



Vanadium oxide supported on porous clay heterostructure for the partial oxidation of hydrogen sulphide to sulfur



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ABSTRACT

Vanadium oxide supported on porous clay heterostructures (PCH) catalysts have been synthesized, characterized and evaluated in the selective oxidation of H₂S to elemental sulfur. The catalysts were characterized by XRD, adsorption–desorption of N₂ at –196 °C, diffuse reflectance UV–vis, H₂-TPR, Raman spectroscopy and XPS. The catalysts with higher vanadium content are more active and selective, exhibiting a H₂S conversion close to 70% after 360 h on stream with a high selectivity toward elemental sulfur and a low formation of undesired SO₂. The catalysts with V₂O₅ crystallites have shown a higher activity and resistance to the deactivation. The analysis of the spent catalyst has revealed the formation of V₄O₉ crystals during the catalytic test, which has been reported as the active phase in the selective oxidation of the H₂S.

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1. Introduction

Currently environmental regulations oblige to treat hydrogen sulphide (H₂S) generated in petroleum and gas plants prior to emission to the atmosphere. The most popular utilized technology is the Claus Process [1]. However, all H₂S could not be converted because of thermodynamic limitations.

Various commercial processes have been used to treat tail gases from Claus Process [2–4]. Among these processes, the most attractive is the selective oxidation of H₂S to elemental sulfur by using oxygen from air [2]. However, the S oxidation to SO₂ must be avoided, for this reason selective catalysts are required.

Vanadium oxide based materials constitute an interesting group of catalysts which have been reported recently as potential catalysts for the partial oxidation of H₂S to sulfur [5–13]. The supported vanadium oxide has been the most studied catalysts. It is known that the characteristics of metal oxide support and the nature of vanadium species strongly influence the catalytic performance of supported vanadium catalysts. Regarding vanadium species, catalysts with low V-loadings show important catalyst decay,

especially when working at reaction temperatures below 240 °C [11]. However, supported vanadium oxide catalysts presenting V₂O₅ crystallites are more stable, 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 [11]. In both unsupported and supported V₂O₅-containing catalysts, the formation of V₄O₉ during the oxidation reaction has been confirmed by operando and in-situ conditions using Raman and XAS spectroscopies, respectively [12].

V₄O₉ is a vanadium oxide of the series V_nO_{2n+1}, in which vanadium ions present oxidation state of 4+ and 5+. V₄O₉ can be prepared by reduction of V₂O₅ using reducing agents such as SO₂ [14], sulfur [15], or organic compounds [16]. However, according to previous results, V₄O₉ could be more easily prepared, in-situ, by the treatment of V₂O₅ in H₂S/air mixtures similar to those used during the partial oxidation of H₂S at ca. 200 °C [13]. Since the formation of V₄O₉ from V₂O₅ is carried out in a very short time, this method could be considered also for preparing selectively supported vanadium catalysts using supported–V₂O₅ as precursors [12].

In the last years, new materials have been developed for various catalytic applications. Among them, clays are widely used as catalysts or catalytic supports due to their abundance, low cost, and unique properties, but their use is limited due to their low porosity and poor thermal stability. But these problems currently have been solved through certain modifications, among which the

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pillaring process provides porosity and high thermal stability. Pillared interlayered clays (PILCs) form a well-known family of microporous and mesoporous materials [17]. Among these materials, porous clay heterostructures (PCH), which were synthesized for the first time by Galarneau et al. [18], are a good catalytic support, because these materials present surface acidity. Acid centres are located on surface of the clay layers. Moreover, the acidity of the PCH materials can be increased by incorporation of the suitable cations into the silica walls [19–21]. So the properties of these materials can be changed depending on the features required for the reactions. In the last years, PILCs have been used as a supports for the selective oxidation of H₂S to S [10,22].

In this paper, we present the synthesis, characterization and catalytic activity for the selective oxidation of H₂S to S of supported vanadium oxide catalysts, using a porous clay heterostructures (PCH) as support. Since it is known that this type of catalyst can be modified during the reaction, the used catalysts have been also studied in order to evaluate changes in the structure and oxidation state of active phases after reaction.

2. Experimental

2.1. Catalyst preparation

The raw bentonite was obtained from “Sierra de Níjar”, supplied by Minas de Gador S.A. This material was previously characterized in several researches revealing that the bentonite is formed in a large proportion for montmorillonite (>90%) [23,24].

In order to purify the montmorillonite fraction, the bentonite was collected by sedimentation. Then, the montmorillonite fraction was treated with a saturated solution of NaCl during 1 day leading to the Na-montmorillonite.

PCHs were prepared by means of the following synthetic procedure. 7.5 g of the starting montmorillonite was treated with a solution of 27 g of cetyltrimethylammonium bromide (CTMBr) (Aldrich) in 300 ml of pure *n*-propanol (anhydrous, 99.9% VWR). After 3 days under stirring, the solution was filtered and washed with distilled water till neutral pH was reached. Then the solid was stirred in 750 ml of water during 24 h. After this time, a solution of 2.7 g of hexadecylamine (Aldrich), used as co-surfactant, in 75 ml of *n*-propanol solution was added and stirred for 24 h. The Si-pillars located between the layers of montmorillonite were generated by the incorporation of a solution of 33.3 ml tetraethylorthosilicate (TEOS), as silicon source, dissolved in *n*-propanol (50 vol.%). The obtained gel was stirred during 72 h and then was filtered and washed with water and ethanol and dried at 60 °C in air for 12 h. Finally the surfactant was removed by the calcination at 550 °C with a rate of 1 °C min⁻¹ during 6 h [21].

Vanadium oxides species were incorporated to the PCH using ammonium metavanadate (Aldrich) as precursor by the wet-impregnation method and dried at 60 °C overnight. Finally, all the samples were calcined at 500 °C for 4 h under air flow. The samples were labeled as PCH-*x*V, where *x* refers to the vanadium loading wt% on the support in a range of 2–16 wt%.

2.2. Catalyst characterization

Powder patterns for the samples were collected on a X'Pert Pro MPD automated diffractometer (PANalytical B.V.) equipped with a Ge (111) primary monochromator (strictly monochromatic Cu K α ₁ radiation) and an X'Celerator detector. The diffractograms were determined in the range of 2θ of 1–70° with step size of 0.017°.

The textural parameters (S_{BET} , V_p and d_p) were evaluated from the nitrogen adsorption–desorption isotherms at –196 °C as determined by an automatic ASAP 2020 system from Micromeritics.

Prior to the measurements, samples were outgassed at 200 °C and 10⁻⁴ mbar overnight. Surface areas were determined by using the Brunauer–Emmet–Teller (BET) equation and a nitrogen molecule cross section of 16.2 Å². The total pore volume was calculated from the adsorption isotherm at $P/P_0 = 0.996$.

Raman spectra were recorded in ambient conditions 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.

Temperature-programed reduction with H₂ (H₂-TPR) experiments were carried out using 0.08 g of freshly calcined catalyst placed in U-shaped quartz reactor inside a tubular oven. In order to remove any contaminant, the powders were pre-treated with helium (50 cm³ min⁻¹) to 550 °C for 1 h. After cooling to ambient temperature, TPR experiments were carried out in 10 vol.% H₂/Ar (35 cm³ min⁻¹) increasing the temperature from room temperature to 800 °C with a heating ramp of 10 °C min⁻¹, using a temperature programmable controller. The water produced in the reduction was eliminated with an isopropanol–liquid N₂ trap. Hydrogen consumption was registered using a TCD, mounted in a Shimadzu 14-B gas chromatograph.

X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg K α radiation (300 W, 15 kV, and 1256.6 eV) with a multi-channel detector. Spectra of pelletized samples were recorded in the constant pass energy mode at 29.35 eV, using a 720 μ m diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A 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 Gaussian–Lorentzian curves in order to determine the binding energies of the different element core levels more accurately.

2.3. Catalytic tests

Catalytic tests were carried out at atmospheric pressure in a fixed-bed quartz tubular flow reactor, at 180 °C. A catalyst weight of 0.05 g was mixed with silicon carbide as inert to obtain an adequate bed height to quench the possible homogeneous reactions. A feed mixture composed of H₂S/air/He with molar composition of 1.2/5.0/93.8 and a total flow of 130 ml min⁻¹ was passed through the reactor. Analysis of reactants and products was carried out on-line by gas chromatography using two different chromatographic columns, i.e. Molecular Sieve 5A and Porapak T [12].

3. Results and discussion

3.1. Catalyst characterization

3.1.1. X-ray diffraction

The diffractogram of the raw bentonite is shown in Supplementary information. As was indicated in previous works [21,23,24], the main mineralogical component is montmorillonite. Moreover it is noticeable the presence of minor amounts of plagioclase, cristobalite, calcite and almost undetectable amount of quartz [23,24].

After the purification and the formation of the PCH structure, the diffractogram at low angle reveals the formation of a unique reflection located about $2\theta = 2^\circ$ (not shown), corresponding to the d_{001} diffraction. Moreover, the diffractogram reveals a loss of the basal reflections of the montmorillonite suggesting that the main structural change with the insertion of Si-pillar in the inter-layer space of montmorillonite occurs along the *c*-axis, while the

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