

Document downloaded from:

<http://hdl.handle.net/10251/63765>

This paper must be cited as:

Soriano Rodríguez, MD.; Jimenez-Jimenez, J.; Concepción Heydorn, P.; Jimenez-Lopez, A.; Rodriguez-Castellon, E.; López Nieto, JM. (2009). Selective Oxidation of H₂S to Sulfur over Vanadia Supported on Mesoporous Zirconium Phosphate Heterostructure. *Applied Catalysis B: Environmental*. 92(3-4):271-279. doi:10.1016/j.apcatb.2009.08.002.



The final publication is available at

<http://dx.doi.org/10.1016/j.apcatb.2009.08.002>

Copyright Elsevier

Additional Information

Selective Oxidation of H₂S to Sulfur over Vanadia Supported on Mesoporous Zirconium Phosphate Heterostructure

M.D. Soriano ¹, J. Jiménez-Jiménez ², P. Concepción ¹, A. Jiménez-López ², E. Rodríguez-Castellón ², J.M. López Nieto ^{1,*}

- 1) Instituto de Tecnología Química, UPV-CSIC, Avenida de los Naranjos s/n,
46022 Valencia (Spain)
- 2) Dep. Química Inorgánica, Facultas de Ciencias, Universidad de Málaga, 29071
Málaga (Spain)

*) To whom correspondence should be addressed. E-mail: jmlopez@itq.upv.es

Abstract

Vanadium oxide supported on mesoporous zirconium phosphate catalysts have been synthesised, characterized and tested in the selective oxidation of H₂S to sulphur. The nature of the vanadium species depend on the V-loading of catalyst. Catalysts with a V-content lower than 4 wt% present both isolated vanadium species and V₂O₅ crystallites, while the last are mainly observed for catalysts with higher V-loadings. The catalytic behaviour also depends on V-loading of catalysts. Thus, while the catalytic activity of catalysts can be related to the number of V-sites, the catalyst decay is clearly observed in samples with low V-loading. The characterization of catalysts after the catalytic tests indicates the presence of sulphur on the catalyst, which is favoured on catalysts with low V-loading. However, a clear transformation of V₂O₅ to V₄O₉ can be proposed according to XRD and Raman results of used catalysts with high V-loading. The importance of V⁵⁺-O-V⁴⁺ pairs in activity and selectivity is also discussed.

Keywords: Selective oxidation, hydrogen sulphide; mesoporous zirconium phosphate support, supported vanadium oxide, V₄O₉, V₂O₅.

INTRODUCTION

Hydrogen sulfide is usually removed by the well-known Claus process, a two steps process including thermal oxidation (in which one-third of the hydrogen sulfide is first burned with air to sulphur dioxide in a waste heat furnace) and catalytic reaction (in which SO₂ is reacted with unconverted H₂S to produce elemental sulphur) [1]. However, due to thermodynamic limitations, the process is limited to about 95-97%.

From a practical point of view, the most attractive way of sulfur production from hydrogen sulfide is selective oxidation by using oxygen from air, according to reaction [2-4]: $H_2S + 1/2O_2 \rightarrow H_2O + 1/x S_x$. However, selective catalysts are required since SO₂ can also be formed depending on reaction temperature and H₂S/O₂ ratio.

Vanadium-based catalysts have been reported to be active and selective for the partial oxidation of H₂S to sulphur in the 200-300 °C temperature range [5-19]. Although V₂O₅ is active and selective in the selective oxidation of hydrogen sulphide to elemental sulphur [5-7], other vanadium based catalysts have been also proposed. This is the case of the use of mixed metal oxides, i.e. V-Mg-O [8], rare earth vanadates [10, 11], V-Sb-O [12], Mo-V-O [8, 13], Cu-V-O [14], or supported vanadium oxides [11, 15, 16-19]. Among these, alumina- and titania-supported vanadia catalysts have been the most studied catalysts. Although the characteristics of metal oxide support and the nature vanadium species strongly influence the catalytic performance of supported vanadium catalysts, the nature of active and selective sites is still under discussion.

On the other hand, two important aspects must also be considered in the case of supported vanadium oxide catalysts in order to improve the catalytic performance of these catalysts: i) Catalyst deactivation; and ii) Selectivity to sulphur, since SO₂ can also

be formed by a competitive way. In this way, a catalyst decay could be related to the reduction of vanadium oxide (forming VO_2 or V_2O_3) [6] and/or the formation of less active forms of vanadium, as vanadyl sulfate (VOSO_4) [17]. Thus, the catalyst decay with time on stream could be due to a depletion of labile oxygen on the catalyst surface, which depends on both the redox properties of catalysts and the reaction conditions [6]. However, and depending on the reaction conditions, sulfidation of the metal and metal oxide components could result also in a low stability of the catalysts.

A mesoporous zirconium phosphate heterostructure, prepared using a synthetic strategy that combines the synthesis of pillared layer structures (PLS) and MCM-41 mesoporous solids, where zirconium phosphate is expanded with the formation of silica galleries in the interlayer space, has been proposed as an interesting material as support since it present a high thermal stability, high specific area and acid sites which could favour a relatively high dispersion of vanadium. But also big pores in which metal oxides with relatively low crystal sizes could be formed [21].

In this paper, we present the synthesis, characterization and catalytic performance for the selective oxidation of hydrogen sulphide to sulphur of vanadium oxide supported on a mesoporous zirconium phosphate heterostructure. It will be shown that the vanadium loading influences the catalytic behaviour and how the presence of nanoparticles of V_2O_5 as precursor of the active sites favours a high activity and selectivity. The characterization of used catalysts will be used for understanding the nature of active sites.

2. EXPERIMENTAL

2.1. Catalyst preparation

The mesoporous zirconium phosphate heterostructure, MZP ($S_{\text{BET}} = 556 \text{ m}^2/\text{g}$), was prepared according to a previously reported preparation procedure [21]. The solid was then centrifuged, washed with ethanol and dried at 120°C in air. This precursor material was calcined at 550°C for 6 hours ($1.5 \text{ }^\circ\text{C min}^{-1}$ heating rate). A scheme of the synthesis of the support is shown in Figure 1.

Vanadium oxides supported on mesoporous zirconium phosphate (nV-MZP, in which n is the V-content in wt %) were prepared by the wet-impregnation method of the mesoporous zirconium phosphate using an aqueous solution of ammonium metavanadate (Aldrich). The mixture was rotaevaporated until complete dryness. After that, these materials were dried overnight in an oven at 100°C . Finally the samples were calcined at 500°C for 6 h.

For comparison, a pure V_2O_5 catalyst has been prepared by calcination in air at $500^\circ\text{C}/2\text{h}$ from ammonium metavanadate.

2.2. Catalytic tests

Catalytic tests for the partial oxidation of H_2S to sulphur were carried out at atmospheric pressure in a fixed-bed quartz tubular flow reactor, in the $180\text{-}260^\circ\text{C}$ temperature range. The catalyst weight (0.1g) and a total flow (130 ml min^{-1}) with $\text{H}_2\text{S}/\text{air}/\text{He}$ molar ratio of 1.2/5.0/93.8 have been used for catalytic tests.

Analysis of reactants and reaction products was carried out on-line using gas chromatography and two different chromatographic columns (Molecular Sieve 5A and Porapak T).

2.3. Catalyst characterization

Catalyst surface areas were determined by multi point N₂ adsorption at -196°C, and data were treated in accordance with the BET method. The textural properties of all samples were determined by nitrogen isotherms at liquid N₂ temperature, using a Micromeritics ASAP 2010 apparatus (static volumetric technique). Before determination of adsorption–desorption isotherms the samples (0.2 g) were outgassed for 16 h at 400 °C under vacuum. The specific surface area (S_{BET}) was evaluated by 2-parameters linear BET plot in the range P/P₀ 0.01–0.2. The total pore volume (V_{pore}) was determined from the amount adsorbed at relative pressure of 0.995. Mean pore size was evaluated with the BJH method applied on the adsorption isotherm branch.

X-ray diffraction patterns were collected in an Enraf Nonius PSD120 diffractometer with a monochromatic CuK_{α1} source operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file.

Raman spectra were recorded using a Renishaw system 1000 “in via” attached to a microscope. An argon ion laser (785 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-programmed reduction (TPR) was carried out in a Micromeritics Autochem 2910 equipped with a TCD detector. The reducing gas used in all experiments was 10% H₂ in Ar, with a flow rate of 50 ml min⁻¹. The temperature range explored was from room temperature to 800 °C. The heating rate was maintained at 10 °C min⁻¹ for all samples whilst the sample mass was varied depending on the sample under study. Details of specific conditions are given with the TPR profiles.

Infrared spectra of adsorbed pyridine were obtained in a Nicolet 710 FTIR spectrophotometer. Wafers of 10 mg/cm² were mounted in a pyrex vacuum cell fitted with CaF₂ windows. The samples were pretreated overnight at 400°C and then cooled at room temperature (rt) to obtain the original IR spectra. Then, pyridine was admitted at room temperature, degassed at 150°C for 1h in order to remove the fraction physisorbed, and the spectra registered at room temperature. Pyridine was also desorbed at 250°C.

X-Ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non monochromatic Mg K α radiation (300W, 15 kV, 1253.6 eV) for the analysis of core level signals of C 1s, O 1s, Si 2p, P 2p, Zr 3d, V 2p and S 2p. Spectra of powdered samples were recorded with the constant pass energy values at 29.35 eV, using a 720 μ m diameter analysis area. Under these conditions, the Au 4f_{7/2} line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated by using the Cu 2p_{3/2}, Ag 3d_{5/2} and Au 4f_{7/2} photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. During data processing of the XPS spectra, binding energy values were referenced to the C 1s peak (284.8 eV) from the adventitious contamination layer. The PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves, in order to determine the binding energy of the different element core levels more accurately. The error in BE was estimated to be *ca.* 0.1 eV. Short acquisition time of 10 min was first used to examine C 1s, V 2p regions in order to avoid, as much as possible, photo-reduction of V⁵⁺ species. Satellite subtraction was always performed to study the V 2p and S 2p regions.

3. RESULTS AND DISCUSSION

3.1. Catalytic test in the Selective Oxidation of H₂S to Sulfur

Figure 2 shows the variation of the conversion of H₂S with the time on stream (TOS) during the oxidation of H₂S over supported-vanadia catalysts at 200°C. For comparison, the catalytic results achieved over pure V₂O₅ and V-free support have been also included. In all cases, sulphur and water were the only reaction products, while SO₂ was only observed as minority (selectivities lower than 3%) in the first minutes of these experiments. It can be seen how the conversion of H₂S increases with the vanadium content.

Initial catalyst decay during the first hours of each experiment can be observed on catalysts with low V-loadings. However, no appreciable catalytic activity decay was observed for samples with V-content higher than 12 wt% of V-atoms as well as over pure V₂O₅. In this way, catalytic results achieved at W/F= 32.1 g_{cat} h mol_{H₂S}⁻¹ shows an initial H₂S conversion of ca. 98% over samples 12V-MZP and 16V-MZP after 6 h of time on stream. This catalytic activity is higher than that observed over pure V₂O₅ (ca. 75%).

Table 1 shows comparatively the turnover frequency (TOF) for H₂S oxidation and the space time yield (STY) for sulphur formation achieved at a TOS of 0.5 h obtained on catalysts with different V-loading. The TOF decreases with the V-content of catalysts. However, when considering the formation of elemental sulphur, it can be seen that a space time yield (STY) of ca. 1000 gs h⁻¹ kg_{cat}⁻¹ can be achieved over sample 12V-MZP, while lower productivities have been observed for samples with lower or higher V-loading. Accordingly, the conversion of H₂S increases with the V-loading of catalysts presenting a maximum over the catalysts with a V-loading of 12 wt%. In all cases, any considerable emission of SO₂ has been detected at this time on stream.

In order to comparatively study the catalytic behaviour of stabilized catalysts, a second series of experiments were carried out after a catalyst pre-treatment at 250°C with diluted H₂S (1% in helium) and a total flow of 125 ml min⁻¹ during 4 h. The catalytic results for catalysts containing from 4 to 16 wt% of V-atoms in the reaction temperature range of 180 to 260°C are shown in Figure 3. The hydrogen sulphide conversion increases with the reaction temperature and no catalyst deactivation was observed after these catalytic tests. This trend is similar to that previously observed over supported vanadia catalysts [7-20]. On the other hand, the catalytic activity increases initially with the V-loading presenting a maximum for the catalysts with a 12 wt% of V-atoms. These results indicate that V-sites are active and selective for the oxidation of hydrogen sulphide in both fresh and pre-treated catalysts.

3.2. Characterization of fresh Catalysts

Table 1 shows comparatively some characteristics of fresh catalysts. It can be seen that both the surface area and the pore volume of catalyst decrease when increasing the vanadium loading. These results suggest a partial loss of the mesoporous character with the incorporation of vanadium.

Figure 4 shows the XRD patterns of calcined catalysts before (Fig. 4A) and after the catalytic tests (Fig. 4B). No crystalline phases have been observed for catalysts with V-loading lower than 4 wt% of V-atoms.

For fresh catalysts with a higher V-loading it can be seen the appearance of new peaks at $2\theta = 15.3, 18.6, 20.3, 21.5, 23.6, 26.2, 30.2, 31.2, 34.3$ and $35.5, 44.5, 47.3, 49.0, 51.2, 53.5$ and 57.3° (the intensity of these peaks increase with the increase of the V-loading). These results suggest the presence of V₂O₅ [JCPDS: 41-1426] (with diffraction peaks $2\theta = 15.3, 20.3, 26.2, 31.2, 34.3, 47.3^\circ$) in addition to ZrP₂O₇ [JCPDS:

85-896] (diffraction peaks at $2\theta = 18.6, 21.5, 24.1, 26.2$ and 30.2°), the formation of both favoured on catalysts with high V-contents.

We must indicate that it has been reported that mesoporous zirconium phosphate can be partially destroyed during the calcination step [21]. Moreover, the results presented here suggest that this partial destruction of the mesoporous structure (with the formation of ZrP_2O_7) could be favoured by the presence of high V-loading.

Raman spectra of catalysts are presented in Figure 5. The calcined samples show bands at 998, 706, 530, 489, 410, 305, 289, 203 and 159 cm^{-1} , although their intensities increase with the V-loading (Fig. 5A). These bands refer to the vibrational modes of crystalline V_2O_5 [22, 23]. In addition to these, a band at 1024 cm^{-1} is clearly observed in samples with a high V-loading, which is associated to terminal V=O bond of an amorphous cluster [24].

Diffuse reflectance UV-Vis spectra of catalysts are shown in Figure 6. The bands observed in the range of 200-500 nm arise from low-energy O^{2-} to V^{5+} charge-transfer while the d-d transition of V^{4+} species occur at higher energies (600-800 nm) [25, 26]. For the calcined catalyst with the lowest V-loading (2.0 wt %) only one main band centred at ca. 265 nm is observed (Fig 6A, spectrum a). However, an intense broad band at 260-280 nm with a shoulder at 377 nm, which increases when increasing V-loading can be observed for catalysts with V-loadings higher than 4 wt % (Fig 6A, spectra b, c and d). The absorption band at 270-290 nm indicates the presence of isolated tetrahedral V^{5+} while bands at 245 and 370 nm indicate the presence of VO_x particles. In addition to those, a third band around 465 nm is clearly observed in the sample with a V-loading higher than 8 wt%. This band is related to the presence of “bulk-type” polymeric V_2O_5 -like vanadium species.

Pyridine adsorption was followed by infrared spectroscopy to identify the number and nature of acid sites. Figure 7 shows the FTIR spectra of pyridine adsorbed on MZP-supported catalysts after evacuation at 150°C. The bands at 1450, 1492 and 1622 cm^{-1} are associated to pyridine coordinated to Lewis acid sites, while bands at 1540 and 1638 cm^{-1} are related to pyridinium cations in Brønsted acid sites [27]. The intensity of these bands decreases when increasing the V-loading suggesting the partial elimination of acid sites due to the support. On the other hand, the relatively low acid strength of these acid sites is evidence by the partial disappearance of these bands upon desorption at 250°C (spectra not shown), suggesting that only a part of pyridine is retained on Lewis acid sites.

Figure 8 depicts the H_2 -TPR profile of supported vanadia catalysts from room temperature to 800°C. The studied catalysts show one broad peak, which is related to the reduction of the V^{5+} to V^{3+} . The catalysts with low V-loading (2.0 wt %) presents the reduction band at *ca.* 540°C while in the rest of the samples is observed at *ca.* 550°C. Except in the case of the sample with the lower V-loading, the reduction peak can be related to the presence of V_2O_5 crystallites with relatively low crystal size [28, 29]. In this way, the high reduction temperature observed in the TPR pattern of pure V_2O_5 (Fig.8 pattern d) is probably due to the low accessibility of H_2 to the lattice vanadium atoms in the V_2O_5 bulk [29], as a consequence of the higher crystal size in this sample.

Table 2 shows the XPS results of fresh catalysts. Concerning the composition of the fresh catalysts, the surface vanadium content of sample 8VMZP is slightly higher than that of sample 4VZMP in spite of the higher vanadium content of sample 8VMZP. However, as expected, sample 12VMZP has a surface vanadium content triple than that found in sample 4VMZP. This means that with a low amount of vanadium, most part of

vanadium species are inside the pore and a small proportion is at the external surface of the catalyst. When more vanadium is added (sample 8VMZP), these additional vanadium species are also located into the pores of the support. But with a further addition of vanadium, these vanadium oxides are mainly covering the external surface of the catalyst (sample 12VMZP). The binding energy values of the constituent elements of the support are not modified upon the incorporation of vanadium species (see Table 2). The core level V $2p$ signal show interesting facts. With a low V loading (sample 4VMZP) the V $2p_{3/2}$ signal can be decomposed in two contributions at 518.0 and 516.5 eV assigned to V^{5+} and V^{4+} [30, 31], respectively, and where the proportion of V^{4+} is relatively high (35%). Upon the incorporation of more vanadium, the proportion of V^{4+} dramatically decreases, being 7% for sample 12VMZP. The high proportion V^{4+} at the surface of sample 4VMZP may be due to several reasons such as photoreduction or thermal reduction of dispersed vanadia. These effects are moderated with higher contents of vanadium.

3.3. Characterization of used catalysts

In all cases, the catalysts have been also characterized after the catalytic tests (in which the samples were recorded after a time on stream of *ca.* 6 h, see Fig.1). The corresponding XRD patterns of used catalysts are shown in Figure 4B. It can be seen the presence of a diffraction peak at $2\theta = 21.5^\circ$ related to the presence of crystalline ZrP_2O_7 . In addition, other peaks with low intensities can be observed at $2\theta = 18.3, 23.8, 27.6, 35.8$ and 43.6° . When comparing to those achieved from fresh catalysts (Fig. 4 A), it can be concluded the disappearance of V_2O_5 and the formation of V_4O_9 [JCPDS: 23-720], which increase with the V-loading, for catalysts after the catalytic test. A similar behaviour can also be concluded for the pure V_2O_5 , in which is clearly observed

the preferential formation of V_4O_9 . However the presence of sulfur crystals [JCPDS: 8-247] (peak at $2\theta = 23.1^\circ$), as minority, is only observed on catalysts with low V-loading.

The Raman spectra of used catalysts (Fig. 5 B) show a drastic change with respect to those of fresh catalysts (Fig. 5 A). Thus, a band at ca. 905 cm^{-1} is observed in used catalysts, while the main of the bands related to V_2O_5 crystallites (bands at 998, 706, 530, 489, 410, 305, 289, 203 and 159 cm^{-1}) are not observed. Nilson et al. [32], reported a band at 905 cm^{-1} related to V_4O_9 , which was formed during the propane ammoxidation over V_2O_5 . Accordingly, V_4O_9 is also formed in our catalyst during the oxidation of H_2S , probably as a consequence of a low reoxidation of catalyst in the reaction conditions used here. In this way, we can indicate that both V_2O_5 (bands at 998, 706, 530, 489, 410, 305, 289, 203 and 159 cm^{-1}) and V_4O_9 are observed in the case of pure V_2O_5 sample (Fig. 5B, spectrum g). This indicates that only a part of V^{5+} species were reduced after a time of stream of 6 h.

Moreover, we must indicate the absence of VO_2 crystals in used catalysts, which is characterized by the presence of a band at 614 cm^{-1} [33].

On the other hand, bands at 218 and 472 cm^{-1} are observed for samples with a V-loading of 2.0 and 4.0 wt% of V-atoms, while their intensities are very low in the case of sample 8V-MZP (Fig. 5B, spectra c to e). However, these bands are not observed in the case of the sample with higher V-loading. The band at 218 cm^{-1} (with a low intense band at 150 cm^{-1}) can be assigned to S-S-S bending vibration, while the band at 472 cm^{-1} can be related to S-S stretching of polymeric sulfur species adsorbed at multilayer level [34]. However, no bands related to the formation of vanadyl sulphate (bands at 1060 and 984 cm^{-1} [35]) have been observed.

These results suggest that the deposition of sulphur on the catalyst surface is favored in catalysts with low V-loading, while it is disfavoured in catalysts with high V-

loading. In other words, the deposition of sulphur could be favoured on catalysts presenting dispersed vanadia species and/or acid sites in the surface of the vanadium-free support but not in the catalysts presenting only V_2O_5 crystallites and low surface areas.

In the case of the core level S 2p signal (See Figure 9), there are two peaks with S 2p_{3/2} values at 163.2 – 163.6 eV assigned to elemental sulphur [31, 36], and at 168.3 – 168.4 eV assigned to sulphate [31], where the percentage of elemental sulphur is always higher than that of sulphate. These percentages hardly vary with the vanadium loading. On the other hand, the fact that sulphate is observed by XPS but it is not observed by Raman suggest that the amount of this is low and they are only deposited on the surface of catalyst.

Concerning the core level V 2p signal, the V 2p_{3/2} signal can be decomposed in two contributions at 517.5 eV and 516.3 eV, assigned to V^{5+} and V^{4+} , respectively [30] as in the case of the fresh samples. However, now the percentages of V^{4+} are always the same independent of the vanadium loading, in agreement to previous results [13, 14]. This can be attributed to the presence on the surface of V_4O_9 , in all the used catalysts with a theoretical V^{5+}/V^{4+} ratio of *ca.* 1. However, a partial surface oxidation as a consequence of the regeneration of the catalyst surface after some days in contact with air cannot be completely ruled out, although it should be low.

3.4. General remarks

In the experimental conditions at which the different solids were assayed to study the partial oxidation of H_2S to sulphur V-containing samples are active and very selective (>95%), the catalytic activity increasing with the V-loading. However, the V-free support present a low catalytic activity, Accordingly both dispersed vanadium

species (in samples with low V-content) and V_2O_5 crystallites (in catalysts with high V-content) are seems to be active and selective in the selective oxidation of hydrogen sulphide to sulphur, although the catalytic activity of V-sites depend on the V-loading.

Table 1 shows the TOF calculated after 0.5 h of time on stream. It can be seen that the TOF decreases with the V-content. It is clear that catalysts presenting V_2O_5 crystallites must have a low dispersion and accessibility of V-sites than those presenting isolated vanadium species.

It is clear that the formation of V_2O_5 crystallites is favoured when increasing the V-loading, although the crystal size of this could be relatively low with respect to the achieved in pure V_2O_5 . This can explain the lower reduction temperature observed in supported catalysts with respect to the pure V_2O_5 . Accordingly, the catalysts can be described as indicated in Figure 10.

On the other hand, not only the catalytic activity and the STY (Table 1) but also the catalyst stability increases with the V-loading. Thus, catalytic activity decay is clearly observed for the samples with the lower V-content, while the catalysts are practically stable for V-loading higher than 8 wt% (Fig. 1). For this reason, and in order to evaluate the nature of V-sites before and after the catalytic tests, a characterization of catalysts after the catalytic test has been also carried out.

According to the XRD, Raman and XPS results, the vanadium species are partially reduced during the catalytic tests. When comparing the catalysts with different V-contents it can be observed that the ratio V^{5+}/V^{4+} is maintained constant for all the studied catalysts. However, this fact can be explained taking into account that in all used catalysts, V_4O_9 crystals are clearly observed in those presenting V_2O_5 crystals before the catalytic tests. This V_4O_9 seems to be stable. In fact we can notice that no catalysts decay of sample 12V/MZP have been observed after 6 h (working at 200°C,

see Fig. 1) in which V_4O_9 was observed after this catalytic experiment. Thus, V_4O_9 can be proposed as the active and selective phases in the hydrogen sulphide oxidation to sulphur over these catalysts. V_4O_9 has been reported to be formed during the propane ammoxidation over V_2O_5 , as a consequence of a partial reduction of V_2O_5 during the ammoxidation reaction [32]. In our case, V_4O_9 can be formed probably as a consequence of a low reoxidation of catalyst when working at relatively low reaction temperature (200°C). Neither VO_2 nor $VOSO_4$ have been observed in our case. This probably is due to the minor reductive character of the reaction mixture [6] and the lower reaction temperature [17].

The orthorhombic V_4O_9 is characterized by the presence of V^{5+} -O- V^{4+} pairs, with vanadium atoms exclusively in square-pyramidal coordination with oxygen [37, 38]. We must indicate that this crystalline structure can be easily formed by a partial reduction of V_2O_5 [39, 40]. In addition V_4O_9 can be also easily oxidized to V_2O_5 in the presence of O_2 at 200-250°C [40]. So, one particularity of V_4O_9 is its relatively stability and facility to transport lattice oxygen from the bulk to the surface, which could favour a redox mechanism in the selective oxidation of H_2S to elemental sulphur.

We must indicate that V_4O_9 can be achieved by reducing V_2O_5 single crystals at 250°C for 50 h in a sulphur atmosphere, although prolonging the treatment led to the formation of VO_2 [41]. Thus, a partial reduction of V_2O_5 to V_4O_9 seems to be more favoured at 200°C in the reaction conditions used in this study.

On the other hand, the catalyst decay in samples with low V-loading could be related to the low ability to form stable V^{4+} -species (as occurs with the formation of V_4O_9 from V_2O_5 crystallites in catalysts with high V-contents).

However, other factor must be considered to explain the catalyst decay observed in samples with low V-loading. Thus, sulphur and sulphate species are observed on the

surface of used catalysts, while sulphur crystals are observed by Raman and XRD. Since the amount of S decreases when increasing the V-loading one could consider that isolated vanadium species and/or V-free sites of the mesoporous support are involved in the incorporation of sulphur on the catalyst surface. However, the presence of V-O₂-V pairs could favour also a better desorption of the sulphur, while this could be disfavoured in the presence of dispersed vanadium species. So, these aspects should also be studied in the future in order to adequately address the modifications occurring in the catalysts during the catalytic tests.

Finally, the characterization results of calcined samples indicate that the support is partially transformed from the Mesoporous Zirconium Phosphate Heterostructure to ZrP₂O₇ when increasing the V-loading. This loss of the surface area of the support and the appearance of ZrP₂O₇ could favour the disappearance of acid sites (related to the metal oxide support), which could favour a lower deposition of sulphur on the catalyst surface in samples with High V-loading. So, apparently, support with low surface areas seems to be preferred in order to decrease the sulphur adsorption of the catalyst.

In conclusion, vanadium oxide supported on mesoporous zirconium phosphate is active and selective in the partial oxidation of H₂S to elemental sulphur, although its catalytic behaviour, including the catalyst stability, strongly depends on the V-loading. Catalysts with low V-loading with both isolated V⁵⁺ species and V₂O₅ crystallites are less active and show high catalyst decay than pure V₂O₅. However, catalysts with high V-loading, in which V₂O₅ crystallites are mainly observed, show a catalytic activity and stability higher than pure V₂O₅. So, apparently V₂O₅ could be proposed as the active and selective phase in this reaction. However, the characterization results of tested catalysts have demonstrated the formation of V₄O₉ during the catalytic test. In addition,

if SO₂ is initially observed in the first minutes of the reaction, it is practically not observed (the selectivity to sulphur is > 99%) at high time on stream. Accordingly, V₄O₉ seems to be the active and selective crystalline phase in the reaction conditions used in this work, i.e reaction temperature of 200°C and a H₂S/O₂ ratio of 1.2. However, and according to the redox properties of these materials the nature of crystalline phases formed in this reaction could be change depending on the reaction conditions. So, the redox properties of this catalytic system play an important role in both catalytic behaviour and formation of stable crystalline phases.

Acknowledgments

The authors gratefully acknowledge financial support from CICYT, Spain (NAN20004-09267-C01 and NAN2004-09267-C03-02). MDS thanks a fellowship from the Universidad Politécnica of Valencia.

References

- 1) R.E. Kirk, F. Orthmer, J.I. Kroschwitz and M. Howe-Grant, Kirk-Othmer's Encyclopedia of Chemical Technology, John Willey & Sons, New York, 1998.
- 2) a) R. Ketter, N. Liermann, Oil Gas J. 86 (1988) 63; b) J. A. Lagas, J. Borsboom, P. H. Berben, Oil Gas J. 86 (1988) 68.
- 3) a) S.W. Chun, J.Y. Jang, D. W. Park, H.Ch. Woo, J.S. Chung, Appl. Catal. B 16 (1998) 235-243. b) J.H. Uhm, M.Y. Shin, J. Zhidong, J.S Chung. Appl. Catal. B 22 (1999) 293-393.
- 4) T.N. Mashapa, J.D. Rademan, M.J. Janse van Vuuren, Ind. Eng. Chem. Res. 46 (2007) 6338-6344.
- 5) A.A. Davydov, V.I. Marshneva, M.L. Shepotko, Appl. Catal. A 244 (2003) 93-100.

- 6) M.Y. Shin, Ch.M. Nam, D.W. Park, J.Sh. Chung, *Appl. Catal. A* 211 (2001) 213-225.
- 7) K.-T. Li, T.-Y. Chien, *Catal. Lett.* 57 (1999) 77-80.
- 8) K.T. Li, M.Y. Hyang, W.D. Cheng, *Ind. Eng. Chem. Res.* 35 (1996) 621-626.
- 9) K.T. Li, Z.-H. Chi, *Appl. Catal. B* 31 (2001) 173-182.
- 10) K.T. Li, Z.-H. Chi, *Appl. Catal. A* 206 (2001) 197-203.
- 11) S. Yasyerly, G. Dogu, T. Dogu, *Catal. Today* 117 (2006) 271-278.
- 12) D-W- Park, B.K. Park, D.-K. Park, H.C. Woo, *Appl. Catal. A* 223 (2002) 215224.
- 13) B.-G. Kim, W.-D. Ju, I. Kim, H.-Ch. Woo, D.-W. Park, *Sol. State Ionics* 172 (2004) 135-138.
- 14) S. Yasyerli, G. Dogu, I. Ar, T. Dogu, *Chem. Eng. Sci.* 59 (2004) 4001-4009.
- 15) M.I. Kim, D.W. Park, S.W. Park, X. Yang, J.S. Choi, D.J. Suh, *Catal. Today* 111 (2006) 212-216.
- 16) P. Kalinkin, O. Kovalenko, O. Lapina, D. Kjabibulin, N. Kundo, *J. Mol. Catal. A* 178 (2002) 173-180.
- 17) M.W. Song, M.Kang, K.L. Kim, *React. Kinet. Catal. Lett.* 78 (2003) 365-371.
- 18) K.-T. Li, Ch.-H. Huang, *Ind. Eng. Chem. Res.* 45 (2006) 7096-7100.
- 19) D.-W. Park, B.-H. Byung, W.-D. Ju, M.I. Kim, K.-H. Kim, H.-C. Woo, *Korean J. Chem. Eng.* 22 (2005) 190-195; K.V. Bineesh, D.R. Cho, S.Y. Kim, B.R. Jermy, D.W. Park, *Catal. Commun.* 9 (2008) 2040-2043.
- 20) M.I. Kim, W.D. Ju, K.H. Kim, D.-W. Park, S.S. Hong, *Stud. Surf. Sci. Catal.* 159 (2006) 225-228.
- 21) J. Jiménez-Jiménez, M. Rubio-Alonso, D. Eliche-Quesada, E. Rodríguez-Castellón, A. Jiménez-López, *J. Mater. Chem.* 15 (2005) 3466-3472.

- 22) L. Abello, E. Husson, Y. Repelin, G. Lucazeau, *Spectrochim. Acta* 39 (1983) 641-651.
- 23) M.D. Argile, K. Chen, A.T. Bell, E. Iglesia, *J. Catal.* 208 (2002) 139-149.
- 24) S.H. Lee, H.M. Cheong, M.J. Seong, P. Liu, C. Edwin, A. Mascarenhas, J. Roland, S.K. Deb, *Solid State Ionic*, 165 (2003) 111-116.
- 25) V.R. Porter, W.B. White, R. Roy, *J. Solid State Chem.* 4 (1972) 250-259.
- 26) Xingtao Gao and Israel E. Wachs, *J. Phys. Chem. B* 104 (2000) 1261-1268.
- 27) J. Le Bars, J.C. Vedrine, A. Auroux, S. Trautnant, M. Baerns, *Appl. Catal. A* 119 (1994) 341-354.
- 28) T. Blasco, A. Galli, J.M. López Nieto, F. Trifiró, *J. Catal.* 169 (1997) 203-211.
- 29) B. Solsona, J.M. López Nieto, U. Diaz, *Microp. Mesop. Mater.* 94 (2006) 339-347.
- 30) L.E. Briand, O.P. Tkachenko, M. Guraya, X. Gao, I.E. Wachs, W. Grünert, *J. Phys. Chem. B* 108 (2004) 4823-4830.
- 31) J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, *Standard Spectra for Identification and Interpretation of XPS data*, Perkin Elmer, Eden Prairie, MN, 1992.
- 32) R. Nilsson, T. Lindblad, A. Andersson, *J. Catal.* 148 (1994) 501-513.
- 33) C. Poccirillo, R. Binions, P. Parkin, *Chem. Vap. Deposition* 13 (2007) 145-151.
- 34) C. Quijada, F.J. Huerta, E. Morallón, J.L. Vázquez, L.E.A. Berlouis, *Electrochim. Acta* 45 (2000) 1847-1862.
- 35) J.C. Evands, *Inorg. Chem.* 2 (1963) 372-375.
- 36) J. Hrbek, S.Y. Li, J.A. Rodriguez, D.G. van Campen, H.H. Huang, G.-Q. Xu, *Chem. Phys. Lett.* 267 (1997) 65-71.
- 37) K.-A. Wilhelmi, K. Waltersson, *Acta Chem. Scand.* 24 (1970) 3409-3411.
- 38) K.P. Callahan, P.J. Durand, *Inorg. Chem.* 19 (1980) 3211-3217.

- 39) H. Kwon, S. Choi, L.T. Thompson, *J. Catal.* 184 (1999) 236-246.
- 40) J. Haber, M. Witko, R. Tokarz, *Appl. Catal. A* 157 (1997) 3-22.
- 41) G. Grymonprez, L. Fiermans, J. Vennik, *Acta Cryst. A* 33 (1977) 834-837.

Caption to figures

Fig.1. Scheme of the synthesis of the mesoporous zirconium phosphate heterostructure.

Fig.2. Variation of the H₂S conversion with the time on stream (TOS) obtained over MZP-supported vanadium oxide catalysts. Reaction conditions: 0.1 g of catalyst; total flow of 130 mL min⁻¹; H₂S/air/He molar ratio of 1.2/5.0/93.8 (i.e. H₂S/O₂ ratio of 1/0.9); W/F= 31.2 g_{cat} h⁻¹ mol_{H₂S}⁻¹. Symbols: 0V-MZP (◇); 2V-MZP (●); 4V-MZP (▲); 8V-MZP (■); 12V-MZP (□); 16V-MZP (◆); f) V₂O₅ (Δ).

Fig.3. Variation of the H₂S conversion with the reaction temperature of pretreated samples. *Pretreatment conditions*: temperature = 250°C (4 h); total flow of 125 mL min⁻¹ of a 1% of H₂S/He; weight of catalyst= 0.1 g. *Reaction conditions*: 0.1 g of catalyst; total flow of 130 mL min⁻¹; H₂S/air/He molar ratio of 1.2/5.0/93.8 (i.e. O₂/H₂S ratio of 0.85); W/F= 31.2 g_{cat} h⁻¹ mol_{H₂S}⁻¹. Symbols: 4V-MZP (▲); 8V-MZP (■); 12V-MZP (●); 16V-MZP (□).

Fig.4. XRD patterns of MZP-supported vanadium oxide catalysts before (A) and after (B) the catalytic test: a) 0V-MZP; b) 2V-MZP; c) 4V-MZP; d) 8V-MZP; e) 12V-MZP; f) 16V-MZP; g) V₂O₅. Symbols: V₂O₅ (●); ZrP₂O₇ (□); V₄O₉ (▲); elemental sulphur (■).

Fig.5. Raman spectra of MZP-supported vanadium oxide catalysts before (A) and after (B) the catalytic test: a) 0V-MZP; b) 2V-MZP; c) 4V-MZP; d) 8V-MZP; e) 12V-MZP.; f) 16V-MZP; g) V₂O₅.

Fig.6. DR-UV-vis spectra of MZP-supported vanadium oxide catalysts before (A) and after (B) the catalytic test: a) 2V-MZP; b) 4V-MZP; c) 8V-MZP; d) 12V-MZP; e) 16V-MZP; f) V₂O₅.

Fig.7. FTIR spectra of adsorbed pyridine on MZP-supported vanadium oxide catalysts: a) 0V-MZP; c) 4V-MZP; d) 8V-MZP; e) 12V-MZP. After evacuation at 150°C.

Fig. 8. TPR patterns of results on MZP-supported vanadium oxide catalysts: a) 4V-MZP; b) 8V-MZP; c) 12V-MZP; d) V₂O₅.

Fig.9. V 2*p* and S *p* core level spectra for MZP-supported vanadium oxide catalysts after the catalytic test. Samples: a) 4V-MZP; b) 8V-MZP; c) 12V-MZP.

Table 1. Characteristics of supported vanadium oxide catalysts.

Sample	V-content (wt %) ^(a)	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	TPR results ^(b)		H ₂ S Oxidation	
				TCM (°C)	H ₂ -uptake (10 ⁴ mol _{H2} g ⁻¹)	TOF (mol _{H2S} h ⁻¹ mol _V ⁻¹) ^(c)	STY (gs h ⁻¹ kg _{cat} ⁻¹) ^(d)
0V-MZP	0.0	556	0.54		0	-	218
2V-MZP	2.1	212	0.50	550	0.23	22.6	490
4V-MZP	4.1	158	0.56	550	0.69	14.5	785
8V-MZP	8.4	151	0.49	550	1.61	13.0	986
12V-MZP	12.7	89.8	0.43	550	2.99	11.8	1054
16V-MZP	16.0			560	4.20	9.36	1054
V₂O₅	56.0	3.0	-	619	n.d.	2.15	806

a) V-content in calcined samples in wt% of V-atoms.

b) Temperature of maximum hydrogen consumption (TCM) and H₂-uptake (in mol_{H2} g⁻¹) achieved during the TPR results; n.d= not determined.

c) Turnover frequency (TOF) in mol_{H2S} h⁻¹ mol_V⁻¹, calculated after 0.5 h of time on stream. Reaction conditions as in Fig. 1.

d) Space time yield (STY) of sulphur formation, in gs h⁻¹ kg_{cat}⁻¹, calculated after 0.5 h of time on stream. Reaction conditions as in Fig. 1.

Table 2. XPS results of fresh catalysts.

Sample	Surface composition O/Si/P/Zr/V atomic ratio	Core level binding energy (eV)				
		O1s	Si 2p	P 2p	Zr 3d _{5/2}	V 2p _{3/2}
0MZP	71.90/17.48/6.70/3.45/0.00	532.2	102.8	133.5	183.1	-
4VMZP	71.85/17.35/6.24/3.30/0.94	532.1	102.8	133.6	183.1	518.0 (65%) 516.5 (35%)
8MZP	70.54/17.31/6.60/3.35/2.02	531.9	102.8	133.5	182.9	517.8 (75%) 516.5 (25%)
12MZP	71.43/16.54/5.77/2.94/3.11	532.0	102.8	133.4	183.1	517.8 (93%) 516.5 (7%)

Table 3. XPS results of used catalysts.

Sample	Surface composition	Core level binding energy (eV)							
	O/Si/P/ Zr/V/S atomic ratio	O1s	P 2 <i>p</i>	Si 2 <i>p</i>	Zr 3 <i>d</i> _{5/2}	V 2 <i>p</i> _{3/2}		S 2 <i>p</i> _{3/2}	
4VMZP	68.14/17.38/7.32/3.91/1.14/1.10	532.1	133.6	102.8	183.1	517.5 (64%)	163.2 (72%)	516.3 (36%)	168.4 (28%)
8VMZP	68.38/17.11/7.46/3.94/2.02/1.09	531.9	133.5	102.8	182.9	517.5 (66%)	163.2 (70%)	516.3 (34%)	168.3 (30%)
12VMZP	68.50/16.79/6.90/3.70/3.45/0.66	532.0	133.4	102.8	183.1	517.5 (64%)	163.6 (66%)	516.3 (36%)	168.3 (34%)