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Additional Information

Partial oxidation of hydrogen sulphide to sulphur over vanadium oxides bronzes

by

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Abstract

Me-containing V_2O_5 materials (Me= Ag, Cu, Ca and Na) were prepared hydrothermally (from aqueous gels containing $V_2O_5/H_2O_2/MeCl_x$ mixtures, with Me/V ratios of 0.17). The samples were finally heat-treated in air or in N_2 atmosphere. The heat-treated samples have been characterized by several physico-chemical techniques and tested in the partial oxidation of hydrogen sulfide. According to XRD, electron paramagnetic resonance and ^{51}V NMR results, $Ag_{0.35}V_2O_5$ and $Na_{0.33}V_2O_5$ (or NaV_6O_{15}) bronzes with a minority presence of V_2O_5 were mainly obtained in the case of Ag- and Na-containing materials in samples both heat-treated in air or in N_2 atmosphere. In the case of Cu- and Ca-containing samples, V_2O_5 was mainly observed in samples calcined in air. However, $Cu_{0.26}V_2O_5$ and $Ca_{0.17}V_2O_5$ bronzes, with the minority presence of V_2O_5 , have been observed in Cu- and Ca-containing samples heat-treated in N_2 . On the other hand, the catalytic behavior strongly depends on the metal promoter. Thus catalysts presenting vanadium oxide bronzes, i.e. samples presenting $Ag_{0.35}V_2O_5$, NaV_6O_{15} , $Cu_{0.26}V_2O_5$ or $Ca_{0.17}V_2O_5$ shows a catalytic activity during the partial oxidation of H_2S to sulfur higher than that observed over pure V_2O_5 or over promoted catalysts presenting mainly V_2O_5 (i.e. Cu- or Ca-containing samples calcined in air). Moreover, some differences in the selectivity to sulfur were observed. A higher formation of SO_2 at high reaction temperature has been favored over $Ag_{0.35}V_2O_5$ -containing catalyst. This different behavior between samples could be explained by the presence of metallic Ag on the surface of $Ag_{0.35}V_2O_5$, which was detected by XRD. Also, higher formation of SO_2 is favored in the case of catalyst heat-treated in N_2 , in which the presence of VO_2 , as minority, could have a role in combustion of sulfur. Accordingly, this work should be considered as a first approach to relate catalytic activity of the Me-containing vanadium

oxide bronze (containing Ag, Cu, Ca and Na) for the selective oxidation of hydrogen sulfide.

Keywords: $\text{Ag}_{0.35}\text{V}_2\text{O}_5$, $\text{NaV}_6\text{O}_{15}$, $\text{Ca}_{0.17}\text{V}_2\text{O}_5$ bronzes; selective oxidation of hydrogen sulfide to sulfur; Na-, Ag-, Ca- or Cu-doped catalysts, vanadium oxide bronze.

Introduction

Vanadium based catalysts have been proposed as effective in the partial oxidation of hydrogen sulphide to sulfur [1-10], although their catalytic behaviour strongly depends on the reaction conditions (especially reaction temperature). In order to avoid the formation of SO_2 and improve the selectivity to sulphur, the reaction should be carried out in the 180-200 °C temperatures range [8-10], but some V-catalysts are partially reduced to vanadium oxide under these catalytic conditions [8,9]. Indeed, V_4O_9 crystallites have been observed to be formed during the partial oxidation of hydrogen sulphide on catalysts consisting of both bulk and supported V_2O_5 crystallites at temperatures lower than 220 °C [8]. Moreover, in-situ XAS spectroscopy and Operando Raman spectroscopy have shown that the change takes place in the first minutes and the reduced phases remain during the reaction [9].

The incorporation of alkaline metals to both unsupported and supported vanadium oxide catalysts improves the selectivity to sulphur and promotes the formation of a metal oxide bronze, i.e $\text{A}_{0.33}\text{V}_2\text{O}_5$ (A= Na, K, Cs), which is stable during the reaction [10], being Na-containing catalysts the more effective independently on the preparation procedure [10]. A recent investigation on the hydrothermal synthesis of Na-containing V_2O_5 bronze [11] has shown that pure $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ bronze phase is formed

at Na/V molar ratios in the synthesis gel in the range Na/V=0.09-0.33, whereas a mixture of β -Na_{0.33}V₂O₅ and NaV₃O₈ is obtained at Na/V ratios higher than 0.3. The more active and selective catalyst consists mainly of β -Na_{0.33}V₂O₅ and the minority presence of V₂O₅.

The electronic properties and structural phase of Me_xV₂O₅ oxide bronze, where Me is an intercalated cation, depend on the metal Me and the Me/V ratio [12, 13]. Among them, Ag-containing vanadium oxide bronze has been extensively studied paying special attention their synthesis and characterization [13-15], but little is known about their catalytic properties [16,17]. In addition, the incorporation of divalent metals such as Ca or Cu could be of interest in order to modify physico-chemical properties of vanadium oxide bronzes.

In this paper, we present the results obtained on the synthesis, characterization and catalytic activity of Me-containing vanadium oxide bronze (with Me= Ag, Cu, Ca and Na) for the selective oxidation of hydrogen sulfide. The samples have been prepared hydrothermally and then heat-treated treated at 500 °C in air or in N₂. The catalysts have been characterized by several techniques, i.e. DRX, SEM-EDX, ⁵¹V NMR, EPR and XPS, and studied for the partial oxidation of hydrogen sulphide to sulfur.

2. EXPERIMENTAL

2.1. Catalyst preparation

Vanadium oxide bronzes were prepared by hydrothermal synthesis according to a previously reported procedure [11, 18]. V₂O₅ was dispersed in water (10 ml/gV₂O₅) and then 30% H₂O₂ and MeCl salt (Me= Ag, Cu, Ca and Na), with a Me/V atomic ratio of 0.17, were added under magnetic stirring at room temperature (see also supporting

information). The suspension solution was loaded in Teflon-lined stainless-steel autoclaves and heated at 175 °C for 72h. The solid obtained was filtered off, washed with distilled water and dried at 100 °C for 16 h. Finally, the samples were heat treated at 500 °C for 2h in air (A-series) or in N₂ (N-series). The corresponding catalysts were named MeV-**X**, where Me refers to the metal ion added in the synthesis gel (Me = Na, Ag, Cu or Ca), and **X** refers the atmosphere for heat-treatment: air (A) or N₂ (N). Pure V₂O₅ was obtained by the same procedure (without other metals) and calcined in air at 500 °C. Table 1 presents the main characteristics of the catalysts.

2.2. Catalyst characterization

Powder X-ray diffraction patterns (XRD) were collected using a PANalytical X'Pert PRO diffractometer with CuK α radiation and an X'Celerator detector in Bragg-Brentano geometry operated at 40 keV and 30 mA.

X-Ray photoelectron spectroscopic (XPS) analyses were carried out with a Physical Electronics PHI 5700 spectrometer using a non-monochromatic Mg K α radiation (300W, 15 kV, 1253.6 eV). Spectra were recorded with the constant pass energy values at 29.35 eV, using a 720 μ m diameter analysis area. The pressure in the analysis chamber was kept lower than 5x10⁻⁶ Pa. The spectrometer energy scale was calibrated using Cu 2*p*_{3/2}, Ag 3*d*_{5/2} and Au 4*f*_{7/2} photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. A PHIACCESS ESCA-V6.0 F and Multipak software packages were used for data acquisition and analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves to determine more accurately the binding energy of the different element core levels. Short acquisition time of 10 min was first used to examine C 1*s*, V 2*p* regions in order to avoid, as much as possible, photo-reduction of V⁵⁺ species, while satellite subtraction of

the O 1s signal was always performed to study the V 2p region [10]. Binding energy (BE) scale was referenced to the C 1s peak (284.8 eV).

⁵¹V Solid state NMR spectra were recorded with a Bruker Avance 400 WB spectrometer using a 2.5 mm probe with the sample spinning at 25 kHz, pulses of 1 μs corresponding to a magnetization flip angle of π/12, and 1 s relaxation delay. ⁵¹V chemical shifts were referred to VOCl₃ using Mg₃V₂O₈ ($\delta^{51}\text{V} = -554$ ppm) as secondary reference.

EPR spectra were recorded at -170 °C with a Bruker EMX-12 spectrometer working at the X band, with a modulation frequency of 100 kHz and 1 G amplitude.

Scanning electron microscopy (SEM) micrographs were collected in a JEOL 6300 microscope operating at 20 kV. The quantitative EDX analysis was performed using an Oxford LINK ISIS System with the SEMQUANT program.

2.2. Catalytic tests

Catalytic experiments for H₂S partial oxidation were carried out at atmospheric pressure in a fixed-bed quartz tubular flow reactor (see also supporting information). A catalyst weight of 0.1g 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 in a range of temperatures between 160-200 °C. Analysis of reactants and products was carried out on-line by gas chromatography using two different chromatographic columns, i.e. Molecular Sieve 5Å and Porapak T [8].

3. RESULTS AND DISCUSSION

3.1 Catalytic tests for H₂S partial oxidation

Figure 1 shows the variation of the H₂S conversion with the reaction temperature (Fig 1a) and the variation of the selectivity to sulfur with the H₂S conversion (Fig. 1b) achieved during the partial oxidation of H₂S over metal-promoted samples heat-treated in Air (A-series) or in N₂ (N-series), and over pure V₂O₅ for comparison. For NaV-A and NaV-N, AgV-A and AgV-N, and for CaV-N sample, the H₂S conversion increases with the reaction temperature to about 95 % at 180 °C, and then slowly to 100 % at 190 °C. CaV-A sample behaves as V₂O₅, giving the lower H₂S conversion in the whole range, increasing to reach a maximum of 70 % at 200 °C, whereas an intermediate situation is observed for the two copper CuV-N and CuV-A catalysts. Regarding the selectivity to sulfur, it is about 100 % for the catalysts calcined in air (NaV-A, AgV-A, CuV-A, and CaV-A) up to H₂S conversion of ca. 75 %, and at higher conversion, the oxidation of sulphur changes the selectivity depending on the catalyst composition and the atmosphere of heat-treatment.

Figure 2 compares the H₂S conversion at 180 °C and the selectivity to sulphur at a H₂S conversion of 75% in order to evidence the differences among the catalysts. Except for Ca-V-containing catalysts, no important differences are observed for samples heat-treated in air or in N₂. Na- and Ag-containing catalysts (i.e NaV-A, NaV-N, AgV-A, and AgV-N) as well as CaV-N sample give the higher catalytic activity, pure V₂O₅ the lower and Cu-V-containing samples (i.e CuV-A, CuV-N) and CaV-A intermediate H₂S conversion. Then, the trend for the H₂S conversion is: NaV-A ≈ NaV-N ≈ AgV-A ≈ AgV-N ≈ CaV-N > CuV-A ≈ CuV-N ≈ CaV-A > V₂O₅. As the activity, the selectivity to sulphur depends on the catalyst composition, but this is also affected by the atmosphere used during calcination so that the selectivity for a given sample is lower when treated under nitrogen. According to Figure 2, the less selective catalysts are CaV-

N, CaV-A, CuV-N and AgV-N, with selectivity to sulfur lower than 95% at H₂S conversions higher than 75%. Then selectivity decreases following the trend: V₂O₅ > NaV-A ≈ NaV-N ≈ CuV-A ≈ AgV-A > AgV-N ≈ CuV-N ≈ CaV-A > CaV-N.

The results of Figure 2 show that, independently on the atmosphere used in the calcination, Na- and Ag-containing catalysts are the most effective for H₂S oxidation, as they display high activity and selectivity. CaV-N sample also shows high H₂S activity but the selectivity to S is the lowest, in opposition to the results for V₂O₅ which is the less active but the most selective for the reaction. Finally, an intermediate behavior in activity and selectivity is observed for CuV-N and CuV-A and CaV-N catalysts.

3.1 Characterization of catalysts

Figures 3A and 4A shows the XRD patterns of samples heat-treated in air (Figure 3A) and in N₂ (Figure 4A). The XRD patterns of **NaV-A** (Fig. 3A, pattern a) and **NaV-N** samples (Fig. 4A, pattern a) indicate the presence of monoclinic NaV₆O₁₅ (JCPDS: 00-024-1155) with minor amounts of V₂O₅. The XRD patterns of AgV-A (Fig. 3A, pattern b) and AgV-N samples (Fig. 4A, pattern b) show peaks at 2θ = 12.3, 12.7, 18.8, 23.2, 25.4, 26.4, 29.3, 30.7, 31.0, 32.9, 34.3, 36.8, 38.1° which are due to Ag_{0.35}V₂O₅ (JCPDS: 00-028-1027), though V₂O₅ (JCPDS: 00-09-0387) and metallic Ag (JCPDS: 01-087-0719) are also observed as minority phases.

V₂O₅ seems to be the main crystalline phase for samples CuV-A and CaV-A, (Fig. 3A, pattern c and d, respectively) and in sample CuV-N (Fig. 4A, pattern c), with some amounts of the corresponding vanadium oxide bronze. However, the mixed oxide phase present in these samples depends on the atmosphere used during the calcination; i.e. CuV₂O₆ (JCPDS: 01-074-2117) and CaV₂O₆ (JCPDS: 00-023-0137) in samples CuV-A and CaV-A (Fig. 3A, pattern c and d, respectively), respectively, and Cu_{0.261}V₂O₅ (JCPDS: 01-079-0796) and monoclinic Ca_{0.17}V₂O₅ (JCPDS: 00-026-1165)

in samples CuV-N and CaV-N treated under nitrogen (Fig. 4A, pattern c and d, respectively). These results suggest that Na- and Ag-containing vanadium bronzes are stable under oxidizing conditions, whereas the Ca-containing vanadium oxide bronze ($\text{Ca}_{0.17}\text{V}_2\text{O}_5$) is formed only when the heat-treatment is carried out under N_2 . Moreover, Cu-containing vanadium oxide bronze is not formed in the preparation procedure described here (independently of the heat-treatment).

Figures 3B and 4B shows the XRD patterns of heat-treated samples after the catalytic tests, i.e. heated at 200 °C under reaction conditions. The common feature in all samples is the reduction of V_2O_5 to V_4O_9 , which appear as impurities in Na- and Ag-containing samples, remaining the corresponding metal-containing vanadium oxide bronze stable (Figs. 3B and 4B, patterns a and b). V_2O_5 or V_4O_9 dominate the XRD patterns of samples CuV-A and CaV-A (Figs. 3B, patterns c and d), as well as in CuV-N sample (Figs. 4B, pattern c). It must be noted that a new phase is formed in sample CaV-N (Figs. 4B, pattern d). On the other hand, and since crystals of VO_2 [JCPDS: 01-81-2392] can be observed at $2\theta = 25, 32, 56$ and 70° [19], the presence of this phase cannot be completely excluded. Therefore, metal-oxides bronzes are relatively stable whereas V_2O_5 is transformed into V_4O_9 during the catalytic tests.

In order to get more information on the nature and proportion of the species formed, ^{51}V NMR and EPR spectroscopies has been used to identify V^{5+} -containing compounds (i.e. V_2O_5 crystallites or other compounds) and V^{4+} species, respectively.

Figure 5 compares the ^{51}V MAS NMR spectra of Me-promoted samples, heat-treated in air or in N_2 , presenting both V_2O_5 and Me-containing vanadium oxide bronzes. All spectra are similar and consist of a unique or almost unique vanadium site characterized by an intense spinning side band pattern due to the effects of chemical shift anisotropy and quadrupole interactions of ^{51}V (100 % natural abundant, $I = 7/2$) of

diamagnetic V^{5+} . Recording the spectra at various spinning rates has allowed the identification of the isotropic peak at $\delta^{51V} = -610$ ppm, which is typical of polycrystalline V_2O_5 and indeed the spectra have been successfully simulated according the parameters previously reported for this oxide [20, 21]. The spectra of Figure 5 are represented in absolute intensity mode and indicate the amount of V_2O_5 in each sample. Quantification using pure V_2O_5 as external reference (Table 1) indicates that **Ag-** and Na-containing samples contain about 7.5-10 wt% V_2O_5 , independently of the atmosphere used during the heat-treatment, in agreement with the 16% of V_2O_5 encountered by Rietveld analysis of a sample similar to NaV-A. [11]). As shown in Figure 5, much more intense ^{51}V NMR signal of V_2O_5 was obtained for sample CuV-N, corresponding to about 56 wt% of V_2O_5 . However, much weaker spectrum is recorded sample CaV-N (see multiplication factor) indicating the presence of small amount of V_2O_5 and the superimposition of an extra signal which cannot be studied because of its weak intensity. It must be noted that no ^{51}V NMR signals which could be attributed to V^{5+} in bronzes are observed in the spectra of Figure 5, which can be explained because vanadium is mainly as V^{4+} in bronzes, or by the interaction of V^{5+} with the strong electron magnetic moment of neighbouring paramagnetic V^{4+} .

Figure 6 shows the EPR spectra of catalysts presenting metal-containing vanadium oxides bronzes. In all cases, the spectra consist of a broad signal at $g = 1.96$ and do not display the hyperfine structure expected for the interaction of the unpaired electron with the nuclear spin of ^{51}V ($I = 7/2$, 99.76 % natural abundance) due to spin-spin exchange reaction between close V^{4+} centres [22]. Comparison of the EPR intensity shows a trend similar to the bronze content in the sample (Table 1): AgV-N > CaV-N > NaV-A = NaV-N > AgV-A >> CuV-N.

The XPS results of catalysts heat treated in air (A-series) or in N₂ (N-series) are summarized in Table 2. The deconvolution of the V 2p_{3/2} region of these samples show the presence of V-species with oxidation state of 5+ (peak centered at 517.2 eV) and 4+ (peaks centered at 515.7 eV), although the V⁴⁺/V⁵⁺ ratio changes depending on the metal added for Na, Ag and Cu containing catalysts : 0.28 (NaV-A), 0.22 (NaV-N), and 0.32 (AgV-A), 0.27 (AgV-N), 0.12 (CuV-A), 0.12 (CuV-N). For Ca-containing samples, the V⁴⁺/V⁵⁺ ratio is determined by the heat treatment: 0.15 (CaV-A) and 0.37 (CaV-N). These results suggest that the formation of vanadium oxide bronzes favors a surface V⁴⁺/V⁵⁺ ratio near to those proposed for vanadium oxide bronze [11], and higher than those of Cu-containing materials or CaV-N sample which contain high amounts of V₂O₅.

On the other hand, the amount of metals on the surface of catalysts also varies depending on the metal and heat-treatment procedure (Table 2). Thus, no changes in the Me/V ratio with the heat-treatment has been observed for samples containing Cu or Na: 0.04 (for CuV-A or CuV-N) and 0.05 (for NaV-A or NaV-N). This is agreement to the fact that no changes in the nature of crystalline phases with the heat-treatment procedure were observed in each case.

However, important differences between samples calcined in air and samples heat-treated in N₂ have been observed in the case of Ag- and Ca- containing samples: 0.10 (CaV-A) and 0.19 (CaV-N) or 0.21 (AgV-A) and 0.10 (AgV-N). This different behaviour can be explained from the fact that in cases, the nature and concentration of crystalline phases changes depending on the activation procedure (in air or in N₂).

The determination of the silver oxidation state by XPS is a matter of large controversy [23, 24]. The dispersion of the reported Ag 3d_{5/2} binding energy values is from 367.9 to 368.4 eV for Ag⁰; from 367.6 to 368.5 eV for Ag₂O; and from 367.3 to

368.1 eV for AgO. The recent paper from Ferraira et al. [25] gives orientation concerning the use of the Auger parameter, peak shape and width to distinguish Ag⁰, Ag⁺ and Ag³⁺. They studied metallic silver, AgNO₃, Ag₂O, AgO and a mechanical mixture (MM) of Ag₂O and AgO, being the Ag 3d_{5/2} binding energy values and the Auger parameters (APs) 3d_{5/2},M₄N₄₅N₄₅ and 3d_{5/2},M₅N₄₅N₄₅ the following: Ag⁰ (368.3/726.5/720.5); AgNO₃ (368.8/723.8/718.3), Ag₂O (368.3/723.9/717.8); AgO (367.8,368.4/724.4/718.1) and MM (367.6, 368.2, 368.7/724.2/718.1). The Auger parameters are calculated according the equation (1):

$$APs = BE \text{ Ag } 3d_{5/2} + KE_{AgMNN} \quad (1)$$

where BE Ag 3d_{5/2} is the binding energy (in eV) of the Ag 3d_{5/2} signal and KE_{AgMNN} the kinetic energy of the Auger electrons AgMNN. The observed values for the AgV-A sample were (367.6/724.3/718.6) and the spectra are shown in Figure 6. The shape of the AgMNN spectra and the observed values of Ag 3d_{5/2}, APs Ag 3d_{5/2},M₄N₄₅N₄₅ and 3d_{5/2},M₅N₄₅N₄₅ point to the presence of Ag⁺ and Ag³⁺ at the surface. However, although the Auger parameter allows distinguishing Ag⁰ from the oxidized forms, it does not allow distinguishing Ag⁺ from other oxidation states. The main difference between Ag 3d in Ag₂O and in AgO is really the shape of the photoelectron peak: that is, a single doublet for Ag₂O and a complex doublet for AgO. The shape of the Ag 3d core level signal is clearly a single doublet (see Figure 6) and the observed spectrum corresponds to Ag⁺ as oxide. Ag⁰ was not detected at the surface because this is easily oxidized to Ag⁺, but its presence in the bulk cannot be ruled out by XPS.

The XPS spectrum of Cu 2p_{3/2} shows a peak at 933.0 eV, which can be related to Cu²⁺ ions [26, 27], and a component at 931.7 eV to Cu⁺ species (Table 2), and about, 88% of Cu species on the catalyst surface are present as Cu²⁺. The XPS spectrum of Ca 2p_{3/2} presents a peak at 347.1 eV suggesting the presence of Ca²⁺ species [28]; and that

of Na 1s shows a peak at 1071.2 eV indicating the presence of Na⁺ [29]. Finally, it must be noticed that the relative intensity of the O 1s bands changes depending on the metal added (Table 2), so that the peak at 529.9-530.2 characteristic of oxygen with lower nucleophilicity accounts for 82% of total oxygen species in CaV-A, CuV-N and CuV-A, (with ca. 80-82% of the total oxygen species), higher than those of AgV-A , NaV-A (with ca. 72% of the total oxygen species), and AgV-N , NaV-N and CaV-N (with ca. 73-75% of the total oxygen species).

General remarks

It is well known that the catalytic performance in the partial oxidation of H₂S of metal-containing vanadium oxide bronzes strongly depends on the preparation procedure [12,13]. In the case of Na-promoted materials, it has been previously reported that mixtures of NaV₆O₁₅ and V₂O₅, containing 35 %, 66 % and 88 % of vanadium oxide bronze (determined by Rietveld from the XRD patterns) were achieved using Na/V ratios in the synthesis gel of 0.09, 0.17 and 0.33, respectively. The higher yield to sulfur (during partial oxidation of hydrogen sulfide) is achieved on the sample prepared from a Na/V ratio in the synthesis gel of 0.17 and calcined in air at 500°C [11].

Here we have used a catalyst preparation procedure similar to those previously reported [11], i.e. hydrothermally from mixtures containing V₂O₅, MeCl_x and H₂O₂. The obtained oxides have been activated in air or in N₂ in order to study the influence of the heat-treatment atmosphere on the nature of the crystalline phases formed and their catalytic behavior.

The characterization results indicate that the Ag- and Na- vanadium oxide bronzes are obtained by calcination in air or in N₂ of Na- and Ag- containing samples with only minor amount of V₂O₅. However, V₂O₅ is the more abundant crystalline

phase in Cu-V-containing samples and in CaV-A sample and only the $\text{Ca}_{0.17}\text{V}_2\text{O}_5$ bronze is obtained uniquely when the Ca promoted oxide is heat-treated under N_2 . Accordingly, the $\text{Ca}_{0.17}\text{V}_2\text{O}_5$ bronze is not formed when the calcination of the oxide precursor is carried out in air, and the Cu-containing vanadium oxide bronze is not formed in air and N_2 in our catalyst preparation conditions.

These results suggest that the crystallization of a pure bronze phase would require the optimization of the Me/V ratio in the synthesis gel. Regarding AgV-containing catalysts, XPS data confirm the presence of Ag^+ (in $\text{Ag}_{0.35}\text{V}_2\text{O}_5$) on the surface and XRD shows the presence of metallic Ag.

The catalytic tests clearly indicate that catalysts containing metal oxide bronzes as the main crystalline phase (i.e. Ag- and Na-containing catalysts and CaV-N) are more active than those in which V_2O_5 is mainly observed (i.e. CuV-A, CuV-N or CaV-A) or than pure V_2O_5 , in agreement with the higher activity of alkali promoted vanadium oxide bronzes catalysts compared to pure V_2O_5 reported previously.

The selectivity to the main reaction product (i.e. sulfur) of Ag-containing samples is lower than that of Na-containing samples, especially at high reaction temperature. This difference can be explained by the presence of metallic silver in AgV-A and AgV-N catalysts revealed by XRD which is known to be active in the partial oxidation of H_2S to SO_2 [30] and have a negative influence on selectivity to sulfur. Therefore, the synthesis of this type of materials should be optimized in order to favor the crystallization of the vanadium oxide bronze avoiding other undesired crystalline phases such as metallic Ag.

The samples heat-treated in N_2 seem to be relatively less selective to sulfur than those calcined in air, which can be tentatively attributed to the presence of minor amounts of VO_2 formed by partial reduction of V_2O_5 favored under N_2 . Indeed, VO_2

has been observed in **CuV-N** samples after the catalytic tests. Therefore, although metal-containing vanadium oxide bronzes are active and selective for the partial oxidation of H₂S, the presence of other crystalline phases such as VO₂ has a negative effect on the catalytic performance of the sample [31].

V₂O₅ has been described as a layered structure built up from VO₅ square pyramids sharing edges and corners, in which V₂O₅ sheets held together via weak vanadium–oxygen interactions (V–O distance of ca. 2.791 Å). However, at the reaction conditions used here, i.e. in the temperature range 160–200 °C, V₂O₅ is transformed into V₄O₉ [11], an orthorhombic *Cmcm* structure with lattice parameters $a= 10.356\text{Å}$, $b= 8.174\text{Å}$ and $c= 16.559\text{ Å}$, which contains three types of vanadium species: distorted VO₆ octahedron, VO₅ pyramid and VO₄ tetrahedron [32] with oxidation states of 4+ (both distorted VO₆ octahedron and VO₅ pyramid) and 5+ (VO₄ tetrahedron), i.e. with a V⁴⁺/V⁵⁺ ratio of 1.

The monoclinic bronzes, i.e. NaV₆O₁₅ (or β-Na_{0.33}V₂O₅), β-Ag_{0.35}V₂O₅ and Ca_{0.17}V₂O₅, can be considered as active and selective crystalline phases. β-Ag_{0.35}V₂O₅, monoclinic, assigned to a space group of *C2/m*, with $a=11.742\text{Å}$, $b=3.667\text{Å}$, $c=8.738\text{Å}$ and $\beta= 90.48^\circ$ [14d] comprises three distinct vanadium oxide chains (chains of edge-sharing [VO₆] octahedra, corner-sharing [VO₆] octahedra, and edge-sharing [VO₅] square pyramids), which enclose a quasi-1D tunnel where Na⁺ or Ag⁺ cations are included [12, 13]. Two of these vanadium atoms (named as *V1* and *V2*) have oxygen neighbors at the corners of a distorted trigonal bipyramid (with V–O distances in the range of 1.42–1.95 Å (*V1*) or 1.54–2.10 Å (*V2*) and an additional oxygen at ca. 2.43 and 2.35 Å, respectively, responsible of the distortion of octahedron [15b]). The *V1* and *V3* atoms form zigzag-type double chains along the *b* axis (forming edge-shared *V1O6* octahedra and *V3O5* square pyramids, respectively). In contrast, the *V2* atoms form a

two-leg ladder composed of corner-shared V_2O_6 octahedra along the b axis [15d]. In this case, the V^{4+}/V^{5+} ratio in monoclinic $\beta\text{-Me}_x\text{V}_2\text{O}_5$ is 1/5 [33].

In contrast to V_2O_5 crystallites, which are transformed to V_4O_9 (stable in our reaction conditions), both $\beta\text{-Na-}$, $\beta\text{-Ag-}$ and $\beta\text{-Ca-}$ containing vanadium oxide bronzes are stable under reaction conditions, with a V^{4+}/V^{5+} ratio lower than in V_4O_9 . Accordingly, $V^{4+}\text{-O-}V^{5+}$ pairs, which can be stabilized by the crystalline structure (as occurs in V_4O_9) or by the presence of metal cations such as Na^+ , Ag^+ or Ca^{2+} in a specific structure (such as in monoclinic $\beta\text{-Me}_x\text{V}_2\text{O}_5$) are active, selective and stable sites for the partial oxidation of H_2S to sulfur. Accordingly, the catalyst activation procedure influences the selectivity to H_2S by changing the relative content of $V^{4+}\text{-O-}V^{5+}$ pairs. In this case, the samples heat-treated in N_2 seem to be less selective to sulfur than those calcined in air. However, in these cases, the presence of VO_2 cannot be completely excluded, which could improve the combustion of sulfur to SO_2 .

This work should be considered as a first approach to relate catalytic activity of the Me-containing vanadium oxide bronze (containing Ag, Cu, Ca and Na) for the selective oxidation of hydrogen sulfide and additional aspects must be study.

Conclusions

Me-containing vanadium oxides (Me= Ag, Na, Cu and Ca) have been prepared by hydrothermal synthesis using a Me/V ratio in the synthesis gel of 0.17, and then heat-treated in air or in N_2 at 500 °C. The calcined samples have been studied as catalysts in the partial oxidation of H_2S to S.

$\beta\text{-Ag}_{0.35}\text{V}_2\text{O}_5$ and $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ bronzes with the minority presence of V_2O_5 are the crystalline phases formed in Ag- and Na- containing samples, respectively, independently of the atmosphere used for catalyst activation. The $\text{Ca}_{0.17}\text{V}_2\text{O}_5$ bronze

was only achieved when the Ca-containing precursor was activated in N₂ at 500 °C, whereas V₂O₅ was the main phase when the activation is carried out in air. However, in the case of Cu-containing catalysts, V₂O₅ was mainly formed independently of the atmosphere used during the activation of catalyst.

The EPR, ⁵¹V NMR and XPS results agree with the crystalline phases present in the samples, and the relative amounts of V₂O₅ and of bronze phases have been estimated by quantification of the ⁵¹V NMR signals and of the V⁴⁺ species by EPR spectroscopy.

The catalytic behavior in the partial oxidation of H₂S of these catalysts strongly depends on the nature of crystalline phases. Thus Ag- and Na-containing materials (calcined in air or in N₂), as well as the Ca-containing sample heat-treated in N₂, consist mainly of Me-containing vanadium oxide bronzes, i.e. monoclinic β-Ag_{0.35}V₂O₅ β-Na_{0.33}V₂O₅ and Ca_{0.17}V₂O₅ bronzes, respectively, and are more active and selective than the Cu- and Ca-containing materials mainly presenting V₂O₅. The XRD patterns of the samples presenting Me-containing vanadium oxide bronzes after the catalytic test, show only small changes in the nature of crystalline phases, indicating that Me-containing vanadium oxide bronzes (Me= Na, Ag or Ca) are stable under reaction conditions. Meanwhile, the XRD patterns of catalysts based on V₂O₅ after reaction consist of V₄O₉ as the main crystalline phase, and show lower activity and selectivity to sulfur than Me-containing vanadium oxide bronzes, especially if they were activated in air (i.e. AgV-A and NaV-A). Probably, the different V⁴⁺/V⁵⁺ ratio can favor a better partial oxidation of H₂S to S avoiding the formation of non-desired SO₂.

However, the catalyst preparation procedure (including both the hydrothermal synthesis and the catalyst activation method) must be optimized in order to improve activity and selectivity. In fact, some aspects have been detected as possible responsible of the lower selectivity in some samples: i) the no formation of metal containing vanadium oxide

bronze; ii) the presence of metallic Ag particles, or iii) the possible presence of VO₂ (as minority), which can have a negative influence on the selectivity to S.

Certainly, it is necessary to study more in details some specific aspects on used catalysts and on the reaction mechanism. This paper can be considered as the first step on this study.

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