



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)

## Use of pillared clays in the preparation of washcoated clay honeycomb monoliths as support of manganese catalysts for the total oxidation of VOCs

José M. Gatica<sup>a,\*</sup>, Jorge Castiglioni<sup>b</sup>, Carolina de los Santos<sup>b</sup>, M. Pilar Yeste<sup>a</sup>, Gustavo Cifredo<sup>a</sup>, Martín Torres<sup>b</sup>, Hilario Vidal<sup>a</sup>

<sup>a</sup> Departamento C.M. I.M. y Química Inorgánica, Universidad de Cádiz, Puerto Real 11510, Spain

<sup>b</sup> Laboratorio de Fisicoquímica de Superficies, DETEMA, Facultad de Química, Universidad de la República, 11800 Montevideo, Uruguay

### ARTICLE INFO

#### Keywords:

Environmental catalysis  
Honeycomb monoliths  
Manganese  
Pillared clays  
VOCs oxidation

### ABSTRACT

Manganese catalysts supported by impregnation onto honeycomb monoliths extruded from commercial clay, previously coated with aluminium-pillared clay, were prepared and tested in the total combustion of propane and acetone. Samples characterization included chemical analysis, nitrogen physisorption, electron microscopies (SEM-EDS, HAADF and EELS), XRD, TPR and O<sub>2</sub>-TPD experiments. The active phase (around 5 wt%), consisting of MnO<sub>2</sub> particles as majority phase, with homogeneous size and shape, that tends to concentrate in some regions of the surface of the clay support, exhibited high efficiency to oxidize the two model VOCs investigated and stability in severe reaction conditions. Light-off temperatures as low as 225 and 330 °C were found for the oxidation of acetone and propane respectively. The better performance observed in comparison to the monoliths without pillared clay was attributed to the higher active phase loading. Differences found as function of the VOC's nature and concentration were related to the different oxidation mechanisms proposed in literature, either just Mars-van Krevelen or this with also Eley-Rideal contribution, for acetone and propane respectively. These results combined with the intrinsic advantages of the honeycomb monolithic design open up new possibilities for using pillared clays as catalytic support in VOCs oxidation under more affordable conditions.

### 1. Introduction

Literature related to the use of manganese-based oxides as alternative to noble metals for the abatement of VOCs is so far extensive, dealing with both pure manganese oxides [1–4] or Mn-containing mixed oxides [5] and MnO<sub>x</sub> deposited onto various supports [6–8], not only in the form of powders but also onto honeycomb monoliths, either using cordierite, washcoated with high surface alumina [9], or metallic substrates [10–12]. On the contrary, it is surprising that references which employ Mn-based catalysts supported onto clays for this application are much scarcer [13], in spite of the fact that clays are cheap and abundant materials, and that many of them possess ideal rheological properties for preparing structured supports by extrusion.

Pillared clays with large surface area can be also used as supports for metal catalysts to achieve homogeneous dispersion, increased reactant adsorption area, and shape selectivity [14]. The utilization of clays pillared with transition metal oxides has been extended to reactions such as the dehydrogenation of cyclohexane to benzene [15], the Fischer–Tropsch synthesis [16], the selective catalytic oxidation of H<sub>2</sub>S [17], the selective catalytic reaction of NO [18], the

hydrodesulfurization of thiophenes [19], and selective organic transformations [20], among others. In these examples, the activity is intrinsically associated to the metal oxides acting as pillars, but in other occasions the active phase is further incorporated by impregnation on the pillared clays surface area, which has been also done to prepare supported Mn oxides [21].

The traditional methods for preparing pillared clays are carried out in very diluted systems, so the contact between the clay in suspension and the intercalating solution allows diffusion of cations, used as pillared precursors, into the clay sheets, generating a homogeneous pillars structure [22,23]. However, their scale up for their industrial production remains a challenge (time-consuming processing, high volumes handling and lack of reproducibility) [24,25]. Therefore it is of great interest the development of optimized standard procedures or experimental techniques for the use of such materials. Recently the use of concentrated dispersions and microwave or ultrasound irradiation during the intercalation step have been proposed [26–28]. Another alternative might be to deposit pillared clays onto honeycomb monoliths as a way to minimize the amount of pillared clay needed, maximizing the contact with active phases, while taking profit of the

\* Corresponding author.

E-mail address: [josemanuel.gatica@uca.es](mailto:josemanuel.gatica@uca.es) (J.M. Gatica).

<http://dx.doi.org/10.1016/j.cattod.2017.04.025>

Received 12 January 2017; Received in revised form 28 March 2017; Accepted 10 April 2017  
0920-5861/ © 2017 Elsevier B.V. All rights reserved.

extra advantages of structured supports with respect to packed bed reactors [29,30]. In this sense, our group has demonstrated the possibility of preparing clay-based honeycomb monoliths with great potential for several environmental applications as a cheaper alternative to commercial structured supports such as those based on commercial high-tech cordierites [31–37]. On the other hand, in previous studies we also prepared aluminium-pillared clays and used them as catalytic support of manganese oxides for the total oxidation of acetone and propane [38,39].

With the above precedents, the novel aim of this research was to prepare and characterize manganese catalysts supported onto honeycomb monoliths extruded from commercial clay, and to test them in the total combustion of propane and acetone, two model VOCs which are often present in end-of-pipe emissions. Moreover, before the incorporation of the manganese phase by using a simple impregnation technique, the clay honeycomb monoliths were also coated with a pillared clay by a washcoating procedure in order to further improve the physicochemical properties of the catalyst and consequently its performance. On this regard, the bare clay honeycomb support [34], this impregnated with the manganese phase [40] and the one just washcoated with the pillared clay were also studied as references of the ternary system.

## 2. Experimental

### 2.1. Materials and catalyst preparation

The clay employed in this work to prepare clay honeycomb monoliths, named as ARG1, was provided by VICAR S.A., and came from deposits located at the east of Spain. It was received as a powder with a grain size of 100  $\mu\text{m}$  and a nominal composition (induced couple plasma, ICP, analysis) as follows: 57%  $\text{SiO}_2$ , 28.4%  $\text{Al}_2\text{O}_3$ , 1%  $\text{Fe}_2\text{O}_3$ , 1.5%  $\text{TiO}_2$ , 0.5%  $\text{CaO}$ , 2.5%  $\text{K}_2\text{O}$ , 0.5%  $\text{MgO}$ , 0.3%  $\text{Na}_2\text{O}$  and 7.8% of undetermined ashes (mass contents for the dry sample).

Extrusion of this clay was achieved without needing other additives except water (0.3–0.4 ml/g of paste) and following the methodology previously reported [41]. The resulting green monoliths were dried overnight at 90  $^\circ\text{C}$  and finally calcined at 440  $^\circ\text{C}$  for 4 h to enhance their mechanical resistance without altering the clay structure [34]. The monoliths finally obtained (Fig. 1), presented a honeycomb-type circular section with a diameter of 1.4 cm, a density of approx. 50 cells/ $\text{cm}^2$ , 0.33 mm of wall thickness and a 72% open frontal area.

The resulting monoliths (from now on ClayM) were subsequently washcoated by an aluminium pillared clay, named as PILC. This was previously prepared from a calcium-rich montmorillonite with low sodium and potassium content from Uruguay as reported elsewhere [42] leading to a material with the following textural properties:  $S_{\text{BET}} = 235.2 \text{ m}^2/\text{g}$ ; pore volume = 0.167  $\text{cm}^3/\text{g}$ ; micropore volume = 0.096  $\text{cm}^3/\text{g}$ ; and average pore diameter = 10.7 nm. Deposition of this PILC over the ClayM monoliths was conducted using a similar

methodology to that employed by other authors for depositing clays onto metallic monoliths [43]. Briefly, the synthesized powder pillared clay was used to prepare a stable aqueous suspension (1.7 wt%). The adequate amount of solid was dispersed in deionised water and the mixture was sonicated for 3.5 h. After this time, a polyvinyl alcohol (PVA) solution was added to the suspension to improve its stability in clay/PVA ratio of 1:1 by weight. The mixture was kept under vigorous stirring for 24 h and then, the ClayM monolith was immersed in it during 1 h under ultrasounds (110 W). After careful withdrawal, the excess of colloidal solution was removed by blowing. Then the monolith was dried overnight at 60  $^\circ\text{C}$  and finally calcined at 450  $^\circ\text{C}$  for 2 h at a heating rate of 1  $^\circ\text{C}/\text{min}$ .

The above resulting PILC/ClayM monoliths were impregnated by immersion with a 1 M 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. These active phase-loaded monoliths were further dried by using microwaves (500 W, 1 min), and finally submitted to calcination at 450  $^\circ\text{C}$  for 2 h using a heating rate of 2  $^\circ\text{C}/\text{min}$ . According to previous Temperature-Programmed Oxidation (TPO) experiments [40], this treatment ensures metal precursor decomposition, while keeping structural stability of the clays supports [29]. Hereafter the final monoliths will be referred to as Mn/PILC/ClayM. A similar procedure, skipping the intermediate washcoating step or the last impregnation, was followed to prepare Mn/ClayM [40] and PILC/ClayM monoliths respectively, both used as reference samples.

### 2.2. Characterization

The samples prepared in this investigation were characterized by means of different techniques such as chemical and textural analyses, Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), X-ray diffraction (XRD), High-angle annular dark-field (HAADF) electron microscopy, Electron Energy Loss Spectroscopy (EELS), Temperature-Programmed Reduction (TPR) and  $\text{O}_2$  Temperature-Programmed Desorption ( $\text{O}_2$ -TPD).

The metal content of the supported catalysts was estimated by inductively coupled plasma spectroscopy (ICP) analysis, using a NexION (Perkin-Elmer) mass spectrometer and an IRIS Intrepid Thermo Elemental instrument, for Mn/PILC/ARG1 and Mn/ARG1 monoliths respectively.

Textural characterization was performed by means of  $\text{N}_2$  physisorption at  $-196 \text{ }^\circ\text{C}$  using a Micromeritics ASAP2020 instrument. For this analysis the monoliths were pre-evacuated at 200  $^\circ\text{C}$  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 the BJH method from the desorption branch of the isotherms.

SEM images and 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. In addition, EDS maps corresponding to the distribution of Mn and Si were recorded in a Field Emission Gun (FEG) scanning electron microscope (Nova NanoSEM 450) equipped with an EDAX system.

XRD studies were carried out in a Bruker diffractometer, D8 Advance 500 model, to study ClayM and Mn/ClayM monolithic samples, previously crushed and sieved. In this case diffractograms were recorded using  $\text{Cu K}\alpha$  radiation and a graphite monochromator. The  $2\theta$  angle ranged from 2 $^\circ$  to 130 $^\circ$ , with a step of 0.03 $^\circ$  and a counting time per step of 45 s. In the case of PILC/ClayM and Mn/PILC/ClayM samples, similar equipment was employed but using  $\text{Mo K}\alpha$  radiation. Measurements were performed from 0.9 $^\circ$  to 49.4 $^\circ$  during 7 h. The tube operated at 50 kV and 50 mA, and the sample turned at 10 rpm. The XRD data were properly processed to allow comparison between diagrams recorded using different radiation. Complementary analysis

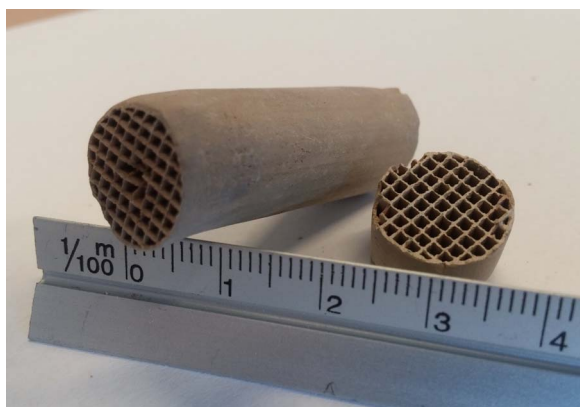


Fig. 1. Image of a typical clay honeycomb monolith extruded in this work.

Download English Version:

<https://daneshyari.com/en/article/4756805>

Download Persian Version:

<https://daneshyari.com/article/4756805>

[Daneshyari.com](https://daneshyari.com)