

Clay honeycomb monoliths as support of manganese catalysts for VOCs oxidation

J. M. Gatica^{a,c}, J. Castiglioni^b, C. de los Santos^b, M. P. Yeste^a, G. A. Cifredo^a, M. Torres^b and H. Vidal^a

^a *Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Puerto Real 11510, SPAIN.*

^b *LAFIDESU, DETEMA, Universidad de la República, Montevideo 11800, URUGUAY.*

^c *Corresponding Author: E-mail: josemanuel.gatica@uca.es*

Abstract:

Integral honeycomb monoliths were prepared from a Spanish clay by extrusion without using additives. The resulting monoliths were employed as support of manganese catalysts deposited by impregnation method. The supported catalysts were characterized by means of different techniques such as chemical analysis, nitrogen physisorption, scanning electron microscopy, X-ray diffraction and Temperature-Programmed Reduction. Additionally, they were tested in the oxidation of both propane and acetone. The results obtained demonstrate that the active phase present (3 wt.%), being highly and homogeneously dispersed onto the surface of the clay support and consisting of MnO₂, exhibits high efficiency to oxidize the two model volatile organic compounds (VOCs) investigated. In particular, light-off temperatures as low as 250 and 330 °C were found for the oxidation of acetone and propane respectively, the catalytic activity being stable for 24 hours. This result combined with the advantages of the honeycomb monolithic design show the potential of the proposed formulation including clay as a more advantageous material in comparison to high-tech cordierites for a real application of interest in the environmental protection field.

Keywords: CaZnO₂; Catalysis; Clay; Honeycomb monoliths; Manganese; VOCs oxidation.

1. Introduction

Volatile Organic Compounds (VOCs) are chemicals which are harmful to health and serious air pollutants because their toxic, smelly, mutagenic and carcinogenic nature. In addition, they are smog precursors and contribute to ozone layer depletion. There are several techniques for their abatement such as thermal combustion or incineration, adsorption and catalytic oxidation. The latter is considered an excellent method to remove VOCs due to its low reaction temperature, NO_x emission level and operative costs along with its high efficiency to destroy fully the pollutant.

The catalysts most usually employed for this application consist of supported noble metals (typically Pt or Pd). However, other transition metals (Co, Cu, Ni, Mn) in the form of oxides have also shown high catalytic activity in VOCs oxidation, with the extra advantage of being cheaper and more resistant against deactivation by poisons [1-3]. Manganese oxide-based catalysts (Mn₃O₄, Mn₂O₃, MnO₂) have been specifically identified as the active phase responsible for the oxidation of several hydrocarbons [1,2].

Nevertheless, when high volumes of gaseous effluents containing low VOCs concentration must be treated, it is additionally necessary to deposit the active phase onto

high open area structured supports to ensure the gas flow with low pressure drop. The most used ones are honeycomb monoliths, which may be manufactured either from ceramic or metallic materials. In particular, those made of cordierite are the most popular due to their extended use in automotive industry.

In this sense, it is noteworthy that existing literature related to the use of manganese oxide-based catalysts for VOCs oxidation either deals with them alone [4-8] or if supported onto clays they are in the form of powders [9,10], the only reference about honeycomb monoliths using cordierite as catalytic support [11].

The novel objective of this work is to prepare and characterize manganese catalysts supported onto honeycomb monoliths obtained from a natural clay, as cheaper alternative to commercial structured supports, and to test them in the total combustion of propane and acetone, two model VOCs which are often present in end-of-pipe emissions.

2. Material and Methods

2.1. Catalyst Preparation

The clay employed in this work, named ARG1-2000, was provided by VICAR S.A., and proceeded from deposits located at the east of Spain. It was received in the form of

powder with a grain size of 100 μm and a nominal composition (wt.%) of 57% SiO_2 , 28.4% Al_2O_3 , 1% Fe_2O_3 , 1.5% TiO_2 , 0.5% CaO , 2.5% K_2O , 0.5% MgO , 0.3% Na_2O and 7.8% of undetermined ashes.

Its extrusion was performed following a methodology previously developed for carbon [12] and other clay materials [13], without using additives except water (0.3–0.4 ml/g of paste). Geometric characteristics of the monoliths obtained (Figure 1) were analogous to those described in [14] (honeycomb-type circular section with a density of 64 cells/cm²), other physico-chemical properties being reported in [15].

The clay honeycomb monoliths, upon being calcined at 440 °C for 4 h to enhance their mechanical resistance, were impregnated by immersion with a 1M solution of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (from Sigma Aldrich, 98.5% pure) with continuous stirring for 30 min. The resulting monoliths were further dried by using microwaves (500 W, 1 min), and finally submitted to calcination at 440 °C for 2 h. According to Temperature-Programmed Oxidation (TPO) experiments, this treatment ensures metal precursor decomposition (Figure 2) without altering the clay structure [15].



Figure 1. Extrusion machine and dye used for preparing the clay honeycomb monoliths (up), and dissectioned manganese-coated clay monolith (down).

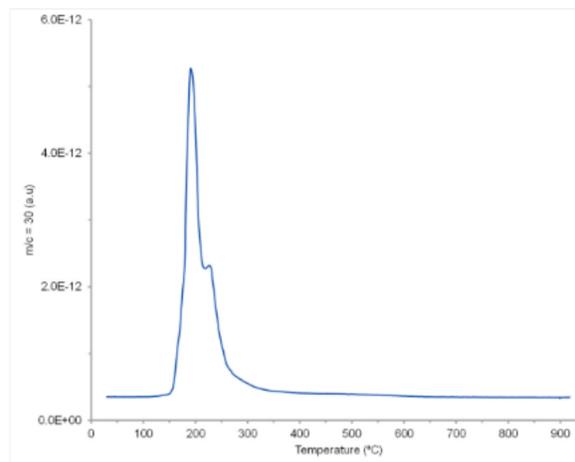


Figure 2. TPO-MS diagram showing NO_x evolution as obtained for the manganese-coated clay honeycomb monoliths after the impregnation and drying steps.

2.2. Characterization Techniques

The metal content of the supported catalysts was estimated by inductively coupled plasma spectroscopy (ICP) analysis using an IRIS Intrepid Thermo Elemental instrument.

X-ray diffraction (XRD) studies were carried out in Bruker diffractometer, D8 Advance 500 model. The diffractograms were recorded using $\text{Cu K}\alpha$ radiation and a graphite monochromator. The 2θ angle ranged from 2° to 130° , with a step of 0.03° and a counting time per step of 45 s. For this study the monolithic samples were crushed and sieved.

Textural characterization was performed by means of N_2 physisorption at -196°C using a Micromeritics ASAP2020 instrument. For this analysis the monoliths (both entire and crushed into pieces) were pre-evacuated at 200°C for 2 h. Specific surface area was measured by the BET method. Total pore volume (V_p) was calculated from the amount of nitrogen adsorbed at relative pressures around 0.99. Pore size distribution and pore mean size diameter were determined by BJH method from the adsorption branch of the isotherms.

Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) compositional data corresponding to small pieces of the monoliths were obtained using a QUANTA-200 scanning electron microscope equipped with a Phoenix Microanalysis System using a nominal resolution of 3 nm.

Programmed-Temperature Oxidation (TPO) and Reduction (TPR) experiments were carried out using both a SDT Q600 thermobalance (TA instruments) and a Thermostat QMS 200 (Pfeiffer) mass spectrometer (MS), employing a flow of 60 ml/min of $\text{O}_2(5\%)/\text{He}$ and $\text{H}_2(5\%)/\text{Ar}$, respectively, over crushed monolith pieces (50 mg) and with a heating rate of $10^\circ\text{C}/\text{min}$.

2.3. Activity Testing

Catalytic tests were run over entire monolith pieces with different lengths, 2 cm (approx. 3 g), 4 cm and 6 cm, placed inside a Pyrex glass reactor. Before the reaction, each monolith was subjected to a pretreatment at 450 °C for 30 min under Ar stream.

In the case of propane oxidation, the activity was measured operating at atmospheric pressure between 200 and 500 °C, with a feedstock of 79.6% Ar, 19.6% O₂ and 0.8% C₃H₈ (167 ml/min). Propane conversion and reaction products were analysed by gas chromatography (GC14B Shimadzu).

Regarding acetone oxidation, the activity was also measured at atmospheric pressure between 150 and 450 °C, using a reactant mixture containing 1200 ppm of C₃H₆O in a gas stream, 97.2% Ar and 2.8% O₂, total flow being 124 ml/min. Acetone conversion and reaction products were analysed by gas chromatography (GC2014 Shimadzu).

3. Results and Discussion

3.1. Catalysts Characterization

Chemical analysis by ICP revealed that the clay honeycomb monoliths impregnated with manganese nitrate and finally calcined at 440 °C exhibited a Mn massive content of 3.07±0.01 (wt.%). Nevertheless, analysis by means of X-ray diffraction (Figure 3) only showed peaks characteristics of the clay support [12]. This is attributed to a very high metal dispersion, and it is in good agreement with results obtained by other authors [16] who studying TiO₂-supported manganese catalysts only detected peaks related to the metal phase for loadings higher than 11% by weight.

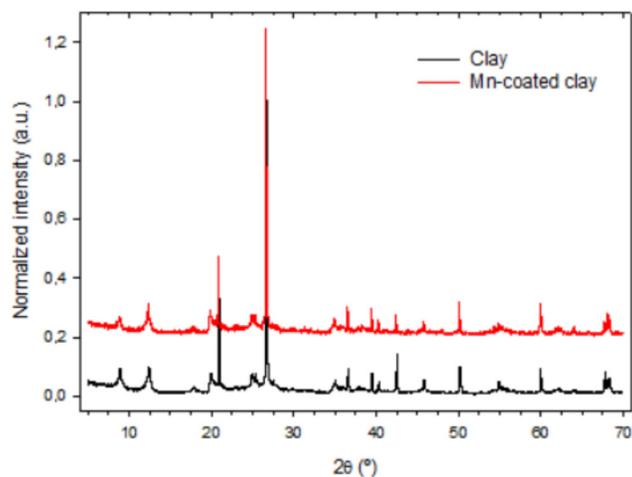


Figure 3. X-ray diffractograms corresponding to the bare and manganese-coated clay honeycomb monoliths.

Images obtained by SEM (Figure 4) were similar to those previously observed for the clay honeycomb monoliths alone [15]. However, the quantitative analysis by EDS of different zones of the calcined manganese-coated monoliths (Figure 5) indicated that Mn is homogeneously distributed with a surface content of 4.87±1.07 (wt.%), which is consistent with results commented above. Also remarkable, this amount is lower than that deposited onto cordierite honeycombs by other authors [11].

Figure 4. Scanning electron micrographs obtained for a small piece of external wall of the manganese-coated clay honeycomb monolith at two different magnifications.

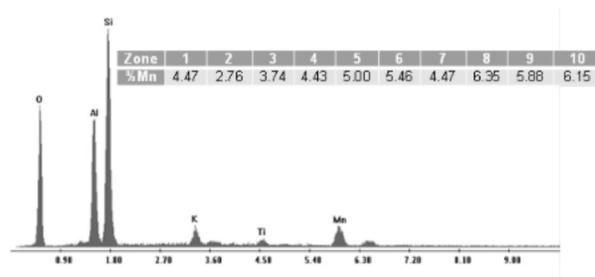


Figure 5. Typical EDS spectrum and result of analyses performed in different surface zones of the manganese-coated clay honeycomb monoliths. Besides Mn, the other elements which appear (Si, O, Al, K and Ti) proceed from the clay used as support. The table accounts for the manganese content in ten different zones of the sample.

On the other hand, textural characterization (Figure 6 and Table 1) demonstrated that coating of the clay honeycomb monoliths with the manganese phase hardly affects neither the specific surface area (around 30 m²/g) nor the porosity of the support (mesoporous samples with a pore diameter of 50 nm) (Figure 7). These textural properties are better than those reported for cordierite honeycombs washcoated by manganese oxides [11].

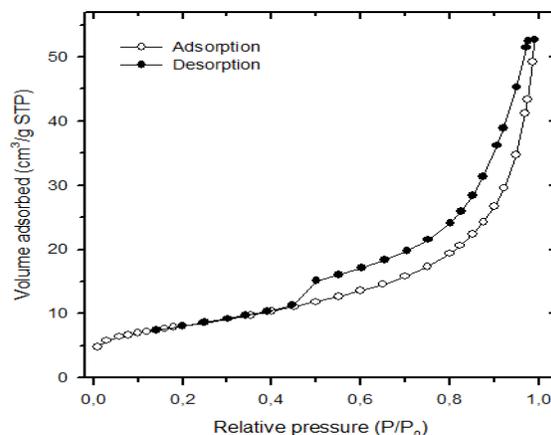


Figure 6. Nitrogen physisorption isotherm of the manganese-coated clay honeycomb monolith, obtained using an entire piece. Similar results were obtained with a crushed monolith.

Table 1. Textural properties of the honeycomb monolithic samples

Sample	S_{BET} (m^2g^{-1})	V_p^a (cm^3g^{-1})	V_{micro}^b (cm^3g^{-1})	V_{meso}^c (cm^3g^{-1})	D_p^d (nm)
Clay	29.3	0.084	0.001	0.083	11.7
Mn-coated clay	28.9	0.064	0.002	0.062	11.4
Mn-coated clay (crushed sample)	29.6	0.066	0.001	0.065	12.0

^a Estimated from the amount of nitrogen adsorbed at $P/P_0=0.99$; ^b Estimated by means of t-plot (Harkins-Jura) analysis from N_2 physisorption data; ^c ($V_p - V_{\text{micro}}$); ^d Determined from the adsorption branch of the N_2 physisorption isotherm following the BJH method.

Concerning the TPR study, the reduction profile obtained can be interpreted as characteristic of the presence of MnO_2 as major metal phase [16,17]. This is suggested by the hydrogen consumption in the 250–350 °C temperature range (Figure 8). Other authors also proposed the formation of this phase on cordierite honeycombs after impregnation with manganese nitrate followed by drying at 120 °C during 4 h and final calcination at 500 °C for 2 h [11].

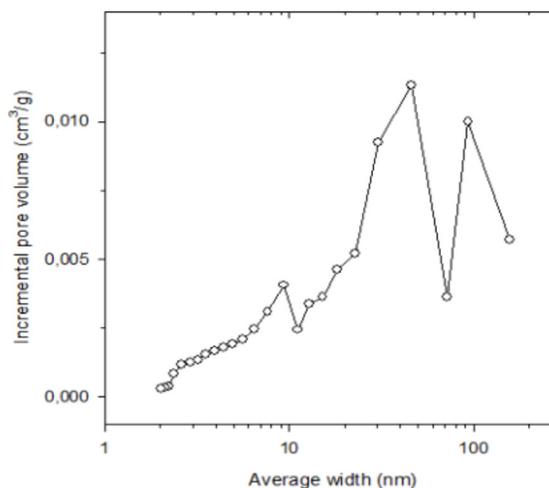
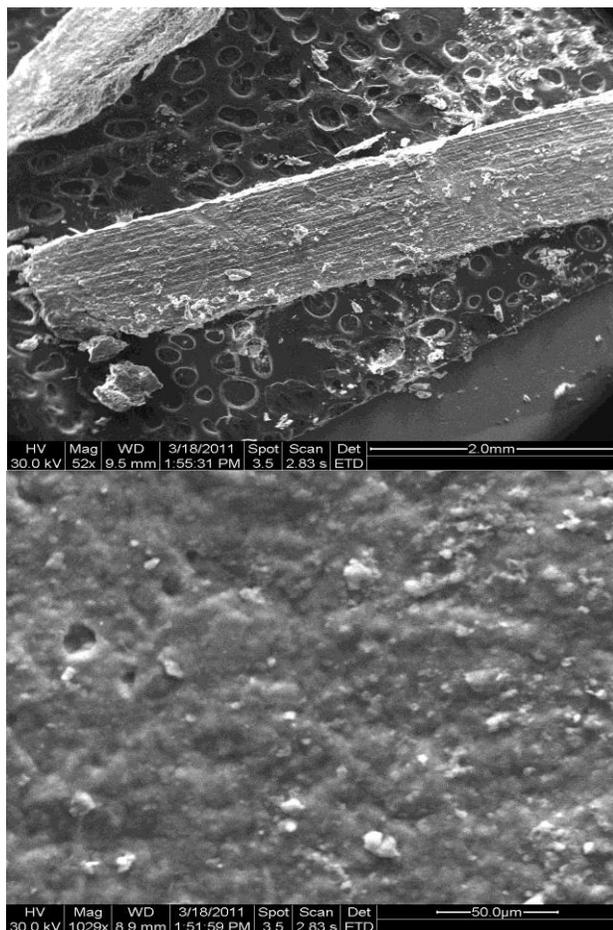


Figure 7. Pore distribution curve of the manganese-coated clay honeycomb monolith, obtained using an entire piece. Similar results were obtained with a crushed monolith.

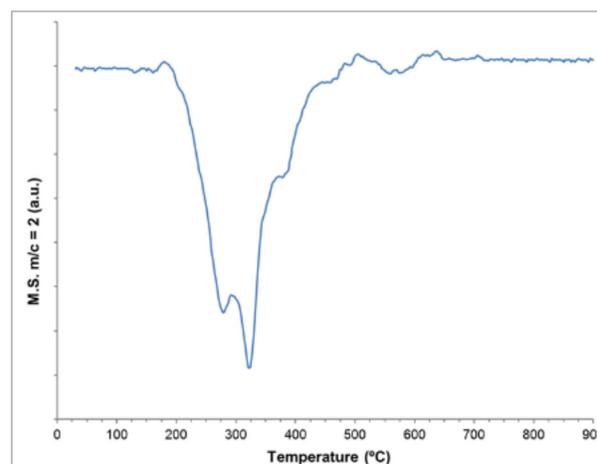


Figure 8. TPR-MS diagram showing the H_2 consumed by the supported manganese catalyst.

3.2. Catalytic Performance

The study of the propane oxidation reaction indicated that the activity of the bare clay honeycomb monolith was negligible under our experimental conditions while those containing manganese showed activity even from 200 °C, reaching a conversion of ca. 92 % at 450 °C (Figure 9). Also significant, only total combustion products (CO_2 and H_2O) were detected. These results are competitive if compared with other catalysts employed in this reaction, for example with high surface area ceria for which a 90% of conversion at 450 °C was reported [18]. The activity found in our work for the oxidation of propane is also in the order of that observed for coprecipitated manganese aluminium $\text{Mn}_3\text{O}_4/\text{Al}_2\text{O}_3$ mixed oxide catalysts [7].

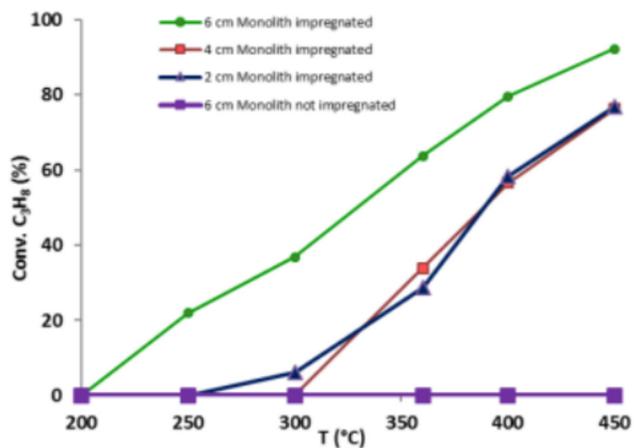


Figure 9. Catalytic activity of the bare and manganese-coated clay honeycomb monoliths in the propane oxidation as function of their length.

In the case of the acetone oxidation (Figure 10), a similar behaviour was observed (although this time the bare clay support showed some activity) with a light-off temperature as low as 250 °C, and full conversion below 400 °C for all the Mn-coated samples no matter the length of the honeycomb monolith used for the catalytic test. Moreover, during an experiment performed at 300 °C (with 80% of conversion) over a 4 cm long monolith the conversion remained constant for 24 hours so showing the stability of the catalysts prepared. This result is even better than those reported for the complete oxidation of acetone over manganese oxide catalysts supported on alumina- and zirconia-pillared clays [9].

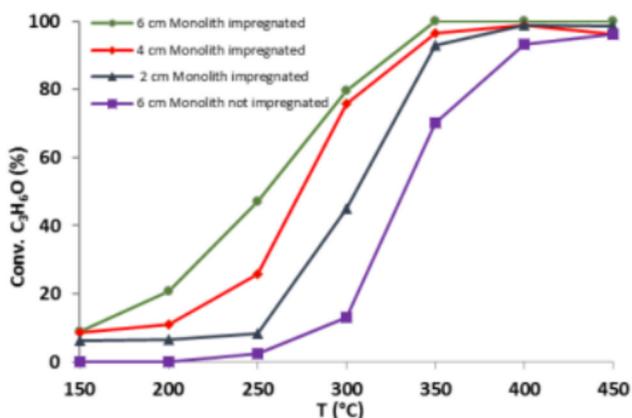


Figure 10. Catalytic activity of the bare and manganese-coated clay honeycomb monoliths in the acetone oxidation as function of their length.

4. Conclusion

Clay honeycomb monoliths-supported manganese (3 wt.%) catalysts were prepared by means of the impregnation method for the oxidation of propane and acetone. Their high activity at moderate temperatures

($T_{\text{light-off}} = 330$ and 250 °C, respectively) was associated to a highly and homogeneously disperse MnO_2 phase. Such result along with the advantages of the honeycomb monolithic design make these catalysts good candidates for real scale application, avoiding both the use of high-tech structured honeycombs as support and of noble metals as active phase.

ACKNOWLEDGMENT

The authors thank the Ministry of Economy and Competitiveness of Spain (Project MINECO/FEDER MAT2013-40823-R), the Junta Andalucía (FQM-110 group) and the ANII from Uruguay (Project FCE_1_2011_1_7004) for their financial support. They also acknowledge the SC-ICYT of the University of Cadiz for using its XRD, AS and electron microscopy division facilities.

REFERENCES

- [1] S.C. Kim and W.G. Shim, "Catalytic combustion of VOCs over a series of manganese oxide catalysts", *Applied Catalysis B: Environmental*, 98, 180 – 185, 2010.
- [2] F.N. Agüero, B.P. Barbero, L.C. Almeida, M. Montes and L.E. Cadús, "MnO_x supported on metallic monoliths for the combustion of volatile organic compounds", *Chemical Engineering Journal*, 166, 218 – 223, 2011.
- [3] V. Balcaen, H. Poelman, D. Poelman and G.B. Marin, "Kinetic modelling of the total oxidation of propane over Cu- and Ce-based catalysts", *Journal of Catalysis*, 283, 75 – 88, 2011.
- [4] L.M. Gandía, A. Gil and S.A. Korili, "Effects of various alkali-acid additives on the activity of a manganese oxide in the catalytic combustion of ketones", *Applied Catalysis B: Environmental*, 33, 1 – 8, 2001.
- [5] M. Baldi, E. Finocchio, F. Milella and G. Busca, "Catalytic combustion of C3 hydrocarbons and oxygenates over Mn₃O₄", *Applied Catalysis B: Environmental*, 16, 43 – 51, 1998.
- [6] M. Baldi, V. Sanchez Escribano, J.M. Gallardo Amores, F. Milella and G. Busca, "Characterization of manganese and iron oxides as combustion catalysts for propane and propene", *Applied Catalysis B: Environmental*, 17, L175 – L-182, 1998.
- [7] E. Finocchio and G. Busca, "Characterization and hydrocarbon oxidation activity of coprecipitated mixed oxides Mn₃O₄/Al₂O₃", *Catalysis Today*, 70, 213 – 225, 2001.
- [8] B. Puértolas, A. Smith, I. Vázquez, A. Dejoz, A. Moragues, T. Garcia and B. Solsona, "The different catalytic behaviour in the propane total oxidation of cobalt and manganese oxides prepared by a wet combustion procedure", *Chemical Engineering Journal*, 229, 547 – 558, 2013.
- [9] L.M. Gandía, M.A. Vicente and A. Gil, "Complete oxidation of acetone over manganese oxide catalysts supported on alumina- and zirconia-pillared clays", *Applied Catalysis B: Environmental*, 38, 295 – 307, 2002.
- [10] A. Gil, M.A. Vicente and S.A. Korili, "Effect of the nature and structure of pillared clays in the catalytic behaviour of supported manganese oxide", *Catalysis Today*, 112, 117 – 120, 2006.

Clay honeycomb monoliths as support of manganese catalysts for VOCs oxidation

- [11] S. Azalim, R. Brahmi, M. Agunaou, A. Beurain, J.-M. Giraudon and J.-F. Lamonier, "Washcoating of cordierite honeycomb with Ce-Zr-Mn mixed oxides for VOC catalytic oxidation", *Chemical Engineering Journal*, 223, 536 – 546, 2013.
- [12] J.M. Gatica, J.M. Rodríguez-Izquierdo, D. Sánchez, C. Ana, J.B. Parra and H. Vidal, "Extension of preparation methods employed with ceramic materials to carbon honeycomb monoliths", *Carbon*, 42, 3251- 3254, 2004.
- [13] T. Chafik, S. Harti, G.A. Cifredo, J.M. Gatica and H. Vidal, "Easy extrusion of honeycomb-shaped monoliths using Moroccan natural clays and investigation of their dynamic adsorptive behavior towards VOCs", *Journal of Hazardous Materials*, 170, 87 – 95, 2009.
- [14] Z. Tian, T. Chafik, M. Asseban, S. Harti, H. Vidal, J.M. Gatica, G.A. Cifredo, N. Bahlawane, P.M. Kouotou and K. Khose-Höinghaus, "Corrigendum to: Towards biofuel combustion with an easily extruded clay as a natural catalyst", *Applied Energy*, 108, 528 – 529, 2013.
- [15] G. Cifredo, J.M. Gatica, S. Harti and H. Vidal, "Easy route to activate clay honeycomb monoliths for environmental applications", *Applied Clay Science*, 47, 392 – 399, 2010.
- [16] P.R. Ettireddy, N. Ettireddy, S. Mamedov, P. Boolchand and P.G. Smimiotis, "Surface characterization studies of TiO₂ supported manganese oxide catalysts for low temperature SCR of NO with NH₃", *Applied Catalysis B: Environmental* 76, 123 – 134, 2007.
- [17] D. Delimaris and T. Ioannides, "VOC oxidation over MnO_x-CeO₂ catalysts prepared by a combustion method", *Applied Catalysis B: Environmental*, 84, 303 – 312, 2008.
- [18] C. De los Santos, D. Gómez, H. Vidal, J.M. Gatica, M. Sergio and J. Castiglioni, "Combustión completa de propano sobre catalizadores a base de dióxido de cerio de alta superficie específica" [Libro de Actas SECAT-2013 Catalizadores y reactores estructurados, Seville, Spain, P62, 335 – 336, 2013].