DOLOMITE SURFACE MODIFICATION WITH TITANIA AND SILICA PRECURSORS AND ITS MORPHOSTRUCTURAL AND THERMAL CHARACTERISATION

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The aim of the paper is to modify the surface of dolomite with titania (TiO_2) and silica (SiO_2) precursors, in order to use it as a potential reinforcement material in a polymeric matrix or for environmental applications (photocatalyst for the degradation of organic pollutants based on TiO_2). The dolomite surface modification was performed by 2 methods. The first method consisted in modifying the direct dolomite surface with SiO₂ and TiO₂. The second method consisted in the initial treatment of dolomite with TEOS, in order to form silanol bonds, followed by the addition of SiO₂ and TiO₂ precursors. The obtained powders were characterized by FTIR, SEM-EDS and DSC-TG. The FTIR spectra prove the formation of the silica network while the samples modified with PDMS exhibit the characteristic peaks of methyl groups from PDMS. In EDS, the presence of the characteristic elements of dolomite (calcium, magnesium, oxygen and carbon) can be observed. When analyzing the modified dolomite powders the presence of titanium and silicon can be observed. The characteristic morphology of the dolomite is preserved in all the samples but, the surface of the larger particles is decorated with smaller particles proving the functionalization of the dolomite, according to the two routes. The thermal analysis is characteristic for dolomite-based materials, the main difference between the samples appearing as a consequence of the burning of the organic part of PDMS, which occur between 400 and 600°C.

Keywords: Dolomite, SiO₂, TiO₂.

INTRODUCTION

Dolomite is a mineral composed of layers of carbonate ions (CO_3^{-2}) separated by alternating layers of the calcium (Ca^{2+}) and the magnesium (Mg^{2+}) ions. Dolomite has properties similar to calcite (CaCO₃), but is harder and has a higher resistance to acid attack (DeArmitt, 2019). Due to its high abundance in nature, dolomite has a low price (Correia et al., 2015). Dolomite is considered a promising catalyst in obtaining biofuel, due to its composition (mainly CaCO3 and Mg), which is decomposed at high temperatures (thermal activation/calcination) into CaO and MgO (Ñústez-Castaño et al., 2019). Other applications of dolomite include: adsorbent for retaining heavy metals (Zn, Ni, etc.) from wastewater, photocatalyst for degradation of organic pollutants (bisphenol A, chlorophenols, etc.) in the presence of UV light (Nagase et al., 2014), filler in various polymeric matrices (polyester resins, alginates, polypropylene, etc.) (Saidi et al., 2019; Huang et al., 2019; Ozdemir et al., 2017). Although dolomite can be used in a wide range of applications, it is not exploited to its true potential, at the industrial level. This is because it requires additional surface treatments to induce specific features of interest. These functionalities are reflected in improved mechanical, chemical, flame retardant properties, etc., which makes it a viable material at the industrial level, the

Dolomite Surface Modification with Titania and Silica Precursors and Its Morphostructural and Thermal Characterization

quality / price ratio being superior to carbon nanotubes, carbon fibers, etc. Therefore, this paper aims to modify the surface of dolomite powder with SiO_2 and TiO_2 precursors, by two simple methods, in order to use it as a potential reinforcing material in polymer matrices or for environmental applications (photocatalyst for degradation of organic pollutants based on TiO_2).

MATERIALS AND METODS

Materials

The following raw materials were used in the experiments: Dolomite powder type DOLOFLOR, with 30-33% CaO, 18-20% MgO, pH=9.67, from SC CEMROM SA; Tetraethyl orthosilicate (TEOS) - reagent grade, 98%, 208.33 wt%; Poly(dimethylsiloxane) – viscosity 500cSt (25° C) (lit.), mol wt ~17,250; Titanium (IV) isopropoxide, \geq 97%, molecular weight: 284.22, density: 0.96g/mL at 20°C (lit.) from Sigma Aldrich, Ethyl Alcohol – for analysis, molecular weight: 46.07 acquired from Chimreactiv SRL.

Method

Dolomite powder was treated according to a methodology published by Sonmez *et al.* (2019).

Method 1: 100 g of dolomite was transferred to a plastic container over which excess ethanol was added (so as to cover the entire surface of the powder) and magnetically stirred at 300 rpm and 40-50°C for 30 min. Then, the functionalizing agents (10 mL polydimethylsiloxane-PDMS or 10.5 mL titanium isopropoxide - TiO₂) were added as fine droplets, and stirring was continued at the same parameters as above, for another 2h. Into the glass containing the dolomite powder/10% titanium isopropoxide, 10 mL of distilled water was added for the hydrolysis process to occur, and stirring was continued for another 20 min. The two types of powders (Dolomite/10% PDMS, symbolized in the paper as **Sample 7** and Dolomite/10% TiO₂ - **Sample 8**) obtained, were filtered under vacuum, washed with ethanol in abundance (at least 3 times to eliminate unreacted agents), dried in an oven with hot air at 80°C for ~ 24 h, ground and characterized (**FTIR, EDS, SEM, DSC-TG**).

Method 2 (sol-gel): involves, compared to method 1, the initial treatment of dolomite with TEOS in order to form reactive Si-OH bonds on the surface (at 300rpm, 40-50°C for 1 h), followed by the addition of functionalizing agents (PDMS or titanium isopropoxide). The amount of TEOS (18.6 mL) was calculated to obtain in the end 5g SiO₂ and 5g of TiO₂ (24.67 mL titanium isopropoxide), the rest of the stages being identical to method 1. Thus, 2 powder variants were also obtained: Dolomite/5%TEOS/5%PDMS – **Sample 9** and Dolomite/5%TEOS/5%TiO₂ – **Sample 10**.

RESULTS AND DISCUSSION





Figure 1. FTIR spectra of raw dolomite powder / modified with SiO₂ and/or TiO₂ precursors

The FTIR spectrum obtained on raw dolomite, highlights the bands from 1416.78, associated with the asymmetric stretching vibration (v_{as}) of $(CO_3)^{2-}$ groups, the band from 873.3 cm⁻¹ (associated γ – out of plane bending vibration of bonds O–C–O) and the 727.93 cm⁻¹ band, associated with δ – in plane bending vibration of O–C–O in (CO₃)^{2–} group (Mroczkowska-Szerszeń and Orzechowski, 2018). In Sample 7, in addition to the characteristic dolomite bands, the PDMS bands can also be identified. Thus, the band from 2962.3 cm⁻¹ (is associated with the stretching vibration of CH_3 bonds) and the bands from 1088.98, 1016.15 cm⁻¹ are associated with the vibration of Si-O-Si bonds. The band from 1258.78 cm⁻¹ s associated with symmetrical deformations of the CH₃ bonds from the Si-CH₃ group, and the one from 796.69 cm⁻¹ represents the stretching vibration of the Si-O bonds (Cui et al., 2018). In the spectrum obtained on Sample 9 can be identified both the characteristic bands of PDMS and silica. In the case of Sample 10, the adsorption band from 3383.68 cm⁻¹ associated with the stretching vibration of hydrogen bonds and the Si-O-Si band from silica can be identified. The characteristic bands of the TiO₂ group could be revealed by FTIR (Sample 8 and 10), only at values below 500 cm⁻¹. However, the presence of the element Ti has been proven by EDS in the case of both powders containing TiO₂ precursor.

SEM-EDS Analysis of Raw and Modified Dolomite Powders

The SEM images obtained on raw dolomite (Figure 2, image A) show a high heterogeneity of particle sizes with variations from 1,512 μ m to 14.08 μ m. According to the literature, generally in raw dolomite, two types of aggregates can be observed: fine with dimensions between 1-4 μ m and large with dimensions between 5-14 μ m (Gruszecka-Kosowska *et al.*, 2017; Huang *et al.*, 2019). Moreover, the shape of the particles in dolomite is not well defined (irregular) and the aggregates have a smooth surface, without visible pores. The characteristic morphology of dolomite is preserved in all modified powders (Figure 2, B-E), with the mention that the surface of large particles is decorated with smaller particles which demonstrates the functionalization of dolomite, according to the two methods. Thus, in the case of Samples 7 and 9 (Fig. 2, B and C), the particle size from SiO₂ precursors varies between 718.3 and 956.5 nm. Smaller particle sizes could be observed in Sample 10, especially at large magnifications-20.000x, with size variations between 113.6, 145.2 and 154 nm. The EDS spectrum obtained on raw dolomite (Figure 2, A) highlights the main elements in its composition: Ca, Mg, C and O

Dolomite Surface Modification with Titania and Silica Precursors and Its Morphostructural and Thermal Characterization

without identifying other elements considered impurities, which demonstrates the advanced purity of the dolomite used.

Figure 2. SEM–EDS analysis of: (A) raw dolomite, (B) Sample 7, (C) Sample 9, (D) Sample 8 and (E) Sample 10, magnification 5000 and 20000x

In Sample 7 (B) and Sample 9 (C) in addition to the dolomite elements, the presence of Si can also be observed, which confirms that the chosen modification route was optimal. Similar, in Sample 8 (D) the element Ti can be identified, and in Sample 10 (E) the elements Ti and Si.

Thermal Analysis

To evaluate the thermal decomposition behavior of raw dolomite and modified with TiO₂ and/or SiO₂ precursors, the DSC-TG analysis was performed, and the obtained curves are shown in Figure 3. In raw dolomite (Figure 3Error! Reference source not found., A), a mass loss of 1.57% is observed in the range RT-600°C. A weak endothermic effect below 100°C indicates an initial water loss (water physically absorbed into the mineral). After 600°C the sample loses 45.81% of the mass up to 900°C, the residual mass being 52.97%. This is the interval in which $MgCO_3$ and $CaCO_3$ decompose by eliminating CO₂. The endothermic effect that accompanies this decomposition process is wide, asymmetrical, with a minimum at 849.5°C, and a shoulder at 813.8°C. According to data from the literature (Yang et al, 2019), the first to decompose is MgCO3 (endothermic effect at 813.8°C). CaCO₃ decomposes at a higher temperature (endothermic effect at 849.5°C). The inflection point on the DTG curve is at 829°C (until there the decomposition of MgCO₃ dominates, and at temperatures > 829° C the decomposition of CaCO₃ dominates). By decreasing the water and considering the total decompositions, a (mass) composition of MgCO₃ ~ 26% and CaCO₃ ~ 73% can be estimated. In Sample 7 (image B) a mass loss of 6.05% up to 600°C is observed. In addition to traces of water removed up to 150°C (according to the weak endothermic effect at 75°C) there is a higher mass loss after 300°C most likely generated by oxidation of PDMS and transformation into SiO₂ (weak exothermic effect at 386.5°C). After 600°C the decomposition of the two carbonates takes place. Besides the mass loss of 13.71% between 725-793°C attributed to the decomposition of MgCO₃ (endothermic effect at 757.9°C) and the mass loss of 25.03% between 793-900°C attributed to the decomposition of CaCO₃ (endothermic effect at 818.6°C) a mass loss between 600-725°C of 4.66% can also be observed, with a weak endothermic effect at 690.6°C. It can be

attributed to the formation of a Ca or Mg silicate (MSiO₃ type). In this case there is a decrease in carbonate decomposition temperatures, more pronounced for MgCO₃.



Figure 3. Thermal analysis of powders: (A) Dolomite; (B) Sample 7; (C) Sample 9; (D) Sample 8 and (E) Sample 10

In Sample 9 (image C) there is a mass loss of 4.22% up to 600°C. In addition to traces of water removed up to 150° C (according to the weak endothermic effect at 80° C) there is a greater loss of mass after 300°C, most likely generated by oxidation of PDMS and transformation into SiO₂ (weak exothermic effect of at 387.7°C). The smaller amount of PDMS in the sample leads to a lower weight loss. Considering the thermal analysis from Sample 10 (image E), the oxidative degradation of TEOS occurs without being able to revealing sudden mass losses or thermal effects. After 600°C the decomposition of the two carbonates takes place. In the range of 600-719°C the reaction between SiO_2 and carbonates takes place (obtaining $MSiO_3$) with a mass loss of 4.22% and a weak endothermic effect at 687.6°C. The decomposition of MgCO₃ occurs predominantly in the range of 719-793°C (endothermic effect at 761.1°C), the mass loss being 15.47%. Between 793-900°C, CaCO₃ decomposes predominantly (endothermic effect at 818.6°C), with a mass loss of 24.68%. In this case there is a decrease in the decomposition temperatures of carbonates. In Sample 8 (image D), a mass loss of 3.08% up to 600°C is observed. Below 100°C a weak endothermic effect is observed, generated by the loss of water absorbed in the sample. After 150°C there are a number of weak endothermic effects, which can be attributed to the decomposition of traces of organic matter. Considering the thermal analysis from Sample 10, the oxidative degradation of titanium isopropoxide occurs without any sudden loss of mass or visible thermal effects. The main decomposition stage starts after 600°C and represents 43.50% up to 900°C. At this stage, the decomposition of MgCO₃ takes place, with the endothermic effect from 768.2°C and the decomposition of CaCO₃ with the endothermic effect from 818.7°C. The inflection point on the DTG curve occurs at 788°C, and can be considered that below 788°C the decomposition of MgCO₃ predominates and then the decomposition of CaCO₃ predominates. It is observed that the addition of Ti isopropoxide (which is already TiO_2) decreases the decomposition temperatures of carbonates. Sample 10 (image E) records a mass loss of 4.83% up to 600°C. In addition to traces of water removed at low temperature (endothermic effect at 75.2°C), there is an oxidative degradation of TEOS and Ti isopropoxide, without major thermal effects. After 600°C the decomposition of the two carbonates takes place in stages. Up to 791°C the decomposition of MgCO₃ predominates (endothermic effect at 767.6°C) with a mass loss of 17.57%. After 791°C the decomposition of CaCO₃ predominates accompanied by the endothermic effect at 813.3°C, with a mass loss of 21.55 %. For this sample, the formation of Mg or Ca silicate

Dolomite Surface Modification with Titania and Silica Precursors and Its Morphostructural and Thermal Characterization

is not observed before the decomposition of MgCO₃. There are two possible explanations, either the formation of the silicate overlaps with the decomposition of the carbonate and can no longer be revealed as separate processes, or SiO_2 has already combined with TiO_2 .

CONCLUSIONS

The dolomite powder was modified according to the two methods presented, in order to be used as a reinforcing agent in obtaining composite materials. Additionally, the presence of TiO_2 can ensure the photo-catalytic activity, and the obtained powders can be used in environmental applications.

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