Research paper

# Promoting effect of cerium on the characteristic and catalytic activity of Al, Zr, and Al–Zr pillared clay ☆

S. Mnasri-Ghnimi [a,1], N. Frini-Srasra [a,b,1]

[a] Laboratoire de Physico-chimie des Matériaux Minéraux et leurs Applications, Centre National des Recherches en Sciences des Matériaux, Technopole Borj Cédria, BP 95-2050 Hammam Lif, Tunisia
[b] Départements de Chimie, Faculté des Sciences de Tunis, 1060 Tunis, Tunisia

## ABSTRACT

A series of pillared interlayered clays (PILCs) including Al-, Zr- and Al–Zr-PILC have been prepared and characterized by X-ray diffraction, elemental analyses, $N_2$ adsorption, cationic exchange capacity and IR measurements after n-butylamine adsorption. Cerium introduced in the $Zr^{4+}$ and/or $Al^{3+}$ intercalated solution allows for an improvement of the stability and crystallinity of PILC and creates pillared clays with new properties. The resulting materials were used for the synthesis of 1,3-dioxolane. The addition of cerium has a major influence in this reaction.

© 2013 The Authors. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Although clays are very useful for many applications in the field of catalysis, adsorption and ion exchange, they have one main disadvantage: their lack of permanent porosity. Smectites swell upon hydration, but upon severe dehydration (heating) the layers collapse and the interlayer surface becomes no longer accessible for chemical processes. To avoid this problem, researchers found a way to prop open the clay layers by the introduction of stable pillars in the interlayer region. Pillared clays (PILCs) are an interesting class of 2-dimensional microporous materials. These materials are prepared by the intercalation of organic or inorganic compounds between the silicate layers of the clay, resulting in an increase of basal spacing, pore volume and specific surface area. Due to their high specific surface area and permanent porosity they are very attractive solids for adsorption and catalysis purposes. PILCs are not sufficiently stable and collapse with a loss of specific surface area and catalytic activity at high temperatures. To avoid sintering of the pillared clay, the thermal stability of the pillars must increase. One way to achieve this goal is to introduce mixed-oxide pillars; A1–Ga (Coelho and Poncelet, 1991), A1–Zr (Canizares et al., 1999; Occelli, 1986), A1–Fe (Bergaya et al., 1993; Lee et al., 1989; Oades, 1984), and

Al–Cu (Frini et al., 1997). Another appropriate way to overcome such a problem of collapse is the addition of rate earth. Sterte (1991) found that the incorporation of lanthanide elements in the preparation of the pillaring agent resulted in materials whose basal spacing was greater than that of conventional materials. An improvement of the thermal stability of Al-pillared clays was reported by Tokarz and Shabtai (1985), who prepared pillared clay catalysts by first exchanging the clay with $Ce^{3+}$ or $La^{3+}$, then exchanging these clays with refluxed, partly hydrolyzed $Al^{3+}$ solutions. The migration of the protons from the interlayer to the clay octahedral sheets and the hydrolysis of structural $Si-O-Al$ bonds by protons are largely prevented by the presence of the $Ce^{3+}$ ions (Tichit et al., 1991). The addition of rate earth improves not only the thermal stability but also the adsorptive and catalytic properties of the pillared products. The presence of $Ce^{3+}$ in Al-pillared clays produces a substantial increase in the conversion of n-heptane and in the selectivity towards cracking products owing to the increase in the number of acid centers (Hernando et al., 1996). Similarly, the presence of the $Ce^{3+}$ ions in the Zr-pillared clays has been found to improve its catalytic activity for cyclohexanol dehydration by preserving the Brönsted acid center (Mishra and Rao, 2003).

On the other hand, acetals are an important class of compounds that have found direct applications in diverse areas in the chemical industry such as in perfumes (Bauer et al., 1990; Yang et al., 2005), flavors (Clode, 1979), solvents (Ley and Priepke, 1994), pharmaceuticals (Franchini et al., 2010; Luo et al., 2000), and polymer chemistry (Stao et al., 1990). Acetals are commonly used in protecting group chemistry for carbonyl functional groups because dimethyl acetals and 1,3-dioxolanes are stable under neutral and basic conditions (Chapuzet et al., 2001;

E-mail addresses: saidamnasri@gmail.com (S. Mnasri-Ghnimi), nfrini@gmail.com (N. Frini-Srasra).
[1] Tel.: +216 71 430 470; fax: +216 71 430 934.

Greene, 1981). Acetalization reaction is generally performed in the presence of protic acid catalysts commonly sulfuric acid, hydrochloric acid, phosphoric acid and p-toluenesulfonic acid (Greene, 1981; Ogata and Kawasaki, 1970). These homogenous catalysts are harmful and corrosive. In recent years, green catalysis has been found to be the method of choice for the production of acetals. Acidic clays have many advantages over other catalysts, such as facile modification of acidity via the exchange of cations in the interlayer, ease of handling, non-corrosiveness, low cost and ability to be regenerated. Moreover, they are environmentally benign. The present study aims to evaluate the promoting effect of cerium on the structural and textural properties as well as on the catalytic activity of Zr- and/or Al pillared clays. The characterization of catalyst was performed by X-ray diffraction, $N_2$ adsorption, cationic exchange capacity, chemical analysis, and FTIR spectroscopy.

## 2. Experimental

### 2.1. Materials

The starting material for the pillaring procedure was the sodium form of a purified Tunisian interstratified illite/smectite (Na-bentonite). Its chemical composition expressed in the oxide form/100 g of the calcined sample, is $SiO_2$ 61.38, $Al_2O_3$ 24.80, $Fe_2O_3$ 8.03, $Na_2O$ 3.06, MgO 1.38, CaO 0.13, and $K_2O$ 1.40 with a structural formula of $[Si_{7.43} Al_{0.57}]^{IV}$ $[Al_{2.96} Fe_{0.73} Mg_{0.24}]^{VI} Na_{0.71} K_{0.21} Ca_{0.01}; O_{22}$. The cation exchange capacity (CEC) of Na-bentonite is 78 meq/100 g. Its specific surface and micropore volume are respectively 107 $m^2 g^{-1}$ and 0.06 $cm^3 g^{-1}$.

### 2.2. Synthesis of PILC with single and mixed oxide pillars

PILCs were synthesized by cationic exchange reaction of sodium clays with hydroxy-oligomeric solutions of simple cations ($Al^{3+}$ or $Zr^{4+}$) or mixed ones (Al–Zr, Ce–Zr, Ce–Al or Ce–Al–Zr). Zirconium tetrachloride ($ZrCl_4$) is used as a source of zirconium polycations. In spite of the extensive literature reported about PILC synthesis using zirconium oxychloride $ZrOCl_2$, and zirconyl hydroxyacetate, there is practically few papers that reported the use of zirconium tetrachloride ($ZrCl_4$) as a source of zirconium polycations (Dominguez et al., 1998). The aluminum pillaring solution was prepared using Al $(NO_3)_3$–9$H_2O$ as the precursor salt. The source of cerium was Ce $(NO_3)_3$–6$H_2O$. Pillaring solutions of different cations were prepared by slowly adding of a basic solution (NaOH 0.2 M) to the corresponding cationic solution ($Al^{3+}$, $Zr^{4+}$, Al–Zr, Ce–Zr, Ce–Al or Ce–Al–Zr) (0.1 M) under constant stirring at home temperature until a desired pH was reached (Table 1). In the case of zirconium polyoxocations, the pH was 2.8. This value of pH is the most useful in the literature (Awate et al., 2004; Dominguez et al., 1998). The obtained solution was aged under stirring at room temperature for 24 h. Then, the pillaring solution was added drop wise to a 1 mass% bentonite suspension in distilled water with a metal/clay ratio equal to 10 mmol $g^{-1}$. The mixture was allowed to react at room temperature for 24 h. After intercalation, the resulting products were centrifuged, washed by dialysis with distilled water, dried at 77 °C and finally calcined for 2 h at 550 °C. The samples are labeled as a function of the nature of pillars (Zr, Al, Al–Zr, Ce–Zr, Ce–Al or Ce–Al–Zr).

### 2.3. Catalytic study

The acetalization reaction of 7.68 g (124 mmol) of ethylene glycol and 3.64 g (63 mmol) of acetone in the presence of 0.1 g of PILC was carried out in the autoclave (100 $cm^3$) at 40 °C under autogenously pressure and without solvent. Then, the reaction mixture was cooled and filtered to separate the clay catalyst. The filtrate was treated with 20 ml of distilled water (3 times) to eliminate the residual ethylene glycol. The organic phase was extracted with diethyl ether. After evaporation of the solvent (ether and acetone) the 2,2-dimethyl-1,3-dioxolane was recuperated.

### 2.4. Characterization methods

The X-ray diffraction (XRD) study was done in a 'PANalylitical X'Pert HighScore Plus' device, which operates with Cu Kα radiation.

$N_2$ adsorption–desorption experiments were carried out at − 196 °C on a Quantachrome, USA instrument. The $N_2$ isotherms were used to determine the specific surface areas (SAs) using the BET equation. The micropore volume was determined using the t-plot method and the total pore volume of the samples, Vt, was calculated at $P/P_0 = 0.99$. Before each measurement the samples were outgassed for 2 h at 130 °C.

The chemical analysis of the starting material and modified samples was determined by atomic adsorption, the spectrometer used is of the type AAS Vario.

Cation exchange capacity was determined by Kjeldhal method. Samples of 200 mg were exchanged with the ammonium acetate (1 M) three times and then washed with anhydrous methanol; a final wash was performed with deionized water three times. The amount of ammonium retained was determined using a unit Kjeldhal. The CEC is expressed as milli-equivalent per gram of the calcined sample.

Brönsted and Lewis acid centers were determined by FT-IR spectroscopy method on the basis of adsorption of butylamine. With this method 10 ml of prepared butylamine in a cyclohexane solution was added to 0.1 g of catalyst. The mixture was shaken at room temperature. After drying, each sample was calcined at different temperatures. FT-IR spectra were recorded in the region 1800–400 $cm^{-1}$ on a Perkin-Elmer infrared Fourier transform spectrometer using the KBr pellet technique.

For the $^1H$ NMR and $^{13}C$ NMR study, different spectra were recorded at respectively 300 MHz and 75 MHs on a Bruker AM 300 spectrometer using 5 mm outer diameter spinning sample tubes. Temperature was fixed at 25 °C using a Bruker VT 1000 variable temperature control unit, measured by a calibrated Pt-100 resistance thermometer. The chemical shifts are given in ppm with respect to external TMS reference at 0 ppm.

## 3. Results and discussion

### 3.1. Characterizations of the pillared clays

#### 3.1.1. XRD

Fig. 1 shows the XRD patterns of samples obtained by Zr-, Al- and Al–Zr-bentonite with and without incorporation of cerium. The interlayer spacing in the sample of Na-bentonite increases from 12 to 18.2 after Zr-pillared treatment, indicating an expansion of the clay layer during the pillaring process. This proves that the bigger Zr oligomer must be located in the interlayer space of the bentonite layer and causes structural changes. Furthermore, the interlayer spacing of Zr–G increases from 18.2 to 19.3 after cerium adding into Zr-pillared bentonite. Concerning crystallinity, it can be seen that, the Zr–G sample shows a wider and broad peak: the broadness of 001 diffraction peak mostly reported in the literature (Colin et al., 2005; Maes et al., 1997) indicates the heterogeneity in the size of the pillars and possible delamination of the clay structure due to the low pH of the Zr oligomeric solution. This is not evident for the Ce–Zr–G sample which presents a sharp (001) peak showing that the layers of the clay are homogenously spaced. The increase observed in the basal spacing value and crystallinity of Ce–Zr–G shows that favorable conditions are met to form zirconium pillars by conventional treatment because of the presence of cerium. This observation has been reported by Carriazo et al. (2007), Chen et al.

**Table 1**
pH used for the synthesis of PILC with single and mixed oxide pillars.

| Samples | Al–G | Zr–G | Al–Zr–G | Ce–Al–G | Ce–Zr–G | Ce–Al–Zr–G |
|---------|------|------|---------|---------|---------|------------|
| pH      | 4.1  | 2.8  | 3.8     | 4.1     | 2.8     | 3.8        |