Catalysis Today 155 (2010) 296–301

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Operando XAS and Raman study on the structure of a supported vanadium oxide catalyst during the oxidation of H_2S to sulphur

J.P. Holgado [a], M.D. Soriano [b], J. Jiménez-Jiménez [c], P. Concepción [b], A. Jiménez-López [c], A. Caballero [a], E. Rodríguez-Castellón [c], J.M. López Nieto [b,*]

[a] *Instituto de Ciencia de Materiales de Sevilla and Dep. Química Inorgánica (CSIC-Universidad de Sevilla), Sevilla, Spain*
[b] *Instituto de Tecnología Química, UPV-CSIC, Campus de la Universidad Politécnica de Valencia, Valencia, Spain*
[c] *Dep. Química Inorgánica, Universidad de Málaga, Málaga, Spain*

ARTICLE INFO

Article history:
Available online 1 April 2010

Keywords:
Operando
RAMAN
EXAFS
XANES
Partial oxidation of hydrogen sulphide
Vanadium oxides supported on mesoporous zirconium phosphate

ABSTRACT

The modification of crystalline phases of a vanadium oxide supported on mesoporous zirconium phosphate during the partial oxidation of H_2S to sulphur has been studied by using an *operando* Raman-GC approach and XAS in reaction conditions. The catalyst, mainly presenting crystalline V_2O_5, is transformed during the oxidation of H_2S at 200 °C, presenting crystals of V_4O_9, which is identified by the presence of a band at ca. 900 cm^{-1} in the Raman spectra (using a 785 nm line of an Argon ion laser) and by the presence of a pre-edge at 5469.8 eV (and a main-edge at 5482.2 eV) in XANES spectra. At the same time, it is observed a high conversion of H_2S to sulphur (the main reaction product) and SO_2 (as minority). Both activity and selectivity depend on the time on stream. In this way, the selectivity to SO_2 decreases from ca. 5 to 1% with the time on stream. This change could be explained on the basis of the nature of V-species: the initial presence of V^{5+}–O–V^{5+} pairs and the appearance of V^{5+}–O–V^{4+} pairs at high time on stream.

1. Introduction

Supported vanadium oxide catalysts are interesting in a well number of reactions such as the partial oxidation of hydrocarbons or in the selective reduction of NO_x [1–5]. In addition to the oxidative dehydrogenation of short chain alkanes [4,5], an important effort to study these catalytic systems in the partial oxidation of H_2S to elemental sulphur has been carried out in the last years [6–10]. At the moment, it is known that the characteristics of the metal oxide support and the nature of vanadium species strongly influence the catalytic performance and stability of supported vanadium catalysts during the partial oxidation of H_2S [6–10], although the catalysts could be modified during the reaction depending on the characteristics of catalysts and/or the reaction conditions. In this way, the reducing power of reactants seems to be an important factor in the partial oxidation of H_2S over V_2O_5 catalyst [11]. Thus, it has been reported that a reduced vanadium oxide, achieved by a reduction of V_2O_5 at 600 °C for 24 h, showed a stable reactivity and an excellent conversion of H_2S and selectivity for the elemental sulphur. Recently we have observed how catalysts based in vanadium oxide supported on a mesoporous zirconium phosphate heterostructure change depending on the V-loading and the reaction conditions [12]. Accordingly, the nature of active and selective sites working during the reaction is still under discussion.

Raman studies have been carried out to determine the structure of vanadium oxide catalysts [13], while X-ray absorption spectroscopy (XAS) have been used to determine the oxidation state and coordination of vanadium-based catalysts [14]. More recently, they have been also used in operando conditions in order to clarify the nature of active and selective sites [15–17].

In the present paper we show for the first time an X-ray absorption spectroscopy (XAS) and Raman study, both working *in operando* conditions, on the selective oxidation of H_2S to sulphur using a vanadium oxide supported on a mesoporous zirconium phosphate heterostructure as catalyst. In addition, the reduction or reoxidation of catalyst after the catalytic test has been also studied.

2. Experimental

2.1. Catalyst preparation

A vanadium oxide supported on mesoporous zirconium phosphate (with 12 wt% of V-atoms, named as $12VO_x$/MZP) has been prepared by the wet-impregnation method of the mesoporous zirconium phosphate (MZP, $S_{BET} = 556\ m^2/g$), using an aqueous solution of ammonium metavanadate. The mixture was rotae-

---

[*] Corresponding author. Fax: +34 963877809.
E-mail address: jmlopez@itq.upv.es (J.M.L. Nieto).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.02.050

vaporated until complete dryness, dried overnight at 100 °C and then calcined at 550 °C for 6 h. The resulting catalyst presents a surface area of $90\,m^2\,g^{-1}$. The mesoporous zirconium phosphate heterostructure, MZP ($S_{BET} = 556\,m^2/g$), was prepared according to a previously reported preparation procedure [18].

For comparison, commercial $VOSO_4.3H_2O$ (Aldrich), V_2O_5 and V_4O_9 have been also used. V_2O_5 has been prepared from ammonium metavanadate by calcination in air at 550 °C for 1 h. A V_4O_9 sample has been prepared according to the preparation procedure previously described [19]. The sample shows an X-ray power diffraction pattern with lines at 2θ = 13.7, 21.6, 27.7, 28.1, 33.9, 35.5, 35.7, 41.2, 53.2, 56.0° in agreement to that previously reported for pure V_4O_9 [JCPDS-23-720].

2.2. Catalyst characterization

The *operando* FT-Raman spectra were recorded with an “in via” Renishaw spectrometer, equipped with a microscope (Olympus). The samples were excited by the 785 nm line of an Argon ion laser (Spectra Physics Model 171) with a laser power of 2.5 mW. Spectra were collected using a backscattering geometry with a 180° angle between the illuminating and the collected radiation. A micro quartz reactor (i.d. 6 mm, length 200 mm) located in a furnace has been used for in situ Raman studies. The furnace is provided with a small hole in order to allow focalization on the sample with the laser spot (spatial resolution of approx. 1.5 μm). The reactor was positioned below the microscope objective, using a ×50 long working distance objective (WD = 10.6 nm). The flow of the reactant has been controlled by mass flow controllers using a total flow of 65 ml/min, with a $H_2S/air/N_2$ molar ratio of 1.2/5.0/93.8. The reaction has been performed on 50 mg of catalysts powder at a reaction temperature of 200 °C. Analysis of reactants and reaction products was carried out on-line using gas chromatography and two different chromatographic columns (Molecular Sieve 5Å and Porapak T). The gas line after the reactor has been heated to 150 °C in order to avoid condensation of sulphur. Previous to venting the gases sulphur has been collected on a cold trap.

Vanadium K-edge X-ray absorption spectroscopy (XAS) measurements were performed at the beamline X10DA (superXAS) located at the Swiss Light Source (SLS), Villigen, Switzerland, using a Si(1 1 0) monochromator. The measurements were performed in transmission mode using ion chambers filled with Ar/N_2 as detectors. A modified commercial infrared (Specac) cell, equipped with Kapton windows was used for in operando measurements. Typically, 50 mg of catalyst powder were pressed in a stainless steel sample holder in order to obtain self-supported discs of samples with appropriated transmission properties. Due to formation of sulphur in the reaction, heating of pipes after the cell is necessary, to avoid the condensation of this element. Collection of formed sulphur in the reaction will be done in a cold trap previous to vent the gases into the exhaust. Mass flow controllers were used for dosing the gases to the cell, using a total flow of 100 ml/min, with $H_2S/O_2/He$ molar ratio of 1/1/98. For comparison, the spectra of catalyst before and after the catalytic tests have been also achieved at room temperature in helium. The XAS spectra were analyzed using the IFEFFIT programs package [20]. A factor of k^2 was used for obtaining the Fourier Transforms (FT) of the EXAFS region of the spectra.

The catalytic tests were carried out in a fixed-bed tubular reactor at 200 °C and atmospheric pressure, 50 mg of catalyst and a H_2S/air/He mixture with a molar composition of 1.25/5.0/93.8 and a total flow of $130\,ml\,min^{-1}$. The analysis of reactants and products has been carried out using the same procedure to that described previously for the *operando* Raman study.

3. Results and discussion

3.1. Characterization of catalysts before and after catalytic tests

Fig. 1 shows the XRD patterns (Fig. 1A), and Raman (Fig. 1B) and XANES (Fig. 1C) spectra of supported catalyst ($12VO_x$/MZP sample) before and after the catalytic test. For comparison, the corresponding spectra of the as-synthesized V_4O_9 are also included (Fig. 1, patterns c and spectra f and i). We must indicate that the used supported catalyst was recovered after a time-on-stream 300 min. During the catalytic test the H_2S conversion decreased from ca. 80 to 63%, while the selectivity to elemental sulphur was higher than 99%.

The XRD patterns of fresh catalysts shows the presence of V_2O_5 [JCPDS: 41-1426] and ZrP_2O_7 [JCPDS: 85-896]. When comparing to those achieved from used catalysts (Fig. 1A, pattern b) and pure V_4O_9 (Fig. 1A, pattern c), it can be concluded the disappearance of V_2O_5 and the formation of V_4O_9 [JCPDS: 23-720] after the catalytic tests [12].

On the other hand, fresh catalyst is characterized by the presence of bands at 998, 706, 530, 489, 410, 305, 289, 203 and 159 cm^{-1}

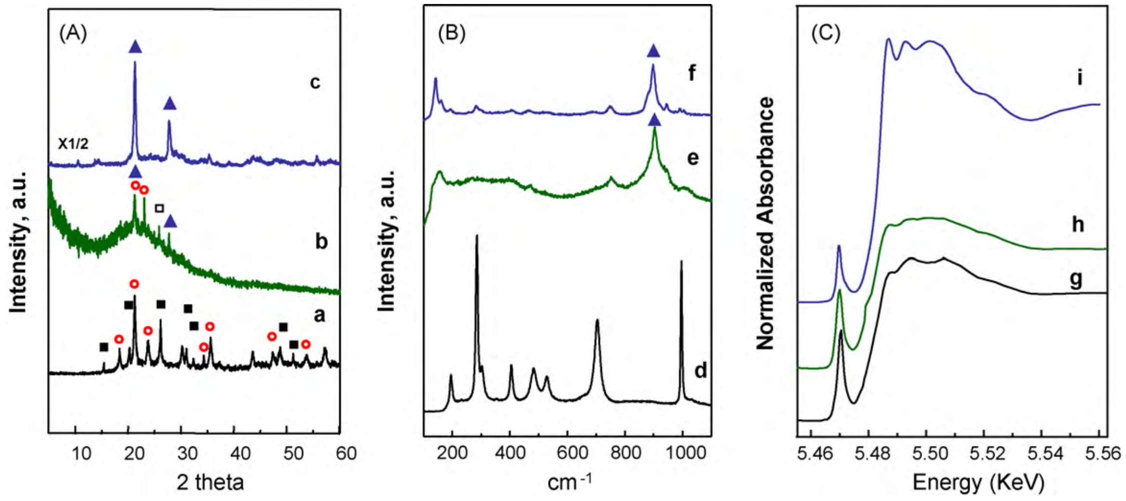

Fig. 1. XRD (A), Raman (B) and XANES (C) results of fresh (a, d and g) and used (b, e and h) supported vanadium oxide catalyst ($12VO_x$/MZP). For comparison, the corresponding spectra of the as-synthesized V_4O_9 are also included (c, f and i). Symbols: V_2O_5 (■); ZrP_2O_7 (○); V_4O_9 (▲); elemental sulphur (□). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 1
Pre-edge and main peak observed in XANES spectra of $12VO_x/MZP$ catalysts and references.

Sample	Treatment[a]	Pre-edge peak position (eV)	Main-edge position (eV)	Δ (eV)[b]
V_2O_5	He/rt	5470.6	5483.7	13.1
V_4O_9	He/rt	5469.8	5482.2	12.4
$VOSO_4$	He/rt	5469.8	5480.1	10.3
$12VO_x/MZP$	He/rt	5470.4	5483.2	12.8
$12VO_x/MZP$	He/200 °C	5470.4	5482.9	12.5
$12VO_x/MZP$	RC, after a TOS of 120 min	5469.9	5482.1	12.2

[a] Treatment of samples: in Helium at room temperature (rt) or at 200 °C; in reaction conditions (RC) as in Fig. 2.

[b] Difference between main-edge position and pre-edge peak position.

in the Raman spectrum, which indicate the presence of crystalline V_2O_5 [13] (Fig. 1B, spectrum d). However the presence of isolated vanadium species on the surface of the support as minority cannot be ruled out. After the catalytic tests the Raman spectrum of catalyst changes (Fig. 1B, spectrum e). Thus, a band at *ca.* 900 cm^{-1} is observed in used catalysts, while the main features of the bands related to V_2O_5 crystallites are not observed. This spectrum is very similar to that achieved with the as-synthesized V_4O_9 (Fig. 1B, spectrum f), which is also in agreement to one reported by Nilson et al. [21] during the study of the propane ammoxidation over V_2O_5 and one recently proposed from our group for this type of catalysts during the partial oxidation of H_2S [12].

We must indicate that the Raman band at ca. 900 cm^{-1} characteristic of V_4O_9 [20] is only observed when excited with radiation of 785 nm while not observed when using an excitation wavelength of 514 nm [22]. This effect, explained by resonance effects in reduced vanadium oxides, makes their characterization possible by properly selecting the laser excitation wavelength. Similar resonant effects have already been observed by Mestl et al. [23,24] in partially reduced molybdenum oxide.

Fig. 1C shows the V K-edges XANES spectra of catalyst before (Fig. 1C, spectrum g) and after the catalytic test (Fig. 1C, spectrum h), as well as the spectrum achieved with the as-synthesized V_4O_9 (Fig. 1C, spectrum i). For comparison, the pre-edge features for the XANES spectra are shown in Table 1. According to previous XANES results of V-based compounds [14], it can be concluded that V_2O_5 is mainly present in fresh catalyst while V_4O_9 seems to be the main phase in the used catalyst. In this case, the V_4O_9 phase in the catalyst seems to be more amorphous than the massive oxide phase, according to the more attenuated oscillations observed by XAS.

3.2. *Raman study on catalysts during the H_2S partial oxidation*

Fig. 2 shows *operando* Raman spectra and their on-line simultaneous catalytic results for sample $12VO_x/MZP$ during the selective oxidation of H_2S with time on stream, TOS, from 0 to 180 min.

The Raman spectrum of the sample at 200 °C in helium shows the same bands to that obtained for fresh catalyst (bands at 998, 706, 530, 489, 410, 305, 289, 203 and 159 cm^{-1}) indicating the presence of bulk V_2O_5 (Fig. 2, spectrum b). However, after some minutes in contact with the reaction mixture, the bands related to V_2O_5 disappear appearing a band at ca. 900 cm^{-1} (Fig. 2, spectra c to j). The band at ca. 900 cm^{-1}, observed during all the experiment (after 180 min of time on stream), was also observed during the characterization of the catalyst after a catalytic tests in a fixed-bed reactor. Thus, and according to that previously indicated, the band at ca. 900 cm^{-1} can tentatively be assigned to V_4O_9 [21]. In addition, we can also conclude that this non-stoichiometric vanadium oxide is formed during the partial oxidation of H_2S at 200 °C.

On the other hand, Fig. 2 also shows the catalytic results obtained during the *operando* Raman-GC measurements. It can be seen that the conversion of H_2S decreases from 99 to 90% after 120 min. In this way, we must indicate that a similar behavior is also observed when the catalytic tests were carried out in a fixed-bed reactor.

In all cases, sulphur has been the main reaction product while SO_2 was observed as minority. However, a small difference in the

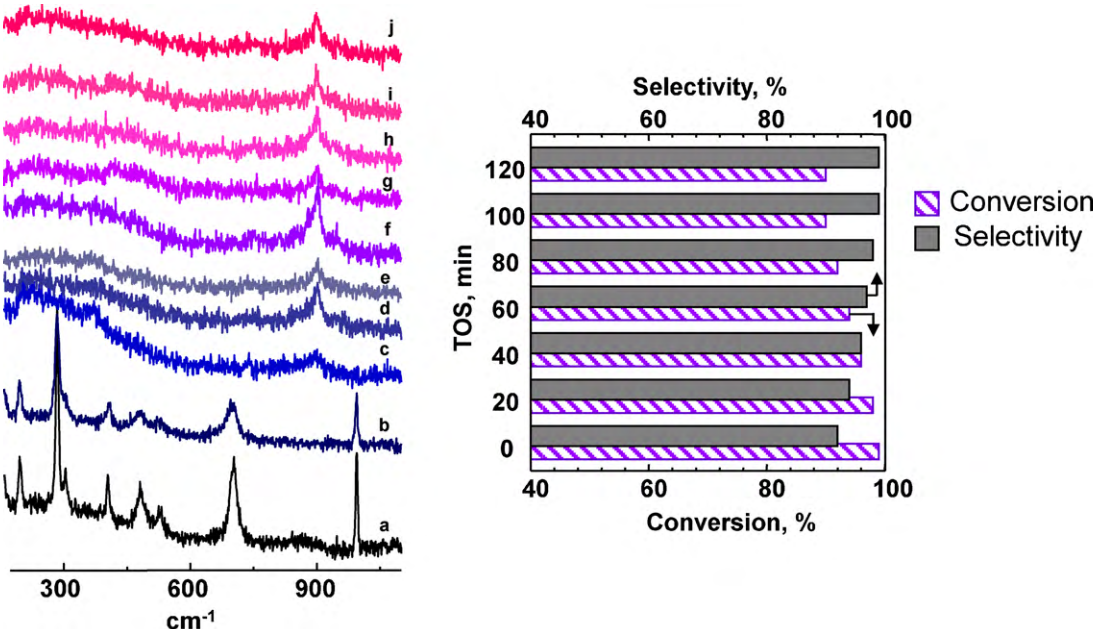

Fig. 2. Operando Raman spectra (left) of $12VO_x/MZP$ catalyst during partial oxidation of H2S and the corresponding catalytic results, i.e. H_2S conversion (▨) and selectivity to elemental sulphur (■) (right). Spectra: (a) at r.t. in He; (b) at 200 °C in He; (c) during reaction at a TOS of 15 min; (d) during reaction at a TOS of 30 min; (e) during reaction at a TOS of 45 min; (f) during reaction at a TOS of 60 min; (g) during reaction at a TOS of 75 min; (h) during reaction at a TOS of 90 min; (i) during reaction at a TOS of 120 min; (j) during reaction at a TOS of 180 min. Reaction conditions: 50 mg of catalyst, total flow 65 ml min^{-1}; H_2S/air/He molar ratio of 1.2/5.0/93.8. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

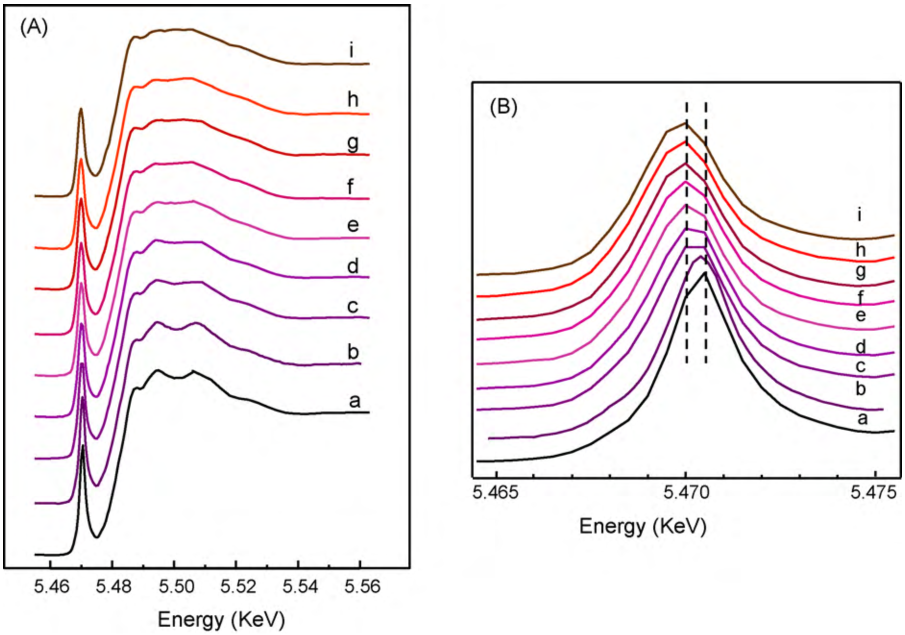

Fig. 3. Normalized absorption spectra (XANES) for the $12VO_x$/MZP catalyst at different time on stream (A). For comparison, the enlarged pre-edge region of V–O bond is also included (B). Spectra: at room temperature in He (a); at 200 °C in He (b); spectra in reactions conditions at a TOS (in min) of 15 (c), 30 (d), 45 (e), 60 (f), 75 (g), 90 (h) and 120 (i).

S/SO_2 ratio is also observed with the time on stream. Thus, an initial selectivity of ca. 8% was observed for SO_2 although it decreases with time on stream until selectivity to SO_2 lower than 1% at a TOS of 120 min. In an opposite trend, the initial selectivity to elemental sulphur of ca. 92% increases until 99% after 120 min of time on stream.

3.3. *XANES/EXAFS measurements during the H_2S partial oxidation*

Fig. 3 shows the XANES spectra of $12VO_x$/MZP catalyst during the treatment at 200 °C, while Table 1 shows the pre-edge peak position, the main-edge position as well as the difference between main-edge and pre-edge peak position in fresh and used catalysts. For comparison, Fig. 4 shows the XANES spectra of reference compounds, i.e. V_2O_5, during the partial oxidation of H_2S.

In the case of $12VO_x$/MZP catalyst, it can be seen that in a He stream at room temperature (r.t.) or 200 °C the XANES spectra indicate the presence of bulk V_2O_5 (Fig. 3, spectra a and b, respectively), which is characterized by a pre-edge position at 5470.6 eV and a main-edge peak at 5483.7 eV. However, the XANES spectra are clearly modified during the reaction at 200 °C, and completely different XANES spectra are observed after the first 30 min of time on stream. Thus, the pre-edge peak shifts from 5470.4 (Fig. 3, spectrum b) to 5469.9 eV (Fig. 3, spectrum d). At the same time, the main-edge position shifts from 5483.2 (in helium at room temperature) to 5482.9 (in Helium at 200 °C) and finally to 5482.1 eV (when obtained in reaction conditions after a time of stream of 120 min, Fig. 3, spectrum g). This final spectrum is quite similar to that of the V_4O_9 (Fig. 1, spectrum f) suggesting that a partial reduction of V(V) to V(IV) species has occurred during the reaction.

The XANES spectrum of pure V_2O_5 shows a similar behaviour during the treatment with a reaction mixture (Fig. 4). Thus, V_2O_5 is clearly modified when in reaction conditions in the same way than that observed in supported catalyst. At this point we must indicate that the XANES spectrum of pure V_4O_9 remains mainly unmodified (spectrum not shown), presenting a great stability of this mixed valence compound in reaction conditions. So, after about 2 h of time on stream, the XANES of all three samples (catalyst and reference materials) are similar, with the pre-edge peak shifted to about 5469 eV, with the main-edge located at 5481 eV. The fact that in all cases the final spectra are quite similar to that of the V_4O_9 shows that a partial reduction of V(V) to V(IV) species occurs in reaction conditions. These results are in agreement to the Raman spectrum achieved in the same conditions.

These assertions are fully confirmed by the results obtained by Fourier Transforming the EXAFS region of the XAS spectra. Fig. 5 shows the Fourier Transforms (FTs) obtained from the EXAFS spectra of the sample during the He treatment at 200 °C and after 2 h of reaction. For comparison Fig. 6 shows the EXAFS spectra achieved with V_2O_5 (Fig. 6A) and V_4O_9 (Fig. 6B) after the same treatments. Due to the high complexity of the vanadium oxides coordination shells, with four different V–O shells between 1.60 and 1.91 Å, and three V–V distances at 3.15–3.65 Å, no fitting procedure of the signals have been accomplished. However, a direct comparison with the FT of the vanadium oxides references allows us to establish that in all cases, the FTs after reaction are similar to the V_4O_9 reference, with two peaks centered at about 1.25 and 1.95 Å, respectively. The fact that the peaks in the supported catalyst are wider than in the vanadium oxides references is related to a more heterogeneous and disordered state of the supported phases, an effect frequently observed in many supported catalytic systems [25]. This finding totally confirms the previous conclusion from the XANES spectra that the bulk V_2O_5, originally presents in the catalysts, and even the V_2O_5 reference, are partially reduced to a V_4O_9-like phase, which remains stable all along the catalytic reaction (Fig. 6B).

3.4. *General remarks*

It is known that the catalytic performance of supported vanadia catalysts strongly depends on the supports and the V-loading, which determine the nature of V-species [12]. In this way, it has been reported that catalysts presenting V_2O_5 crystallites are more active and present lower catalyst decay than catalysts presenting isolated vanadium species on the surface of the support. For this reason, the catalytic behavior of our catalyst can be related to the presence of V_2O_5 crystallites, although the contribution of surface vanadium species cannot be completely ruled out.

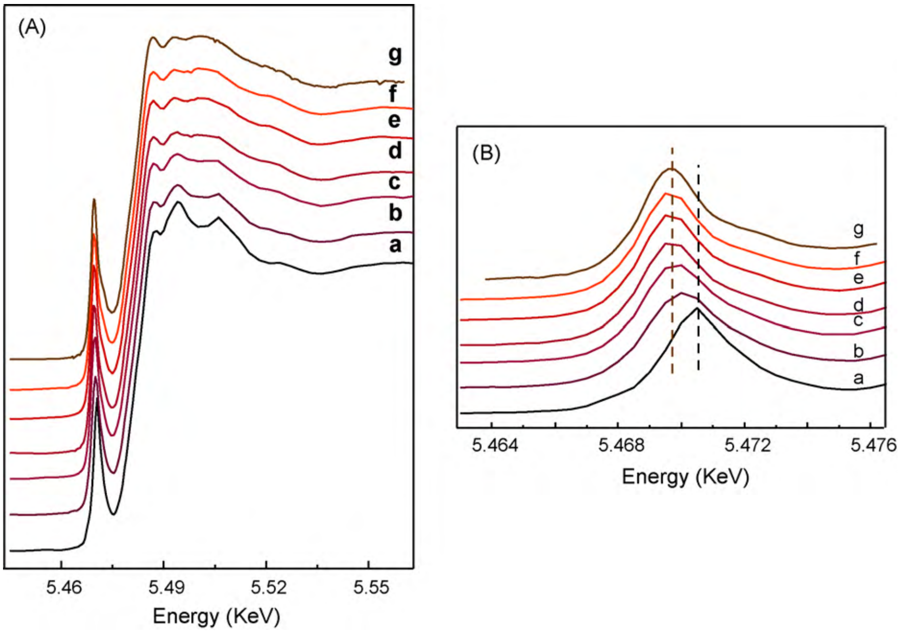

Fig. 4. Normalized absorption spectra (XANES) for the V_2O_5 catalyst at different time on stream (A). For comparison, the enlarged pre-edge region of V–O bond is also included (B). Spectra: at 200 °C in He (a); spectra in reactions conditions at a TOS (in min) of 15 (b), 30 (c), 45 (d), 60 (e), 75 (f), 90 (g).

The Raman and XAS results of our catalysts before and after the catalytic tests show the transformation of catalyst by changing the nature of crystalline phases in fresh (V_2O_5) and in used (V_4O_9) catalyst. Thus, one could propose the formation of a partially reduced V-compound during the catalytic tests as a consequence of the catalyst reduction. However, the extension of the partial reduction of V_2O_5 crystallites cannot be directly determined by the characterization of used catalysts since this could be also reoxidized during the characterization step.

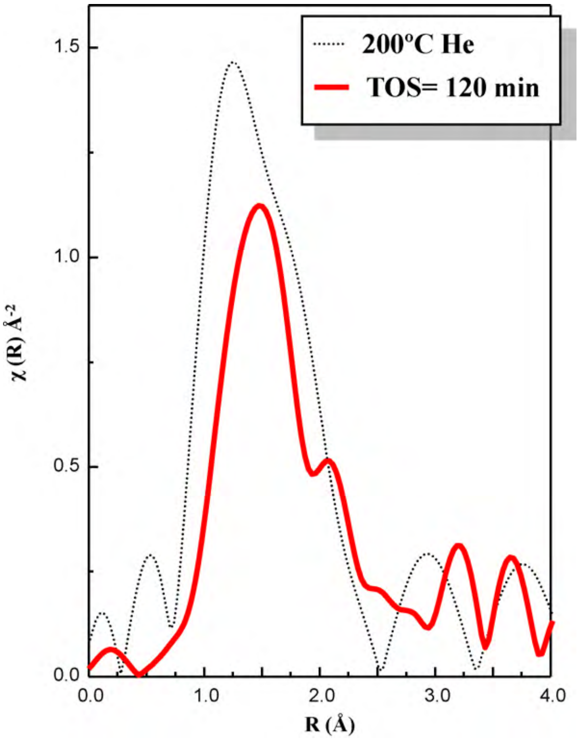

Fig. 5. Fourier transforms of the EXAFS region obtained for the $12VO_x$/MZP catalyst before (dashed line) and after a treatment in reaction conditions at a TOS of 120 min (solid line). Reaction conditions as in Fig. 3.

In this way, we must remember that VO_2 or V_2O_3 have been proposed as the final crystalline phase formed during the oxidation of H_2S at 235 or 335 °C over pure V_2O_5 or V/SiO_2 catalysts [6]. However, they are not observed in our case. For this reason, we considered that a study on the catalyst modification during the reaction should be performed more effectively by using the same characterization techniques in *operando* condition.

The characterization results carried out by Raman and EXAFS-XANES in *operando* conditions confirm that V_4O_9 is mainly formed during the reaction and it remains in the catalyst after the catalytic tests. At this point we must indicate that V_4O_9 can be easily formed by treating V_2O_5 with sulphur [26], and it is an intermediate product during the preparation of vanadium nitrides [27]. In fact, by the temperature-programmed reaction of V_2O_5 with NH_3 the following sequence has been proposed: $V_2O_5 \rightarrow V_4O_9 \rightarrow VO_2 \rightarrow V_2O_3 \rightarrow VO_{0.9}$, last being transformed by the topotactic substitution of nitrogen for oxygen.

It has been proposed that the selective oxidation of H_2S is carried out by a redox mechanism involving lattice oxygen [6–10]. Our results suggest that the catalyst reoxidation could be the determining-reaction step, favoring a partial reduction of the catalyst. However, V^{5+}–O–V^{4+} pairs can be proposed as the active and selective sites in steady-state conditions since a high selectivity to elemental sulphur is achieved over partially reduced catalysts (i.e. V_4O_9 with V^{5+}–O–V^{4+} pairs) instead of over total oxidized catalyst (i.e. V_2O_5 with V^{5+}–O–V^{5+} pairs).

On the other hand, the different oxidation state observed in our catalyst, but also in V_2O_5 after the reaction, with respect to that proposed by Shin et al. [6] can be explained by the different reaction conditions used in each case. Thus, Shin et al. observed VO_2 and VO_3 when the reaction is carried out at 325 °C and a H_2S/O_2 ratio of ca. 2 in the presence of NH_3 and steam and a time of stream of 20 h [6]. It is clear that in the last conditions a higher reduction should be achieved. In this way, it has been proposed that the catalytic performance of V-based catalysts strongly depends on the reductor character of the reaction mixture [11], the reducing power of reactants being the most important factor in the selective

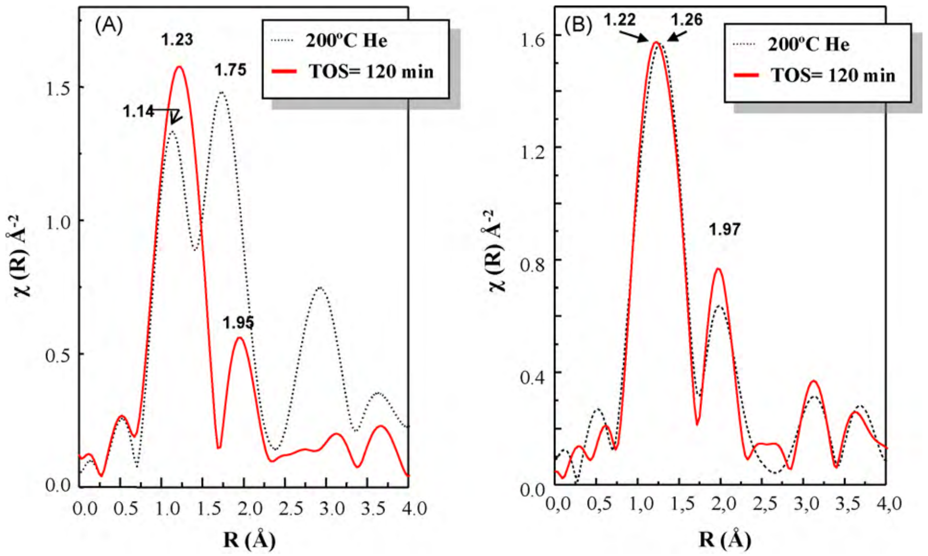

Fig. 6. Fourier transforms of the EXAFS region obtained for the V_2O_5 (A) and V_4O_9 (B) catalyst before (dashed line) and after a treatment in reaction conditions at a TOS of 120 min (solid line). Reaction conditions as in Fig. 3.

oxidation of H_2S. For this reason, it is evident that the nature of crystalline phases in the catalyst could be changed when using reaction mixtures with a high reductor character and/or when working at different reaction temperature. However, in the reaction conditions studied here, the catalysts achieved a steady-state condition when forming the partially reduced phase.

4. Conclusions

In this paper we have studied the modification of a V-based catalyst (a vanadium oxide supported on a mesoporous zirconium phosphate, 12 wt% of V-atoms) during the selective oxidation of H_2S to sulphur by *operando* Raman and EXAFS-XANES. These results have been compared with those carried out with a used catalysts. In addition, and for a better understanding, we have also follow the modification of pure V_2O_5 and V_4O_9 during the catalytic test.

According to the results presented here bulk V_2O_5 which is mainly observed in the fresh supported catalysts, is clearly transformed into a like-V_4O_9 phase during the partial oxidation of hydrogen sulphide to sulphur at 200 °C, confirming previous results obtained during the characterization of used catalysts [12]. This like-V_4O_9 phase is characterized by the presence of a band at ca. 900 cm^{-1} in the Raman spectrum (achieved with 785 nm line of an Argon ion laser) and a pre-edge peak at 5469.9 eV and a main-edge at 5482.1 eV in the XANES spectrum (achieved in vanadium K-edge X-ray absorption spectroscopy).

On the other hand, this like-V_4O_9 phase is also observed when the *operando* XAS study is carried out by using pure V_2O_5 as catalyst. However, no changes were observed in the nature of the catalyst when pure V_4O_9 was used as catalyst. These results are in good agreement to those achieved during the characterization of an used catalyst confirming a partial reduction of catalyst during the catalytic test for the partial oxidation of hydrogen sulphide to sulphur.

This conclusion is quite different to those previously proposed over V_2O_5 and SiO_2-supported vanadium catalysts, suggesting that the reaction conditions, i.e the reduction power of the fed and/or the reaction temperature, are a key element in the transformation of the active phase.

Finally, it is also observed that the selectivity to sulphur increases when increasing the formation of V_4O_9 in the catalyst. May be, the presence of V^{5+}–O–V^{4+} pairs (as proposed in V_4O_9) instead of V^{5+}–O–V^{5+} pairs (as proposed in V_2O_5) favors a higher selectivity to partial oxidation products (i.e. sulphur). In this sense, the formation of more oxidized products (i.e SO_2) in addition to sulphur seems to be more favored in oxidized catalysts but decay with the time of stream in catalytic tests.

Acknowledgments

The authors gratefully acknowledge financial support from CICYT, Spain (NAN20004-09267-C03-01 and NAN2004-09267-C03-02). We also thank Swiss Light Source (SLS) at the Paul Scherrer Institut (Proposal 20081090).

References

[1] J.M. López Nieto, Top. Catal. 41 (2006) 3.
[2] J.N.J. van Lingen, O.L.J. Gijzeman, B.M. Weckhuysen, J.H. van Lenthe, J. Catal. 239 (2006) 34.
[3] I.E. Wachs, B.M. Weckhuysen, Appl. Catal. A 157 (1997) 67.
[4] T. Blasco, J.M. López Nieto, Appl. Catal. A 157 (1997) 117.
[5] F. Cavani, N. Ballarini, A. Cericola, Catal. Today 127 (2007) 113.
[6] M.Y. Shin, Ch.M. Nam, D.W. Park, J.Sh. Chung, Appl. Catal. A 211 (2001) 213–225.
[7] M.Y. Shin, D.W. Park, J.S. Chung, Appl. Catal. B 30 (2001) 409.
[8] M.W. Song, M. Kang, K.L. Kim, React. Kinet. Catal. Lett. 78 (2003) 365.
[9] M.I. Kim, W.D. Ju, K.H. Kim, D.W. Park, S.S. Hong, Stud. Surf. Sci. Catal. 159 (2006) 225.
[10] K.V. Bineesh, D.R. Cho, S.Y. Kim, B.R. Jermy, D.W. Park, Catal. Commun. 9 (2008) 2040.
[11] J.D. Lee, N.K. Park, S.O. Ryu, T.J. Lee, Appl. Chem. 8 (2004) 601.
[12] M.D. Soriano, J. Jiménez-Jiménez, P. Concepción, A. Jiménez-López, E. Rodríguez-Castellón, J.M. López Nieto, Appl. Catal. B 92 (2009) 271.
[13] B.M. Weckhuysen, J.-M. Jehng, I.E. Wach, J. Phys. Chem. B 104 (2000) 7382.
[14] G. Silversmit, J.A. van Bokhoven, H. Poelman, A.M.J. van der Eerden, G.B. Marin, M.F. Rayniers, R. De Gryse, Appl. Catal. A 285 (2005) 151.
[15] G. Mul, M.A. Bañares, G. Garcia Cortez, B. van der Linden, S.J. Khatib, J.A. Moullijn, Phys. Chem. Chem. Phys. 5 (2003) 4378.
[16] A. Bruckman, Chem. Commun. (2005) 1761.
[17] S.T. Tinnemans, J.G. Mesu, K. Kervinen, T. Visser, T.A. Nijhuis, A.M. Beale, D.E. Keller, A.M.J. van der Eerden, B.M. Weckhuysen, Catal. Today 113 (2006) 3.
[18] J. Jiménez-Jiménez, M. Rubio-Alonso, D. Eliche-Quesada, E. Rodríguez-Castellón, A. Jiménez-López, J. Mater. Chem. 15 (2005) 3466–3472.
[19] T. Miyake, T. Doi, Appl. Catal. A 131 (1995) 43.
[20] M. Newville, J. Synchrotron Rad. 8 (2001) 322.
[21] R. Nilsson, T. Limblad, A. Andersson, J. Catal. 148 (1994) 501.
[22] Y. Zang, M. Meisel, A. Martin, B. Lücke, K. Witke, K.-W. Brzeinka, Chem. Mater. 9 (1997) 1086.
[23] G. Mestl, J. Raman Spectrosc. 33 (2002) 333.
[24] M. Dieterle, G. Weinberg, G. Mestl, Phys. Chem. Chem. Phys. 4 (2002) 812.
[25] D.C. Koningeberger, R. Prins, X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES, Wiley, New York, 1988.
[26] G. Grymonprez, L. Fiermans, J. Vennik, Acta Cryst. A 33 (1977) 834.
[27] H. Kwon, S. Choi, L.T. Thompson, J. Catal. 184 (1999) 236.