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Pillaring of bentonite clay with Al and Co

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ABSTRACT

This work describes the synthesis and characterization of mixed Al/Co pillared clays. The materials were prepared using different Co concentrations: 10%, 25%, 50%, 75% and 100%. The samples were analyzed by XRD, N_2 physisorption, chemical analysis (AA), ^{27}Al NMR, FTIR and EPMA. The use of small amounts of Co (10% and 25%) resulted in the formation of pillared clays, and the material containing 25% cobalt exhibited superior characteristics compared to an Al pillared clay (basal spacing of 18 Å and BET surface area higher than 300 m^2/g). The ^{27}Al NMR results confirmed the formation of mixed Al/Co pillars; the ratio of the Al^{VI}/Al^{IV} signal intensities decreased, indicating that the Al^{VI} content decreased while the Co content increased. Thus, the Co ions isomorphically substituted for Al in the Keggin ion structure (pillaring agent). When the Co content was 50%, 75% and 100%, pillared clays did not form. Therefore, it is possible to obtain clays with mixed Al/Co pillars for Co contents of up to 25%.

1. Introduction

When oil prices increased in the 1970s and 1980s, pillared clays (PILC) began to attract much attention as catalysts that could overcome the limitations of zeolites. Zeolites have relatively small pores, and therefore, large molecules must be preprocessed before zeolites can be used in the cracking of heavy oil fractions. Pillared clays, which might have larger pores than zeolites, are a promising alternative to zeolites [1].

The pioneers in clay pillarization used amines as pillaring agents; however, organic molecules are not resistant to high temperatures (higher than 250 °C) [2]. Several metals, including Al, Fe, Zr, Cr, Ti, Ga and Mn, have been used to prepare pillared clays [3–5]. In addition, mixed pillars, such as Al/Fe, Al/Ga and Al/Ce/Fe pillars have been used [6–8]. Despite being lodged between the lamellae, the metal oxide pillars are easily accessible due to the lamellar (two-dimensional) clay structure. The choice of pillar depends on the application of the material. Several reviews on the applications of pillared clays have appeared in the literature [9,10].

The pillaring procedure involves the formation, intercalation and subsequent fixation of polynuclear cations between the clay layers. Thus, the lamellar spacing and specific area increase, making these materials attractive catalysts for various reactions. Several methods of preparing pillared clays are outlined in the literature, and variations in the synthesis result in materials with different characteristics [11–13]. However, no general rules for the best synthesis conditions exist.

Pillared clays are interesting because their structures and textural properties can be controlled by the nature and density of the pillars. When pillared clays are employed as supports for active phases, such as metals, the product size can be controlled by the pore size due to a molecular sieve effect [14].

Although various types of pillars are described in the literature, few studies have utilized cobalt pillars. Most of these reports examine pillared clays with Al or another metal that have been impregnated with Co [14–17]. Thomas et al. [18] synthesized a cobalt pillared clay. The Co complexes $[Co_3(OC_2H_4NH_2)_6]^{3+}$ and $[Co_3(OC_2H_4NH_2)_6]^{2+}$ were used as the pillaring agents. However, the authors showed that these complexes have low thermal stability, indicating that the materials are only useful for low-temperature (below 200 °C) catalytic applications.

Urruchurto et al. [19] synthesized mixed Al/Co, Al/Cu and Al/Co/Cu pillared clays. Although the samples had basal spacings of approximately 17 Å, the XRD reflections were rather weak, suggesting the presence of some structural disorder. In addition, the BET surface areas were in the range of 140 m^2/g. Following the reasoning of Sanabria et al. [7] and Galeano, Gil and Vicente [20], when mixed pillars are formed using Al and cations larger than Al, it is assumed that the difference in the ionic radii of the cations causes the basal spacing of the pillared clay to increase. Therefore, mixed Al/Co pillars are expected to have larger interlayer spacings than the corresponding Al pillars.

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Banković et al. [21] also synthesized Al/Co pillared clays. The resulting clay had a basal spacing of 17.2 Å, which was larger than that of the corresponding Al pillared clay (16.0 Å). The Al/Co PILC surface area was smaller than the Al PILC surface area (142 m^2/g vs. 179 m^2/g). However, no further evidence that mixed Al/Co pillars were formed was given.

Kollár et al. [22] also prepared Al/Co pillared clays. However, the authors did not provide the basal spacings, and the BET surface areas were low (64.6 m^2/g for the pillared montmorillonite and 178 m^2/g for the pillared beidellite).

To the best of our knowledge, the few studies of the synthesis of Al/Co pillared clays in the literature do not prove that mixed pillars were formed. Thus, this work aimed to synthesize mixed Al/Co pillared clays and verify their formation for future use in catalytic reactions such as Fischer–Tropsch synthesis.

2. Experimental

In this study, a bentonite clay consisting of mostly montmorillonite was used. To prepare the pillared clays, the following synthesis procedures were employed.

2.1. Pillaring agent synthesis

The concentrations of the $CoCl_2{\cdot}6H_2O$ (Vetec Fine Chemicals), $AlCl_3{\cdot}6H_2O$ (Vetec Fine Chemicals) and NaOH (Sigma–Aldrich) solutions used in the synthesis were all 0.2 mol/L. The NaOH solution was dripped slowly into the Al and Co solutions under constant stirring at 60 °C. After, the pillaring agent remained for 24 h under stirring at 60 °C.

2.2. Clay suspension

Subsequently, 3 g of clay were stirred in 300 mL of distilled water for 2 h at room temperature to hydrate the interlayer cations and expand the lamellae.

2.3. Intercalation

The pillaring agent was added to the clay suspension, and the mixture was stirred for 2 h at room temperature to allow the natural clay cations to be exchanged with the prepared polyhydroxy cations (pillaring agent).

2.4. Stabilization of the pillars

The material was vacuum filtered, washed with distilled water and dried in an oven at 60 °C. The OH/metal ratio was 2, and 0.05 mol (total) of Al or Co were used in all the syntheses.

This procedure was used to synthesize five pillared clays containing different amounts of Al and Co: PCo10Al90 (10% Co, 90% Al), PCo25Al75 (25% Co, 75% Al), PCo50Al50 (50% Co, 50% Al), PCo75Al25 (75% Co, 25% Al) and PCo100 (100% Co).

The novelty of this method compared to the traditional methods described in the literature [1,14] is: the synthesis uses the clay as received (without any purification); the preparation of the pillaring agent takes just one day with heating at 60 °C; the cation exchange and pillaring steps take just 2 h. Another interesting point is that it is the first time described in the literature pillared clays with Co and Al.

The samples were calcined at different temperatures. Some of the samples were first heated at a rate of 5 °C/min to 120 °C and held at that temperature for 30 min. Then they were further heated at the same rate to 250 °C and held at that temperature for 3 h. The rest of the samples were calcined at 150 °C for 30 min and then at 450 °C for 3 h (the heating rate was 5 °C/min). To indicate the calcination temperature of the samples, a suffix was added to their names: c1 for calcination at 250 °C and c2 for calcination at 450 °C.

2.5. [Co–Al–CO_3] LDH synthesis

A cobalt layered double hydroxide (LDH) was synthesized for comparison. For this synthesis, two solutions, A and B, were prepared. Solution A consisted of a mixture of $Al(NO_3)_3{\cdot}9H_2O$ (Vetec Fine Chemicals) and $CoCl_2{\cdot}6H_2O$. Solution B consisted of Na_2CO_3 (Kinetics) and NaOH. The Co/Al molar ratio was 2. First, solution B was heated to 80 °C, and then solution A was slowly dripped into solution B. The solution color changed during this procedure. After the solutions were combined (after approximately 1.5 h), the mixture was pink. The sample was stirred at 78 °C for 24 h. Then the material was washed with distilled water until the pH was approximately 7. Subsequently, the pinkish material was dried at 60 °C.

2.6. Material characterization

The prepared materials were characterized by X-ray diffraction (XRD) on a Bruker D2 Phaser using Cu radiation (λ = 1.54 Å), a 10 mA current, a 30 kV voltage and a LynxEye detector (192 channels). A 0.02° step size, 0.2 mm divergent slit, 0.4 s length and 1 mm anti-air-scattering screen were employed in the measurements. For the Co-containing samples, the detector parameters were adjusted; a low discrimination value of 0.18 V and high discrimination value of 0.25 V were used to minimize the effect of fluorescence. For the other materials, the default values (low discrimination = 0.11 V and high discrimination = 0.25 V) were employed. Infrared vibrational spectroscopic data were collected using a Perkin-Elmer Spectrum 65 FT-IR spectrometer coupled to a Perkin-Elmer Universal ATR sampling accessory. The analysis range was 650–4000 cm^{-1}. N_2 physisorption isotherms were measured using a Micromeritics TriStar II 3020 V1.03 apparatus. Prior to analysis, the samples were degassed for 16 h at 250 or 300 °C (depending on the material calcination temperature) under vacuum. The surface areas were obtained using the BET method, and the micropore volumes and external areas were calculated by the t-plot method using the Harkins-Jura-de Boer t-equation. The total pore volume was calculated at a partial pressure p/p_0 of 0.98. The micropore area was calculated as the difference between the BET and external surface areas. For some samples, chemical analyses were performed using a Shimadzu EPMA (electron probe microanalyzer)-1720H microprobe with an accelerating voltage of 15 kV and BC range of 50 nA to 0.01 nA. For this analysis, the samples were dispersed in a carbon ribbon and metallized with gold. ^{27}Al nuclear magnetic resonance (NMR) spectra were collected using a Bruker AV-400 spectrometer with a BL4 mm probe at a spinning speed of 10 kHz and frequency of 104.26 MHz. Chemical analyses were performed on a Perkin-Elmer Model AAnalyst 200 flame atomic absorption spectrophotometer (FAAS – flame atomic absorption spectrometry). The samples were first digested in 2 mL HF (40% hydrofluoric acid, EMSURE® ISO, Reag. Ph Eur, Merck) and 1 mL of inverted aqua regia (HNO_3:HCl = 3:1) (65% nitric acid (EMSURE® ISO, Merck) and 37% fuming hydrochloric acid (EMSURE® ACS, ISO, Reag. Ph Eur, Merck)).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the natural, PCo10Al90 and PCo25Al75 clays. The shift of the first reflection, which was due to the (001) plane, to smaller angles (2 theta axis) as the Co content increased shows that the basal spacing increased, indicating that pillarization occurred. For the natural clay, the