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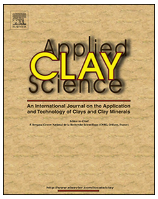

Research paper

Investigation of the initial stages of the montmorillonite acid-activation process using DFT calculations

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ABSTRACT

Many important properties of the clay minerals such as montmorillonite (Mt) arise from their surface chemistry especially when this material is submitted to an acid activation process which will result in materials catalytically active for a variety of reactions. The acid activation preferentially occurs on the edge surfaces, in this sense *ab initio* calculations were performed in order to determinate the most probable models for (010) and (110) surfaces in both pyrophyllite and Mt clay minerals, the edge stability, the initial stages of the acid activation process and the main acid sites present in the structures. The calculations predicted that the (110) edge surface is more stable than the (010) edge surface at pyrophyllite, on the other hand, at Mt the (010) surface has shown to be more stable, thus the pyrophyllite edge surfaces should not be used as representative models of Mt edge surfaces. The microstructural evolution of the Mt during the acid activation was investigated by ^{29}Si and ^{27}Al SSNMR simulations and these calculations could assist in the correct assignment of the silicon and aluminum chemical environments. The reactivity of the surfaces was evaluated and the calculations indicate that the acid character of the acid-activated Mt mainly comes from the H sites present in silanol and aluminol groups. These sites might be responsible for the catalytic activity of these materials.

1. Introduction

Clay minerals are considered very promising materials due to low cost, high availability and simple and inexpensive process of activation. Acid-activation is a chemical treatment typically used on clay minerals such as kaolinite (Yan et al., 2018), halloysite (Fu et al., 2017) and montmorillonite (Zatta et al., 2013; Wang et al., 2010) in order to obtain materials with enhanced surface properties toward environmental, technological and industrial applications. The resulting compound present high surface area, pore volume and density of Lewis and Brönsted sites (Komadel, 2016; Zatta et al., 2013; Wang et al., 2010).

Acid-activated clay minerals have proved to be effective catalysts for tetrahydropyranylation of ethanol, deacetylation of benzaldehyde (Wallis et al., 2007), catalytic cracking of petroleum (Tong et al., 2014; Moraes et al., 2018), and catalysts supports for $ZnCl_2$ Friedel-Crafts alkylation (Rhodes et al., 1991). Santos et al. (2016), Zatta et al. (2012, 2013, 2014) and Kanda et al. (2017) evaluated the role of acid activated clays in the methyl or ethyl esterification of free fatty acids (FFA) to obtain Biodiesel, a biodegradable and environment friendly fuel from effective renewable sources. Biodiesel is normally obtained from esterification of FFA and transesterification of vegetable oils and animal fats with linear primary alcohols with short alkyl chains and these solid acid catalysts can simultaneously catalyze both reactions. The alteration of the acid activated clay minerals by functionalization of the leached groups with organic molecules, which can hydrophobize the basal surface, constitutes a new front because that result in more efficient and effective catalysts and can also be applied in the field of materials polymer nanocomposites (Moraes et al., 2018; Yan et al., 2018; Kooli et al., 2005). The use of the activated material as sorbent toward some environmentally hazardous contaminants have also been reported (Wang et al., 2010).

The acid-activation consists of the reaction of clay minerals with a mineral acid solution, commonly sulfuric, hydrochloric, nitric and phosphoric acids. It is broadly accepted that in early stages of the acid attack, the hydrated cations naturally present in the interlayer space are exchanged by hydrated protons, then, the H^+ penetrate into the layers as a result, there is the leaching of the metals. During decomposition stage, octahedral cations are preferentially released from the layered structure creating Lewis and Brönsted acid sites that must be responsible for the observed catalytic activity of these materials (Yan

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et al., 2018; Fu et al., 2017; Komadel, 2016; Zatta et al., 2013; Wang et al., 2010). In the case of Na^+-Mt, the decomposition is accompanied by the decrease in the Al, Mg, Fe and Na contents and consequently by the increase in the Si/Al molar ratio (Komadel, 2016; Zatta et al., 2013; Zatta et al., 2012; Wang et al., 2010; Yang et al., 2006). The precipitation of amorphous silica with a three-dimensional framework was also identified during the extensive acid activation (Komadel, 2016; Hongping et al., 2002). The extent of these modifications depends on the type and origin of the clay mineral and the conditions of the acid-activation, such as the acid concentration, acid strength, acid/clay mineral ratio, time and temperature of the reaction (Komadel, 2016; Zatta et al., 2013; Yang et al., 2006; Komadel, 2003).

The main techniques used to characterize this process, that provide substantial evidences on the structural modification, are chemical analysis, X-ray diffraction (XRD), ^{29}Si and ^{27}Al solid state nuclear magnetic resonance (SSNMR) and Infrared spectroscopy (IR) (Komadel, 2016; Bergaya et al., 2013). The increase of the Si/Al ratio can be observed by chemical analysis of the solid or leached solutions, indicating that the octahedral cations were preferably leached (Zatta et al., 2012; Yang et al., 2006). The XRD analysis performed during the acid activation showed that the 001 reflection became progressively broader and less intense compared to precursor, consequently the partial delamination of the structure with an increase in time and acid concentration can occur (Zatta et al., 2013; Wang et al., 2010; Okada et al., 2006). In general, mild activations with dilute acid are recommended if the intension is to obtain less leached structures. 100 is one of the reflections that contribute to the edge surfaces of Mt. and almost disappears with the acid-attack, indicating that H^+ attacks preferentially the edge surfaces (Wang et al., 2010). In IR spectra the bands related to Al-OH-Al, Al-OH-Mg and Al-OH-OSi vibrations decrease in intensity and thus reflect the leaching in octahedral sheets (Bergaya et al., 2013; Wang et al., 2010; Reddy et al., 2009). By means of ^{29}Si and ^{27}Al SSNMR have been possible to evaluate locally changes in coordination of the Si and Al cations before and after acid activation (Borah et al., 2010; Okada et al., 2006; Hongping et al., 2002).

The edge surfaces are preferentially attacked by mineral acids, however crystallographic planes that contribute predominantly to the edge surfaces of the clay minerals have not been conclusively defined (Komadel, 2016; Bourg et al., 2007). The interfacial acid chemistry of the edge planes is very complicated due to the high surface heterogeneity and the experimental evidences is lacking, thus isolation of the edges is a difficult task. In this sense some theoretical works have been published with the purpose of analyzing the structure and stability of edge surfaces of the 2:1 dioctahedral phyllosilicates (Newton et al., 2017; Kwon and Newton, 2016; Lavikainen et al., 2015; Liu et al., 2014; Martins et al., 2014; Kremleva et al., 2012; Liu et al., 2012; Yang et al., 2006; Churakov, 2006). In most of these works, pyrophyllite ($Al_2[Si_4O_{10}](OH)_2$) has been used as simplest structural model to represent all clay minerals because of its chemical simplicity, lack of isomorphic substitutions in the layers and hydrated counterions in the interlayer space. Some of these theoretical works suggest that due to the symmetry and stability, the face (110) is considered the most dominant followed by face (010) for pyrophyllite. These conclusions are also extended to other clay minerals (Kwon and Newton, 2016; Lavikainen et al., 2015; Martins et al., 2014; Churakov, 2006), however significant influence of the isomorphic substitutions in edge-water interfacial structures was detected by Liu et al. (2012), consequently the stability order and the physico-chemical properties might also be affected.

The versatile chemical and physical properties of the Mt mostly arises from diversified structure arrangements and composition, thus they are valuable in various applications such as adsorption and catalysis. Most of their properties are related to the surface chemistry in aqueous solution, large surface area and chemically active surfaces, in this way, models closest as possible to the true structure of the material should be used to represent a clay mineral such as Mt.

In the present work, a comprehensive DFT study on the edge surfaces of the acid-activated Mt is introduced. Initially, a survey over a range of Mt and pyrophyllite edge geometry variations for (110) and (010) planes was performed and after the Gibbs free energy of the distinct surfaces as a function of water coverage was estimated in order to distinguish the most probable edge structures. The process of acid activation was investigated, and the resulting models were characterized by simulation of the ^{29}Si and ^{27}Al SSNMR parameters. To access the reactivity of the main surface sites, the acid-basic properties were examined by the absorption of the probe molecules (CO and NH_3) on the Mt acid-activated surfaces. The changes in the electronic and acid-basic properties were also evaluated by projected density of states (PDOS). The structural characterization of the acid-activated edges and the Brönsted and Lewis acid sites are still a complex task that could be clarified by further theoretical calculations.

2. Computational details

2.1. Methodology

Ab Initio calculations were performed using the codes available within the QUANTUM ESPRESSO package (Giannozzi et al., 2009), which implements the Density Functional Theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) with periodic boundary conditions and a plane-wave basis set (Makov and Payne, 1995). The effect of exchange-correlation (XC) potential was explored by Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (Perdew et al., 1996). The inclusion of dispersion corrections was done according to the DFT-D2 scheme (Grimme, 2006). Valence orbitals were described with PAW for all elements with a cutoff value of 65 Ry. Integrations over the Brillouin zone were carried out with a 2 × 2 × 1 Monkhorst-Pack grid (Monkhorst and Pack, 1976). The simulation of SSNMR parameters was performed with the gauge including projector augmented wave (GIPAW) approach (Pickard and Mauri, 2001; Yates et al., 2007). The vibrational modes were obtained from phonon calculations, which were based on the harmonic approximation by density functional perturbation theory (DFPT) (Baroni et al., 1987, 2001) at the Γ q-point. The vibrational data were used to calculate both the contribution of the lattice thermal vibration and the zero-point energy (ZPE). The Gibbs free energy (G) can be calculated using the equation $G = H - TS$. The enthalpy H(T) and the entropy S(T) were calculated for the systems in the solid state by statistic thermodynamics formulations, including translational and rotational states, beyond vibrational and electronic, as done in our previous works (Fonseca et al., 2017b; Fonseca et al., 2017a; Moraes et al., 2016; Alvim et al., 2013; Vaiss et al., 2011).

2.2. Structural models

The bulk models for pyrophyllite and montmorillonite were constructed based on the crystallographic parameters found for Drits et al. (2012) and Viani et al. (2002) respectively. The cell parameters reported for pyrophyllite are $a = 5.1600$ Å, $b = 8.9660$ Å, $c = 9.3400$ Å and $\alpha = \gamma = 90$ and $\beta = 100{,}5^\circ$ (Drits et al., 2012; Lee and Guggenheim, 1981). For Mt structure was used the more stable model for the composition "M-M" obtained in our previous work (Fonseca et al., 2016). In these models, only isomorphic substitutions of Al^{3+} by Mg^{2+} in the O-sheet (octahedral sheet) were evaluated. Some XRD data indicate a decrease of the basal spacing because of the substitution of Ca^{2+}, Na^+ or K^+ intercalated counter-ions by hydrated protons (Moraes et al., 2018; Zatta et al., 2013). For these simulations the hydrated protons, with four water molecules, were used as counter-ions resulting in the basal spacing reported by Yang et al. (2006) around 12.3 Å. For both structures a supercell $2\times1\times1$ was used and the molecular formulas are $[Al_8][Si_{16}O_{40}](OH)_8$ for pyrophyllite and $(H^+)_2.8H_2O[Al_6Mg_2][Si_{16}O_{40}](OH)_8$ for Mt. The free molecules used in this work were optimized using a cubic supercell of 20 Å × 20 Å × 20 Å with just one molecule.