

Theoretical study of the molecular fragmentation mechanism of the hybrid δ -FeOOH/PMMA

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Abstract: The organic-inorganic hybrid materials are synthesized using an organic phase comprised of polymers and an inorganic phase which may be a variety of materials, such as metal nanoparticles, oxide nanoparticles, nanotubes or clays. The synthesis of these materials with optimized properties constitutes an area in constant expansion, with potential application in the area of catalysis and chemical sensors [1,2]. The use of magnetic materials, to synthesize inorganic organic hybrids with polymer matrix and developed to explore as physical and chemical properties. The polymers may be shaped to allow inorganic particles to be incorporated. Hybrids based on poly(methylmethacrylate) - PMMA and iron oxides have been studied in recent years, especially with magnetic iron oxides. The magnetic properties are guaranteed only if they are found in a maximum dispersion of iron oxide in the polymer matrix, PMMA is considered a good dispersant of magnetite nanoparticles. Among iron oxide oxides, ferroxhyte (δ -FeOOH) attracted particular attention to its stability in biochemical media. Due to its superparamagnetic properties, it is a potentially interesting material to be used in modern medicine. Despite its great importance, detailed computational and experimental work on this subject soon appeared [1,3]. Thus, this work aims to propose and understand the mechanism of molecular fragmentation of the hybrid δ -FeOOH/PMMA using theoretical calculations. The theoretical study used the ADF package with the DFT method, the functional density PBE. The set of functions of the Slater type TZP. The computations performed for the fragmentation mechanism of the δ -FeOOH/PMMA hybrid are described in Figure 1. According to the experimental data using the PMMA-maghemite hybrid, the order of loss intensity of the fragments is: $\text{COH}^+ > \text{CH}_3^+ > \text{CO}_2\text{CH}_3^+$. However the order of stability found by theoretical calculations was $\text{CH}_3^+ > \text{COH}^+ > \text{CO}_2\text{CH}_3^+$. The activation energy (ΔE) for COH^+ was 56 kcal.mol⁻¹ higher than that of CH_3^+ . In comparison to CO_2CH_3^+ , the difference of ΔE is 119 kcal.mol⁻¹ and 175.29 kcal.mol⁻¹, respectively. The order of theoretical stability found showed good agreement with previously published experimental studies. Thus, the kinetic control can occur in the process of δ -FeOOH/PMMA fragmentation.



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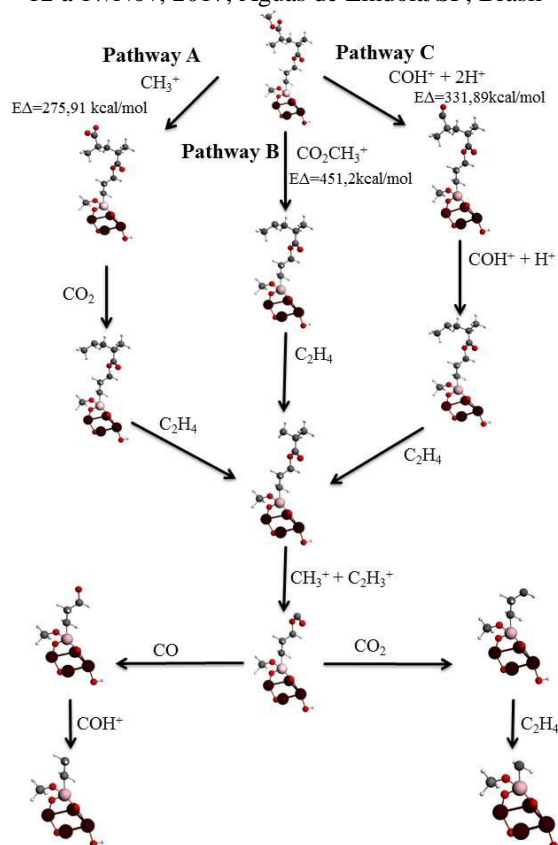


Figure 1: Fragmentation mechanism of δ -FeOOH/PMMA hybrid.

Through the theoretical calculations it was possible to predict and propose a mechanism of fragmentation for the material. Allowing to discuss the best pathways of formation of the fragments and the chemical factors that influence the losses.

Key-words: DFT, PMMA, Feroxyhyte, fragmentation mechanism

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