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Review Article

A review on characterization of pillared clays by specific techniques

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ABSTRACT

The use of specific characterization techniques, namely Thermal Analysis, Near Infrared Spectroscopy, Ultraviolet–Visible Spectroscopy, Electron Paramagnetic Resonance, Mössbauer Spectroscopy and Neutron Scattering, in the characterization of pillared clays is reviewed. Special emphasis is placed in the information provided by each of these techniques in the characterization of pillared clays.

1. Introduction

In recent years, Pillared InterLayered Clays (PILCs) have been widely used in several applications; in particular in adsorption and catalysis. Thus, the research interest in this family of solids has increased considerably. These solids are obtained from smectite clay minerals with the following three-step synthesis procedure: a) polymerization of a multivalent cation (such as Al^{3+}, Ga^{3+}, Ti^{4+}, Zr^{4+}, Fe^{3+}, and Cr^{3+}, among others), leading to polycations; b) intercalation of these polycations into the interlayer space of smectite clays, involving the substitution of natural exchangeable charge-compensating cations; and c) calcination at moderate temperatures. The latter step is necessary because the solids obtained after the second one, usually called *intercalated clays*, are metastable, like the polycations themselves. Calcination transforms the polycations into stable oxi-hydroxide phases named *pillars*, the solids obtained thus being called *pillared clays*.

Since polycations, and hence pillars, are voluminous, their insertion into the clay mineral layers involves layer separation to a long distance, while at the same time the clay mineral layers prevent the aggregation of the pillars during calcination, maintaining their dispersion. Thus, pillared clays show a characteristic porous structure, influenced by the number and size of the pillars in the interlayer region, which is in turn influenced by the cation exchange capacity of the original clay mineral and the charge of each individual polycation, among other factors. The intense research on PILCs carried out in the last decades means that more than one thousand references can be found in the literature, including several review articles and books reporting synthesis procedures, and the characterization and applications of these solids (only those published in the last decade are cited here as references: Gil et al., 2000, 2008, 2010; Ding et al., 2001; Serwicka and Bahranowski, 2004; Kloprogge et al., 2005; Bergaya et al., 2006).

Two techniques are by far the most widely used in the characterization of PILCs: X-ray diffraction and gas adsorption. The first provides immediate information about the success of the intercalation/pillaring process, evidenced by the shifting of the basal spacing to higher values; i.e. lower angles in the diffractograms. Moreover, such intercalation can be observed even faster by carrying out the diffraction of oriented films obtained by a single drop of suspension during synthesis. Nitrogen adsorption at −196 °C allows the estimation of specific surface area values, reported in almost all works in this field, and information about porosity by application of several models, reported to a lesser extent. These two techniques have been used to confirm the intercalation and pillaring processes. FT-Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy are probably the next most widely used techniques used to characterize these materials. FTIR has been widely used to verify the pillaring process, describing the anchoring of the pillars to the clay mineral layer and cross-linking bonding, and also for analyzing the acid properties of these solids, mainly studied by pyridine adsorption. In the case of NMR, this allows study of the environment of ^{27}Al and ^{29}Si atoms in clays, and in the case of the solids pillared with Al-polycations it also allows the intercalating solutions, and the intercalated and pillared solids, to be studied, thus offering very interesting structural information.

Other techniques have been used to a much lesser extent; in some cases reported only in a few articles. Some of them can be used only

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for a certain type of PILCs: i.e., visible spectroscopy is only applicable to PILCs containing transition elements, while temperature-programmed reduction can be applied to PILCs containing reducible cations (in both cases, only Fe- and Cr-PILCs can be studied). In other cases, the information provided by a given technique is very specific and such a technique might not be easily accessible, explaining its scant use in the study of these solids (e.g., Neutron Scattering). However, the information afforded by these specific techniques about the properties of pillared clays may be very interesting, and this is why we were prompted to review their usefulness for the study of these solids.

2. Specific techniques for characterization of pillared clays

As indicated earlier, besides the techniques most frequently used for the characterization of pillared clays – X-ray diffraction, nitrogen adsorption, infrared spectroscopy and nuclear magnetic resonance – many other techniques have been used, although to a lesser extent. Among them all types of techniques may be cited: spectroscopic techniques such as Ultraviolet–Visible, Near Infrared, Electron Paramagnetic Resonance or Mössbauer Spectroscopy; thermal techniques such as Thermogravimetry–Differential Thermal Analysis, Temperature Programmed Reduction, etc. Although an exhaustive review of all the studies carried out on pillared clays using these techniques is out of the scope of this short review, some relevant points of these studies are addressed in ensuing sections.

2.1. Ultraviolet–Visible Spectroscopy (UV–Vis)

As indicated, Fe^{3+} and Cr^{3+} are the only *d*-block elements used for the intercalation of pillared clays, and hence the only cations studied by visible spectroscopy. However, two important points should be noted before continuing. One is the fact that the UV–Vis region has been studied in some clay minerals, mainly in those pillared with Ti and Zr species, obtaining information from the Ultraviolet region (this information is not reviewed here). The second is that visible spectroscopy has also been used to study *doped* PILCs; that is, pillared clays into which small amounts of other element(s) have been incorporated by adding it (them) to the intercalating solution. The same is applicable when transition elements are incorporated by impregnation onto pillared-clay minerals. Although these solids are evidently very important, in a strict sense, the transition elements are not the constituents of pillaring solutions. Additionally, many elements have been incorporated in pillared clays, such as V, Cr, Mn, Co, Ni, Cu, Pd, Ag, and Pt, among others, and a review of these solids is beyond the scope of the present study. Thus, only the *true* pillared clays containing Cr- or Fe-polycations will be considered here.

In the case of Cr-PILCs, the polymerization of Cr^{3+}, and hence the nature of the intercalating species, can be monitored by visible spectroscopy. Polymerization of this cation leads to the formation of the dimer $[Cr_2(OH)_2(H_2O)_8]^{4+}$, the trimer $[Cr_3(OH)_4(H_2O)_9]^{5+}$, the tetramers $[Cr_4(OH)_6(H_2O)_{11}]^{6+}$ and $[Cr_4(OH)_5O(H_2O)_{10}]^{5+}$, and even of a pentameric and a hexameric polycation, hitherto not described in detail. The position of the two bands appearing in the visible spectra varies strongly: between 408–426 and 575–584 nm, depending on the degree of polymerization, the ratio between their extinction coefficients also varying between 1.17 and 1.60 (Finholt et al., 1981; Thompson and Connick, 1981; Stünzi and Marty, 1983; Spiccia and Marty, 1986; Spiccia et al., 1987, 1988). The nature of the polymeric species present in a given solution can be deduced by comparing the spectra with reported results.

Brindley and Yamanaka (1979) used these data to conclude that their intercalating solution may have been composed of the dimer $[Cr_2(OH)_2(H_2O)_8]^{4+}$, while Volzone et al. (1993) and Volzone (1995, 2001) described the change in color of the intercalating solution, obtaining peaks at 424 and 585 nm, although they did not discuss the composition of the solution in detail. Toranzo et al. (1997) and Mata et al. (2007) studied the polymerization process of a series of Al–Cr mixed solutions, from the Al alone- to the Cr alone-containing cases. Those authors reported that the degree of polymerization depended on the Al^{3+}/Cr^{3+} ratio, since the acidity of both cations elicits a strong competition by the OH^- added to the solution during the polymerization process. The formation of the trimer was found for the pure- and rich-chromium solutions, while the dimer, and even no polymerization of this cation, was found when the more acidic Al^{3+} was the major cation in the solution. The nature of the polycations once incorporated in the saponite clay may be different to that of the polycations in solution. It should be considered that the intercalating solutions are added to clay suspensions, which are slightly alkaline ($pH \approx 8$), which can alter the polymerization before the polycations enter the basal spacing.

Diffuse reflectance spectra of the intercalated solids reveal three well defined bands, close to 230, 420 and 590 nm, corresponding to the three spin-allowed transitions in Cr^{3+}, and a shoulder close to 690 nm, corresponding to the spin-forbidden ruby line (Fig. 1). The position of these bands changes, depending on the Cr^{3+}/Al^{3+} atomic ratio in the intercalating solution. The position of the bands also changes strongly under calcination, shifting to lower wavenumbers: that is, the crystal field stabilization energy and the Racah parameter also decrease. This allows a follow-up of the transformation from the polycations (fairly ionic, with hydroxyl groups and water molecules) to the covalent pillars, which are close to Cr_2O_3-eskolaite, as shown by the evolution of the β parameter, which is closer to 1.0 in the pillared solids (Table 1, Vicente et al., 1998).

The incorporation of iron to PILCs does not elicit such clear effects, since Fe^{3+} in the polycationic species does not have spin-allowed bands, owing to its d^5 configuration. Belver et al. (2004a) have reported the DR-UV–Vis spectra of mixed Al–Fe-PILCs prepared from saponite and solutions containing various Al/Fe ratios (Fig. 2). These spectra show a broad band with a maximum in the UV region, close to 300 nm, and a large shoulder at higher wavelengths, reaching the visible region and typical of the charge transference of Fe^{3+} in hydroxo-complex species. These patterns were similar for all Fe samples, and clearly differed from that of the Fe-free Al-PILC, which showed a narrower band in the UV region, also due to the charge transfer process. While calcining the intercalated solids, no changes in the spectra were observed, although the color of the samples changed from pale brown to dark brown or even black, the wide charge transference shoulder remaining almost unchanged.

2.2. Near Infrared Spectroscopy

Near Infrared (NIR) is the region of the electromagnetic radiation with a wavelength between 800 and 2500 nm and a wavenumber between 12,500 and 400 cm^{-1}, and it is the most energetic infrared region, close to the visible region. It has been much less used than the *usual* infrared radiation: between 4000 and 300 cm^{-1}. In fact, this spectroscopy is carried out on UV–Vis devices, not on IR apparatus. Overtones and combination bands are the effects observed by means of this spectroscopy.

NIR spectroscopy has been little used for the characterization of pillared clays. Vicente et al. reported the characterization of pillared Ballarat saponite (Vicente and Lambert, 1999, 2001; Vicente et al., 2004) with this technique. The overtone of the stretching vibration of the structural OH of the original saponite was found at 1389 nm, while the overtone of this vibration in water molecules was observed as two effects at 1408 and 1461 nm, suggesting the presence of two kinds of water molecule, as corroborated by the fact that these effects were not observed in the intercalated solid, in which a broad band was observed at this position. The $\nu + \delta$ combination band of water was reported at 1907 nm, while that from structural OHs appeared as