



High catalytic activity at low temperature in oxidative dehydrogenation of propane with Cr–Al pillared clay

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HIGHLIGHTS

- A montmorillonite was pillared with Al and/or Cr and tested in ODP.
- All catalysts (Al–C, Cr–C, Al–Cr–C) were active in ODP.
- The highest propylene yield (10.3%) was obtained with the Al–Cr–C catalyst at 450 °C.
- Even at 350 °C a promising propylene yield of 9.3% was obtained with Al–Cr–C.

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ABSTRACT

A montmorillonite was pillared separately with chromium and aluminum polyoxocations (Cr–C and Al–C respectively) and also with an equimolar mixture of both polyoxocations (Al–Cr–C). The resulting solids were characterized by scanning electron microscopy, energy dispersive spectrometry, thermal analysis, Fourier transform infrared spectroscopy, X-ray diffraction and nitrogen adsorption at –196 °C. The inclusion of polycations in the interlamellar space led to modifications in the properties of the clay. An eleven fold increase in specific surface area with respect to the calcined starting clay was found for the Al–C, whereas a twofold increase was observed for the Cr–C; the value for the Al–Cr–C was only slightly higher than that for the latter. Diffractograms of the Cr–C showed the occurrence of a Cr₂O₃ phase. Catalytic activity in oxidative dehydrogenation of propane was assayed in the temperature range from 350 °C to 450 °C using Ar/C₃H₈/O₂ (80/10/10) as reactant gas mixture. Propylene selectivity was found to be temperature-dependent, showing a maximum in the studied temperature range for the catalyst containing only aluminum, whereas remaining practically constant for the Cr-containing catalysts. Highly promising propylene yields at low temperature were obtained with the catalyst containing Al and Cr (Al–Cr–C): 9.3% at 350 °C and 10.3% at 450 °C.

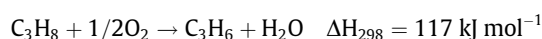
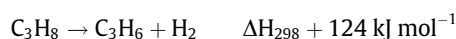
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1. Introduction

Light alkanes, including propane, are abundant in natural gas and as by-products of oil refining and are commercialized mainly for their fuel value. Their transformation into the corresponding olefins, via dehydrogenation or oxidative dehydrogenation, converts them into raw materials for petrochemical industry, thus increasing dramatically their value. Particularly for propane an industrial process has not yet been developed as Cavani et al. [1] assure in a recent review on the topic. The authors conclude: “it

is evident that, in the future, the greatest efforts will be devoted to the study of catalysts and/or reactor configurations that are capable of maintaining high selectivity to propylene under conditions leading to high propane conversion”. In consequence the researchers’ attention is focused still nowadays on the topic.

Dehydrogenation so well as oxidative dehydrogenation is thermodynamically favorable and for propane the reactions are as follows:



Catalytic propane dehydrogenation requires high temperature (over 700 °C) to attain propene yields that assure the economic balance of the process. In these conditions coke deposition on

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the catalyst is unavoidable requiring regenerations cycles to restore catalyst activity [2–4]. Oxidative dehydrogenation of propane (ODP) allows comparable yields at relative lower temperatures (under 600 °C) which in addition to the presence of oxygen in the reaction mixture diminish the risk for coke deposition. The use of lower temperatures and the fact to avoid regeneration cycles contribute to the economy of the process. As the reaction is exothermic high temperatures are reached during the process, that although favorable from a kinetic point of view, they contribute to undesired side reactions as cracking and total oxidation of reactants and products.

As an extra drawback the high temperatures compromise the catalyst structure in detriment of the catalytic performance [5]. Finding a highly active catalyst at low temperature or even at moderate temperatures –but not compromising catalyst's structure– represents a great challenge nowadays. The catalytic activity of chromium in paraffin dehydrogenation –especially C₃ and C₄– for olefin production has been reported. Generally the active species is supported on a solid having a high specific surface area as alumina [6–8], silica [9,10] mesoporous solids [11] and microporous materials [12].

Clays, due to their abundance and low cost, are interesting materials to be used in catalysts synthesis. Their low specific surface area represents a drawback for their direct application. However the smectites, particularly montmorillonites, owing to their high exchange capacity and expandable character, can be transformed into solids with high microporosity and specific surface area, which are referred to as pillared clays (PILC: Pillared Inter Layered Clay). The pillaring technique involves the exchange of the interlayer cations of the clay by bulky ones; the subsequent controlled calcination leads to the formation of oxidic species between the clay layers [13] and generates an open and rigid structure. Polioxocations of aluminum, known as Al₁₃, have been widely used to prepare alumina-pillared clays (Al-PILCs), also polyhydroxy species of Fe, Ti, Cr, Ga as well as of mixed metal cations have been reported and are summarized in comprehensive reviews [14–16]. An improvement of Al-PILCs thermal stability was verified when the polioxocation was prepared by basic hydrolysis of a solution containing Ga and Al in a ratio of 1:12 [17].

Preparation of chromium-polioxocations has been reported by several authors [18–20] and has enabled the synthesis of chromium-pillared clays (Cr-PILCs) [21–28]. Heat treatment conditions –temperature and atmosphere– influence greatly the structural and textural properties of these solids. Most authors report that the basal spacing (*d*₀₀₁) achieved for the Cr-PILC is not stable at high temperatures. Volzone [29] reported a decrease of the specific micropore volume as well as the presence of Cr₂O₃ when the solids were heated at temperatures above 420 °C in the presence of oxygen. Hopkins et al. [19] reported for Cr-PILC a *d*₀₀₁ value of 15.4 Å stable up to 300 °C. The structure of the solid is more stable when the calcination is performed in inert atmosphere instead of air [30,31]. Zhao et al. [25] prepared the pillaring solution using both Al and Cr and showed that thermal stability of the PILC reduced with increasing of Cr/Al ratio. Toranzo et al. [27] prepared Al–Cr mixed pillars by basic co-hydrolysis of their salts. Tomul and Balci [32] prepared Al–Cr-PILCs mixing different amounts of solutions containing each of the hydroxylated species; the resulting solutions were aged before use.

Tzou and Pinnavaia [33] and Moini et al. [34] reported good catalytic activity for Cr-PILCs in the reaction of dehydrogenation of cyclohexane to produce benzene. Mata et al. [28] reported the catalytic activity in propene oxidation of Al–Cr-PILCs prepared using oligomers obtained by co-hydrolysis of the corresponding metal chlorides. Kar et al. [35] used Cr-PILCs as catalysts for octahydroanthrenes synthesis in solvent free conditions. Catalytic activity in oxidative dehydrogenation of propane (ODP) of rare earth

phosphates supported on Al-PILCs is reported by De Los Santos et al. [36] verifying the highest propylene yields in the temperature range from 400 °C to 600 °C.

To improve thermal stability of Cr-PILCs different preparation routes have been proposed: (a) the co-hydrolysis of a solution containing aluminum and chromium salts at different Al/Cr ratios [25,28], the presence of aluminum in the pillaring solution is proposed to improve thermal stability of the PILC; (b) the hydrolysis of the Al₁₃ Keggin polycation in the presence of a chromium salt [26], it has been proposed that chromium can replace aluminum during hydrolysis. In any case no conclusive evidence of mixed species is presented.

The aim of this study was to obtain new and cheap catalysts by pillaring of a Uruguayan montmorillonite with high catalytic activity in the oxidative dehydrogenation of propane. Chromium polyhydroxy cations and Al₁₃ were prepared separately. Solutions containing either one of them or a mixture (Cr/Al molar ratio equal to 1) were used for pillaring a montmorillonite. Structural and textural properties of the PILCs were determined and their catalytic activity in ODP was evaluated in the temperature range from 350 °C to 450 °C.

2. Materials and methods

2.1. Starting material

A raw mineral extracted from Bañado de Medina (32° 23' 0" South, 54° 21' 0" West), Uruguay, was used. Over 80% of it is constituted by a calcium-rich montmorillonite with low sodium and potassium content [37]. Cation exchange capacity (CEC) of the mineral, as determined by the ammonium acetate method (1 M and pH = 7), was 1.12 meq per gram of the dry clay. The interlayer cations were analyzed by atomic absorption spectroscopy and atomic emission spectroscopy. The results in meq/g are as follows: Ca⁺² 0.82; Mg⁺² 0.29; Na⁺ 0.012; K⁺ 0.002 [38]. The raw mineral was oven dried at 110 °C for 24 h, ground and sieved. The fraction with aggregates size less than 250 μm was selected and named as M.

2.2. Preparation of catalysts

The solid M was exchanged with solutions containing Cr and/or Al hydroxylated species.

Al-polyhydroxylation solution was prepared from a 0.1 M AlCl₃ solution over which a 0.2 M solution of NaOH was slowly added while vigorous stirring was kept. Volumes were selected to give a final molar ratio OH[−]/Al³⁺ of 2. The resulting solution was aged for one hour at 50 °C [39]. According to Bottero [40] in those conditions, the 95% of the aluminum is embodied in the Al₁₃ cation.

Cr-polyhydroxylation solution was prepared from a 0.1 M Cr(NO₃)₃ solution over which a 0.2 M solution of NaOH was slowly added while vigorous stirring was kept. Volumes were selected in order to attain a final molar ratio OH[−]/Cr³⁺ of 2. The solution was aged for 24 h at 60 °C [41].

A third solution was obtained by mixing equal volumes of the above aged solutions, resulting in a molar ratio Cr³⁺/Al³⁺ = 1.

Each of the three solutions was added to 10% (w/w) slurry of the solid M. In all cases the volume of the intercalating solution was the necessary to achieve a ratio of 10 mmol of total metal per gram of dry clay and the contact time was 2 h. The resulting solids were separated by filtration and repeatedly washed with deionized water. The exchanged clays obtained (M-samples) were named as Al–M, Cr–M and Al–Cr–M according to the intercalating solution used in the preparation. The M-samples were calcined in air in a tubular furnace, Carbolite, CTF-12/65/550, at a heating rate of 1 °C min^{−1} up to 450 °C, and maintained at this temperature for 2 h. The PILCs thus obtained were identified as Al–C, Cr–C and Al–Cr–C, according

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