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Spray-drying for the preparation of Al–Co–Cu pillared clays: A comparison with the conventional hot-drying method

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ABSTRACT

This work reports the synthesis of pillared clays with Al, Al–Co, Al–Cu, and the new ternary system Al–Co–Cu. Natural clay (bentonite) was intercalated with aqueous metal-ion polyhydroxycationic solutions and further dried by either conventional oven-drying or spray-drying. The two drying methods were compared to optimize the pillaring process. The obtained powders were characterized by different techniques, revealing several advantages and an enormous reduction in the process time with spray-drying. X-ray powder diffraction, X-ray fluorescence, and nitrogen adsorption analyses showed successful pillaring of the solids. Textural analyses showed higher surface areas and larger pore volumes for spray-dried pillared clays. Comparable thermal behavior (TGA-DSC analyses) was observed for pillared solids obtained by both drying methods. Scanning electron microscopy (SEM) revealed better control of particle size and shape when spray-drying was used.

1. Introduction

Pillared interlayered clays (PILCs) are an important group of microporous inorganic solids with huge potential for applications in adsorption and catalytic processes [1–4]. Many researchers have shown interest in these materials, whose application as catalysts covers a wide range of reactions, such as oxidation, hydrogenation, dehydrogenation, hydroxylation, esterification, catalytic cracking, and others [5–8]. All of the above-mentioned reactions are potentially interesting in general industrial processes, fine chemistry procedures, or environmental handling. The synthesis of pillared clays involves the initial introduction of (large) polyhydroxycationic species of metal ions, such as Al^{3+}, Fe^{3+}, Zr^{4+}, Cu^{2+}, or Cr^{3+}, by cationic exchange in the interlayer spacing of a smectite-type clay mineral. These voluminous species separate the clay sheets; after drying and calcinations, they yield oxyhydroxide nanoparticles that permanently prop open the clay layers. In addition to improving clay mineral strength and stability, the introduction of inorganic pillars increases the microporosity and provides greater surface area on the solid, thereby facilitating reagents' access to potential active sites for the catalysis of some reactions [9].

The synthesis of PILCs involves several parameters, such as the type of clay mineral, OH/metal ratio, temperature, aging time, and metal ion concentration. Some steps of the synthesis must be stringently controlled; for example, drying and calcination are two important unit operations that determine the dehydration/dehydroxylation necessary to form the oxide nanoclusters (pillars). These operations have a critical influence on the final microporosity of the synthesized solids. Calcination allows higher dehydroxylation and fixes the pillars on the clay sheets, but the drying process has a strong effect on the formation of micropores and consequently the texture of these materials. Drying is described as elimination of the solvent from the pores of a solid, but the removal of solvent might result in collapse of the structure; therefore, the drying operation must be carefully controlled if high porosity is desired [10]. Several drying methods, such as freeze-drying (lyophilization), hot-drying (in an oven), drying under vacuum, air-drying, air-drying after ethanol extraction and supercritical drying have been used for the synthesis of PILCs [11–16]. However, spray-drying is the least studied process for the preparation of this type of solid. The technique is appropriate for producing dried powders with controlled morphology and grain size in a short amount of time because the powder can immediately be obtained from a liquid suspension.

Spray-drying is a unit operation that involves the atomization of a liquid sample (solution, emulsion or suspension) in a hot gas current (usually air) to instantaneously obtain a powder [17–19]. This technology is well established, rather inexpensive and straightforward for tailoring micro-particles by controlling their size and morphology according to the technical conditions [20,21]. By using spray-drying, many powders can be formed with spherical or semi-spherical morphology and regular particle size distribution, depending on the surface tension and rheological properties of the suspension, as well as on the nature of the dispersed molecules. Furthermore, when the suspension consists of colloidal primary nanoparticles, the resultant particles are comprised of nanoparticles that form a nano-structured powder [20].

On the other hand, the synthesis of pillared clays has been widely described in the literature [4–7,13,16,22–24], and several techniques for characterizing their structure and texture have been recently

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Table 1
Elemental chemical analyses (wt.%) of the natural clay (B) and the modified solids dried by the conventional method (B–Al, B–Al–Cu, B–Al–Co, B–Al–Co–Cu) or the spray technique (BSP–Al, BSP–Al–Cu, BSP–Al–Co, BSP–Al–Co–Cu).

Solid	SiO_2/Al_2O_3	Co_2O_3 (wt.%)	CuO (wt.%)	CaO (wt.%)	Na_2O (wt.%)
B	2.89	–	–	2.93	0.65
B–Al	2.31	–	–	0.53	0.75
BSP–Al	2.25	–	–	0.66	0.60
B–Al–Cu	2.32	–	0.71	0.47	0.76
BSP–Al–Cu	2.20	–	0.64	0.41	0.61
B–Al–Co	2.26	0.10	–	0.43	0.67
BSP–Al–Co	2.20	0.09	–	0.34	0.52
B–Al–Co–Cu	2.21	0.11	0.76	0.53	0.61
BSP–Al–Co–Cu	2.18	0.09	0.69	0.38	0.54

reviewed [1,4], but as far as we know, studies on cobalt or aluminum-cobalt pillared clays are very scarce in the scientific databases. Recently, we found that cobalt–copper oxides supported (by wet impregnation) over alumina or on Al-delaminated clays constitute a mixed catalytic system with interesting cooperative behavior for redox reactions [25,26]. Thus, the aim of this study was to synthesize Al–Co–Cu-pillared clays to be used as catalysts in further work. This process was optimized by spray-drying, and to the best of our knowledge, the synthesis of PILCs from this ternary mixed pillar (Al–Co–Cu) has not yet been studied.

2. Materials and methods

2.1. Solid synthesis

A commercial clay (bentonite from Valle del Cauca-Colombia, supplied by Bentocol company), previously characterized [27] and separated by particle size to collect the <2 μm fraction, was used as starting raw material (labeled as B). This natural clay was exchanged with a 1 M $CaCl_2$ solution, washed with distilled water and dried at 60 °C.

For pillaring the clay mineral, several clay samples were exchanged with an appropriate aqueous metal ion polyhydroxycationic solution of Al, Al–Co(10%), Al–Cu(10%) or Al–Co(10%)–Cu(10%). These solutions were prepared from a 0.2 M Al^{3+} solution containing calculated quantities of Co^{2+} and/or Cu^{2+} to obtain molar ratios of 10% ($100 \times Co / (Al + Co + Cu) = 10$; $100 \times Cu / (Al + Co + Cu) = 10$). In all cases, hydrated nitrates (analytical grade Merck) were used as the precursor salts. Then, a 0.2 M NaOH solution was slowly added (dropwise) to the aqueous metal-ion solutions to reach a molar ratio of $OH / (Al + Co + Cu) = 2.2$. The final pillaring solution was used to intercalate the clay samples, 2% clay aqueous suspensions that had been previously hydrated for 24 h, by cationic exchange of the clay mineral with the polyhydroxycations contained in the aqueous medium. A ratio of 20 milliequivalents of total metal ions per gram of clay was used. The pillaring solution was added dropwise to the clay aqueous suspension (2%) under constant stirring at room temperature, and then the resulting suspension was heated with continuous stirring at 60 °C for 3 h. Finally, the solids were removed by centrifugation and washed with distilled water until nitrate free.

Intercalated solids were dried by two methods. One set of solids was conventionally dried at 60 °C in a static air atmosphere in an oven, and another set of solids was spray-dried using a laboratory scale spray-drier LabPlant SD-06 (Huddersfield, England), with a main spray chamber of 1110 mm × 825 mm × 600 mm. The optimal conditions for spray-drying were determined in several previous experiments. A 2% aqueous suspension was fed to the drying chamber at a 10 mL/min flow rate, adjusting the inlet and outlet air temperatures at 180 °C and 80 °C, respectively, with an air flow rate of 100 m^3/h and a compressor air pressure of 4 bar. A 2.0 mm diameter nozzle was used. Finally, all the dried solids were calcined at 400 °C for 2 h under a static air atmosphere using a heating ramp. The solids were labeled as B–Al, B–Al–Co, B–Al–Cu or B–Al–Co–Cu according to the pillaring system. For the spray-dried solids, SP was used in each name, as in BSP–Al–Co–Cu.

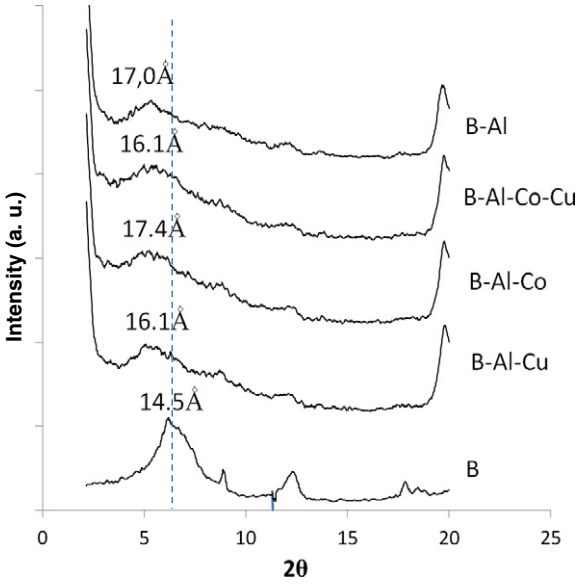

Fig. 1. X-ray diffraction profiles of the natural clay and pillared solids dried by the conventional method (in an oven at 60 °C).

2.2. Solid characterization

The solids were characterized by powder X-ray diffraction (XRD) using a SHIMADZU LAB-X XRD D-6000 equipment (Cu Kα, λ = 1.5406 Å) with 2θ geometry and Bragg–Brentano configuration. Diffractograms were recorded at room temperature, using a 0.02° 2θ step size and 10 s step time. Elemental chemical analyses were performed in a Philips MagixPro PW-2440 X-ray fluorescence spectrometer. Morphological analyses were carried out using a JEOL JSM-5910LV scanning electron microscope, taking several images at different points of the solids. Nitrogen adsorption isotherms were taken at

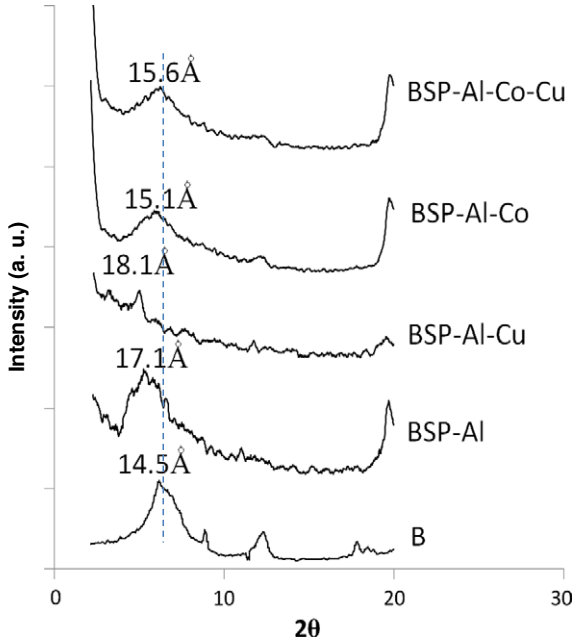

Fig. 2. X-ray diffraction profiles of the natural clay and the pillared solids dried by the spray technique.