

DFT investigation of Montmorillonite edge surfaces stability and their acid-basic properties in Biodiesel production context

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Abstract: Renewable energies make up the industrial sector with the greatest growth in the world. The synthesis of biodiesel from renewable biological sources, including animal fats and vegetable oils, has received considerable attention due to its environmental advantages and sustainable production in comparison with fossil fuels [1]. In general, biodiesel is produced by transesterification of vegetable oils or animal fats or by esterification of fatty acids with short chain alcohols, in homogeneous or heterogeneous catalytic conditions. Heterogeneous catalysis based on clays such as Montmorillonite (Mt) have received considerable attention due to their environmental compatibility, low cost, selectivity, thermal stability and recyclability [2].

Montmorillonite is classified as a 2:1 cationic exchanger phyllosilicate family and their acid properties can be enhanced by acid activation, these include: the edges of the crystals are opened and Al^{3+} and M^{2+} cations of the octahedral sheet are leached from the structure, causing an increase in both surface area and pore diameter. The acid-activated Mt proved to be reusable, besides presenting structural improvements and maintenance of catalytic activity. It show to be a promising catalyst for the production of fatty acid esters by esterification of different fatty materials [2,3].

Crystallographic planes that contribute predominantly to Mt edge surfaces are (010) and (110) and they are the catalytically active plans in these applications. In the present work, a comprehensive DFT study on the stability of Mt edge structures is introduced. The aim is to carry out a survey over a range of Mt edge geometry variations for (010) and (110) planes, estimate the Gibbs free energy of the surface formation in order to distinguish the most probable edge structures. To assess the reactivity of these sites, we examined the acid-basic properties by adsorbing a probe molecule CO on the Mt acid-activated surfaces. The changes in the electronic and acid-



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basic properties were also investigated by density of states calculations and projected density of states. Solid-State Nuclear Magnetic Resonance analyzes of ^{29}Si and ^{27}Al were performed with the neat and acid-activated Mt. To better understand the reaction mechanism, the theoretical study of the aspects of the esterification reaction catalyzed by Mt edge surfaces were also done.

The quantum mechanical calculations were performed using the codes available in Quantum ESPRESSO (QE) package [4]. Electronic structure calculations were based on density functional theory (DFT) implemented with periodic boundary conditions using plane wave functions as basis set. The electronic correlation and exchange terms were employed using GGA with the PBE functional. The NMR calculations was performed by means of gauge including projector augmented wave (GIPAW) method.

In the presence of water, the stabilization of the lateral facets is achieved through chemisorption of H_2O molecules. Surface Gibbs free energy, ΔG_{surf} , as a function of the water coverage of the (010) and (110) facets are 0.55 and 0.70 kcal mol $^{-1}$ Å $^{-2}$ respectively. Thus, the (010) surface was found to be the most dominant face for Mt. The acid-activated Mt surfaces were simulated and the reactivity of the Al_V sites was checked by means of the CO adsorption. CO is a common Lewis basic probe molecule used to describe the Lewis acidity. The data confirm that the sites of the face (110) are slightly more acid than the sites of the face (010), the adsorption energies were -5.9 kcal/mol and -4.9 kcal/mol, respectively. The density of states (DOS) shows that the gap found for the Mt bulk is greater than the gap of both edge acid-activated surfaces, 4.9 compared to 4.6 and 4.3 regarding to (010) and (110), respectively. The edge (110) is slightly more acid. The projected density of states (pDOS), shows that the H^+ sites present in the hydroxyl groups linked to Si atoms (HO-Si sites) on the surface and the protons present in the hydroxyl groups (HO- Al^V sites), are more acidic than the surface Al_V sites for both acid-activated surfaces. Probably these are the sites responsible for the catalytic activity of the acid-activated Mt. By means of NMR simulation of ^{27}Al and ^{29}Si it was possible to characterize both the Al^IV and Al^V sites on the edge surfaces in accordance with the propositions made in literature. The attribution of affected Si environments by the site Al^IV was also be discussed. Based on the adsorption energies, we can infer that the esterification mechanism begins with the adsorption of acetic acid, better stabilization of the molecule by both surfaces compared to methanol. The formation of alkoxide has also been verified and does not occur on the surfaces.

Key-words: Montmorillonite, Clay minerals, Edge surfaces, *Ab initio* calculations, Biodiesel, Heterogeneous catalysis.

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