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The Co-Grinding of Z/Cao/Al(OH)₃ (Z = ZnO Or $Zn_4CO_3(OH)_6$) Powder Compositions as Technique for Preparation of Sorbents

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Abstract

The co-grinding processes for ZnO/CaO/Al(OH)₃ and Zn₄CO₃(OH)₆/CaO/Al(OH)₃ powder compositions in a vibratory mill with an impact-shear loading were studied. The solid phase was investigated by the methods of X-ray diffraction, IR spectroscopy, scanning electron microscopy, synchronous thermal analysis and other methods. It was found that the formation of new Ca(Zn₂(OH)₆) phase takes place only in the ZnO-containing mixtures. The detected calcium hexahydroxodizincate dehydrate crystals had a prismatic shape. The experimental data showed also that the co-activation process is accompanied by the hydration of the particle surface due to the alignment of the basic properties of the initial compositions. The amount of glibbsite in the composition influences the changes in a crystal structure. The co-grinding of both compositions allows one to obtain the pellets which keep the mechanical durability after the saturation with HCl vapors. It was shown that the compositions with the basic zinc carbonate are characterized by the higher absorption capacity for the HCl vapors.

Keywords: Co-grinding; Zinc oxide; Basic Zinc carbonate; Calcium oxide; Gibbsite; Calcium hexahydroxodizincate dehydrate; Hydrochloric acid vapors adsorption

Introduction

Both catalytic and absorbing systems often have a nature of complex systems composed by oxides, hydroxides, carbonates, aluminates and other compounds [1]. For the manufacturing of such systems, the Zn, Ca and Al – containing compounds are widely used [2-6]. Here, the role of each component may be different and include such functions as promoter, binder and the active component itself. For example, ZnO plays the role of an active component, CaO can act as a promoter, binder or an active component while Al(OH)₃ or Al₂O₃ may be a carrier or also an active component.

For the synthesis of aluminates, the variety of hydrothermal methods is used [2,3,5,6]. The use of microwave power allows one to intensify the hydrothermal process [7] as well as to obtain the calcium hexahydroxodizincate dehydrate [8]. Another pathway for the synthesis of Zn, Ca and Al-containing compounds is the sol-gel process which involves corresponding oxides, hydroxides, carbonates, nitrates and other salts [6,9]. Also, the sol-gel process requires water or organic solvents as a liquid phase. The use of large amounts of liquids is the main disadvantage of this method.

An advanced way for the modification of powder materials is the mechanochemical activation [10]. The rapid development of mechanochemistry has attracted the great interest to the processes based on the co-grinding of several ingredients [11-13]. It was shown that the processing of solid material in mills-activators may result in the synthesis of many new products [11,12]. Based on these studies, Avvakumov introduced the term of "soft mechanochemistry" [11]. The conditions of soft mechanochemistry are realized if the treated substances produce the water when reacting one with other.

The processes taking place in the vibration mill during the dry cogrinding of the calcium- and aluminum-containing compounds have been described in detail [14-16]. In these works, it was found that the most reactive mixture is a composition of aluminum hydroxide and calcium oxide powders. Since the mentioned components have a maximum difference between their acid-base properties, the synthesis of the calcium hydroaluminates easily occurs. The use of calcium carbonate instead of calcium oxide leads to the deformation and destruction of aluminum hydroxide particles. The reason is a very high hardness of the CaCO₃ crystals.

The purpose of this work was the study of physical and chemical phenomena occurring in the Z/CaO/Al(OH)₃, where Z = ZnO or $Zn_4CO_3(OH)_6$, co-grinding process in the impact-shear vibratory mill. Another goal was to examine the sorption activity of these systems in relation to the HCl vapors.

Experimental

Materials and preparation procedures

The investigations were carried out for 4 types of mixtures with different initial compositions (Table 1). For the preparation of these mixtures, the following substances and ingredients were used:

- Al(OH)₃ in a form of commercial aluminum hydroxide (RusAl, Russia). It contained 98.8 wt% of gibbsite while the remaining part consisted of the impurities, such as Na(K)O₂, SiO₂, Fe₂O₃ and moisture.
- CaO in a form of the fluffy white powder obtained from CaCO₃ during the calcinations process at 850°C for 4 h. For this purpose, we used the precipitated calcium carbonate (Reaktiv, Ukraine). The content of CaCO₃ was 99.1 wt%, and the remaining part was represented by the admixtures of Fe₂O₃, Al₂O₃ and others.
- Zn₄CO₃(OH)₆ in a form of commercial basic zinc carbonate (Wuhan Xuyadi Chemicals Co., China). The Zn₄CO₃(OH)₆

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Num	Composition	Molar ratio ZnO:CaO:Al ₂ O ₃	Amount of ingredient per 100 g of mixture, g					
			ZnO	Zn ₄ CO ₃ (OH) ₆	CaO	AI(OH) ₃		
1	720(020(4)(01))	1:1:1	27.7	-	19.1	53.2		
2	2110/Ca0/AI(OH) ₃	1:1:2	18.1	-	12.5	69.4		
3	7- 00 (011) (0-0(4)(011)	1:1:1	-	51.7	12.8	35.5		
4	$\simeq 11_4 CO_3 (OH)_6 / CaO/AI(OH)_3$	1:1:2	-	38.2	9.4	52.4		

Table 1: Proportion of mixtures.

content was 96.7 wt%, the moisture content was 2.5 wt%, and the rest were the impurities. Before introducing into the mixture, the basic zinc carbonate was dried at 150° C for 2 h.

- ZnO in a form of fine-dispersed white powder prepared by the calcination of basic zinc carbonate at 500°C for 4 h.

In order to provide the mechanochemical activation (co-grinding) of the mixtures listed in Table 1, the vibratory roller-ring mill VM-4 (Česká Republika) was used. The diameter of the milling chamber was 98 mm, and the total volume of the chamber was 0.302 l. The oscillation frequency was 930 min⁻¹, the amplitude was 10 mm. The mixture was placed into the mill in the amount of 100 g. The grinding time was 10 min. After the grinding, the water was added to the mixture. The resulted content was stirred in order to obtain the homogeneous plastic paste. The optimum water content was ranged from 25 to 30 wt%. The granules with diameter of 3 ± 0.1 mm were molded from the paste using the piston extruder. Then, the granules were dried at 110°C for 4 h.

Control methods and devices

The chemical and physical properties for both original mixture components and resulting content were examined by following methods:

- Powder X-ray diffraction (XRD) spectroscopy. The patterns were recorded on DRON-3M X-ray diffractometer. The Cu K_{α} -radiation ($\lambda = 0.15406$ nm, Ni-filter) was used with a power supply settings of 40 kV and 20 mA. For the identification of the crystal phases, we used the ASTM database.
- Fourier transformed infrared (IR) spectroscopy. The spectra were measured using the Avatar 360 FT-IR ESP spectrometer working in the wave number range of 4000–400 cm⁻¹. The samples were prepared by the KBr method, and the sample to KBr ratio was 1:100. For the identification of the absorption bands [17-19].
- Scanning electron microscopy (SEM). The measurements were performed with the JSM-6460 LV microscope.
- Synchronous thermal analysis (STA). The measurements were provided by the STA 449 F3 Netzsch device. The heating rate was 5°C·min⁻¹ in an air.

Also, the N₂ adsorption-desorption isotherms were measured at 77 K on the Micromeritics ASAP-2400 analyzer. The samples were outgassed at 573 K before the measurements. The specific surface area was calculated from nitrogen adsorption data in the relative pressure range from 0.05 to 0.2 using the BET (Brunauer-Emmett-Teller) equation.

The amount of surface sites was calculated by potentiometric data obtained on the S500 SevenExcellence. The treatment of the titration curves were carried out according to pK Spectroscopy [20]. In order to measure the static capacity of the pellets for the HCl vapours, these were placed into the extractor under the 2% solution of HCl and were kept there for 7 days. The partial pressure of HCl vapors was $4.4 \cdot 10^{-5}$ mm Hg. Then, the pellets were dissolved in aqueous NaOH, and the

content of Cl-ions was determined by the titration.

The dimension of the coherent scattering region (CSR) as well as the density of dislocations was calculated from the broadening of the X-ray diffraction profile. Here, the first step was the extraction of the physical components from the total broadening profile using a Gaussian distribution:

$$\beta_s^2 = \beta_{ph}^2 + \beta_{st}$$

where β_s is the integral half-width of the sample profile, β_{ph} is the physical component of the broadening, and β_{st} is the integrated half-width of the standard sample. For the standard sample, it was assumed that the measured broadening is equal to the instrumental broadening only and is associated with both device characteristics and exposure conditions. In this work, the accurately crystallized gibbsite (Ecolan, Russia) was used as the standard sample. In order to calculate the CSR dimension of (D_{CSR}), we used the Scherrer equation

$$\beta_{ph} = \lambda / (D_{CSR} \cos \Theta)$$

where λ is the wavelength, and Θ is the position of the profile centroid of the sample. The density of dislocations was evaluated as

$$\rho = \beta_o^2 tan^{-1} \Theta / (2B)^2$$

where β_g is the Gaussian component of the physical broadening, *B* is Burgers vector.

Results

The preliminary experiments showed that the pelletized compositions prepared from starting materials are characterized by the very good sorption capacity in relation to the HCl vapors (Table 2). However, the mechanical strength of such pellets was found to be unsatisfactory low, so that after removing from the exiccator the pellets were completely destroyed. This allows one to conclude that the pregrinding of the original mixture ingredient is required in order to provide the better durability for the given sorption material. Previously, it has been reported that the mills with an impact-shearing action are frequently used for the grinding of oxide materials [10]. An optimal grinding time is determined by such factors as the process energy efficiency [14] and/or the completeness of the mechanochemical interactions [11,12]. In our case, since the initial compositions already have high absorption capacity and the grinding is the quite powerintensive process, the long grinding time seems to be not reasonable. That is why, in this study the grinding time was set as 10 minutes.

Composition ZnO/CaO/Al(OH)₃

The XRD patterns (Figure 1a) show that the gibbsite in the initial samples is in a good crystallized form. Such conclusion is based on the small broadening of the reflexes, for example in the range of 17.5-21 deg 2 Θ . At the same time, the wide reflexes of ZnO (for example, in the range of 31-37 deg 2Θ) allow one to conclude that the particles are in the highly dispersive state. Also, the weak peaks of CaO indicate the X-ray amorphous state of this phase (Figure 1).

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Num	Composition	Molar ratio ZnO:CaO:Al ₂ O ₃	Grinding time, min	Mechanical strength of pellets, MPa	Parametrs of a sorbent on it being kept over an HCl solution (P _{HCl} = 4.4×10 ⁻⁵ mm Hg)			
					mechanical strength of pellets, MPa	gain in mass, %	Cl⁻ content, mg·g⁻¹	
1a	ZnO/ CaO/ Al(OH) ₃	1:1:1	0	<0.5	Destroyed	3.63 ± 0.05	0.30 ± 0.02	
1b			10	3.7 ± 0.3	1.8 ± 0.2	4.25 ± 0.07	0.21 ± 0.01	
2a			0	<0.5	Destroyed	3.54 ± 0.06	0.17 ± 0.01	
2b			10	3.4	2.0 ± 0.2	4.16 ± 0.07	0.18 ± 0.01	
3a	Zn ₄ CO ₃ (OH) ₆ /CaO/Al(OH) ₃	3 1:1:1 3 1:1:2	0	<0.5	Destroyed	6.94 ± 0.06	0.50 ± 0.02	
3b			10	2.3 ± 0.2	2.2 ± 0.3	10.9 ± 0.07	0.34 ± 0.01	
4a			0	<0.5	Destroyed	7.05 ± 0.05	0.38 ± 0.01	
4b			10	3.2	3.2 ± 0.3	7.19 ± 0.06	0.29 ± 0.01	

Table 2: Characterization of the sorbent. Sample numbers correspond to Table 1.



ZnO:CaO:Al_2O_3 are 1:1:1 (1) and 1:1:2 (2). Sample numbers correspond to Table 1.

After the grinding in a vibratory mill, some new reflexes were detected on the XRD patterns (Figure 1b). These reflexes belong to Ca $(Zn_2(OH)_6)$ ·2H₂O (PDF #701561). The crystal lattice of the new phase is monoclinic, and the unit cell parameters are given in Table 3. Also, the data of Figure1b show that the grinding results in the reduction of both ZnO and CaO peaks intensities. This is a quite expectable phenomenon because the grinding process leads to amorphization of ZnO and CaO as well as to their consumption for the formation of Ca(Zn₂(OH)₆)·2H₂O. From Table 4, it can be seen that the composition with the oxide ratio of 1:1:2 shows a decrease in the intensity for the



Figure 2: IR spectra of the compositions $ZnO/CaO/AI(OH)_3$ before (a) and after (b) co-grinding in a vibratory mill during 10 min. Molar ratios $ZnO:CaO:AI_2O_3$ are 1:1:1 (1) and 1:1:2 (2). Sample numbers correspond to Table 1.

gibbsite reflexes in Table 4 (2ab). At the same time, behavior of the gibbsite peak in the composition with the oxide ratio of 1:1:1 requires the special comments. After co-grinding process, the intensity of reflexes from the <002> plane increases Table 4 (1ab). The calculations of the crystal structure demonstrate a decrease in the D_{CSR} of gibbsite particles in the sample 2 as well as point out on more than 25% increase on the gibbsite particle size in the sample 1 (Table 5). Accordingly, in the first case, the co-grinding procedure results in increasing gibbsite defectiveness while, in the second case, one can speak about more than 20% decrease in the density of dislocations. The unit cell parameters

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Num Molar ratio ZnO:CaO:Al ₂ O ₃		a, Å b, Å		c, Å	β, °	
1b	1:1:1	6.41 ± 0.01	11.03± 0.02	5.76 ± 0.02	78.46 ± 0.05	
2b 1:1:2		6.40± 0.03	11.03 ± 0.03	5.78 ± 0.02	78.52 ± 0.06	
ASTM PDF #701	561	6.384	10.97	5.756	78.02	

Table 3: Unit cell parameters	r Ca($Zn_2(OH)_6$)·2H ₂ O. Sample numbers correspond to Table 1.	

Num	Molar ratio ZnO:CaO:Al ₂ O ₃	Grinding time (min)	Parameters of the	e reflection peak from gibbsite (d = 4.87 Å)	Specific surface,	Amount of surface			
			Maximum intensity, imp·s ⁻¹	Integrated intensity, imp·s ⁻¹ ·deg	Integral half-width, deg	m²∙g ⁻¹	mmol·m ⁻²		
Composition ZnO/CaO/Al(OH) ₃									
1a	1.1.1	0	185 ± 2	87 ± 3	0.171 ± 0.001	30 ± 3	0.35 ± 0.01		
1b	1.1.1	10	295 ± 3	63 ± 2	0.158 ± 0.002	17 ± 2	0.31 ± 0.01		
2a	1.1.0	0	431 ± 5	83 ± 2	0.130 ± 0.001	22 ± 3	0.45 ± 0.01		
2b	1.1.2	10	371 ± 4	73 ± 3	0.145 ± 0.001	25 ± 2	0.39 ± 0.01		
Composition Zn ₄ CO ₃ (OH) ₆ /CaO/Al(OH) ₃									
3a	1.1.1	0	280 ± 3	94 ± 4	0.172 ± 0.001	19 ± 2	0.66 ± 0.01		
3b	1:1:1	10	396 ± 4	103 ± 4	0.141 ± 0.002	23 ± 2	0.30 ± 0.01		
4a	1.1.0	0	378 ± 4	73 ± 2	0.129 ± 0.001	21 ± 2	0.47 ± 0.01		
4b	1.1.2	10	454 ± 5	81 ± 3	0.138 ± 0.001	22 ± 2	0.40 ± 0.01		

 Table 4: Characteristics of compositions. Sample numbers correspond to Table 1.

	Compositions	Molar ratio ZnO:CaO:Al ₂ O ₃	CSR dimension, nm	Dislocations density, ρ·10⁻¹², cm⁻²	Unit cell parameters				
Num					a, Å	b, Å	c, Å	β, °	
				Initial gibbsite					
1-4a	All composit	ions	80 ± 2	1.89 ± 0.02	8.71 ± 0.02	5.11 ± 0.01	9.69 ± 0.02	94.12 ± 0.04	
	After grinding for 10 min								
1b	ZnO/CaO/ Al(OH) ₃	1:1:1	100 ± 4	1.48 ± 0.02	8.89 ± 0.02	5.09 ± 0.02	9.70 ± 0.03	93.73 ± 0.05	
2b	ZnO/CaO/ Al(OH) ₃	1:1:2	70 ± 2	2.43 ± 0.03	8.81 ± 0.02	5.05 ± 0.01	9.80 ± 0.02	94.67 ± 0.04	
3b	Zn ₄ CO ₃ (OH) ₆ / CaO/Al(OH) ₃	1:1:1	165 ± 5	1.13 ± 0.02	8.70 ± 0.02	5.10 ± 0.02	9.67 ± 0.03	93.85 ± 0.05	
4b	Zn ₄ CO ₃ (OH) ₆ / CaO/Al(OH) ₃	1:1:2	75 ± 2	2.10 ± 0.03	8.71 ± 0.02	5.10 ± 0.01	9.68 ± 0.02	93.76 ± 0.04	

Table 5: Characterization of the microstructure of the crystal lattice of gibbsite. Sample numbers correspond to Table 1.

of the gibbsite are also changed after the co-grinding. It should be noted that the co-grinding of the composition with oxides ratio of 1:1:1 causes a decrease in the specific surface area by almost 2 times Table 4 (1ab) while a decrease in the number of basic surface cites is observed for all oxide ratios. Probably, these phenomena are connected with the formation of new Ca($Zn_2(OH)_6$)·2H₂O phase in the mechanochemical synthesis process.

Figure 2 illustrates the analysis of the samples by the Fourier transformed infrared spectroscopy. It can be seen that, in the low-frequency region 800-400 cm⁻¹, there are several unclear absorption bands (Figure 2 (1a, 2a)) which cannot be identified correctly. The intensive absorption band at 1022 cm⁻¹ corresponds to the asymmetric vibrations in the Al–OH groups. The double band in the range of 1600–1300 cm⁻¹ belongs to the surface carbonate-hydroxyl groups adsorbed in the monodental form, and the band at 2100 cm⁻¹ point out on the possibility of condensation for both surface and internal hydroxyl groups. In the near-infrared region, one can see a clear band at 3640 cm⁻¹. This band reflects the stretching vibrations in the internal hydroxyl groups of the gibbsite. The broad band in the range of 4000-2500 cm⁻¹ represents the combined signal from the stretching vibrations in both Me–OH groups and hydroxyl groups in water molecules [21]. Since the layered hydroxides contain the interlayered carbonate, the absorption

band at 2925 cm⁻¹ can be associated with the vibrations in the bridgetype bonds between carbonate ions and water in the interlayer region [18,19]. After the grinding in a vibratory mill, the new absorption bands were found in the far-infrared 1000-400 cm⁻¹ region (Figure 2 (1b, 2b)). These bands correspond to the deformation vibrations in Me–O (Me = Al³⁺, Ca²⁺, Zn²⁺) bonds. The coalescence of the double band with an absorption maximum at 1425 cm⁻¹ demonstrates the appearance of a new spatial lattice. Also, a substantial increase in the absorption intensity in the range of 3300-2700 cm⁻¹ takes place. This is caused by the overlapping of the absorption bands for Me(II)–O groups formed due to the hydration of the particle surface [18,19].

Summarizing the XRD and IR data, one can conclude that the ratio of components in the initial $ZnO/CaO/Al(OH)_3$ mixture does not influence the reaction pathways in this system and, in fact, results only in the variations of quantitative parameters. That is why the further data will relate only to the composition with 1:1:1 oxides ratio.

The SEM images of the initial composition (Figure 3a) show that it contains the irregularly shaped particles with a predominant size of 0.5-4 μ m. These particles are the agglomerates of crystals with the sizes of 0.1-0.2 μ m. After the co-grinding, the crystals of a new phase with the prismatic shapes are clearly seen on the SEM images (Figure 3b). The size of these particles varies from 0.5 to 4 μ m while some of them



Figure 3a: SEM images of the composition ZnO/CaO/Al(OH)₃ (molar ratio ZnO:CaO:Al₂O₃ is 1:1:1) before.



Figure 3b: SEM images of the composition ZnO/CaO/Al(OH)₃ (molar ratio ZnO:CaO:Al₂O₃ is 1:1:1) before and after (b) co-grinding in a vibratory mill during 10 min. Scale bars are 0.5µm (left) and 1 µm (right).

reach are greater than 10 μ m. According to the XRD data described above, this new crystal phase is Ca(Zn₁(OH)₆)·2H₂O.

The thermal decomposition of the initial mixture exhibit the basic four step mechanism (Figure 4a) mentioned for many layered hydroxides [22]. The first mass loss occurring up to 200°C accounts for 1.98% of total mass loss. The nature of this stage is the removing of the weakly adsorbed and interlayer water. The second and third mass losses at 284°C are in agreement with the temperature range for the dehydroxylation of the gibbsite (Figure 4). These stages represent the largest mass loss of 12.71% from the total loss value, and their nature is the simultaneous dehydroxylation and removing of the interlayer anions from the gibbsite. A small maximum on the left side of the dehydroxylation peak on the DSC curve for this region consists of two overlapped peaks with the maximums at 221 and 284°C. This reflects the two-step decomposition of gibbsite: 0.5H₂O is removed on the first step, and the remaining 1.5H,O go out on the second step. Then, an increase in the temperature over 335-450°C caused the decarbonization of particles surface. An finally, the heating of the samples over 500°C results in complete dehydroxylation of aluminum hydroxide. After the co-grinding, the double peak on the DSC curve in the range of 200-330°C is merged into a single one (Figure 4b). Also, the maximum thermal effect is shifted to 286°C, and the mass loss is about 13.31% of the total mass loss. It is important to note that the value of endo effect falls down to 345 J·g⁻¹.

Composition Zn₄CO₃(OH)₆/CaO/Al(OH)₃

The XRD analysis shows that the co-grinding does not lead to the formation of a new phase. As can be seen from Figure 5, only the reflexes form the initial ingredients are present in the XRD patterns. Also, one can see both decrease in intensity and broadening of the peaks related to $Zn_4CO_3(OH)_6$ and CaO. For the <002> gibbsite plane, the peak intensity increases independently on the contents of the ingredients

in the initial mixture (Table 4 (3ab, 4ab)). The calculation show that, after the co-grinding, the value of $D_{\rm CSR}$ in a mixture with oxides ratio of 1:1:1 increases by 2 times (Table 5 (3ab)). This is accompanied by a decrease in the dislocation density by 40%. On the contrary, for the mixture with odes ratio of 1:1:2, the co-grinding results in a decrease in $D_{\rm CSR}$ of aluminum hydroxide while the density of dislocations shows an increase (Table 5 (4ab)). Simultaneosly, the unit cell parameters of gibbsite keep near-to-constant values.

After the co-grinding, the change of the specific surface is not observed (Table 4 (3ab, 4ab)). It was found also that the co-grinding causes a decrease in the number of basic surface sites. The last effect has a maximum value for the composition with oxides ratio of 1:1:1.

The IR spectra of the initial muxture in the long-wave region 1000–400 cm⁻¹ contain the bands corresponding to Me–O deformation vibrations (Figure 6 (3a,4a)). The double band at 1395 and 1515 cm⁻¹ belongs to carbonate groups. Similarly to the above discussed mixture of ZnO/CaO/Al(OH)₃, the near IR region also represent the absorption bands from the Me–OH stretching vibrations (Figure 6 (3b,4b)). After the co-grinding, the double band at 1395 and 1515 cm⁻¹ is merged into a single broad band with an absorption maximum at 1424 cm⁻¹. Also, a group of superimposed bands appears in the region of 3300–2700 cm⁻¹. This is a result of hydration of the particle surface with the formation of Me(II)–O groups. It should be noted that such phenomenon is more typical for the composition with oxides ratio of 1:1:1.

Again, the results of XRD and IR spectroscopy show that the ratio of components in $Zn_4CO_3(OH)_6/CaO/Al(OH)_3$ mixture affects only the quantitative parameters. That is why the below data will relate to the mixture with oxides ratio of 1:1:1 only. As can be seen from Figure







Figure 5: XRD patterns of the compositions $Zn_4CO_3(OH)6/CaO/AI(OH)_3$ before (a) and after (b) co-grinding in a vibratory mill during 10 min. Molar ratios $ZnO:CaO:AI_2O_3$ are 1:1:1 (3) and 1:1:2 (4). Sample numbers correspond to Table 1.



Figure 6: IR spectra of the compositions $Zn_4CO_3(OH)_8/CaO/Al(OH)_3$ before (a) and after (b) cogrinding in a vibratory mill during 10 min. Molar ratios $ZnO:CaO:Al_2O_3$ are 1:1:1 (3) and 1:1:2 (4). Sample numbers correspond to Table 1.

7, the qualitative changes in the composition after the co-grinding are not observed. Particularly, the particle aggregates with a size of $1-3 \mu m$ dominate in the mixture while the larger aggregates are also present. After the co-grinding, a large amount of particles with the sizes of $0.25-1.5 \mu m$ appear in the composition. Also, there are the aggregates with a size of 10 μm and more. The Thermal analysis showed that the thermolysis of this composition follows the four-step mechanism (Figure 8), as was mentioned above for the ZnO-containing mixture. The removing of the interlayer and weakly bound water (about 2.89 % of the total mass loss) occurs up to 200°C. The biggest mass loss of 16.52 % takes place in the temperature range of 230–330°C. This loss can be attributed to the dehydroxylation of gibbsite and decarbonization of basic zinc carbonate. After the co-grinding, the value of the total endo effect decreases from 446 to 439 J·g⁻¹, and the maximum on the DSC curve is shifted from 284 to 289°C.

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HCl vapors sorption

It was found that the maximum adsorption capacity for HCl vapours is for the composition based on basic zinc carbonate (Table 1). The XRD analysis did not point out on the formation of new crystalline phases because of their small amount. However, the halo appeared at the middle angles of diffraction indicates the formation of new X-ray amorphous structure. The absorption ability for the pellets made from the co-grinded ingredients was found to be lower. Such phenomenon is due to the complete destruction of the pellets prepared from the initial compositions to powdery state that provides higher absorbtion surface area.

After the exposure in acid vapors, the initial mechanical strength is kept on the same level only for the $Zn_4CO_3(OH)_6/CaO/Al(OH)_3$ compositions. In the case of ZnO-based mixtures, the strength of the pellets decreases by more than 2 times. According to the SEM data (Figure 9), this effect can be directly associated with the restructuring of the pellets during the absorption of water and acid vapors. Particularly, it can be seen that the new finely dispersed phase with a typical size of 0.2-1.5 µm is present on the surface of the particles. The formation of this phase weakens the contacts between the particles in the pellets and thus, results in decreasing strength of the overall pellet.

Discussion

According to the general concept of the soft mechanochemical synthesis [11], one must use the solids substances with higher reactivities compared with anhydrous oxides. The group of such substances includes solid acids, bases, acidic and basic salts and crystal hydrates which can react one with other with other releasing the water. Accordingly, in the compositions containing CaO, Al(OH)₂, ZnO and Zn₄CO₄(OH)₆ one can expect chemical reactions between gibbsite, calcium oxide or basic zinc carbonate with the formation of calcium/ zinc aluminates. However, the co-grinding process does not result in the formation of new compounds in the $Zn_4CO_3(OH)_6$ – based mixture. At the same time, the calcium and zinc oxides yielded the formation of $Ca(Zn_2(OH)_6) \cdot 2H_2O$, and the water required for the reaction comes from the ambient air. Therefore, in our case, the oxides exhibit the greater solid-phase reactivity compared with the carbonized and hydrated compounds. The similar regularities have been found for the alumocalcium bicomponent mixtures [15]. We believe that the results obtained in present study as well as published literature [15,16] do not contradict with the general concept of soft mechanochemical synthesis [10-13]. Really, the co-grinding process in air atmosphere leads to the formation of Ca-OH and Zn-OH, and the surface hydroxide groups



Figure 7: SEM images of the composition Zn₄CO₃(OH)₆/CaO/AI(OH)₃ (molar ratio ZnO:CaO:Al,O, is 1:1:1) before (a) and after (b) co-grinding in a vibratory mill during 10 min. Scale bars are 0.5 µm (left) and 1 µm (right).



facilitate the solid-phase synthesis in a vibratory mill. This conclusion is supported by the data of IR spectroscopy (Figures 2 and 6) as well as confirmed by published data [18,19].

The ratio of ingredients in the initial compositions influences the parameters of the gibbsite after the co-grinding process. In the case of relatively small content of Al(OH), (that corresponds to ZnO:CaO:Al,O, = 1:1:1), the co-grinding results in increasing D_{CSR} as well as in decreasing density of dislocations (Table 5). These phenomena can be explained by the following processes. The motion of dislocations in the gibbsite crystal lattice is observed under mechanical loading. Both Caand Zn-containing compounds which are present in the initial mixture with the predominant amounts damp the action of milling bodies. This results in the exit of dislocations on the surface as well as in their annihilation without the crack of the crystal. Accordingly, the number of dislocations decreases, and the length of the defectless region (D_{scr}) increases. The lower contents of Ca- and Zn-containing compounds in the initial mixture (for example, in the case of $ZnO:CaO:Al_2O_2 = 1:1:2$) leads to the dispergation of the gibbsite crystalls and to the growth of crystal lattice defects (Table 5). Here, these compounds play the role of surfactants.

It is important to note that the maximum increase in the gibbsite particle size is obtained for the Zn₄CO₃(OH)₆ - containing compositions with the oxides ratio of 1:1:1 while the maximum reduction of aluminum hydroxide particle size was found for ZnO - containing mixtures with the oxides ratio of 1:1:2. In order to explain these phenomena, one can account for the hardness of crystals. Particularly, the hardness of the gibbsite crystals on the Mohs scale is 2.5-3, and the hardnesses of CaO, ZnO and Zn₄CO₃(OH)₆ are 2.5, 4-5 and 2-2.5, respectively. Thus, the harder ZnO crystallites may easily crack crystals of gibbsite while the softer crystals of basic zinc carbonate are able to reduce the surface energy and to provide the annihilation of dislocations without destruction of the aluminum hydroxide crystallites.

Conclusions

It was shown that the co-grinding of ZnO/CaO/Al(OH)₃ and Zn₄CO₃(OH)₆/CaO/Al(OH)₃ compositions with ZnO:CaO:Al₂O₃= 1:1:1 or 1:1:2 molar ratios in a vibratory mill with an impact-shear loading leads to the formation of new of Ca(Zn₂(OH)₄) phase in the form of prismatic crystals only in the ZnO-based mixtures. This is accompanied by a decrease of the specific surface area by more than 1.5 times. In the Zn₄CO₃(OH)₆ - based mixtures, the co-grinding causes only the amorphization of zinc and calcium containing compounds



Figure 9: SEM images of ZnO/CaO/Al(OH) $_3$ (a) and Zn4CO $_3$ (OH) $_6$ /CaO/Al(OH) $_4$ (b) compositions (molar ratio ZnO:CaO/Al $_2O_3$ is 1:1:1) after HCl vapor sorption. Scale bars are 1 µm (left) and 5 µm (right).

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while the specific surface area remains almost constant.

The co-grinding process results in the hydration of the surface of the particles with the formation of Me(II)–OH groups. Such process yields the equalization of the acid-base properties of the compositions.

For the relatively small contents of $Al(OH)_3$ (the molar ratio of oxides in the initial mixture is 1:1:1), the milling process is characterized by the aggregation of the particles as well as by a decrease in their defectness. With higher contents of $Al(OH)_3$ (the molar ratio of oxides in the initial mixture is 1:1:2), the co-grinding process reduces the dimension of the coherent scattering region of the gibbsite. This leads to the slightly decreasing endothermic effect of dehydroxylation and is accompanied by an increase in the thermolysis temperature.

It was found that the $Zn_4CO_3(OH)_6/CaO/Al(OH)_3$ compositions is characterized by 1.5 times greater HCl vapors absorption capacity compared with the ZnO/CaO/Al(OH)_3 system. The pellets prepared from both initial mixtures have low mechanical strength. These are destroyed completely after the adsorption of HCl vapors. The cogrinding allows one to increase the strength of pellets and, as a result, to save shapes after the exposure in HCl vapors under the HCl solution.

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