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Original scientific paper

DTA/TG ANALYSIS OF MECHANOCHEMICALY ACTIVATED SODIUM CARBONATE

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Abstract: Sodium carbonate is a material that is very good sorbent of carbon dioxide from the atmosphere, and it is a reason of it is increasing importance in environmental protection. In order to improve it is sorption characteristics, activation of Na_2CO_3 was performed by mechanochemical procedure and monitoring of changes during the relaxation time. This research is based on differential thermal analysis with thermogravimetry, in order to determine the changes that occurred on the activated samples during the relaxation period under controlled conditions. Sodium carbonate was activated for 2 and 7 minutes in a vibro mill, and then the activated samples were deposited in at room temperature and atmosphere of carbon dioxide at a humidity of 95% for 96h.

Keywords: mechanical activation, Na_2CO_3, thermal analysis

1 INTRODUCTION

Material activation process has widely been accepted method for an additional energy introduction to the system in order to stimulate a control reaction. This enables the system to overcome the "energy barrier" of the reaction. Generally, materials can be activated by chemical, thermal, mechanical activation method. The activated system carbons from lingocellulosic materials by chemical and/or physical activation was presented in paper (Rodrigues and Molina-Sabio, 1992), and chemical activation process of a lignocellulosic material with KOH by XPS and XRD microporous and mesoporous materials (Díaz-Terán, 2003); physical activation vs. chemical activation (Maciá-Agulló et al, 2004) are presented in papers. Authors have also investigated the enhanced capacitance of carbon nanotubes through chemical activation (Frackowiak et al. 2002), preparation of fibrous porous materials by chemical activation (Yue et al. 2002), the effect of mineral matter on the physical and chemical activation of low rank coal and biomass materials (Vamvuka et al. 2006), and compering different chemical reactions (Lillo-Ródenas et al., 2003).

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Thermal activation of materials was interesting field for researchers. Thermal activation and viscosity is presented in paper (Galligan and Mckrell, 2000), and the kinetics of thermally activated processes in cordierite-based ceramics in paper (Obradović et al., 2019).

Mechanical and mechanochemical method of material activation has increasing application. Development of different activation methods facilitated further novel materials investigations like the kinetic reaction tracking in the solid phase as well as possibilities for huge savings related to classical material activation methods. Mechanical activation has been applied in hydrometallurgy (Wang et al., 2005, Baláž, 2003,), solid state materials (Maurya et al., 2009), such as ceramics materials (Castro et al., 2004), mechanical activation on the preparation of $SrTiO_3$ and Sr_2TiO_4 ceramics from the solid state system $SrCO_3$–TiO_2 (Berbenni et al., 2001). Functional ceramics of nanocrystallinity by mechanical activation is presented in paper (Xue et al. 2002) and the effect of mechanical activation on synthesis and properties of $MgAl_2O_4$ ceramics in paper (Obradović et al., 2019).

Sodium carbonate reacts on mechanical activation extremely well. Namely, its chemical activity is considerably enhanced as a result of bond weakening. Based on these characteristics of sodium carbonate, there is an ample of applications for mechanochemical synthetic reactions different substances that can be used instead of classical methods in extreme conditions.

It is observed that the sodium carbonate activation leads to a substantial increase of the free surface and as a consequence this increases its absorption abilities. It is observed that sodium carbonate after being aged for a while enables better absorption of carbon dioxide and moisture from air. As well as, the absorbed amount of gasses is a function of a material activated degree (Djordjević et al., 2020). In this communication we presented a control a change of mass inactivated and activated sodium carbonate aged for 96 hours (relaxation period) in three different environments: in vacuum, carbon dioxide and room conditions. The result showed that mass of examined samples in vacuum (inactivated and activated sodium carbonate) did not change. The samples stayed in carbon dioxide and at room conditions had an enhanced mass of 2 % for inactivated and 14-21 % for activated samples. On the other hand, the samples stayed at room temperature conditions had a mass increase of 10 % (inactivated Na_2CO_3), up to 32 % (Na_2CO_3 activated for 7 minutes). This substantial increase of the mass of activated samples during relaxation time is the result not just of the enlarged free surface but also of disrupted crystal lattice and increase of the total energy of the system as a result. In this case, this was carbon dioxide and water from air which were absorbed on activated samples of sodium carbonate. It is worth emphasizing that this topic has a special importance taking into account higher contamination of environment.

2 EXPERIMENTAL PROCEDURE

Sodium carbonate was used in this work. The sample was p.a. purity, MERCK index 11.8541. The values of the binding energy represented by sodium carbonate are (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). The specific weight is 2500 kg / m^3. The chemical composition of sodium carbonate according to the MERCK index 11.8541 is given in Table 1.

Table 1 Chemical analysis of sodium carbonate

Σ Na_2CO_3=99,5	Conc. %
Cl^-	0,002
SiO_2	0,005
Pb	0,0005
Fe	0,0005
Al	0,01
Mg	0,0005
K	0,01
SO_4^{2-}	0,005
Ca	0,005
Ignition loss at 180°C	0,5

The Na_2CO_3 sample, weighing 50 g, was activated by a mechanical process for 2 and 7 minutes in a high-energy mill "KHD HUMBOLDT VEDAGAG" with torsion springs and ring elements. The volume of the working vessel of the mill was 2 dm^3, and the optimal mass of material that can be activated is 200g. The engine power was 0.8 kW. Intense vibratory movement of the working part of the mill with massive rings causes the working temperature of the grinding vessel to rise to 80° C.

After activation sodium carbonate samples were placed in carbon dioxide environment with 95% humidity for 96 h. The samples were exposed to room temperature. Depending on the activation time in the mechanochemical reactor, the retention time of the sample after activation changes (relaxation time) was monitored by the change of decay temperature of activated Na_2CO_3 samples, as well as mass loss and degree of Na_2CO_3 to $NaHCO_3$ conversion as a function of activation time and relaxation time.

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed for simultaneous thermogravimetric and differential thermal analytical measurements on activated samples on a METZSCH apparatus in the temperature range 20-1000 °C, with a heating rate of 10 °C / min.

3 RESULTS AND DISCUSSION

Sodium carbonate samples that were activated in a vibro mill for 2 and 7 minutes and then deposited in an atmosphere of carbon dioxide with humidity rate about 95 % were subjected to differential thermal analysis with thermogravimetry. The aim of this analysis was to determine the changes in decomposition (loss of mass during decomposition and the temperature at which decomposition occurs) as a function of the time of activation and the time of relaxation of Na_2CO_3 samples. Based on these data, it would be possible to determine a quantitative assessment of the conversion of activated sodium carbonate to $NaHCO_3$ in controlled catches according to reaction (1).

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

Change in decomposition temperature and mass loss and degree of conversion of activated Na_2CO_3 samples in the process of Na_2CO_3 to $NaHCO_3$ conversion as a function of sample activation time and sample relaxation time are shown in Table 2.

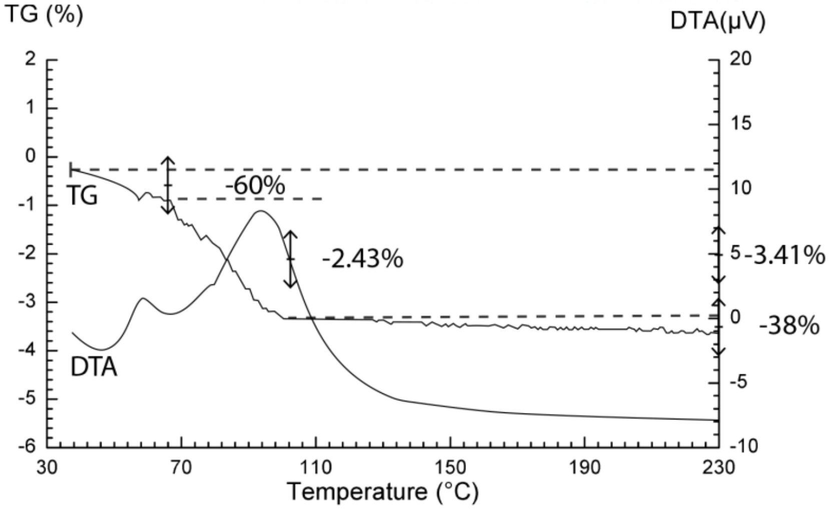
Table 2 Loss of decomposition mass and temperature and degree of conversion of activated Na_2CO_3 samples in the process of Na_2CO_3 to $NaHCO_3$ conversion as a function of sample activation time and relaxation time.

Relaxation time, h	Activation time, min					
	2 min			7 min		
	t, °C	Δm , %	Conversion rate, %	t, °C	Δm, %	Conversion rate, %
0	94,1	2.43	6,57	77,8	0,81	2,19
3	118,6	7,55	20,40	127,1	12,78	34,54
6	130	13,71	37,05	131,6	14,62	39,51
9	132,4	15,76	42,60	136,4	16,46	44,49
24	158	27,07	73,16	161,5	27,07	73,16
48	156,3	33,81	91,38	159,8	34,08	92,11
72	155,2	35,23	95,22	158,6	35,69	96,46
96	_	_	_	156,3	34,63	93,60

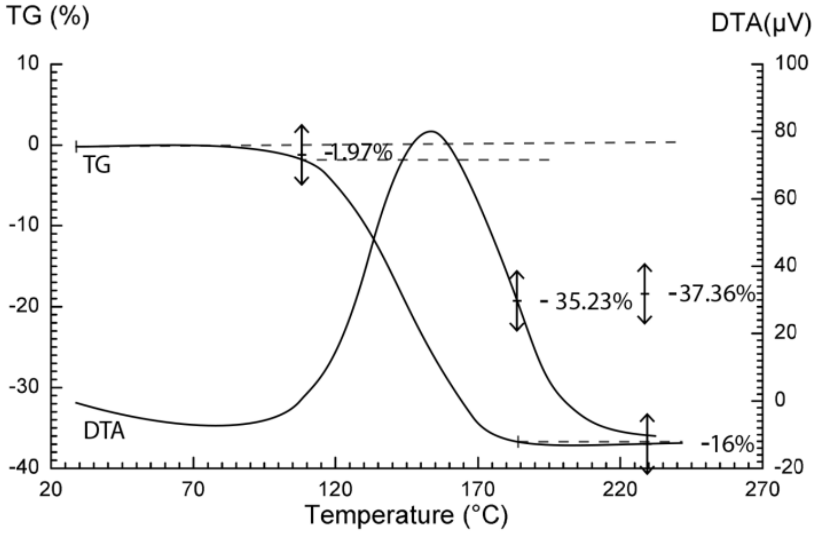
According to Table 2, the changes in the decomposition temperature as a function of the relaxation time and the activation time, it can be seen that in the first 24 hours the decomposition temperature tends to increase, while in the first three hours the temperature rises sharply. Since the decomposition temperatures for the samples that were analyzed immediately after activation (relaxation time 0h for 2 and 7 minutes of activation), values below 100 ° C, this is a simple loss of moisture. The value of moisture loss is below 2.5% for both samples.

By the third hour of standing the samples in a controlled environment, due to the absorption of moisture and carbon dioxide, such changes occur in the samples of sodium carbonate, which lead to an increase in the decomposition temperature to about 120 °C. The weight loss is 7.55 % (for samples activated 2 min.) and almost 13 % (for samples activated 7 min.).

This indicates that the standing of activated sodium carbonate in an atmosphere of carbon dioxide and the presence of moisture probably leads to chemical changes in the sample, i.e. to the conversion of Na_2CO_3 to $NaHCO_3$ after reaction (1). By 24 hours, the decomposition temperature rises to 160 °C, after which it stabilizes until the end of the experiment. The weight loss of the samples is 27 % by the 24th hour, after which it continues to grow to the value of 35 %, and 36 % by the 72.nd hour, after which it stabilizes.

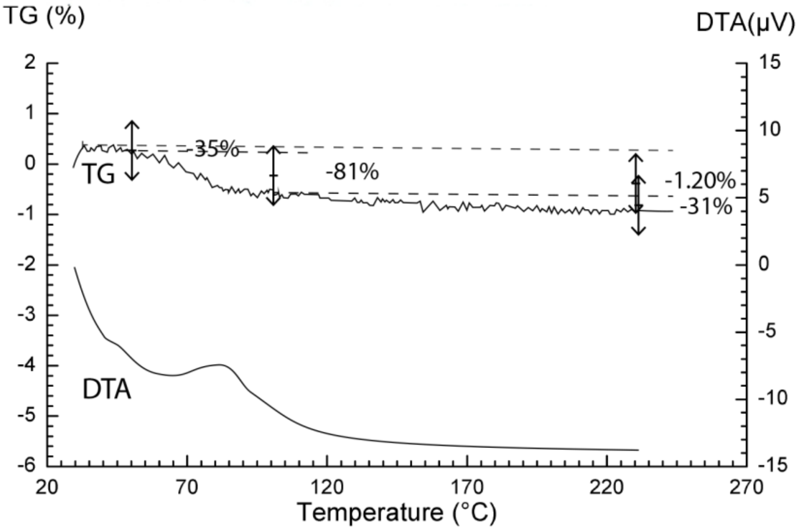


a)

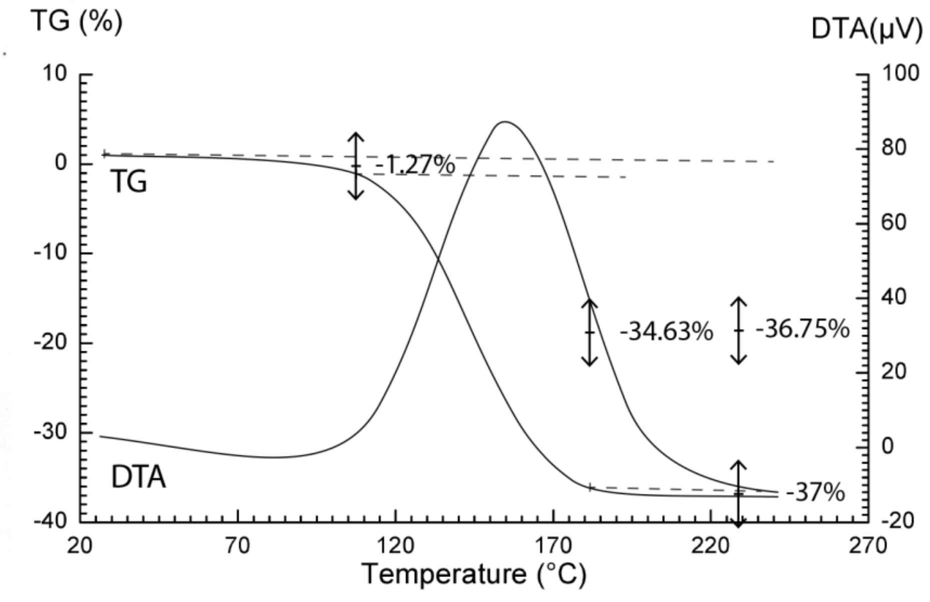


b)

Figure 1 DTA / TG diagram of the Na_2CO_3 sample activated 2 min after the relaxation time a) 0 h and b) 72 h in a CO_2 atmosphere and 95% humidity



a)



b)

Figure 2 DTA / TG diagram of the Na_2CO_3 sample activated 7 min after the relaxation time a) 0 h and b) 72 h in a CO_2 atmosphere and 95% humidity

If it is assumed that the standing of activated sodium carbonate under the given conditions leads to the conversion to $NaHCO_3$ after reaction (1), then the decomposition at elevated temperatures takes place after the opposite reaction, as follows:

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

When the mass loss of the samples given in Table 2 is calculated by reaction (2) to carbon dioxide and water, the data given in the same table under the heading conversion rate are obtained. From the data it can be concluded that by standing the samples in excess carbon dioxide and moisture and their absorption over the entire volume of the sample, conversion to sodium bicarbonate occurs, and that within 72 hours almost complete sodium carbonate is converted to sodium bicarbonate.

That further research is going to engage with a longer duration of the sample activation in a mechanochemical activator in order to determine the maximum effect of activation on the degree and velocity of carbon dioxide and moisture sorption on activated sodium carbonate, so that would probably achieve faster changes and increase the level of the sorption. The results clearly show that the activation of the Na_2CO_3 samples has huge effect regarding the sorption of CO_2 and H_2O. It can be expected that further increasing the activation time and thus increasing the specific surface area of the system would lead to faster and more significant sorption on the sample. The results presented in this study show that even with a very short activation of Na_2CO_3, almost complete conversion to $NaHCO_3$ was achieved, with practically both conversion rate and utilization coefficient of about $\eta = 0.96$.

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