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Thermodynamic Aspect of Sodium Carbonate Mechanical Transformations under Different Environment

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Abstract:

During mechanical activation, the energy of treated material is raised to a higher level that can lead to the chemical transformation of the activated material. This is the point that should be considered as a phenomenon of the mechanochemical transformations appearing as a result of mechanical activation. Sodium carbonate as a substance that is often subjected to mechanochemical synthesis was mechanically activated in this study. The subject was the monitoring of changes in the physico-chemical characteristics of sodium carbonate after exposure to different degrees of activation time within the range of 1-28 minutes. After activation, the samples were deposited in three environments, CO_2, air, and vacuum, at room temperature, in a period of 64 days. The mass changes occurring during the treatment were measured depending on the processing environment. Increasing the mass was evident and was attributed to the chemisorption of moisture and carbon dioxide present in the air as a consequence of the sodium carbonate activation. The methods also used were calcimetric chemical analysis and X-ray structural 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 environment.

Keywords*: Mechanical activation; Sodium carbonate; Mechanochemical transformation.*

1. Introduction

Mechanical activation (MA) of materials achieved by using high-energy milling is widely used for common to increase the reactivity of material and to begin a controlled reaction. This treatment is usually relating to the activation of solid materials, which is why they more often use in practice throughout the world. The primary effect of the milling is comminution or breakage of particles causing the creation of a new particle surface area and thus its specific surface area increase. These effects occur as a consequence of the process of bringing additional energy to a system. The results achieved by numerous researchers show that mechanical activation generates the accumulation of mechanical energy in processed material accompanied by various changes more precisely by improving physico-chemical characteristics of the solids. Namely, the change in reactivity can significantly exceed those provoked by particle size decrease. The change of reactivity during milling originate from the combined effect of an increase of the specific surface area together with a structural disorder, enhanced strain, amorphization of the crystals, microtopography, phase transformations, and thermal reduction. These changes contribute to faster, simpler, and qualitatively better development of certain processes usually performed by conventional chemical methods. MA

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allows the system to be moved across the "energy barrier" that is in the reaction's path. This treatment also causes significant savings in time and cost of the process preparation. Moreover, certain chemical processes proceeding in one way can change their course during or after the mechanical treatment thus providing quite different products [1-11]. Various materials nowadays are prepared by MA, such as cordierite-based, alumina-based, titanate-based, spinels, slag, fly ash, and many others [12-16]. 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 [17]. It is also noted that a significant increase in activation causes a significant increase in its absorption capacity. Due to these characteristics, there is a possibility of extensive use of sodium carbonate in the mechanochemical reactions of the synthesis of various substituents, which would replace the classical chemical processes in extreme working conditions.

Former studies observed that carbon dioxide and moisture from the air can be absorbed by the sodium carbonate [18]. The use of the sodium-based sorbent precursor is usual in the process to separate/capture carbon dioxide that originating from fossil fuel combustion in a single-cycle and multi-cycle process as a function of calcination and carbonation reactions [17]. Namely, the global climate has been changed in warming direction since the 1950's, increasing the temperature in the atmosphere and oceans, reducing the levels of snow and ice, and raising the level of seas. The main reason for climate change is attributed to the emissions of greenhouse gases, while the carbon dioxide is of the principal interest because of "its large current greenhouse forcing, its substantial projected future forcing and its long persistence in the atmosphere" [19-23]. Since the amount of adsorbed gases presents a function of the degree of activation, a study regarding the MA of sodium carbonate is considered a very interesting field for investigation since it assumes the increase of its sorption capacity.

The basics of mechanochemical treatment of materials were established by V. V. Boldyrev, B. V. Deryagin, P. A. Rebinder, E. D. Shchukin, and others [24-28]. There are different approaches and fields of interest in studying the mechanochemical action on materials. Some studies were engaged in considering the influence of several types of devices for transferring mechanical energy to materials and the development of new ones [29-31]. Besides, the effects of different conditions (temperature, atmosphere, intensity, and mode of mechanical energy transmission, etc.) on the kinetics and mechanism of mechanochemical processes were also investigated [32, 33].

The aims of numerous researches were focused on monitoring the effects that mechanochemical reaction can provoke on treated materials such are the occurrences of defects, crystal structure destruction, and amorphous phase formation [34-38]. Different methods and possibilities of new testing methods for characterization of materials after mechanical activation have been studied as in a function of different parameters (relaxation time, temperature, the atmosphere in which the sample is located, possible reactions in multicomponent systems) [39-42].

As already mentioned, solid materials are characterized by a stable crystalline structure. During the mechanochemical treatment, mechanical energy is transferred to the material–resulting in the accumulation of energy and thence on defects in the crystal and disruption in the arrangement of the structural elements. As a consequence, the thermodynamic instability and a change in the free Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) occur. The amount of accumulated energy in the material to be ground depends on the intensity of the added energy, material properties, grinding time, etc [7].

Mechanochemistry is a scientific approach occupied with the physico-chemical changes of substances exposed to the action of mechanical energy. Studying the reactions in the solid phase after mechanical activation, the information of certain properties of material acquired during mechanical treatment can be obtained. Therefore, the aim of the research was to get acquainted with the changes that accompany the process of MA of this substance

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(change of crystal structure, the appearance of defects in the lattice of crystals, change of mass due to the gas-phase chemisorption, as well as examining the possibility of using new methods for qualitative and quantitative assessment of the degree of activation.

2. Materials and Experimental Procedures

During this research, the sodium carbonate system (p.a. MERCK index 11.8541) was activated by a mechanochemical process. The bond energy values of sodium carbonate are as follows [16]:

a) Na–O (364 kJ/mol)
b) C–O (1076.4 kJ/mol)
c) 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 [43]. The chemical composition of sodium carbonate according to the MERCK index 11.8541 is given in Table I.

Tab. I Chemical composition of sodium carbonate.

Compound (element)	Na_2CO_3	Impurity content (max.)									
		Cl^-	In total SO_4^{2-}	SiO_2	Pb	Fe	Al	Mg	Ca	K	loss by drying 180°C
The conc. %	99.5	0.002	0.005	0.005	0.0005	0.0005	0.01	0.0005	0.005	0.01	0.5

Sodium carbonate was mechanochemically activated in a high energy mill with torsion springs and "KHD HUMBOLDT WEDAG AG" ring elements. The volume of the mill's working vessel was 2 dm^3 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. The intense vibration movement of the mill work-piece with massive rings causes the vessel to warm up to a temperature of 80 °C.
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 at room temperature under different surroundings, in a carbon dioxide, air, and in a vacuum. The sample residence time was from 1 to 85 days. Depending on the activation time in the mechanical-chemical reactor and the environment type and duration of samples residence after activation, changes were monitored on activated sodium carbonate using different methods.

The effects of MA sodium carbonate were monitored by measuring the change in mass of the activated sample, calcimetric analysis, and X-ray diffraction. 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. X-ray diffraction of polycrystalline samples was performed on a PHILIPS PW-1700, an automated copper tube diffractometer operating at 40 kV and 35 mA. The unit is supplied with a graphite monochromator and with a proportional counter filled with xenon. Shooting angle (2Θ) was in the 4-15 range.

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3. Results and Discussion
3.1 Change in sample mass as a function of activation time

Changes in the sample`s mass were monitored as a function of activation time as well as the time of exposure to certain environmental conditions. Namely, 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 samples, non-activated and activated, were deposited at room temperature under a carbon dioxide environment, air surrounding, and in a vacuum for 64 days. It was noted that the activated and non-activated samples of sodium carbonate deposited in vacuum had no mass changes for 64 days. Therefore, the measured results of mass changes shown in Fig. 1 include the other two environments, air and CO_2.
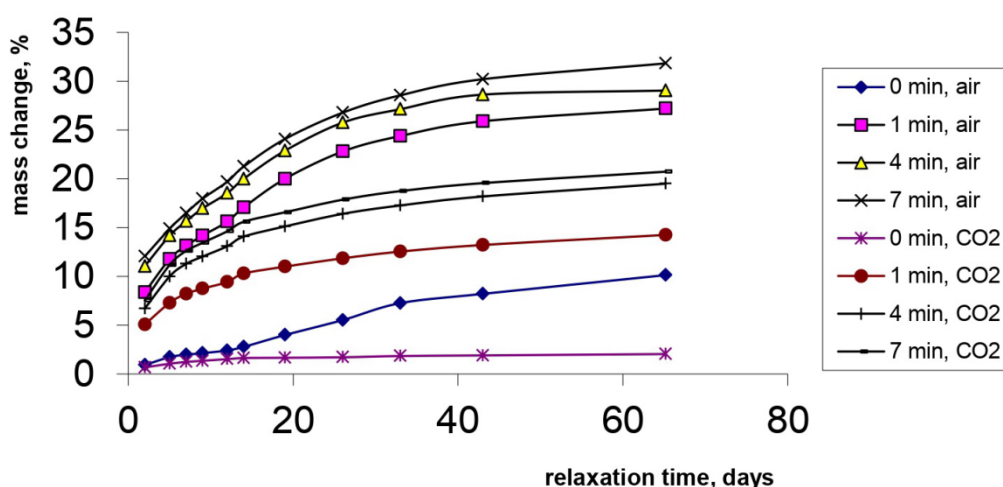
Fig. 1. Mass increase of non-activated and activated Na_2CO_3 samples in the air atmosphere and CO_2 environment.

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.

In the case of deposited samples in air surrounding and room temperature, mass of non-activated sodium carbonate increased by 10.13 % for 64 days. After 1 minute of activation, the mass increased by 27.20 %, and after 4 minutes by 29.05 %, while after 7 minutes of activation increased by 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

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atmosphere, in which, besides 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 non-activated sodium carbonate samples have also included in this investigation. The results are shown in Fig. 2.
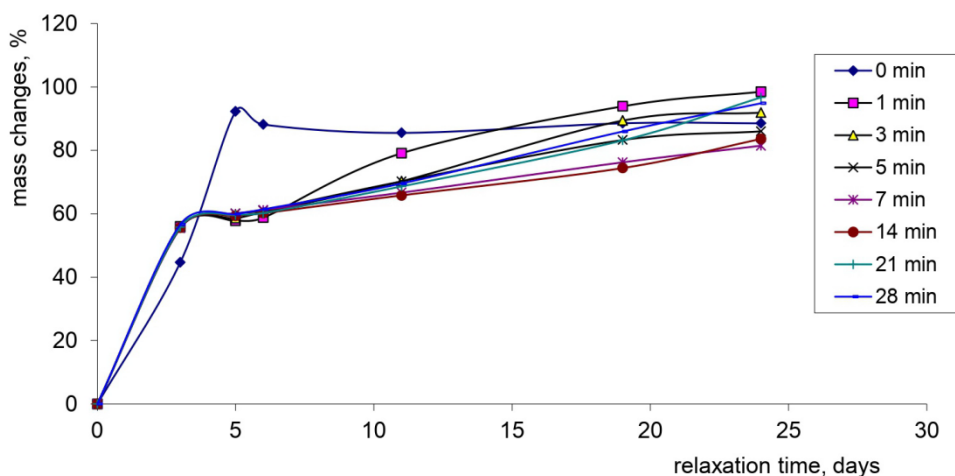
Fig. 2. Changes in mass of non-activated and activated Na_2CO_3 in a CO_2 atmosphere at 95 % humidity in a function of the relaxation time.

Fig. 2 show that the non-activated 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 non-activated sample remained almost unchanged. This behavior of the non-activated 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 non-activated sample. This can be assumed due to the hygroscopicity of the anhydrous sodium carbonate.

All samples that were subjected to MA in the first 3 days of the relaxation time increased their mass almost identically up to 60 %. After the third day, one period of stagnation occurs and lasts until the sixth day. However, the mass of samples again tends to increase from 6 to 24 days of relaxation, while in a function of the activation time, it increased by 80-90 %. It can be noticed a significant difference in the behavior of non-activated and activated Na_2CO_3. Unlike the simple absorption that occurs with non-activated 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:

$$2Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)} \rightarrow 2NaHCO_{3(s)} \qquad (1)$$

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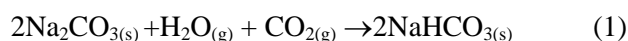
Due to the behavior of the samples during the relaxation time, further analyses were necessary to confirm the assumption that the activation of sodium carbonate increases chemical activity and, consequently, due to the presence of CO_2 and moisture in the atmosphere, conversion to $NaHCO_3$ occurs.

3.3 Crystallographic studies of activated Na_2CO_3

Activated samples of Na_2CO_3 (1, 3, 5, 7, 14, 21, and 28 minutes) were given for X-ray diffraction analysis. The samples were isolated from the outside atmosphere, so that no additional effect on the activated samples could occur. The aim of this analysis was to determine how the structure of sodium carbonate behaved as a function of milling time in a vibrating mill. Comparing the diffractograms of the activated samples with the unactivated sample, it is shown that the grinding of the samples of sodium carbonate led to the destruction of the crystal structure.

In order to monitor the change in the intensity of diffraction peaks as a function of the time of activation, five characteristic peaks at certain values of the diffraction angles were selected from the data given by the diffractograms. The diffractogram of Na_2CO_3 activated for the period of 1-21 minutes in a vibrating mill are given in Fig. 3. The dependence among the intensity of the diffraction peaks in the function of activation time is shown in Fig. 4.
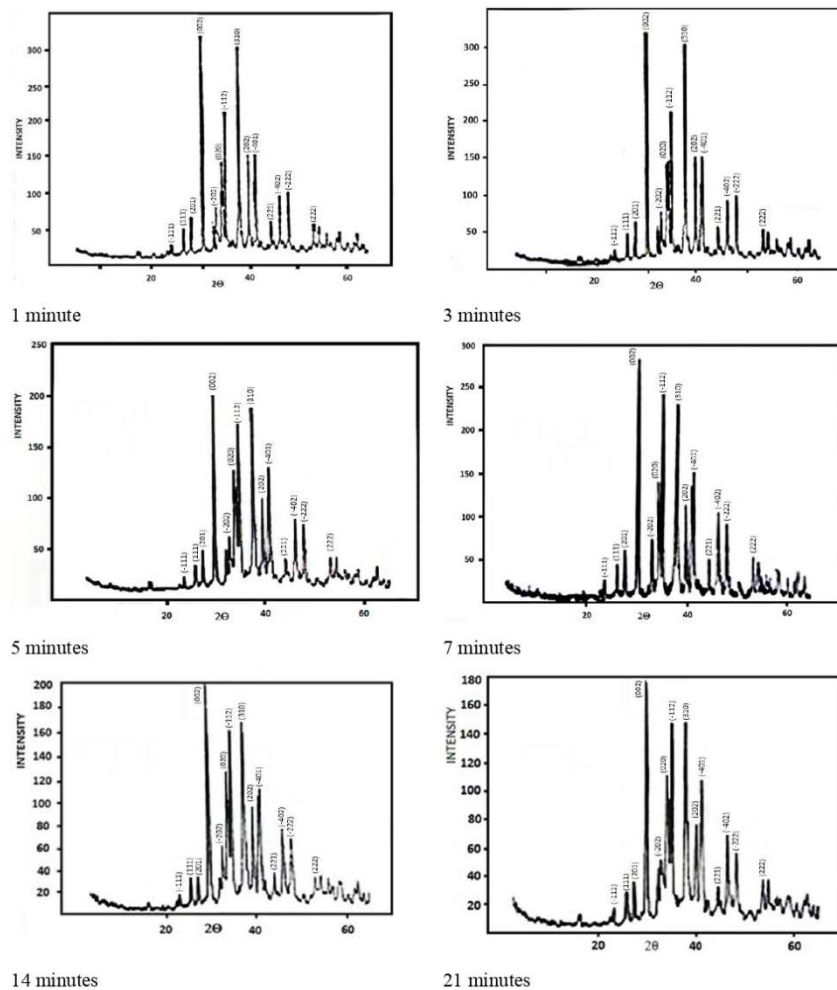

Fig. 3. Diffractograms of Na_2CO_3 activated for a period of 1-21 min in a vibrating mill.

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From Fig. 4, it can be concluded that during the first five minutes of activation there is a sharp decrease in the values of the intensity of diffraction maxima indicating that the destruction of the crystal structure was being happened at all angles of diffraction. This is due to the fact that the introduced mechanical energy is consumed by the fragmentation of the existing grains of sodium carbonate, which then leads to the destruction of the internal structure of the Na_2CO_3 crystals. Between the fifth and the seventh minutes of grinding, the values of the maximum intensity increase, also at all diffraction angles. The increase in the intensity of diffraction peaks can be explained by the fact that after five min of grinding, or after the destruction of the crystal structure, the mechanical energy supplied to the system allows certain recrystallization of the existing system, that is, to partial rearrangement of the destroyed structure. After that, the intensities decrease again until the fourteenth minutes of grinding, after which the change in maximum intensity would be stationary, more precisely showing a slight tendency to increase with grinding time.

This almost stationary part of the curve can be explained by the assumption that after the destruction of the newly formed structure, meaning after 14 minutes of milling changes in the structure of the activated sample are not observed. It can also be supposed that extension of the milling time, for more than 28 minutes, would not result in further changes in the structure of the activated material.
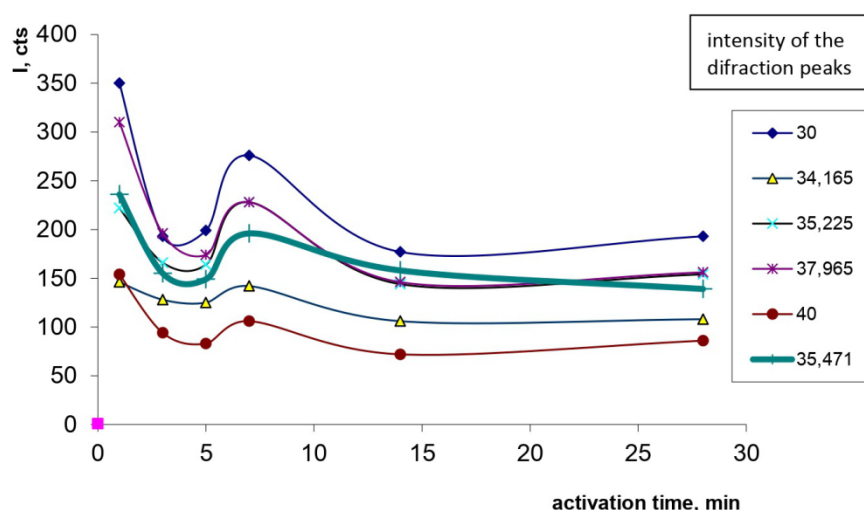

Fig. 4. The dependence of the intensity of the diffraction peaks as a function of activation time.

3.4 Thermodynamic aspects of mechanochemical transformations

Given the results obtained experimentally, it was interesting to analyze the thermodynamic aspect of the reactions that were assumed to occur during the relaxation time of activated Na_2CO_3. The reactions considered relate to inactive substances. Thermodynamic data were analyzed using the HSC Chemistry software version 2.03. containing a database that includes thermochemical data for numerous compounds. Relevant data can be used to calculate thermochemical equilibrium based on the free energy minimization approach [45]. The reactions of the conversion of sodium carbonate to sodium bicarbonate in the presence of carbon dioxide and moisture were studied (Table II), as well as the decomposition of sodium bicarbonate (Table III), and the decomposition of sodium carbonate (Table IV).

Table II gives the thermodynamic data of the reaction (1) given above, wherein the reaction relates to inactivated sodium carbonate. Based on the change in Gibbs energy, it can

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be seen that this reaction at temperatures up to 120°C is thermodynamically possible if the energy barrier is overcome (activation energy according to Fig. 4). Considering that data from experimental monitoring of changes occurred in mechanochemically activated sodium carbonate, it is obvious that changes after reaction (1) occur spontaneously during the relaxation time.

Tab. II Thermodynamic data for the reaction of Na_2CO_3 with carbon dioxide and water at temperatures from 0 to 200 °C.

$Na_2CO_3 + CO_2{}_{(g)} + H_2O_{(g)} = 2NaHCO_3$				
T (°C)	ΔH (kJ)	ΔS (J)	ΔG (kJ)	K
0	-135.344	-337.363	-43.193	1.82E+08
20	-135.489	-337.878	-36.440	3.12E+06
40	-135.602	-338.251	-29.679	8.93E+04
60	-135.68	-338.493	-22.911	3.91E+03
80	-135.722	-338.617	-16.14	2.44E+02
100	-135.729	-338.636	-9.367	2.05E+01
120	-135.701	-338.562	-2.595	2.21E+00
140	-135.639	-338.407	4.175	2.97E-01
160	-135.543	-338.183	10.941	4.79E-02
180	-135.417	-337.899	17.702	9.11E-03
200	-135.263	-337.565	24.456	2.00E-03

Under certain atmospheric conditions, in controlled conditions with carbon dioxide and at a humidity of about 95 %, it is evident that the energy barrier (activation energy) is overcome by the transfer of mechanical energy to the system. In this case, mechanical energy had been initially used to destruct the existing crystalline structure of sodium carbonate, and subsequently, it was accumulated in the system. MA of sodium carbonate increased the state of crystal structure to maximum energy level (transition state), which resulted in spontaneous reaction and conversion to sodium bicarbonate by subsequent standing of sodium carbonate in a controlled conditions, which was experimentally shown.

The mechanical energy transferred to sodium carbonate during the mechanochemical treatment had the greatest effect on the weakening of the Na-O bond in the Na_2CO_3 structure. Since changes were subsequently made at this connection, that is, hydrogen bonded from the moisture present, and in the atmosphere of carbon dioxide $NaHCO_3$ was converted by reaction given in Table II.

Table III gives thermodynamic data for the decomposition reaction of $NaHCO_3$ at temperatures from 0 to 200 °C. Based on Gibbs energy, it can be concluded that the reaction is thermodynamically possible at temperatures over 140 °C. DTA/TG analysis of the activated sodium carbonate also showed that at temperatures above 120 °C [17] the decomposition of the system that occurred during the previous relaxation time of the activated sodium carbonate, under the controlled atmosphere of carbon dioxide and moisture had passed into sodium bicarbonate.

Tab. III Thermodynamic data for the decomposition reaction of $NaHCO_3$ at temperatures from 0 to 200 °C.

$2NaHCO_3 = Na_2CO_3 + CO_{2(g)} + H_2O_{(g)}$				
T (^{o}C)	ΔH (kJ)	ΔS (J)	ΔG (kJ)	K
0	135.344	337.363	43.193	5.49E-09
20	135.489	337.878	36.440	3.21E-07
40	135.602	338.251	29.679	1.12E-05
60	135.680	338.493	22.911	2.56E-04
80	135.723	338.617	16.140	4.10E-03
100	135.729	338.636	9.367	4.88E-02
120	135.701	338.562	2.595	4.52E-01
140	135.638	338.407	-4.174	3.37E+00
160	135.543	338.183	-10.941	2.09E+01
180	135.418	337.899	-17.702	1.10E+02
200	135.263	337.565	-24.456	5.01E+02

Table IV gives thermodynamic data for the decomposition reaction of sodium carbonate to carbon dioxide and sodium oxide. This reaction is also potentially possible as a consequence of the mechanochemical reaction. However, the data show that this reaction is not thermodynamically possible at room temperature, and no traces of Na_2O were found by FTIR analysis [17]. The detailed study of DTA/TG and FTIR result presented in 1, is going to be published soon.

Tab. IV Thermodynamic data for Na_2CO_3 decomposition reaction at temperatures from 0 to 1200 °C.

$Na_2CO_3 = CO_{2(g)} + Na_2O$				
T (^{o}C)	ΔH (kJ)	ΔS (J)	ΔG (kJ)	K
0	319.441	150.059	278.308	5.95E-54
100	318.932	148.979	263.340	1.36E-37
200	318.131	147.113	248.525	3.64E-28
300	316.281	143.605	233.973	4.73E-22
400	312.844	138.118	219.870	8.66E-18
500	309.379	133.224	206.377	1.14E-14
600	308.054	131.624	193.126	2.79E-12
700	305.784	129.172	180.080	2.15E-10
800	304.276	127.704	167.231	7.24E-09
900	270.746	97.842	155.963	1.14E-07
1000	279.131	104.536	146.042	1.02E-06
1100	275.766	101.990	135.718	6.87E-06
1200	320.562	133.887	123.326	4.23E-05

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4. Conclusion

The results of the study show that by holding the activated Na_2CO_3 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.

X-ray diffraction analysis of activated Na_2CO_3 showed that grinding of the samples in a function of grinding time at the first moment led to the destruction of the crystalline structure, and then partial recrystallization of the damaged system, followed by breaking of the crystal lattice again. Further grinding of the samples did not lead to new changes in the structure of the tested sample.

Thermodynamic analysis of the reaction of the conversion of sodium carbonate to sodium bicarbonate revealed that the mechanical energy was transferred by mechanochemical treatment of sodium carbonate, which, by destroying the crystal structure, accumulated in the system. During this process, the accumulated energy was sufficient to overcome the energy barrier and bring the system to a maximum level of potential energy, thanks to which the activated sodium carbonate in the atmosphere of carbon dioxide and the present moisture was spontaneously converted to sodium bicarbonate.

Acknowledgments

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Сажетак: Током механичке активације, енергија третираног материјала подиже се на виши ниво што може довести до хемијске трансформације активираног материјала. Ово је тачка коју треба посматрати као феномен механохемијских трансформација које настају као резултат механичке активације. Натријум карбонат као супстанца која се често подврагава механохемијској синтези је механички активирана у овом истраживању. Предмет је био праћење промена у физичко-хемијских својстава натријум карбоната након излагања различитим времена активације у интервалу од 1-28 минута. Након активирања, узорци су депоновани у три средине, CO_2, ваздух и вакуум, на собној температури, у периоду од 64 дана. Промене масе које су се јављале током третмана мерене су у зависности од средине у којој су биле одложене. Повећање масе било је очигледно што се може приписати хемисорпцији влаге и угљендиоксида присутних у ваздуху, као последица активације натријум карбоната. Коришћене методе биле су калциметријска хемијска анализа и рендгенска структурна анализа. Према добијеним резултатима, установљено је да се активирани натријум карбонат у великој мери трансформише у натријум-бикарбонат, при чему ове промене зависе од времена активације и средине у којој је активирани материјал одложен.
Кључне речи: механичка активација; натријум карбонат; механохемијска трансформација.