

Document downloaded from:

<http://hdl.handle.net/10251/64198>

This paper must be cited as:

Soriano Rodríguez, MD.; Cecilia, JA.; Natoli, A.; Jimenez-Jimenez, J.; López Nieto, JM.; Rodríguez Castellon, E. (2015). Vanadium oxide supported on porous clay heterostructure for the partial oxidation of hydrogen sulphide to sulfur. *Catalysis Today*. 254:36-42. doi:10.1016/j.cattod.2014.12.022.



The final publication is available at

<http://dx.doi.org/10.1016/j.cattod.2014.12.022>

Copyright Elsevier

Additional Information

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

M.D. Soriano¹, J.A. Cecilia¹, A. Natoli¹, J. Jiménez-Jiménez¹, J.M. López Nieto², E. Rodríguez-Castellón^{1*}

- 1) Departamento Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga (Spain)
- 2) Instituto de Tecnología Química, UPV-CSIC, Campus Universidad Politécnica de Valencia, Avenida de los Naranjos s/n, 46022 Valencia (Spain)

*) To whom correspondence should be addressed. E-mail: castellon@uma.es

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 hours on stream with a high selectivity towards elemental sulphur and a low formation of undesired SO₂. The catalysts with bigger V₂O₅ particles 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.

Keywords: V₂O₅, V₄O₉, Porous clay heterostructure, H₂S, selective oxidation

INTRODUCTION

Currently environmental regulations oblige to treat hydrogen sulphide (H_2S) generated in petroleum and gas plants prior to emission to the atmosphere. The most popular utilized technology is the Claus Process [1]. However, all H_2S 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 H_2S to elemental sulfur by using oxygen from air [2]. However, the S oxidation to SO_2 must be avoided, for this reasons 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 H_2S 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 $240\text{ }^\circ\text{C}$ [11]. However, supported vanadium oxide catalysts presenting V_2O_5 crystallites are more stable, as a consequence of the partial reduction of V_2O_5 to V_4O_9 which can be proposed as the active and selective crystalline phase when working at reaction temperatures lower than $240\text{ }^\circ\text{C}$ [11]. In both unsupported and supported V_2O_5 -containing catalysts, the formation of V_4O_9 during the oxidation reaction has been confirmed by *operando* and *in-situ* conditions using Raman and XAS spectroscopies, respectively [12].

In the last years, new materials have been developed for various catalytic applications. Among them, clays are widely used as a 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 pillaring process provides porosity and high thermal stability. Pillared interlayered clays (PILCs) form a well-known family of microporous and mesoporous materials [14]. Among these materials, porous clay heterostructures (PCH), this were synthesized for the first time by Galarneau et al. [15], are a good catalytic support, because these materials present a 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 [16-18]. 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 [10,19].

In this paper, we present the synthesis, characterization and catalytic activity for the selective oxidation of H₂S to S over vanadium oxide supports on a porous clay heterostructures (PCH). The used catalysts will be studied to evaluate changes in the structure and vanadium oxidation state 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%) [20,21].

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 hours 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 °Cmin⁻¹ during 6 hours [18].

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 2-16wt. %.

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 $\text{CuK}\alpha_1$ radiation) and an X'Celerator detector. The diffractograms were measured in the range of 2θ of 10-70° 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 $-196\text{ }^\circ\text{C}$ as determined by an automatic ASAP 2020 system from Micromeritics. Prior to the measurements, samples were outgassed at $200\text{ }^\circ\text{C}$ 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 \AA^2 . 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-programmed reduction with H_2 (H_2 -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 ($50\text{ cm}^3\text{min}^{-1}$) to $550\text{ }^\circ\text{C}$ for 1 h. After cooling to ambient temperature, TPR experiments were carried out in 10 vol.% H_2/Ar ($35\text{ cm}^3\text{min}^{-1}$) increasing the temperature from room temperature to $800\text{ }^\circ\text{C}$ with a heating ramp of $10\text{ }^\circ\text{Cmin}^{-1}$, using a temperature programmable controller. The water produced in the reduction was eliminated with an isopropanol–liquid N_2 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 $\text{MgK}\alpha$ 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 μm 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.

2.2. 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 0.05g 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

3.1.1. X-ray diffraction

The diffractogram of the raw bentonite is shown in Supplementary Information. As was indicated in previous works [18,20,21], 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 [20,21].

After the purification and the formation of the PCH structure, 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 interlayer space of montmorillonite occurs along the *c*-axis, while the non-basal reflections (020, 110, 200, 060) suffer a decrease in their intensity by the random displacement between layers along the *a*- and *b*-axis.

The incorporation of vanadium species (Figure 1) diminishes the intensity of the non-basal reflections. This fact can be related with a partial breakdown of the porous structure increasing disorder along the *a*- and *b*-axis. Moreover, the diffractograms reveal that the presence of V-containing crystalline phases have been not detected for V-loadings lower than 8wt.% of V, which suggests a high dispersion of the active phase. New diffraction lines starts to arise for PCH-12V catalyst, being well-defined for PCH-16V catalysts located at $2\theta = 15.3, 18.6, 20.3, 21.5, 23.6, 26.2, 30.2, 31.2, 34.3, 35.5, 44.5, 47.3, 49.0, 51.2, 53.5$ and 57.4° attributed to the presence of V_2O_5 phase [JCPDS: 41–1426].

3.1.2. Textural properties

Adsorption–desorption N_2 isotherms and pore size distributions of PCH-xV catalysts are summarized in Table 1 and Supplementary Information. According to the IUPAC classification [22] and refined by Rouquerol et al. [23], PCH exhibits a type II isotherm associated with monolayer-multilayer adsorption on an open and stable

external surface of a powder with macroporosity. This isotherm is obtained with aggregates of plate-like particles, which therefore possess non-rigid slit-shaped pores. PCH presents a narrow H3 type hysteresis loops with no indication of a plateau at high P/P_0 , which are usually found on solids consisting of aggregates or agglomerates of particles forming slit shaped pores (plates or edged particles like cubes). S_{BET} of the PCH presents a rise of the surface area ($643 \text{ m}^2\text{g}^{-1}$) with respect to the raw bentonite ($99 \text{ m}^2\text{g}^{-1}$) which indicates the formation of a well-defined porous structure. The isotherm reveals that this support exhibits mainly a microporous framework which indicates that this material could be a potential support for small molecule model such as H_2S .

The incorporation of vanadium species provokes a decrease of the surface area and the pore volume mainly by a blockage of the micro- and mesoporous structure, while the macroporosity attributed to inter-particle spaces remains unaltered (Table 1 and Supplementary Information).

3.1.3. Raman spectroscopy

Raman spectra of catalysts in ambient conditions are shown in Figure 2. The spectra of samples with V-loading higher than 8wt.% of V content show bands at 998, 706, 530, 489, 410, 305, 289, 203 and 159 cm^{-1} . These bands refer to the vibrational modes of crystalline V_2O_5 [24, 25]. However, the samples with V-loading lower than 8wt.% of V do not present bands, which suggests a high dispersion of the active phase over PCH. These results are similar to that observed in XRD.

3.1.4. Diffuse reflectance UV-vis

Diffuse reflectance UV-vis spectra of catalysts are compiled in Figure 3A. The band located between 200 and 500 nm has been ascribed to the low-energy O^{2-} to V^{5+} charge-transfer. This band can be deconvoluted in two overlapped contributions for all catalysts. The first contribution located between 230 and 315 nm, with a maximum located about 270 nm indicates the presence of isolated tetrahedral and octahedral V^{5+} . The second contribution, between 315 and 465 nm, is clearly observed in all catalysts by the presence of “bulk-type” polymeric V_2O_5 -like vanadium species. Finally, the signal located between 600 and 800 nm is attributed to the d–d transition of V^{4+} species, being more noticeable for the catalysts with the higher vanadium content [26].

3.1.5. H_2 -TPR

The dispersion of the vanadium oxide species has been studied through H_2 -TPR profiles (Figure 3B). As was described in previous works, all catalysts only show a broad signal ascribed to the reduction of the V^{5+} species to V^{3+} , which is shifted progressively from 485 °C for PCH-2V catalyst towards higher temperatures as the vanadium loading increases (555 °C for PCH-16V). Nonetheless the reduction temperature is still lower than that of bulk V_2O_5 , indicating that the particle size of V_2O_5 is a key factor in the reducibility of the vanadium species. Thus, the catalysts with small particles of V_2O_5 present a higher interaction with the support, favoring the reducibility than bulky ones [11,27].

3.1.6. XPS

In order to gain further insight into the surface composition of the fresh catalysts, XPS technique was employed. Table 2 compiles the binding energy values and the atomic ratios for all samples.

V $2p_{3/2}$ core level spectra, compiled in Figure 4, can be decomposed in two contributions. The main contribution located about 517.7 eV is assigned to V^{5+} in the form of V_2O_5 . The second contribution centered about 516.3 eV is attributed to V^{4+} species due to photoreduction or thermal reduction of the V_2O_5 species on the surface of the catalyst [28,29]. The photoreduction effect is more moderated for the catalysts with higher vanadium content.

O $1s$ core level spectra present a first contribution located about 532.7 eV attributed to the oxygen of the montmorillonite and the silica pillars. The second contribution is a shoulder of the first contribution centered about 530.5 eV, typical value of the V_2O_5 [11].

XPS analyses were also used to determinate the vanadium content on the surface of the catalyst and the V/Si atomic ratio (Table 2), revealing that vanadium content on the surface increases directly with the vanadium content incorporated. However, the catalysts with the higher vanadium loadings, PCH-12V and PCH-16V, the vanadium content remains unaltered, which could indicate that the dispersion of vanadium oxide decreases with the loading charge leading to a covering of the external surface of the catalyst, as was shown un XRD data and textural properties (Fig. 1B and Table 1)

3.2. Catalytic tests in partial oxidation of H_2S

Figure 5 shows the H₂S conversion (A) and elemental sulfur yield (B) over PCH-vanadia catalysts that were evaluated for 360 min at 180 °C with a reactant molar composition of H₂S/air/He = 1.2/5.0/93.8. In all samples, the highest conversion is observed at the initial stage of the reaction, decreasing with the time on stream. However, the initial catalysts decay is more appreciable over catalysts with V-content lower than 8wt%. On the other hand, it can be seen how the conversion of H₂S increases with the vanadium content, reaching the higher conversion values for PCH-12V catalyst. The use of higher V-content (PCH-16V) maintains the conversion values unaltered. So, when V₂O₅ crystallites are formed the activity in these materials is similar, although if we compared with the conversion of V₂O₅ pure [11] the vanadium supported are more active than bulk V₂O₅.

The trend of sulfur yield for PCH-V catalysts (Fig. 5B) is similar to that of H₂S conversion, obtaining the highest yield values for PCH-12V catalyst, reaching a sulfur yield values close to 88% at the first minutes on stream.

Figure 6 plots the variation of H₂S conversion and sulfur selectivity over PCH-8V. For low H₂S conversion the main product is sulfur, but the formation of combustion products (SO₂) increases when increasing the H₂S conversion.

4. DISCUSSION

In order to understand the performance of PCH-xV catalysts during the catalytic test, XRD, Raman spectroscopy, elemental analysis and XPS were carried out on the catalysts after the catalytic tests.

XRD patterns of spent catalysts (Figure 1) show that the diffraction lines ascribed to V_2O_5 species disappear, arising new diffraction lines about 21.3° and 27.7° assigned to V_4O_9 crystals (JCPDS: 23–720) after the catalytic test, mainly in the case of the catalysts with the highest V-loading, which indicates a partial reduction of V_2O_5 under catalytic conditions. Moreover it must be discarded the presence of more reduced crystalline phases such as VO_2 or $VOSO_4$ [30,31], although a prolonging treatment under this catalytic conditions can lead to the formation of more reduced species as VO_2 [32]. It has been reported in the literature that V_4O_9 crystallites present a relative stability and high capacity to transport lattice oxygen in V_4O_9 improving the redox behavior of the catalytic system in the selective oxidation of H_2S to elemental sulfur [11,33]. Although V_4O_9 crystalline phase presents stability, this phase can be re-oxidized to V_2O_5 by the air contact. Finally, it is noticeable the presence of a small and noisy diffraction line located about 23.1° (JCPDS: 8–247) for the spent catalysts with a higher V-content, which is ascribed to the formation of small elementary sulfur crystals.

V_4O_9 has been characterized in the literature using Raman Spectroscopy [11,12,34], so the formation of this specie found by XRD has been also characterized by Raman also. Figure 2 shows the Raman spectrum of the spent PCH-16V catalyst. After catalytic tests the Raman spectrum is modified. The band which indicates the presence of crystalline V_2O_5 disappears and a new band centered at ca. 900 cm^{-1} is observed. This spectrum is similar to one reported supported [34] and unsupported [12] vanadium oxide catalysts, so this band can be assigned to the formation of V_4O_9 crystallites during the partial oxidation of H_2S at 180°C .

The modification and formation of new species was also evaluated by XPS analyses (Table 2). The core level S $2p$ signal for spent catalysts (Figure 7A) shows two

contributions for S $2p_{3/2}$ region located at 163.3-163.7 eV and 168.3-168.6 eV attributed to elemental sulfur and sulfate species, respectively [11,29]. The spent catalysts with the lower vanadium loading present higher sulfur contents on the surface of the catalysts. Moreover the contribution ascribed to elemental sulfur is higher than the contribution of sulfate species. In the case of the catalysts with the higher vanadium content, the sulfur content on the surface is lower and the sulfate species is the main contribution. These results suggest that the catalysts with the lower vanadium content suffer a higher deactivation process by the deposition of elemental sulfur on the surface provoking a decrease of the active centers of the catalyst, while the catalysts with a higher vanadium content, that barely present deactivation, present a lower deposition of elemental sulfur as indicates the V/S atomic ratio.

With regard to the core level V $2p$ signal, similarly to the fresh catalysts, the V $2p_{3/2}$ signal of the spent catalysts can be decomposed in two contributions. The first one located about 517.5 eV assigned to V^{5+} species and the second one located about 516.3-516.0 eV attributed to V^{4+} species. After the catalytic test, the contribution assigned to V^{4+} species increases, although in a similar proportion for all catalysts, due to the formation of V_4O_9 crystallites on the surface of the catalyst during the catalytic test, as was revealed in the XRD data of the spent catalysts (Figure 7B), which has been proposed as active and selective phase in the hydrogen sulfide oxidation to sulfur over these catalysts [11]. The dispersion of the vanadium species can be evaluated from $V/(Al+Si)$ atomic ratio (Table 2). Thus, the catalysts with a lower V-content exhibit minor $V/(Si+Al)$ ratio after the catalytic test due to these catalysts present a higher sulfur content which can cover the surface of the catalyst, diminishing the number of available active centers for the selective oxidation of the H_2S and leading to the deactivation of the catalyst with the time on stream. However, the catalysts with a

higher V-content present an increase of the available vanadium species on the surface of the catalyst after the catalytic test, which suggests a possible nucleation and/or migration of the vanadate species to the surface of the catalyst. Moreover these species are covered in a lower proportion by sulfur species leading that together with the major amount of available active sites leads catalytic systems with a high activity and stability.

CONCLUSIONS

It has been synthesized a porous clay heterostructure (PCH) by the expanding of the basal spacing and formation of pillars between the montmorillonite sheets leading to a material with a high surface area with interesting properties as catalytic support.

Vanadium oxide supported on PCH has been tested in the partial oxidation of H₂S to elemental sulfur showing be active and a highly selective to elemental sulfur. The catalytic behavior and catalytic stability is directly correlated with the vanadium content. Thus, the catalysts with lower vanadium content suffer a deactivation process with the time on stream, while the catalysts with higher vanadium content exhibit a higher resistance to the deactivation. Although the incorporation of higher vanadium content on the PCH produces a decrease of the specific surface area and pore volume, the formation of bigger V₂O₅ crystallites increases the catalytic stability.

The analysis of the spent catalysts have revealed the formation of partially reduced vanadium species in the form of V₄O₉ crystalline phase during the catalytic test, which seems to be the active and selective phase in the selective oxidation of the H₂S according to the high stability and the redox properties of this phase.

Acknowledgments

The authors would like to thank the DGICYT in Spain (Projects CTQ2012-37925-C03-01, CTQ2012-37925-C03-03 and MAT2010-19837-C06-05) and project of Excellence of Junta de Andalucía (project P12-RNM-1565) for financial support.

References

- 1) R.E. Kirk, F. Orthmer, J.I. Kroschwitz, M. Howe-Grant, Kirk-Othmer's, Encyclopedia of Chemical Technology, John Willey & Sons, New York, 1998.
- 2) A. Piéplu, O. Saur, J. C. Lavalley, O. Legendre, C. Nédez, Catalysis Reviews: Science and Engineering; 40 (1998) 409-450.
- 3) A.D. Wiheeb, I.K. Shamsudin, M.A. Ahmad, M.N. Murat, J. Kim, M.R. Othman, Rev. Chem. Eng. 29 (2013) 449-470.
- 4) M. Capone, Encyclopedia of Chemical Technology, in: J. K. Kroschwitz, M. Howe-Grant (Eds.), Wiley, New York, 1997.
- 5) K.T. Li, Z.H. Chi, Appl. Catal. A: Gen. 206 (2001) 197–203.
- 6) X. Zhang, X. Zhang, G. Dou, Zh. Wang, L. Li, Y. Wang, H. Wang, Zh. Hao, J. Hazard. Mat. 260 (2013) 104-111.
- 7) D. Barba, V. Palma, P. Ciambelli, Inter. J. Hydrog. Energy 38 (2013) 328-335.
- 8) K.-T. Li, Ch.-H. Huang, Catal. Today 174 (2011) 25– 30.
- 9) X. Zhang, Z. Wang, N. Qiao, S. Qu, Z. Hao, ACS Catal., 4 (2014) 1500-1510.
- 10) K.V. Bineesh, M. Kim, G.-H. Lee, M. Selvaraj, K. Hyun, D.-W. Park, J. Ind. Eng. Chem. 18 (2012) 1845–1850.
- 11) M.D. Soriano, J. Jiménez-Jiménez, P. Concepción, A. Jiménez-López, E. Rodríguez-Castellón, J.M. López Nieto, Appl. Catal. B: Environ. 92 (2009) 271–279.
- 12) J.P. Holgado, M.D. Soriano, J. Jiménez-Jiménez, P. Concepcion, A. Jiménez-López, A. Caballero, E. Rodríguez-Castellón, J.M. López Nieto, Catal. Today 155 (2010) 296–301.
- 13) M.D. Soriano, J.M. López Nieto, F. Ivars, P. Concepcion, E. Rodríguez-Castellón, Catal. Today 192 (2012) 28-35.
- 14) G. Centi, S. Perathoner, Micropor. Mesopor. Mater. 107 (2008) 3-15.
- 15) A. Galarneau, A. Barodawalla, T.J. Pinnavaia, Nature 374 (1995) 529-531.

- 16) M. Polverejan, Y. Liu, T.J. Pinnivaia, *Cham. Mater.* 14 (2002) 2283-2288.
- 17) L. Chmielarz, B. Gil, P. Kústrowski, Z. Piwowarska, B. Dudek, M. Michalik, J. *Solid State Chem.* 182 (2009) 1094-1104.
- 18) J.A. Cecilia, C. García-Sancho, F. Franco, *Microporous Mesoporous Mater.* 176 (2013) 95-102.
- 19) K. V. Bineesh, D.-K. Kim, D.-W. Kim, H.-J. Cho, D.-W. Park, *Energy Environ. Sci.* 3 (2010) 302-310.
- 20) E. Caballero, J.M. Fernández-Porto, J. Linares, F. Huertas, E. Reyes, *Estud. Geol.* 39 (1983) 121–140.
- 21) E. Caballero, E. Reyes, J. Linares, F. Huertas, *Miner. Petrogr. Acta* 29 (1985) 187–196.
- 22) K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* 57 (1985) 603.
- 23) F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by Powders and Porous Solids*, Academic Press, London, 1999 (Chapter 13).
- 24) L. Abello, E. Husson, Y. Repelin, G. Lucazeau, *Spectrochim. Acta* 39 (1983) 641-651.
- 25) M.D. Argile, K. Chen, A.T. Bell, E. Iglesia, *J. Catal.* 208 (2002) 139-149.
- 26) X. Gao, I.E. Wachs, *J. Phys. Chem. B* 104 (2000) 1261–1268.
- 27) B. Solsona, J.M. López Nieto, U. Diaz, *Microp. Mesop. Mater.* 94 (2006) 339-347.
- 28) L.E. Briand, O.P. Tkachenko, M. Guraya, X. Gao, I.E. Wachs, W. Grünert, *J. Phys. Chem. B* 108 (2004) 4823–4830.
- 29) J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Standard Spectra for Identification and Interpretation of XPS Data*, Perkin Elmer, Eden Prairie, MN, 1992.
- 30) M.Y. Shin, C.M. Nam, D.W. Park, J.S. Chung, *Appl. Catal. A: Gen.* 211 (2001) 213-225.
- 31) M.W. Song, M. Kang, K.L. Kim, *React. Kinet. Catal. Lett.* 78 (2003) 365-371.
- 32) G. Grymonprez, L. Fiermans, J. Vennik, *Acta Cryst. A* 33 (1997) 834-837.
- 33) J. Haber, M. Witko, R. Tokarz, *Appl. Catal. A: Gen.* 157 (1997) 3-22.
- 34) R. Nilsson, T. Lindblad, A. Andersson, *J. Catal.* 148 (1994) 501-513