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TRANSFORMATIONS OF MECHANOCHEMICAL ACTIVATED Na_2CO_3

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Abstract: During mechanical activation, energy of treated material is increase to a higher level. This can lead to chemical transformation of the activated material. This is the point where we can talk about mechanochemical transformations that have occurred as a result of mechanical activation. The subject of this paper is to monitor mass changes of material after different degrees of activation. One of the substances which is often used in the processes of mechanochemical synthesis is sodium carbonate. The mass changes occurring during the treatment were detected and measured by various methods, depending on the processing environment. The mass increase was attributed to chemisorption of moisture and carbon-dioxide present in air, as a consequence of the sodium carbonate activation. The methods we used were calcimetric chemical analysis. According to obtained results, it was found that activated sodium carbonate is mass-transformed into sodium bicarbonate, whereby these changes are functionally dependent on activation time and the processing atmosphere.

Keywords: Mechanical activation, sodium carbonate, mechanochemical transformation

1 INTRODUCTION

Mechanical activation (MA) of materials is widely used as a process of bringing additional energy to a system to begin a controlled reaction. This allows the system to be moved across the "energy barrier" that is in the reaction's path. MA is among the most interesting fields of investigation. It is relating the activation of solid materials, also more often used in practice throughout the world. The results achieved by numerous researchers show that mechanical activation results in accumulation of mechanical energy in processed material, accompanied by various changes and improved physico-chemical characteristics of material. These changes contribute to faster, more simple and qualitatively better development of certain processes usually performed by conventional chemical methods. It also causing significant savings in time and cost of preparation

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process. Moreover, certain chemical processes proceeding in one way may change their course during or after the mechanical treatment, thus providing quite different products which could not be obtained in other ways.

Various materials nowadays are prepared by MA, such as cordierite-based, alumina-based, titanate-based, spinels and many others. Sodium carbonate is a substance that responds extremely well to mechanochemical treatment, with its chemical activity significantly increasing due to the weakening of the chemical bonds in the crystal lattice. Due to these characteristics, there is a possibility of extensive use of sodium carbonate in the mechanochemical reactions of synthesis of various substituents, which would replace the classical chemical processes in extreme working conditions.

Mechanochemistry is a modern scientific problem, and it deals with the physico-chemical changes of substances due to the action of mechanical energy. Studying the reactions in the solid phase after mechanical activation, we can get the information of certain properties of material acquired during mechanical treatment.

The basics of mechanochemical treatment of materials were laid by V. V. Boldyrev, B. V. Deryagin, P. A. Rebinder, A. N. Frumkin, E. D. Shchukin, N. A. Kratove, D. V. Kusnecov, and others (Dunkić et al., 1996). There are different areas of interest in studying the mechanochemical action on materials. Considering the influence of the action of several types of devices for transferring mechanical energy to materials and the development of new ones are presented as well (Dallacqua et al., 1998; Belyaev et al., 1998; Boldyrev et al., 1998). Different conditions (temperature, atmosphere, intensity, and mode of transmission of mechanical energy, etc.) as well as the setting of kinetics and mechanism of mechanochemical processes were also presented (HCS Chemistry; Obradović et al., 2019). As a result of mechanochemical action in materials, defects occur, crystal structure destruction and amorphous phase formation. Monitoring of these effects are given in papers (Filipović et al., 2018; Živojinović et al., 2019). Different methods and possibilities of new testing methods for characterization of materials after mechanical activation have been studied as a function of different parameters (relaxation time, temperature, atmosphere in which the sample is located, possible reactions in multicomponent systems) (Lazarević et al., 2017; Obradović et al., 2016).

2 EXPERIMENTAL PROCEDURE

During this research, the sodium carbonate system, p.a.MERCK index 11.8541, was activated by a mechanochemical process. The bond energy values represented by sodium carbonate are Na–O (364 kJ/mol), C–O (1076.4 kJ/mol), C=O (532.2 kJ/mol).

The decomposition temperature of sodium carbonate is 851 °C. Sodium carbonate has a monoclinic crystal lattice (a = 8.907; b = 5.239; c = 6.043), with a specific mass of 2500 kg/m^3. The chemical composition of sodium carbonate according to the MERCK index 11.8541.

A chemical analysis was performed on a representative sample. Sodium carbonate was mechanochemically activated in a high energy mill with torsion springs and “KHD HUMBOLDT WEDAGAG” ring elements. The volume of the mill's working vessel was 2 dm^2 and the mass of material that can be activated under optimal conditions is 200 g. Engine power was 0.8 kW. The device operates discontinuously in an atmosphere of air. Intensely vibrating movement of the mill work piece with massive rings causes the vessel to warm up to a temperature of 80 ^oC.

A sample of Na_2CO_3, weighing 50.0 g, was activated by a mechanical procedure for 1 to 28 min. Activated samples were deposited under different conditions at room temperature, in a carbon dioxide atmosphere and in a vacuum. The sample residence time was from 1 to 85 days. The samples were exposed to a room temperature. As a function of the activation time in the mechanical-chemical reactor, the residence time of the sample after activation and the atmosphere in which the sample was located, changes were monitored on activated sodium carbonate using different methods.

The effects of MA of sodium carbonate were monitored by measuring the change in mass of the activated sample, calcimetric analysis. The following instrumental technique was used. A standard laboratory calculator was used to quantify the content of sodium carbonate as well as to monitor the process of carbon dioxide chemisorption from the atmosphere in which the sample was located, over the carbonate content of the test sample.

3 RESULTS AND DISCUSSION

3.1 Change in sample mass as a function of activation time

A sample of 50.0 g anhydrous Na_2CO_3 was activated by a mechanochemical process in a vibrating mill for 1, 4 and 7 min. Both inactive and activated samples were deposited at room temperature under carbon dioxide, vacuum and room conditions for 64 days. Mass samples changes was monitored as a function of activation time, and also the time that samples were exposed to the given conditions. The measurement results are shown in Figure 1.

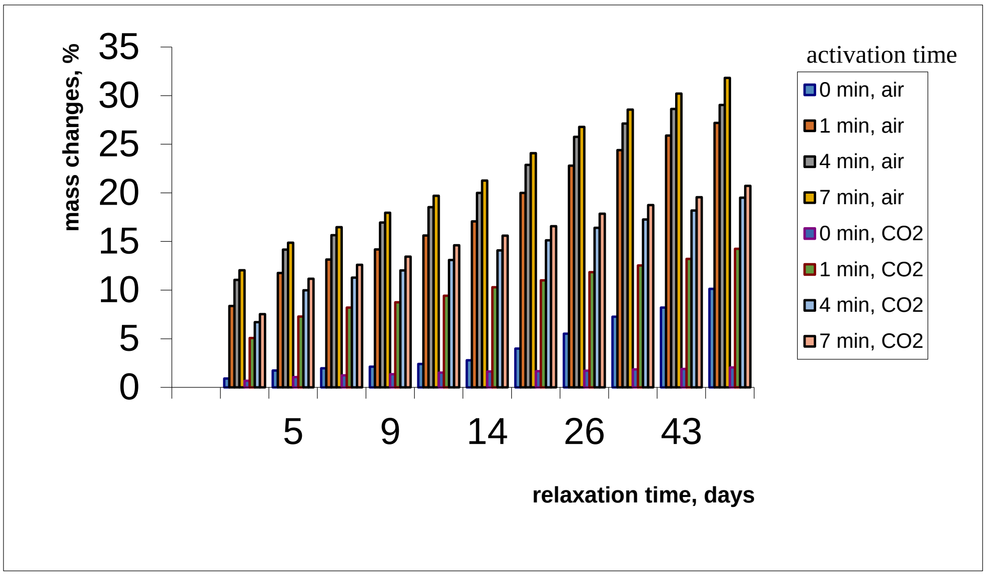

Figure 1 Mass increase of inactivated and activated Na_2CO_3 samples under room conditions and CO_2 atmosphere

The samples activated for 1, 4 and 7 min, as well as the inactivated sample of sodium carbonate that were in vacuum, had no mass changes for 64 days. Samples that were stored in carbon dioxide at room temperature as a function of relaxation time, changed as follows: the non-activated sample of sodium carbonate increased by 2.039 % over a 64-day period. The 1 min activated sample mass increased 14.25 %, the 4 min activated sample weight increased 19.50 %, and the 7 min activated sample mass increased 20.73 %. The increase in sample mass is due to the absorption of carbon dioxide and the moisture present throughout the sample volume. Inactivated sodium carbonate mass change showed that mass increased 10.13 % under room atmosphere and temperature conditions for 64 days. The 1 min activated sample mass increased 27.20 %, the 4 min activated sample 29.05 %, and the 7 min activated sample increased 31.83 %. The increase in the mass of these samples was due to the absorption of moisture and carbon dioxide from the air. Based on these results, it can be concluded that the mass of the samples increases as a function of the time of activation of the sodium carbonate in the vibrating mill, that is, the samples increase the absorption capacity with the extension of the activation time.

3.2 Changing mass of activated Na_2CO_3 in CO_2 atmosphere and increased humidity as a function of activation time

As the activated sodium carbonate samples show a tendency of increased absorption power, the continuation of the experiment of monitoring the changes in the relaxation of the activated samples was carried out in a closed vessel, at room temperature, in a CO_2 atmosphere, in which, beside the samples, there was a water tank. The carbon dioxide pressure was 1 bar and the humidity was about 95 %. The Na_2CO_3 samples were activated 1, 3, 5, 7, 14, 21, and 28 min. The relaxation time was 24 days. Changes in sample mass as a function of activation time and relaxation time were monitored. The measured samples also contained a sample of inactivated sodium carbonate. The results are shown in Figure 2.

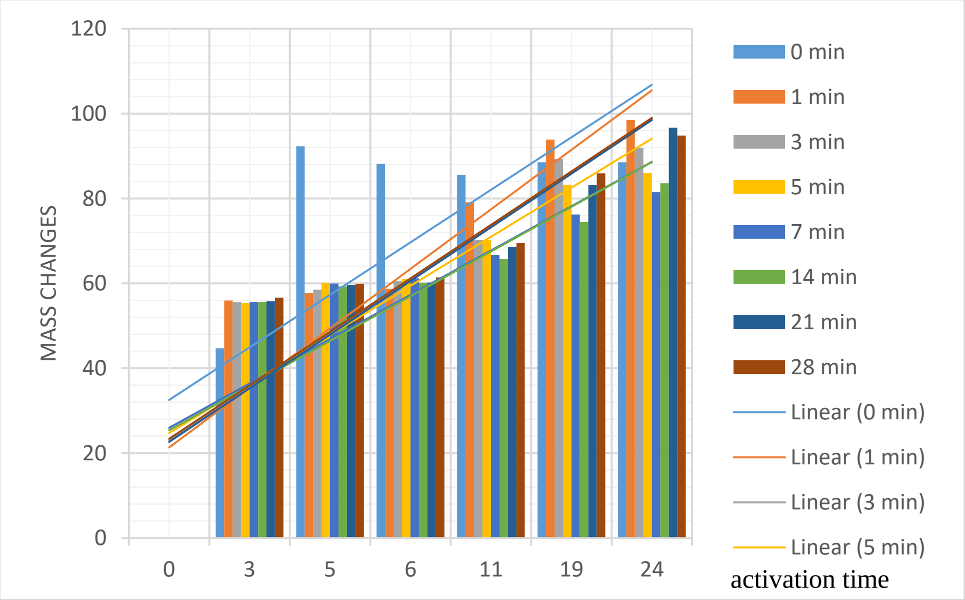

Figure 2 Mass changes of inactive and activated Na_2CO_3 in CO_2 atmosphere at 95 % humidity, as a function of the relaxation time

Figure 2. shows that the inactivated sample under these conditions rapidly increases mass (up to almost 90 %) during the first 5 days of the relaxation time due to the absorption of moisture from the atmosphere by water vapor. After this time, the mass of the inactive sample remained almost unchanged. This behavior of the inactivated sample can be explained by the fact that the entire volume of Na_2CO_3 has been bound by the presence of moisture from the atmosphere in the form of crystalline water. Based on the results obtained, it can be concluded that 5.3 moles of water per mole of sodium carbonate have been absorbed by the fifth day of monitoring the change in mass of the unactive sample. This change in the sample was due to the hygroscopicity of the anhydrous sodium carbonate.

All samples that were subjected to MA in the first 3 days of the mass relaxation time increased almost identically up to 60 %. After the third day, one period of stagnation occurs until the sixth day, after which the mass of samples again tends to increase, so that by the 24th day, as a function of the time of activation, it increased 80–90 %. It can be noticed a significant difference in the behavior of inactivated and activated Na_2CO_3. Unlike the simple absorption that occurs with inactivated sodium carbonate, this behavior of the activated samples can be explained by the assumption that during the mechanical activation there was a weakening and breaking of the chemical bonds in the sample, and thus an increase in the chemical activity of Na_2CO_3. Since such a sample was, after activation, contained in an atmosphere of CO_2 and moisture present, it may be that during the first three days of relaxation, their chemisorption by sample volume and $NaHCO_3$ formation occurred. After three days of stagnation, the sample mass begins to grow again due to the subsequent absorption of moisture by the resulting bicarbonate. The reaction by which the process of chemisorption of carbon dioxide and moisture probably occurs, that is, the possible conversion of sodium carbonate to sodium bicarbonate is as follows:

$$2Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)} \rightarrow 2NaHCO_{3(s)}$$

Due to the behavior of the samples during the relaxation time, further analyses were necessary to confirm the assumption that the activation of sodium carbonate increases chemical activity and, consequently, due to the presence of CO_2 and moisture in the atmosphere, conversion to $NaHCO_3$ occurs.

4 CONCLUSION

The results of the study show that by holding the activated Na2CO3 sample at room conditions, the sample mass grows due to the absorption of moisture and carbon dioxide from the air. The mass of the samples increased as a function of the grinding time of sodium carbonate at the same relaxation time. By the presence of activated samples in the atmosphere of carbon dioxide, the masses of activated samples also increase as a function of the time of activation, while the mass changes are smaller than the samples that were stored at room conditions.

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