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Additional Information

Catalytic behavior of $\text{NaV}_6\text{O}_{15}$ bronze for partial oxidation of hydrogen sulfide

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Abstract

Na-containing V_2O_5 materials have been prepared hydrothermally from gels with Na/V ratios of 0.02 to 0.34, and calcined at 500°C. The calcined samples have been characterized and tested as catalysts in the partial oxidation of H_2S to elemental sulfur. At low Na-contents, V_2O_5 and NaV_6O_{15} bronze are formed, with the NaV_6O_{15}/V_2O_5 ratio increasing with the Na-content. Pure NaV_6O_{15} bronze is mainly formed from gels containing a Na/V ratio of 0.18. However, NaV_6O_{15} and NaV_3O_8 bronzes are formed at from gels with Na/V ratio higher than 0.35. NaV_6O_{15} based catalyst shows high conversion for the oxidation of H_2S with a high selectivity into elemental sulfur. These catalysts are more active and stable than pure or Na-doped V_2O_5 catalysts. V_4O_9 is observed in used catalysts derived from pure and Na-doped V_2O_5 and materials containing NaV_6O_{15}/V_2O_5 mixtures. However, no changes in the NaV_6O_{15} crystalline structure are observed in pure and NaV_6O_{15}/V_2O_5 mixtures catalysts. Accordingly, NaV_6O_{15} crystalline phase is stable for several hours of catalysis at a difference with V_2O_5 . The active sites in V-containing vanadium catalysts are probably $V^{5+}-O-V^{4+}$ pairs as proposed for V_4O_9 crystalline phase. The best catalytic performances were achieved on V_2O_5 - NaV_6O_{15} mixtures which are transformed to V_4O_9 - NaV_6O_{15} mixtures during the catalytic tests. These catalytic results could be due to the intrinsic physical properties of both phases but also because of the optimal dispersion.

Keywords: NaV_6O_{15} bronze, V_2O_5 , V_4O_9 , selective oxidation of hydrogen sulfide to sulfur, Na-doped vanadium oxide catalyst

1. INTRODUCTION

Vanadium oxide based materials is an interesting group of catalysts which have been reported as selective in partial oxidation reactions of alkanes, alkenes and aromatic hydrocarbons [1-5] and, more recently, in the partial oxidation of H₂S to sulphur [6-14].

In the case of the transformation of H₂S to sulphur, the catalytic performance and catalyst stability strongly depend on V-content, especially for supported vanadium oxides. Thus, catalysts with V-loadings lower than the theoretical monolayer show important catalyst decay, especially when working at reaction temperatures lower than 240°C [12]. However, supported vanadium oxide catalysts presenting V₂O₅ crystallites present lower catalyst decay, as a consequence of the partial reduction of V₂O₅ to V₄O₉ which can be proposed as the active and selective crystalline phase when working at reaction temperatures lower than 240°C [12]. The formation of V₄O₉ during the reaction has been recently confirmed by *operando* and *in-situ* conditions using Raman and XAS spectroscopies of both unsupported and supported V₂O₅-containing catalysts [13].

On the other hand, two rate influencing steps could be the chemisorptions of oxygen and the reaction between chemisorbed H₂S and chemisorbed oxygen when the reaction is carried out over V-free catalysts [15]. Moreover, three different types of reactions, i.e. hydrogen atom abstraction, free sulfur atom generation, and oxygen–sulfur exchange, should be considered for V-containing catalysts [16].

According to these results, the characteristics of vanadium oxide-based catalysts should be tailored in order to improve the catalytic behaviour. In this way, it has been recently proposed that small incorporation of alkali metal on V₂O₅, especially sodium, can favoured the formation of an alkali metal-vanadium bronze, i.e. Na_{0.33}V₂O₅, which seems to be also active and selective during the partial oxidation of H₂S to sulphur [14].

In this way, the catalyst with a Na/V ratio of 0.04 was the more active one, in which both V_2O_5 and $Na_{0.33}V_2O_5$ are observed in fresh catalyst but V_4O_9 and $Na_{0.33}V_2O_5$ were observed after the catalytic tests [14]. So, an activation time is required in this case in order to achieve and stable and selective catalyst.

Recently, it has been proposed that $Na_{0.33}V_2O_5$ or NaV_6O_{15} can be synthesized hydrothermally [17]. In this paper, we present the synthesis, characterization and catalytic behaviour for the partial oxidation of H_2S to sulphur of sodium-containing vanadium oxide bronzes in which gels with a Na/V ratio from 0.02 to 0.35 were used. The materials prepared hydrothermally were finally calcined at $500^\circ C$ in order to achieve the desiderate catalysts. The catalytic performance of these catalysts will be also compared with those previously reported for Na- doped V_2O_5 catalysts in order to evaluate the importance of the presence of V_4O_9 and/or NaV_6O_{15} on activity and selectivity.

2. EXPERIMENTAL

2.1. Catalyst preparation

Na-V-O bronzes were prepared by hydrothermal synthesis under autogenous pressure. According to previous synthesis procedure [17], V_2O_5 was dispersed in water, and then 30% H_2O_2 and the required amount of NaCl were added under magnetic stirring at room temperature for 2 h. The suspension solution were loaded in Teflon-lined stainless-steel autoclaves and heated at $175^\circ C$ for 72h. The solid obtained was filtered off, washed with distilled water and dried at $100^\circ C$ for 16 h. Finally, the samples were calcined at $500^\circ C$ for 2h. The catalysts will be named as **HT-x**, where x is referred to the Na/V atomic ratio in the synthesis gel.

For comparison, an unpromoted and a Na-promoted V_2O_5 catalyst have been also prepared. Pure V_2O_5 has been prepared from ammonium metavanadate by calcinations at 550°C for 2h. The sample will be named as **NaV-0**. Na-promoted V_2O_5 catalyst (with a Na/V atomic ratio of 0.04) has been prepared by the impregnation method [14]. An aqueous solution of sodium nitrate was drop wise added to the ammonium metavanadate (NH_4VO_3 , Aldrich) and shaking the mixture with a spatula up to obtain an homogeneous paste. The solid was dried overnight in furnace at 100°C and calcined in air at 550°C for 2h. This catalyst will be named as **I-NaV-4**.

2.2. Catalyst characterization

X-ray diffraction patterns were collected in an Enraf Nonius PSD120 diffractometer with a monochromatic $\text{CuK}\alpha_1$ source operated at 40 keV and 30 mA. Crystalline phases were identified by matching experimental patterns to the JCPDS powder diffraction file.

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, which introduces the ZAF correction.

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FTIR absorption spectra of catalysts (diluted with KBr) were measured in the $300\text{-}4000\text{ cm}^{-1}$ region with a Nicolet 205xB spectrophotometer equipped with a Data station at a spectral resolution of 1 cm^{-1} and accumulations of 128 scans.

Temperature-programmed reduction (TPR) experiments were carried out in a Micromeritics Autochem 2910 equipped with a TCD detector, from room temperature

(RT) to 800 °C (heating rate, 10 °C min⁻¹), under 10% H₂/Ar (vol.%) and a constant flow rate of 50 ml min⁻¹.

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). Binding energy (BE) scale was referenced to the C 1s peak (284.8 eV), originated from the adventitious contamination layer. The error in BE was estimated to be *ca.* 0.1 eV. Spectra were recorded with the constant pass energy values at 29.35 eV, using a 720 μm diameter analysis area. 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, while satellite subtraction of the O 1s signal was always performed to study the V 2p region.

2.2. Catalytic tests

Catalytic tests were carried out at atmospheric pressure in a fixed-bed quartz tubular flow reactor, at 200°C temperature. 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. 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 [12].

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

The X-ray diffraction patterns of calcined catalysts are shown in Figure 1. The Na-free sample shows the characteristic peak of orthorhombic V_2O_5 (JCPDS, 41-1426) (Fig. 1, pattern a). However, a strong influence of the Na/V ratio on the nature of crystalline phases is observed. Monoclinic NaV_6O_{15} (JCPDS, 86-0120) in addition to V_2O_5 are observed for samples with a Na/V ratio lower than 0.18. Moreover, pure monoclinic NaV_6O_{15} crystals are only observed for samples with Na/V ratio of 0.18; whereas NaV_6O_{15} and a Na-rich structure, i.e. NaV_3O_8 (JCPDS, 35-0436) are observed for sample with Na/V ratio of 0.35.

On the other hand, and according to previous results [18], the strongest set at $2\theta = 12.2, 29.18, 30.6$ and 41.5° , related to Bragg peaks (002), (104), (-304) and (106) of NaV_6O_{15} , respectively, suggests that NaV_6O_{15} crystals exhibit mainly (001) growing orientation.

The morphology of catalysts can be observed in the low-magnification SEM images. Thus, if the Na-doped catalyst, i.e. **I-NaV-4** sample, shows the main presence of V_2O_5 and NaV_6O_{15} as minority (Fig.2.a), NaV_6O_{15} crystals are mainly composed of needle-like (or nanorods) particles (Fig.2. b) in agreement to XRD results.

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Infrared spectra of catalysts are shown in Figure 4. For comparison, the spectra of pure V_2O_5 (Fig.4, spectrum a) and Na-doped vanadium oxide (Fig. 4, spectrum g) catalysts are also presented. The spectrum of pure V_2O_5 sample is in agreement to that previously reported by other authors [19] with the presence of bands at 1020 cm^{-1} (assigned to V=O bond stretching vibration), 828 cm^{-1} (related to the V-O-V stretching vibration) and bands in the $450\text{-}650\text{ cm}^{-1}$ (related to and V-O-V rocking vibration)

(Fig.4, spectrum a). Small changes are observed in the case of sample **I-NaV-4**, with the appearance of new bands at 994, 578 and 534 cm^{-1} in addition to those observed for pure V_2O_5 (Fig. 4, spectrum g).

Moreover, the spectrum changes with the increase in sodium content (Fig. 4, spectra b-f): i) the band at 1020 cm^{-1} progressively shifts to lower values 994-991 cm^{-1} (and its intensity decreases when increasing the Na/V ratio) but disappears in sample **HT-35** (Fig.2 spectrum g); ii) new bands at 962 and 955 cm^{-1} are observed when increasing the Na/V ratio in catalyst; iii) the band at 828 cm^{-1} shifted towards the lower energy with increasing Na concentration and a new band is observed at 750 cm^{-1} in Na-promoted catalysts (Fig. 2, spectra c to f); iv) the band at 602 cm^{-1} in V_2O_5 shifts to 535 cm^{-1} in Na-promoted catalysts; v) the intensity of the band at 478 cm^{-1} decreases when increasing the Na/V ratio. These results are in good agreement to previous reported results for Na-promoted V_2O_5 catalysts [20].

The presence of the band at 994 cm^{-1} has been related to a decrease of the bond strength of V=O stretch vibration, while the presence of the band at 960 could be related with the presence of the $\text{Na}_{0.33}\text{V}_2\text{O}_5$ bronze [21, 22]. In addition, the incorporation of Na^+ cation favors a decreases of the V=O bond character, stabilizing the partial presence of V^{4+} species [23]. The changes in the V=O bond by Na addition is caused by the electron transfer from Na to the vanadium ion to form the $\text{V}^{4+}=\text{O}$ group. In the same way, with respect to the V-O-V stretching vibration in pure V_2O_5 , it was broad and shifts toward the low frequency upon the Na^+ addition. On the other hand, the bands at 955 and 970 cm^{-1} in the sample with higher Na/V ratio can be related to the presence of NaV_3O_8 [24].

Table 1 summarizes the H_2 -uptake achieved during the TPR- H_2 experiments. In addition, the TPR- H_2 profiles of catalysts are presented as supplementary information

(Fig. S1). For comparison, the TPR profile of pure V_2O_5 has been also considered, which presents three peaks of reduction at 613, 650 and 671 °C (the first reduction peak related to the partial reduction of V^{5+} species, while the other peaks should be related to the reduction of V^{4+} to V^{3+}) (Fig. S1) [25]. However, the TPR results achieved for Na-containing catalysts indicate a lower H_2 -uptake (Table 1) and a lower reducibility of V-atoms for these samples (Fig. S1), shifting the reduction peaks to higher temperatures when increasing the Na-content in catalysts. In addition, the H_2 -uptake decreases when increasing the Na-content (Table 1), confirming a higher stabilization of V^{4+} species in Na-containing catalysts [22].

The DR UV-vis spectra of samples calcined at 500 °C are shown in Fig. 5. V_2O_5 shows four broad bands, whose deconvolution can be assigned to the absorption bands at 240, 340, 444 and 510 nm, in agreement to previous results [26, 27]. The band at 510 nm is assigned to the absorption of square pyramidal octahedral V^{5+} species [26]. This band remains in both Na-doped sample and sample with low Na/V ratios showed similar spectra to that of V_2O_5 which is in good agreement to the XRD results.

In the case of samples with high Na/V ratio, a new adsorption bands below 250 nm (which can be assigned to the CT of V^{4+} species [28]) and broad bands in the region of 450–800 nm (related to d–d transitions of isolated V^{4+} species [28]) can be observed. Accordingly, the presence of Na^+ cations in Na-containing vanadium bronze stabilizes the presence of V^{4+} species, as concluded from the fact that the presence of (d-d) transitions in the 600-800 nm range (related to the presence of V^{4+} species) increases when increasing the Na/V ratio.

The XPS spectrum of Na-free sample reveals that this sample only consists of vanadium and oxygen (Table 2), while the Na/V ratio increases when increasing the Na-content. The deconvolution of the V $2p_{3/2}$ region confirms that the incorporation of

sodium favors a higher reduction of V-atoms [24, 29]. V^{5+} is mainly present in Na-free sample as deduced from the fact that the peak is centered at 517.2 eV. However, a weak intensity contribution centered at 515.5 eV indicates the presence of a small amount of V^{4+} in Na-containing catalyst, but the V^{4+}/V^{5+} surface ratio increases when increasing the Na-content confirming that the materials consists of mixed valance state vanadium atoms (Table 2). This is in agreement with previous results with Na-containing vanadium oxide bronzes [24].

On the other hand, quantification of the XPS peak areas gives that the surface ratio of V/O in the Na-free sample is about 0.25, which is close to the chemical stoichiometry of V_2O_5 . However, in the case of Na-containing catalysts the V/O ratio increases with Na-content. In addition, the intensity of the band at ca. 530.2 eV increases when increasing the Na content. In this way, the intensity of this band was higher in the case of the sample prepared by impregnation of Na, i.e. **I-NaV-4** sample. On the other hand, the band related to Na 1s appeared in all cases at ca. 1071.2 eV, typical of Na^+ , in agreement to previous results [29,30].

3.2. Catalytic tests in partial oxidation of H_2S

The catalytic results during the partial oxidation of H_2S at 200°C over catalysts prepared with Na/V ratios in gel from 0 to 0.18 are shown in Figure 6. High activity and selectivity are observed for catalysts with Na/V ratios lower than 0.18. However, the catalytic activity over the sample HT-35 was very low. Thus, under the same reactions conditions to those presented in Fig. 6, samples HT-35 presented a H_2S conversion of 10% at a time on stream of 200 min.

Initial catalyst decay is observed at short time on stream for catalysts with low Na/V ratios (Fig.6a). However, very small catalyst decay has been observed for sample

HT-14. On the other hand, the catalysts resulted very selective to elemental sulphur (higher than 97%), with very low selectivity to SO_x.

Figure 6b shows the selectivity to SO_x as a function of time on stream. Apparently the selectivity to SO_x increases with the Na/V ratio of catalyst. However, if the variation of the selectivity to SO_x with the H₂S conversion is considered (supplementary information, Fig. S-2), no important differences are observed among the studied catalysts, although the selectivity to SO_x increases for H₂S conversion higher than 95%.

4. DISCUSSION

The catalytic results presented here have demonstrated that Na-containing vanadium oxide catalysts, presenting a bronze structure of the NaV₆O₁₅ type, are interesting catalysts in the partial oxidation of H₂S to elemental sulfur, presenting a catalytic activity and selectivity to sulfur higher to that achieved over pure V₂O₅ and similar to that achieved over a Na-doped vanadium oxide catalysts. Accordingly, a NaV₆O₁₅ is by its-self active and selective.

One important difference of pure NaV₆O₁₅ with respect to pure V₂O₅ is the higher stability of this crystalline phase. In fact, as presented here and in agreement to previous results, V₂O₅ is transformed into V₄O₉ under the reaction conditions used here [12, 13]. This is also observed in catalysts in which both NaV₆O₁₅ and V₂O₅ are observed in fresh catalysts. Thus, V₄O₉ and NaV₆O₁₅ have been observed after reaction in samples prepared with intermediate Na-content, and in which both V₂O₅ and NaV₆O₁₅ crystalline phases are observed in fresh catalysts. Accordingly, NaV₆O₁₅ is also stable under the reaction conditions used here.

In the case of samples prepared from gels with Na/V ratios between 0.15 and 0.35, only bronzes are detected in fresh catalysts, i.e. pure $\text{NaV}_6\text{O}_{15}$ or mixed $\text{NaV}_6\text{O}_{15}/\text{NaV}_3\text{O}_8$ depending on the Na-content in catalysts. However, no changes in the nature of both crystalline phases have been observed in used catalysts. On the other hand, catalysts presenting mainly $\text{NaV}_6\text{O}_{15}$ bronze structure are active and selective whereas, the catalyst presenting mainly NaV_3O_8 show very low catalytic activity. Probably, the higher Na-content in NaV_3O_8 blocks the active sites. In this way, it has been reported in the case of Na-doped V_2O_5 materials, that the incorporation of high Na-loadings favors a strong decrease in the catalytic activity [14].

On the other hand, the infrared and DR-UV-vis spectra also confirm changes in the characteristics of V species as a consequence of the partial reduction of V^{5+} to V^{4+} with the incorporation of Na^+ cations. Although it will be discussed later, the presence of both V^{5+} and V^{4+} could have a positive effect in the catalytic behavior of these catalysts as suggested previously for catalysts presenting V_4O_9 phase [12-14].

Moreover, and in order to explain the catalytic behavior of Na-containing catalysts, it is interesting to consider the structure of these crystalline phases. It is well known that the incorporation of alkali metal (Li, Na, K) to vanadium oxides, favors the formation of bronzes of general formula MxV_2O_5 [31], which depend on the alkali/V ratio [31-34]: i) α -bronze, isostructural with the orthorhombic V_2O_5 , at very low alkali metal content, i.e. values of x of 0.13 (Li), 0.02 (Na) or 0.006 (K); and ii) β -bronze at higher concentration of Li ($0.22 < x < 0.62$) or Na ($0.22 < x < 0.40$).

β - $\text{NaV}_6\text{O}_{15}$, a vanadium bronze with a monoclinic $C2/m$ crystal structure, is observed in our catalysts. It contains tunnels formed by the VO_6 and VO_5 complexes along the *b* axis, whereas the Na ions are located inside the tunnels. However, these vanadium atoms occupy three crystallographically different positions [32-34]: i) VO_6

octahedron forming zig-zag chains of edge-shared VO₆ octahedra along the *b* axis; ii) VO₆ octahedron forming double chains of angle-shared octahedra, and iii) VO₅ pyramids forming zig-zag chains of edge-shared VO₅ pyramids.

On the other hand, β-NaV₆O₁₅ contains one V⁴⁺ ion and five V⁵⁺ ions in the unit cell. In fact, A_xV₆O₁₅ are in a mixed-valence state of V⁴⁺ and V⁵⁺, so that in the case of NaV₆O₁₅ the formal valence is V^{4.83+} [35], whereas α-NaV₂O₅ and NaV₃O₈ has an average state of vanadium of 4.5 [36] and 4.93, respectively [24].

Thus, sodium cation in vanadium oxide bronze such as β-NaV₆O₁₅ occupies interstitial positions in tunnels and channels between V-O-V layers in the pentoxide lattice, whereas the oxidation state of vanadium in vanadium oxide bronze changes with respect to those in V₂O₅ (the presence of V⁴⁺ species is enhanced by the presence of sodium).

It has been recently reported that V₂O₅ crystallites are selectively transformed into V₄O₉ when during the partial oxidation of H₂S [12, 13]. So, when we are comparing the catalytic behavior on sample **NaV-0** is compared, it is possible to indicate that the catalyst is transformed into V₄O₉ and, with part of V-atoms having an oxidation state of +4.

It is know that V⁴⁺ plays an important role in vanadium-based catalysts, and vanadium is generally reduced to V⁴⁺ during partial oxidation reactions, although it is usually re-oxidized during the reaction, following a concerted redox mechanism. In the case of partial oxidation of H₂S over V₂O₅ this does not occur exactly. In fact, V₂O₅ is partially reduced during the first minutes of reaction forming V₄O₉, which is stable during the reaction at reaction temperatures lower than 240°C. Since V₄O₉ but also NaV₆O₁₅ crystalline phase are more selective than V₂O₅, it can be suggested that the presence of V⁵⁺-O-V⁴⁺ pairs, as occurs in V₄O₉, or V⁵⁺-O-V⁴⁺(Na), with vanadium

atoms partially blocked with Na^+ cations in Na-containing vanadium oxide bronzes such as $\text{NaV}_6\text{O}_{15}$, seems to be not only active and selective but also stable at reaction temperatures lower than 240°C . The absence of $\text{V}^{5+}\text{-O-V}^{5+}$ pairs, which are mainly present in V_2O_5 , could decrease the consecutive oxidation of sulphur to SO_x decreasing the selectivity to partial oxidation reaction.

In this way, it has been proposed that the activation mechanism of S-H bonds during partial oxidation of H_2S could be similar to that observed to the C-H activation in partial oxidation of hydrocarbons, in which asymmetric bridging V-O-V bonds could be involved for selective catalysts [37]. It is clear that reducing reducibility of V-sites could favor a decrease of the rate of consecutive reaction. However, this will depend on the reaction conditions, especially reaction temperature and feed composition [6-13, 38].

Conclusions

Na-containing vanadium oxide bronzes have been prepared hydrothermally from gels with Na/V ratios of 0.02 to 0.35. The samples calcined at 500°C have been characterized (by using several physic-chemicals techniques) and tested in the partial oxidation of hydrogen sulphide to elemental sulphur. XRD, FITR and HREM/SAED results suggest the formation of V_2O_5 and $\text{NaV}_6\text{O}_{15}$ bronze in samples prepared with Na/V ratios in gel lower than 0.18. The presence of V_2O_5 decreases and the presence of $\text{NaV}_6\text{O}_{15}$ increases when increasing the Na/V ratio. However, $\text{NaV}_6\text{O}_{15}$ and NaV_3O_8 are observed at Na/V ratio in gel higher than 0.18. Reducibility of vanadium atoms also decrease when increasing the Na/V in solid.

The catalytic behaviour was improved for samples prepared from gels with Na/V ratios of 0.10-0.20 in which $\text{NaV}_6\text{O}_{15}$, is mainly observed.

On the other hand, nor catalyst decay nor changes in the crystalline phases are observed after 300 min of time on stream in the sample presenting pure $\text{NaV}_6\text{O}_{15}$, while it is known that at the same reaction conditions V_2O_5 is selectively transformed into V_4O_9 . Accordingly, the presence of $\text{V}^{5+}\text{-O-V}^{4+}$ pairs seems to be not only active and selective but also stable at reaction temperatures lower than 240°C , but they are relatively unstable at reaction temperatures higher than 240°C .

Thus, the higher catalytic performance of samples containing V_2O_5 and $\text{NaV}_6\text{O}_{15}$ bronze could be related to changes in the amount of the number of V^{5+} species. Thus, the $\text{V}^{4+}/\text{V}^{5+}$ ratio increases when increasing the Na/V ratio in solid. This is in agreement with previous results achieved over V_4O_9 -containing catalysts, since V_4O_9 is characterized by the presence of $\text{V}^{5+}\text{-O-V}^{4+}$ pairs.

In the case, of Na-containing bronzes, $\text{V}^{5+}\text{-O-V}^{4+}$ pairs are also presented, although they are stabilized by the presence of Na^+ cations. This can influence the reducibility of vanadium species as suggested from the TPR- H_2 results.

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Caption to figures

Fig.1. XRD patterns of catalysts: a) NaV-0; b) HT-02; c) HT-10; d) HT-14; e) HT-18; f) HT-35; g) **I-NaV-4**. Symbols: V_2O_5 (\circ); NaV_6O_{15} (\blacksquare); NaV_3O_6 (\blacktriangledown).

Fig.2. SEM micrographs of catalysts: a) HT-02; b) HT-10; c) HT-18; d) HT-35

Fig.3. HRTEM image of a crystal of V_4O_9 (a) and NaV_6O_{15} (or $Na_{0.33}V_2O_5$) (b) projected along the [001] zone axis. The corresponding structures have been also included.

Fig.4. Infrared spectra of catalysts: a) NaV-0; b) HT-02; c) HT-10; d) HT-14; e) HT-18; f) HT-35; g) **I-NaV-4**.

Fig.5. UV-vis patterns of catalysts a) NaV-0; b) HT-02; c) HT-10; d) HT-14; e) HT-18; f) HT-35; g) **I-NaV-4**.

Fig.6. Variation of the H_2S conversion (a) and selectivity to SO_x (b) with time on stream over catalysts prepared from gels with a Na/V ratios lower than 0.18. Reaction conditions: 0.1 g of catalyst; total flow of 130 mL min^{-1} ; H_2S /air/He molar ratio of 1.2/5.0/93.8.

Supporting information

S-1 TPR- H_2 patterns of catalysts a) NaV-0; b) HT-02; c) HT-10; d) HT-14; e) HT-18; f) HT-35; g) **I-V-4**.

S.-2. Variation of the selectivity to SO_x with the H_2S conversion. Reaction conditions as in Fig. 6.

Table 1. Characteristics of sodium-promoted vanadium oxide catalysts.

Sample	Na/V ratio		TPR results ⁽³⁾		Main Crystalline phases in calcined samples ⁽⁴⁾
	in gel	in catalyst ⁽²⁾	TMC (°C)	(mmol _{H2} /g _{cat})	
NaV-0	0	0	619	5.26	100% V ₂ O ₅
HT -02	0.02	0.02	702	12.1	>90% V ₂ O ₅
HT -10	0.09	0.10	692	12.0	83% V ₂ O ₅ (17% NaV ₆ O ₁₅)
HT -14	0.17	0.14	728	10.9	66%NaV ₆ O ₁₅ (34% V ₂ O ₅)
HT -18	0.33	0.18	723	9.33	88%NaV ₆ O ₁₅ (12% V ₂ O ₅)
HT -35	0.64	0.35	653	3.44	93%NaV ₆ O ₁₅ (7% NaV ₃ O ₆)
I-V-4 ⁽¹⁾	-	0.10	634	10.7 ⁵ 3.94	68% V ₂ O ₅ (32%NaV ₆ O ₁₅)

1) Catalyst prepared by impregnation of NH₄VO₃; 2) Determined by EDS for calcined catalysts; 3) Temperature of maximum hydrogen consumption (TCM) and H₂-uptake (in mmol_{H2} g_{cat}⁻¹); 4) Determined by Rietveld; 5) considering the two reduction peaks, whereas the first reduction peaks was 3.94 mmol_{H2}/g_{cat}.

Table 2. XPS results of sodium-promoted vanadium oxide catalysts.

Sample	Na/V ratio		Core level binding energy (eV) ¹		
	Bulk	Surface	O 1s	Na 2p	V2 p _{3/2}
NaV-0	0	0	530.2 (82)	-	515.8 (7)
			531.9 (12)		517.8 (93)
			533.5 (6)		
HT -10	0.10	0.04	530.2 (71)	1071.2	516.0 (17)
			531.8 (17)		517.5 (83)
			533.3 (12)		
HT -18	0.18	0.09	530.4 (75)	1071.4	516.3 (20)
			531.9 (16)		517.7 (80)
			533.5 (9)		
HT -35	0.35	0.17	530.1 (77)	1071.2	516.1 (13)
			531.7 (17)		517.4 (87)
			533.2 (6)		
I-NaV-4	0.10	0.02	530.6 (87)	1071.4	516.5 (14)
			531.9 (13)		517.8 (86)

1) In parenthesis, intensity in %.

