

# Study of supported vanadium oxide catalysts in the partial oxidation of H<sub>2</sub>S by XAS and Raman in operando conditions

M.D. Soriano<sup>1</sup>, J.P. Holgado<sup>2</sup>, J. Jiménez-Jiménez<sup>3</sup>, P. Concepción<sup>1</sup>, A. Jiménez-López<sup>3</sup>, A. Caballero<sup>2</sup>, E. Rodríguez-Castellón<sup>3</sup>, J.M. López Nieto<sup>1\*</sup>

<sup>1</sup>Instituto de Tecnología Química, UPV-CSIC, Valencia, 46022, Spain

<sup>2</sup>Instituto de Ciencia de los Materiales, CSIC-Universidad de Sevilla, Sevilla, 41092, Spain

<sup>3</sup>Dep. Química Inorgánica, Universidad de Málaga, Málaga, 29071, Spain

\*jmlopez@itq.upv.es

## Introduction

V-containing catalysts seem to be one of the most active/elective in the H<sub>2</sub>S partial oxidation of elemental sulfur [1-2]. X-ray absorption spectroscopy (XAS) have been used to determine the oxidation state and coordination of vanadium in catalysts [3], while Raman studies have been carried out to determine the structure of vanadium in catalysts [4]. In the present paper we present an XAS and Raman study, both working in operando conditions, on the selective oxidation of H<sub>2</sub>S to sulphur using vanadium oxide supported on a mesoporous zirconium phosphate heterostructure and  $\chi$ -Al<sub>2</sub>O<sub>3</sub> (with 4-12 wt% of V-atoms, named nVMZP and nVAI, with n= 4-12) as catalysts. A correlation between catalytic behaviour, catalyst stability and changes in the crystalline phases during reactions will be suggested.

## Experimental

Supported vanadium oxides catalysts were prepared by the wet-impregnation method [2]. The transmission 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. 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 Ar<sup>+</sup> laser (Spectra Physics Model 171) with a laser power of 2.5 mW. All catalytic experiments (including operando measurements) were carried out in the 180-240°C temperature range, using a mixture with a H<sub>2</sub>S/O<sub>2</sub>/N<sub>2</sub>/He molar ratio of 1/1/4/94.

## Results/Discussion

Figure 1 shows the Raman (Fig.1, A and B) and XAS (Fig.1, C and D) spectra achieved over 12VAI and 12VMZP in a He stream at 200°C and during the selective oxidation of H<sub>2</sub>S. It can be seen that V<sub>2</sub>O<sub>5</sub> is initially present. However, after some minutes in contact with the reaction mixture, the bands related to V<sub>2</sub>O<sub>5</sub> disappear appearing a new band at ca. 900 cm<sup>-1</sup>, which can be related to the formation of V<sub>4</sub>O<sub>9</sub> [5]. The XANES spectra also confirm the presence of V<sub>2</sub>O<sub>5</sub> in fresh samples (pre-edge position at 5470.6 eV, being the main-edge peak at 5483.7 eV).

However, when operating in reaction conditions at 200°C and difference time on stream, the XANES spectra change (Fig. 1C, spectra c and d). These are characterized by a pre-edge peak at 5469.9 eV and a main-edge peak at 5482.1 eV. Figure 1-D shows the Fourier Transforms obtained from the EXAFS spectra in a He steam at 200°C (Fig.1, D, spectra a, b) and after 2 hours of reaction (Fig.1-D, spectra c, d). A direct comparison with the TF of V<sub>2</sub>O<sub>5</sub> y V<sub>4</sub>O<sub>9</sub> (spectra not shown) allows us to establish that in all case, the FTs after reaction are similar to the V<sub>4</sub>O<sub>9</sub> with two peaks centred at about 1.25 and 1.95 Å, although some differences are observed, probably due to changes in the crystal size and interaction of V<sub>2</sub>O<sub>5</sub> crystals in each catalyst. These results clearly show the changes occurring in the catalysts (from V<sub>2</sub>O<sub>5</sub> to V<sub>4</sub>O<sub>9</sub>) during the reaction at 200°C. However, the reaction conditions and V-loading have a strong influence on the nature of crystalline phases. In this way, catalysts with high V-loading are active, selective and stable while catalyst with low-loading show low stability. The importance of the presence of V<sub>2</sub>O<sub>5</sub> crystallites and reaction mechanism in H<sub>2</sub>S partial oxidation are discussed.

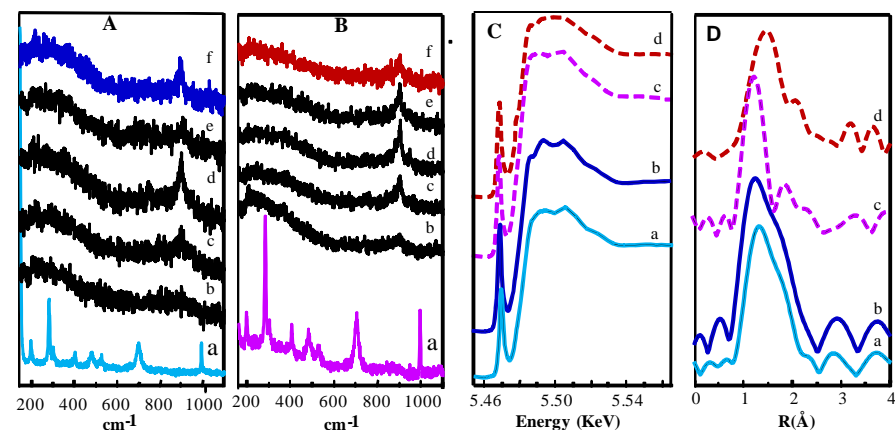


Figure 1. Raman spectra in operando conditions over 12VAI (A) and 12VMZP (B) catalysts at difference time on stream: 0 min (a), 15 min (b), 30 min (c), 60 min (d), 90 min (e) and 120 min (f). XANES (C) and EXAFS (D) spectra: 12VAI (a, c) and 12VMZP (b, d), at difference TOS: 0 min (solid line) and 120 min (dashed line).

## References

1. M.I. Kim, D.W. Park, S.W. Park, X. Yang, J.S. Choi, D.J. Suh, Catal. Today, **11**, 212 (2006)
2. M.D.Soriano, J. Jiménez-Jiménez, P. Concepción, A. Jiménez-López, E. Rodríguez-Castellón, J.M. López Nieto, Appl. Catal., B, **92**, 271 (2009)
3. 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**, 151 (2005)
4. G.G. Cortez G.G, M.A. Bañares, J. Catal., **209**,197 (2002)
5. R. Nilsson, T. Limblad, A. Andersson, J. Catal., **148**, 501 (1994)