, Ag 3d_{5/2}, and Au 4f_{7/2} photoelectron lines at 932.7, 368.2 and 84.0 eV, respectively. In a constant pass energy mode under a 23.5 eV condition, the Au 4f_{7/2} line was recorded with a 0.73 eV FWHM at a binding energy (BE) of 84.0 eV. The PHI Smart Soft-VP 2.6.3.4 software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. The recorded spectra were fitted using Gaussian–Lorentzian curves. The atomic concentration percentages of the characteristic elements of the surfaces were determined taking into account the corresponding area sensitivity factor for the different measured spectral regions. The pressure in the analysis chamber was kept lower than 5 × 10⁻⁶ Pa. During data processing of the XPS spectra, binding energy (BE) scale was referred to the C 1s peak (284.8 eV), originated from the adventitious contamination layer. The error in BE was estimated to be ca. 0.1 eV. Short acquisition time of 10 min was firstly used to examine C 1s, V 2p regions in order to avoid, as much as possible, photo-reduction of V⁵⁺ species.

2.3. Catalyst test

Catalytic tests for the partial oxidation of H₂S to sulphur were carried out in a fixed-bed quartz tubular flow reactor, at atmospheric pressure and 180°C temperature during a time on stream of ca. 5 h. A catalyst weight of 0.1 g was mixed with silicon carbide as inert to obtain an adequate bed height to quench the possible homogeneous reactions. A feed mixture composed of H₂S/Air/He with molar composition of 1.2/5.0/93.8 and a total flow of 130 ml min⁻¹ was passed through the reactor. Analysis of reactants and reaction products was carried out online by gas chromatography using two different chromatographic columns (Molecular Sieve 5A and Porapak T) [10].

3. RESULTS AND DISCUSSION

3.1. Catalytic test for H₂S partial oxidation

Figure 1a shows the variation of the H₂S conversion at times on stream of 1h and 4 h with the Cu/V ratio in the synthesis gel used for the preparation of the catalysts. It can be seen that the catalytic activity but also the catalyst stability increases when increasing the Cu/V ratio. In fact a very small change in H₂S conversion is observed after 4h of time on stream for catalysts with Cu/V ratio in the synthesis gel higher than 0.17 (Fig. 1a and Fig. S1-supporting information). The lower catalytic activity of V₂O₅ at short time on stream has been reported and associated to the time required for the formation of V₄O₉ [10], which is the active and selective phase, stable in the reaction conditions used here. The results reported in Figure 1a show that increasing the Cu content improves catalytic activity and the catalyst stability, suggesting that the formation of V₄O₉ is favored.

Figure 1b shows the variation of the selectivity to sulphur with the H₂S conversion achieved during the partial oxidation of H₂S over Cu-V-O catalysts. In all cases, the selectivity to S is higher than 95% for H₂S conversions below 90% and decreases to 90% when the conversions increase up to 100%. However, samples CuV-25 and CuV-33 show the higher selectivity to sulphur also at near total H₂S conversion. The high selectivity to sulphur, obtained in all cases, indicates that the formation of SO₂ is very low on all catalysts.

3.2. Characterization of catalysts

The changes of phase composition for the catalysts prepared with different Cu/V ratio in the synthesis gel were investigated systematically. Figure 2 shows the powder X-ray diffraction patterns of heat-treated catalysts, which evidences a clear influence of the Cu/V ratio on the nature of crystalline phases. Cu-free sample consists of orthorhombic V₂O₅ (JCPDS: 00-09-0387) and the incorporation of copper promotes the transformation to monoclinic β -Cu_{0.261}V₂O₅ (JCPDS: 1-79-0796), which is characterized by peaks at $2\theta = 9.16, 12.15, 18.80, 24.46, 26.39, 28.65, 31.16, 33.09, 37.25, 39.73, 40.93$ and 46.23° . β -Cu_{0.261}V₂O₅ is the main crystalline phase in sample Cu-V-25, which also contains some CuV₂O₆ and V₂O₅, and in sample Cu-V-33 with some CuV₂O₆ extra phase. CuV₂O₆ (JCPDS: 1-74-2117) is characterized by the presence of peaks at $2\theta = 29.0, 42.2, 45.2$ and 49.1° [24, 25].

Figure 3 shows the Raman (Fig. 3A) and IR (Fig. 3B) spectra of all catalysts. The Cu-free sample and samples prepared with Cu/V contents in the synthesis gel lower than 0.33 shows the presence of bands at 998, 706, 530, 489, 410, 305, 289, 203 and 159 cm⁻¹ due to the presence of V₂O₅ crystallites [26, 27]. Samples Cu-V-025 and Cu-V-0.33 display additional bands at 902, 786, 710, 512, 435, 365, 256, 199 and 147 cm⁻¹

corresponding to crystalline CuV_2O_6 [26]. It must be noticed that no bands associated to Cu-containing vanadium bronze, i.e $\beta\text{-Cu}_{0.261}\text{V}_2\text{O}_5$ are observed in the spectra, which seems to be in contradiction with the XRD data. However, it is known that bands associated to V^{4+} cannot be observed by Raman spectroscopy when using a Laser of 514 nm [9]. For this reason, the samples were also studied by FTIR. Figure 3B shows the FTIR spectra of all catalysts, which display important changes when increasing the Cu/V ratio in catalysts. The Cu-free sample shows bands at 1020, 828 and 650-400 cm^{-1} (Fig. 3B, spectrum a), which have been assigned to V=O stretching vibration, V-O-V stretching vibration and V-O-V rocking vibration, respectively, in V_2O_5 [16]. However, the intensity of the band at 1020 decreases progressively, while a new band is observed at 1007 cm^{-1} , in Cu-containing samples (Fig. 3B, spectra b-e) indicating the presence of $\nu(\text{V}^{5+}=\text{O})$ and $\nu(\text{V}^{4+}=\text{O})$ [28]. Moreover, the IR absorption seems to be attenuated, as the copper content increases, probably because of the high carrier concentration in copper vanadium oxide bronzes that strongly suppresses the infrared absorption [29]. At high Cu/V contents, an additional band at ca. 930 cm^{-1} (Fig. 3B, spectrum e) assigned to CuV_2O_6 [29] is also observed.

Figure 4 shows the UV-Vis diffuse reflectance spectra of Cu-V-O samples and pure V_2O_5 . The spectrum of Cu-free sample (Fig. 4a) shows three bands at around 223, 330 and 478 nm [15, 30]. The band at 330 nm is assigned to the absorption of square pyramidal octahedral V^{5+} species, that at 223 nm to low energy charge transfer of V^{5+} in Td coordination [17, 30], and the band at 478 nm to electron transfer from O^{2-} to V^{5+} in octahedral coordination [15, 30]. These bands are also observed in the catalysts prepared from gels with low Cu/V ratios suggesting predominance of V_2O_5 crystallites, in agreement to XRD results.

However, at higher Cu/V ratios, the low frequency band is further shifted to ca. 240 nm, indicating the contribution of a charge transfer of V^{4+} species [17, 30]. Moreover, a new broad band appears at 620 nm due to d-d transitions of isolated V^{4+} species whose intensity increases when increasing the Cu/V ratio [15, 30]. The evolution of the UV-Vis spectra with the copper content indicates the presence of V^{4+} species associated to the Cu-V-O bronze in agreement to XRD and IR results.

H₂-TPR results of catalysts are shown in Figure 5. The Cu-free sample shows three reduction peaks in the 600-720 °C temperature interval characteristics of V₂O₅ [16]. Meanwhile, the Cu-containing samples show a single broad peak, in which the temperature of the maximum decreases when increasing the Cu content in catalyst: from ca. 600°C (sample **CuV-9**) to 440°C (sample **CuV-33**), suggesting that the presence of Cu-species favors a rapid reduction of V-species. Indeed, it has been reported that Cu-oxides are reduced at lower temperature than vanadium oxide, and that Cu-doped vanadium oxide displays an intermediate reducibility between the two oxides [31,32]. This is in good agreement with the observed increase of the H₂S conversion when the Cu-content in the catalyst increases (Fig. 1).

3.3. Characterization of used catalysts

Figure 6 shows the XRD of all catalysts after 4h of time on stream at 180°C. In agreement to previous results [10,11], the diffraction pattern of the Cu-free sample, i.e. CuV-0 (Fig. 6a) consists mainly of the peaks characteristic of V₄O₉. However, no important changes in the nature of the crystalline phases are observed for the Cu-containing samples after the catalytic tests (Fig. 2). Thus, β -Cu_{0.261}V₂O₅ is the main crystalline phase in the samples prepared with a Cu/V ratios in gel higher than 0.09. Nevertheless, minor amounts of sulphur (JCPDS: 08-0247) or CuS (JCPDS: 06-0464)

are observed in all used Cu-containing catalysts (Fig. 6e). It must be noted that CuV_2O_6 , present in the fresh catalysts, is not observed after reaction, suggesting that this phase has been partially transformed into CuS and $\beta\text{-Cu}_{0.261}\text{V}_2\text{O}_5$. The results obtained for the used catalysts show that while V_2O_5 and CuV_2O_6 crystalline phases are transformed, $\beta\text{-Cu}_{0.261}\text{V}_2\text{O}_5$ oxide bronze is stable in reaction conditions.

The surface chemical composition and oxidation state of the elements in the used catalysts obtained by XPS, shown in Table 1, confirm the changes observed by XRD. Thus, the $\text{V } 2p_{3/2}$ core level signal of the used Cu-free sample presents two contributions at 517.7 and 515.6 eV, confirming the formation of V_4O_9 . Meanwhile, the $\text{V } 2p_{3/2}$ spectra of the used Cu-V-O catalysts show two contributions at about 517.8 and 516.3 eV assigned to V^{5+} and V^{4+} , respectively [15]), whose relative intensity changes indicating modifications in the $\text{V}^{4+}/\text{V}^{5+}$ ratios. For the Cu-free sample, this ratio is 0.50, but it increases to 0.75 and 0.80 for samples CuVO-9 and CuVO-17, respectively, due to the simultaneous presence of V_4O_9 and $\text{Cu}_{0.261}\text{V}_2\text{O}_5$. For samples CuVO-25 and CuVO-33, these values decrease to 0.34 and 0.41, respectively, because of the absence of V_4O_9 (with an increasing presence of CuS). As expected, the surface Cu/V atomic ratio increases with the Cu content, but these values are always higher than that of the nominal values of the gel (see Table 1).

The $\text{S } 2p$ core level signals of the used catalysts are complex (Figure 7 b). All of them show three doublets with $\text{S } 2p_{3/2}$ values at: i) 161.8 eV due to S^{2-} ; ii) 163.3-163.7 eV assigned to elemental sulphur; and iii) 168.3-168.6 eV associated to SO_4^{2-} species [15]. The samples prepared with Cu/V ratios in the synthesis gel of 0.17 and 0.25 showed the highest concentration of sulphur on the catalyst surface, which is also in good agreement to the XRD patterns of the used catalysts (Fig. 2). The formation of S on surface of the catalyst with lower copper content can diminish the accessible of the

active centers causing partial deactivation, which could explain the lower activity of the catalyst. It must be noted that the CuV-33 catalyst, which seems to be more selective for the oxidation to SO₂, present the higher content of SO₄²⁻ on the surface.

The Cu 2*p* core level spectra of all used catalysts (not shown) are very similar and typical of Cu⁺ species, where the Cu 2*p*_{3/2} signal appears at 932.5 eV. The Auger Cu LMM signal was also studied to confirm the oxidation state. The modified Auger's parameters (α') were calculated and resulted to be 1850.2-1850.4. The combination of the binding energy values and the modified Auger' parameter in the corresponding Wagner's diagram indicated the presence of Cu⁺ or Cu²⁺ as CuS because the reported Cu 2*p*_{3/2} binding energy value for CuS is 932.2-932.4 eV [33].

3.4 General Remarks

The results reported here indicate that there are two different approaches for preparing active and selective V₂O₅ based catalysts (Fig. 8). One is the transformation of V₂O₅ into V₄O₉, which is the actual active and relatively selective phase, during the partial oxidation of H₂S at 180°C. The second one is the selectively transformation of V₂O₅ into β -Cu_xV₂O₅ (after heat-treatment at 500°C in N₂) by doping with copper, as this mixed oxide seems to be more active and selective than V₂O₅ and V₄O₉. In fact, according to the results of Figure 1, Cu-V-O mixed oxides bronzes are more active and more selective for the partial oxidation of H₂S to sulphur than V₂O₅, or more specifically than V₄O₉ which is the phase present under reaction conditions.

According to the TPR and catalytic results, the easier reducibility of V-species in Cu-containing catalyst is accompanied by a higher H₂S conversion without decreasing the selectivity to sulphur. This behaviour is associated to the nature of the V-species in Cu-

V-O mixed oxides bronzes. The monoclinic β - $\text{Cu}_x\text{V}_2\text{O}_5$ crystal structure consists of a V_2O_5 -framework containing Cu-cations [34], as shown in Fig. 9. The V_2O_5 -framework is formed by three crystallographically distinct vanadium sites (named as **V1**, **V2** and **V3**) sharing the corners and edges of (**V1**) O_6 , (**V2**) O_6 octahedra and (**V3**) O_5 pyramids, forming three V chains running along the *b*-axis [34] forming a tunnel. According to these authors [34], Cu-atoms occupy lattice positions along the *b*-axis (tunnel sites) forming a ladder-like shape. In this way, a stoichiometric composition of $x = 0.33$ should be correspond to the occupation of 50% of these lattice sites.

According to our results and in agreement with previous publications, V_2O_5 is easily transformed into V_4O_9 in our reaction conditions [10,11] changing also the selectivity to sulphur. This result suggests that the presence of $\text{V}^{5+}\text{-O-V}^{5+}$ pairs favors not only the transformation of hydrogen sulfide to sulphur but also the consecutive reaction (i.e. the deep oxidation of S and H_2S to SO_2). Meanwhile, $\text{V}^{5+}\text{-O-V}^{4+}$ pairs, present in the β - $\text{Cu}_x\text{V}_2\text{O}_5$ (in which V^{4+} species are stabilized by Cu^{n+} -cations), promote the partial oxidation of H_2S to sulphur (due to the higher reducibility of V-species interacting with Cu cations) but with limited deep oxidation products (because of the lower content of V^{5+} -species) (Scheme 1). The role played by metal cation in vanadium oxide bronzes is in good agreement to previous results [35].

4. CONCLUSIONS

In conclusion, Cu-promoted vanadium oxide have been prepared hydrothermally and activated in N_2 at 500°C . The resulting catalysts are more active and selective than pure V_2O_5 catalysts displaying a low activity decay.

The physicochemical characterization of the catalysts, before and after the catalytic tests suggests that $\beta\text{-Cu}_x\text{V}_2\text{O}_5$ bronze oxide is the active and selective crystalline phase although minor amounts of CuV_2O_6 can be also be present at high Cu/V molar ratio. V_2O_5 is transformed into V_4O_9 (in catalysts with low Cu/V ratio). On the other hand, CuV_2O_6 is absent in the used catalyst (with high Cu/V ratios). This suggests a probable conversion of CuV_2O_6 into $\beta\text{-Cu}_x\text{V}_2\text{O}_5$ and CuS phases during the reaction. However, $\beta\text{-Cu}_x\text{V}_2\text{O}_5$ oxide bronze remains as the main crystalline phases in Cu-containing samples after the catalytic tests. According to these results $\beta\text{-Cu}_x\text{V}_2\text{O}_5$ oxide bronze can be considered as active, selective and stable during the partial oxidation of H_2S to sulphur.

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Table 1. Characteristics of V-Cu-O catalysts

Catalyst	Cu/V ratio in gel	TPR-H ₂		XPS of used catalysts ^a						
		(°C)	mmol _{H2} /g _{cat}	Cu/O	V/O	Cu/V	V ⁴⁺ /V ⁵⁺	S ²⁻	S	SO ₄ ²⁻
V ₂ O ₅	0	600-720	12.8				0.50		66	34
CuVO-9	0.09	600	13.5	0.07	0.32	0.22	0.75	38	26	36
CuVO-17	0.17	480	13.4	0.09	0.34	0.27	0.80	45	38	17
CuVO-25	0.25	460	13	0.09	0.29	0.30	0.34	37	26	37
CuVO-33	0.33	440	13.2	0.13	0.26	0.50	0.41	43	22	35

^a Percentages of the total S content determined by deconvolution of the S 2*p* core level signal (see Figure 6).

Caption to figures

Fig.1. a) Variation of the H₂S conversion with the Cu/V ratio in the synthesis gel achieved during the partial oxidation of H₂S over Cu-V-O catalysts at 180°C after 1h or 4h of time on stream (experimental conditions in text); b) Variation of the selectivity to sulphur with the H₂S conversion achieved at 180°C.

Fig. 2. XRD patterns of Cu-V-O mixed oxides catalysts: a) CuV-0; b) CuV-9; c) CuV-17; e) CuV-25; f) CuV-33. Symbols:

Fig. 3. Raman (A) and FTIR (B) spectra of Cu-V-O mixed oxides catalysts: a) CuV-0; b) CuV-9; c) CuV-17; e) CuV-25; f) CuV-33.

Fig. 4. Diffuse reflectance UV-vis spectra of Cu-V-O mixed oxides catalysts: a) CuV-0; b) CuV-9; c) CuV-17; e) CuV-25; f) CuV-33.

Fig. 5. H₂-TPR patterns of Cu-V-O mixed oxides catalysts: a) CuV-0; b) CuV-9; c) CuV-17; e) CuV-25; f) CuV-33.

Fig. 6. XRD patterns of Cu-V-O catalysts after catalytic test (at 180°C during 4h of time on stream): a) CuV-0; b) CuV-9; c) CuV-17; e) CuV-25; f) CuV-33.

Fig. 7. V 2p and S 2p core level spectra for Cu-V-O catalysts after catalytic test (at 180°C during 4h of time on stream): a) CuV-9; b) CuV-17; c) CuV-25; d) CuV-33.

Fig. 8. Selective transformation of V₂O₅: a) During reaction (H₂S/O₂ mixture 180°C); b) During the hydrothermal synthesis (after heat-treatment in N₂ at 500°C).

Scheme 1. Reaction network for partial oxidation of H₂S over β -Cu_xV₂O₅.