



Research paper

Modified clays as catalysts for the catalytic oxidation of ethanol

Alejandro Pérez^a, Mario Montes^b, Rafael Molina^a, Sonia Moreno^{a,*}^a Estado Sólido y Catálisis Ambiental, Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, AK 30 No. 45-03, Bogotá, Colombia^b Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Química de San Sebastián, Universidad del País Vasco, P. Manuel de Lardizabal 3, 20018 San Sebastián, Spain

ARTICLE INFO

Article history:

Received 13 November 2013

Received in revised form 15 February 2014

Accepted 18 February 2014

Available online 24 April 2014

Keywords:

Modification of clays

Pillaring

Delamination

Cooperative effect

Oxidation of ethanol

ABSTRACT

Two methods for modifying a clay mineral by pillaring and delamination were studied to obtain suitable catalyst supports for Co and Cu. The arrangement of the active species and the interaction that they may have with the support will be a fundamental feature for activity and selectivity in the oxidation reactions. Moreover, the use of natural materials such as clay minerals will add value to these materials and allow them to be excellent supports for environmental impact reactions. The combination of transition metals in equimolar ratios leads to cooperative effects between the species, resulting in the excellent catalytic performance in oxidation reactions of VOCs. Based on structural and morphological characterization using XRD, SEM, H₂-TPR, textural analysis and the evaluation of the catalytic activity in the oxidation of ethanol, the delaminated system proved to be a more appropriate support.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

For several decades, modified clay minerals have been an important alternative for the generation of materials with potential applications in catalysis, either as catalysts or catalyst supports, due to their low cost and abundance. Their physicochemical and mechanical properties allow a very wide range of possibilities for structural textural and chemical modifications (De Stefanis and Tomlinson, 2006; Kurian and Sugunan, 2005). The final characteristics of the material can be modulated by varying various parameters of the synthesis such as the nature and mineralogical properties of the solid nature of the modifier species, particle size, material maturation processes, and heat treatments (De Stefanis and Tomlinson, 2006; Pérez et al., 2008).

The process of clay mineral modification can lead to arrangements of the laminar face–face type as in the case of pillared clays, where microporosity is predominant, or edge-type or edge-side edge aggregates, as in the case of delaminated clays, which are predominantly meso and macroporous materials (Carriazo et al., 2007a).

Insertion of large molecules into the clay interlayer space that act as “pillars” and remain separate sheets despite severe heat treatments has emerged as the most suitable method for preventing the loss of physicochemical properties of the material and obtaining a stable microporous solid with a large surface area.

The use of modified smectite clays for pillaring and subsequent employment in oxidation reactions is relatively recent (Mishra et al., 2008; Zuo et al., 2011), particularly their use as supports for transition metals.

On the other hand, the interest in obtaining delaminated clays is primarily because they are materials that have broad pore distributions (meso and macro type porous) and good thermal stability. It is possible to extend their applications as catalysts and adsorbents with high form selectivity to species and large molecules. These textural characteristics favor good dispersion and distribution in the catalyst active phase.

Clays have mostly been used in non-destructive techniques (adsorption) for the removal of VOCs (Arocha et al., 1996; Jarraya et al., 2010; Lake and Rowe, 2005). However, the low efficiency to small percentages of VOCs and complexity in their recovery has motivated the development of more specific and effective methods of removing such contaminants.

Several studies (Pérez et al., 2011; Quiroz-Torres et al., 2010) have focused on catalytic oxidation as an alternative to incineration for the destruction of VOCs. However, the necessity of high temperatures for the removal of some VOCs (>300 °C) and the generation of by-products that could create more contaminants than the initial VOC make obtaining catalysts for this reaction the current challenge.

In this work and in light of the results reported in the literature (Daza et al., 2009; Gamba et al., 2011; Zuo et al., 2009), we selected two methods of modifying a Colombian smectite (pillaring and delamination) to obtain efficient support of the synthesis of Co and Cu catalysts for the VOC oxidation reaction.

2. Experimental

2.1. Starting material

The starting clay mineral (M62) is a smectite from Tolima, Colombia that has been modified and successfully characterized in previous

* Corresponding author. Tel.: +57 1 3165000; fax: +57 1 3165220.
E-mail address: smorenog@unal.edu.co (S. Moreno).

studies (Daza et al., 2009; Gamba et al., 2011). The mineralogical composition shows a montmorillonite content of 62%, with quartz pollutants in low proportions (23%), including feldspar (3%), illite (4%) and kaolinite (2%).

2.2. Modification via pillarization (PIL)

The mineral exchanged with Na^+ was dispersed in water (2% w/v) and allowed to swell for 24 h. The modifier aluminum solution was prepared from a commercial solution of hydrochloride basic aluminum diluted to 0.1 M and aged for 2 h at 60 °C. It was added dropwise to the suspension of the clay mineral (20 meq.g⁻¹) under stirring at 80 °C, and this temperature was maintained for 2 h (Pérez et al., 2008). The resulting suspension was aged for 24 h at room temperature. The solid was washed until the conductivity was close to that of the deionized water and dried at 60 °C. Finally, it was calcined at 500 °C for 4 h (10 °C min⁻¹) to obtain the supports called PIL.

2.3. Modification via delamination (DEL)

The mineral exchanged with Na^+ was dispersed in water at 2% w/v and allowed to swell for 24 h. Subsequently, the suspension was added to a 4% solution of polyvinyl alcohol surfactant (PVA) (Aldrich Co., MW = 26000 and 30,000 g·mol⁻¹) dissolved in water at a surfactant/clay mineral ratio = 1. This mixture was stirred for 30 min at 60 °C (Daza et al., 2009; Gamba et al., 2011). The modifier aluminum solution (shown above) was added dropwise at 60 °C and held at reflux for 24 h. The suspension was subjected to microwave radiation in three intervals of 10 min, each at 640 W and 2.45 GHz using a domestic oven, Sharp Model R-211 HL. The solid was separated by decantation and dried at 80 °C. Finally, it was calcined at 500 °C for 4 h (10 °C.min⁻¹) to obtain the supports called DEL.

Fig. 1 summarizes a scheme obtaining supports from the selected clay mineral.

2.4. Catalyst preparation

The catalysts were prepared by the incipient impregnation method using clay supports prepared as indicated above and amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ appropriate for obtaining catalysts

with a total load weight of 20% metal with equimolar amounts of each metal (Co and Cu) (Huang et al., 2010; Pérez et al., 2011).

2.5. Characterization

Chemical analysis of the catalysts was carried out using X-ray fluorescence by a Philips PW2440 Pro MagiX with samples prepared in pearls. X-ray diffraction was performed by a Philips PW 1710 model with a copper anode. The reducibility of the metals introduced into the clay was evaluated using a Chembet 3000 (Quantachrome) equipped with a thermal conductivity detector and following widely reported methodologies (Gamba et al., 2011). Samples (<250 μm) were previously degassed at 400 °C for 1 h in Ar flow and reduced with 10% H_2 in Ar using a heating rate of 10 °C/min. To study the morphology of the solids, a FEI Quanta 200 in high vacuum and 30 kV voltage was used. Samples were vacuum metallized with gold to a thickness close to 200 Å.

2.6. Catalytic evaluation

Oxidation of ethanol was carried out in a vertical fixed-bed reactor operating in a continuous flow atmospheric pressure, using a total flow of 200 mL/min, 0.200 g of catalyst (sieved <125 μm) and an ethanol concentration of 1000 ppm. The catalysts were pretreated in an air flow at 400 °C for 2 h. The ignition curve was obtained by cooling at 1.0 °C/min from 400 to 50 °C. The conversion was calculated using a mass spectrometer (Balzers Omnistar) based on the disappearance of ethanol and water, and CO_2 production was followed by an online IR detector (VAISALA GTM 220). The curves obtained confirmed a total conversion in all cases, without the generation of intermediates in the reaction.

3. Results and discussion

The Si/Al ratio was calculated from the results of the chemical analyses of the natural clay and the respective modified materials (Table 1). Also shown are the percentages of the compensating cations Na, Ca, K and Mg. The decrease in the Si/Al ratio of the catalyst supports (PIL and DEL) with respect to the starting material (M62) verifies the successful incorporation of Al in the solids.

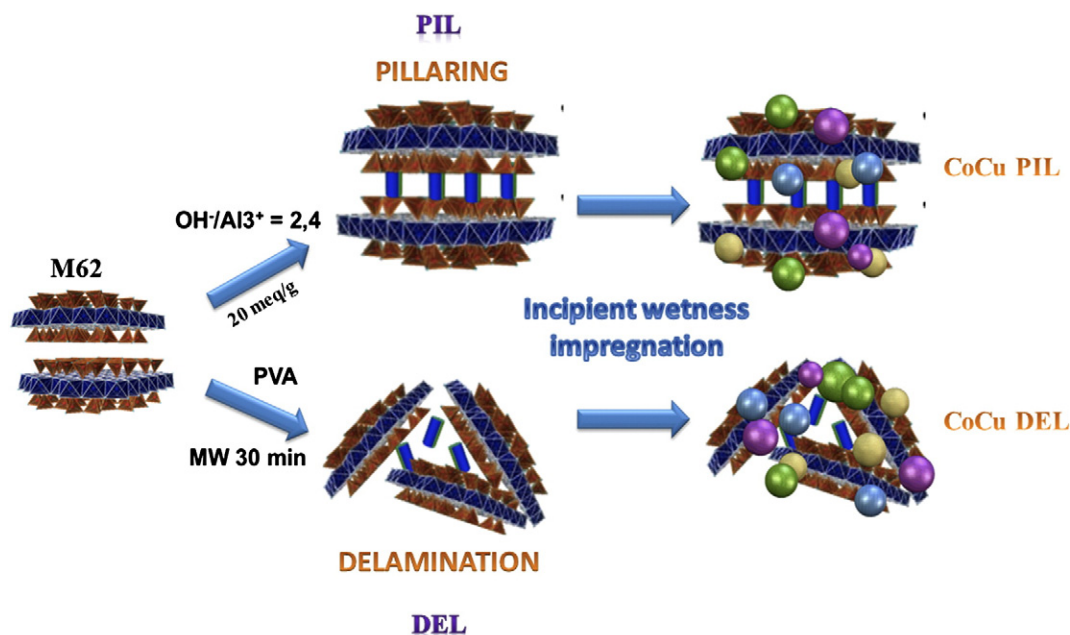


Fig. 1. Scheme of obtaining catalysts.

Download English Version:

<https://daneshyari.com/en/article/1694788>

Download Persian Version:

<https://daneshyari.com/article/1694788>

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