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MECHANOCHEMICAL SYNTHESES AS AN EXAMPLE OF GREEN PROCESSES

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Presented work describes mechanical treatment as a non-conventional solid-state process for preparation of some functional materials. Mechanochemical syntheses may be alternative as waste-free and ecologically safer methods of preparing pigments, composites, catalysts, biomaterials, which obey main principles of Green Chemistry.

Keywords: *catalysts, composites, green chemistry, high-energy ball milling, mechanochemical synthesis, pigments*

Introduction

Green Chemistry is the term dealing with the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances and began as a program of the U.S. Environmental Protection Agency in the early 1990 [1]. Industry is adopting Green Chemistry because it gives economic benefits mainly due to decreasing operating costs. When less waste is generated, environmental compliance, costs go down. One can conclude that Green Chemistry is an environmental, health and safety strategy that emphasizes pollution prevention. The green activity design process includes the selection of safer starting materials, avoiding the use of toxic solvents, using renewable materials, lowering the energy inputs and returning safe substances to the environment. As Green Chemistry, the essence of which is 12 Rules published by Anastas and Warner [2–5], looks to the future the fundamental scientific challenges, facing the field could include:

- the design protocol for molecular structures that are inherently less hazardous to human health and the environment;
- the integration of material and energy systems for the synthesis and isolation of new molecules;
- a molecular level understanding of the nature of chemical synergism in the body and the biosphere;
- design of chemical systems that possess intrinsic ability to resist perturbations that could cause accidents, performance failure or toxicity (resilience);
- design new methods of syntheses more environmentally friendly, energetically effective, e.g. mechanochemical treatments.

Mechanochemical processes – general considerations

Mechanochemistry is a promising branch of solid chemistry for achieving Green Chemistry goals. Mechanochemical treatment is a typical example of non-conventional solid-state process, which can be using for a synthesis of new materials characterized by new properties. However, these processes are not new ones, mechanical activation dates back to the early history of humanity, for example, the use of flints to initiate fire [6, 7].

Milling is very practical, convenient and rational tool for providing chemical reaction especially in solid-state without heating and in large quantities. Specific features of the mechanochemical processes clearly differentiated them from thermally activated ones. Mechanical treatment can change the thermodynamic potentials of reagents and diminish the temperature of the chemical reactions. For many solid-phase chemical reactions, the limiting stage is the diffusion in the solid state while mechanical treatment intensifies transport of the reagents. It is known that mechanically stimulated synthesis can be performed at temperatures up to 50% lower than those in conventional synthesis could. One can encounter situations when traditional synthesis of a compound is impossible while mechanically stimulated synthesis would change e.g. the reaction temperature making the synthesis possible [8].

Mechanochemical processing are differentiated as mechanical milling, mechanical alloying and reactive milling. Mechanical milling refers to the milling of a pure metal or compound, which is in a state of thermodynamic equilibrium at the start of milling. Mechanical alloying refers specifically to the formation of alloys from elemental precursors during processing in

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a ball mill. Reactive milling uses mechanical processing to induce chemical reactions [9, 10].

Mechanochemical technology covers a wide range of important reactions in industrial processes such as intensification of dissolution and leaching processes, faster decomposition and synthesis, preparation of substances with new properties and improvement in sintering properties.

Nevertheless, there are some problems dealing with the mechanochemistry like e.g. understanding unusual properties possessed by nanoscale mechanically treated solids. Moreover, the investigation of the thermal stability and relaxation mechanism of mechanically induced metastable states in solids is required. The problem associated with the mechanically induced structural disorder as well as with the description of the structure of mechanically activated and mechanosynthesized solids needs to be solved. Although mechanochemistry offers direct reaction routes and solvent free, low temperature technologies of synthesis ultrafine powders, amorphous glassy phases alloy from elements difficult to alloying [11, 12].

Practical examples of mechanochemical processes related to Principles of Green Chemistry

Mechanochemical degradation of pollutants

One of the examples of usefulness mechanochemistry in environment protection is a mechanochemical degradation of polychlorinated biphenyls (PCBs), chlorinated pesticides, polychlorinated dibenzodioxins and furans, which make a serious problem for environment [13]. Traditional methods of their degradation based on incineration at high temperature often lead to formation more harmful congeners. Therefore, an effective method of utilisation this kind of substances is searching. Methods based on mechanochemical activation developed by Rowlands *et al.* [14] led to transformation of the reactants to hydrogen, graphite, calcium halide, and/or calcium hydride–halide mixed salt. Monaghedu *et al.* [15] modified this method by providing mechanochemically induced combustion process in which dioxins are mixed with hexachlorobenzene and calcium hydride. The last ones react to each other with evolving high amount of heat according to the equations:

$$6CaH_2+C_6Cl_6=6CaHCl+6C+3H_2 \quad \Delta H=-1804 \text{ kJ mol}^{-1}$$

$$3CaH_2+C_6Cl_6=6CaCl_2+6C+3H_2 \quad \Delta H=-1709 \text{ kJ mol}^{-1}$$

The heat evolved in above reactions burns dioxins. Whole process had realized in one single milling operation (e.g. using Spex Mixer–Mill operated at 875 rpm, in argon atmosphere).

The philosophy of Green Chemistry is also taking into account in the work of Ryou [16], where the improvement on reactivity of cementations waste materials had realized by mechanochemical treatment. Such waste defined as a cement kiln dust (CKD) forms during cement manufacturing. The United States cement industry generates about 5 million tons of CKD every year and only 20% of such amount are utilised. CKD is used as a supplementary cementitious material that owing mechanical treatment has increased surface free energy making material more reactive.

Other waste, which is very hazardous for environment and difficult to treat due to their variability, is asbestos containing wastes (ACWs) [17]. Amount of ACW reaches 30 million tons. These wastes have mechanically treated using a Herzog HSM 100 ring mill equipped with a tungsten carbide bowl. The results of this experiment show that milling of asbestos involves complete disappearance of asbestos fibres after several minutes. These methods of ACW utilization are easy to perform and additionally gas and dust pollution from mechanochemical reactors is low, because whole process is realised in a closed milling vial. In such case, thermal treatment of material could be eliminated.

Mechanochemical syntheses of some functional materials

Pigment production

Chromium is a known element widely used for pigment synthesis because it exists in many states of oxidation, i.e. II–VI what generates different properties, such as stability and coloration. One of the examples of pigments based on chromia is a $Cr_{1.23}Al_{0.77}O_3$ applied as green pigments. The literature data shows some examples of such chromium pigments syntheses, unfortunately mainly based on highly toxic carcinogen Cr(VI) as chromium precursor. Moreover, these syntheses require high temperature and/or using mineralizers to lower synthesis temperature.

From thermodynamic standpoint, Cr_2O_3 and Al_2O_3 oxides form substitution solid solution at the temperature above 950°C. Below this temperature, both phases exist in separate forms. The chromium in the structure of chrome-alumina pigment is present as Cr^{3+}. Colours of this pigment range from green to red, depending on the chromium content.

A conventional ceramic method of synthesis of this pigment is based on calcinations at temperatures above 1300°C. As the diffusion controls the rate of product formation, high reaction temperature is required what involved increasing of pigment synthesis cost. Moreover, such high temperature causes volatile reagents losses changing the stoichiometric conditions

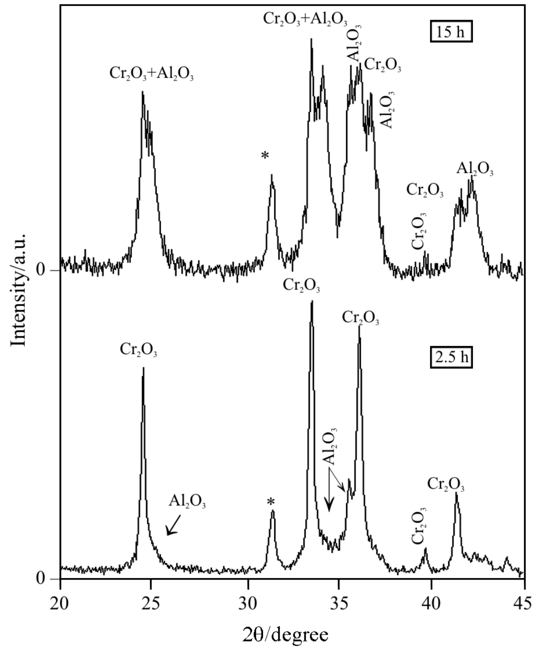

Fig. 1 X-ray diffraction patterns for Cr_2O_3–Al_2O_3 pigment synthesized by mechanochemical treatment for 2.5 and 15 h, respectively; *WC–contamination from milling device

in the system. The alternative for this method is a mechanochemical synthesis that can be realized at room temperature using Cr_2O_3 as a precursor. The additional benefit of the method based on high-energy ball milling is the possibility obtaining the nanocrystalline form of pigment [18–21].

In our laboratory, the attempts of the mechanochemical synthesis of green pigments were undertaken starting from chromium and aluminium oxides using a planetary ball mill Pulverissette 6 Fritsch GmbH. As XRD data indicate the Al_2O_3 is incorporated into Cr_2O_3 matrix and solid solution is formed (Fig. 1). Elongation of milling time causes the total disappearance of chromia reflexes.

Nanocomposites formation

Casting and powder metallurgy processes produce traditionally composite materials. Keeping in mind technological difficulties dealing with their multi-stage character, high temperature synthesis, large amount of wastes in mind, mechanochemical synthesis is an alternative as a dry, waste-free and ecologically safe method of composite formation [22]. The first group of composite materials synthesized mechanochemically was oxide-dispersion-strengthened (ODS) alloys used for high temperature structural applications. In this case, mechanochemical treatment was used for introduction of hard oxide particles (Al_2O_3, Y_2O_3) into relatively soft metal matrix, i.e. Al, Ni. These composite materials have high stability especially at high temperatures due to mixing of each constituent at the atomic level [23]. Currently produced composite materials are based on direct synthesis composite phases by milling. It causes better thermodynamic stability and higher homogeneity in microstructure. An interesting kind of material synthesized in this way is a composite. This material can be applied as a resistance welding electrodes and electrical connectors [24–26]. We have synthesized [27, 28] Cu–Al/Al_2O_3 nanocomposite from two different systems of precursors, i.e. CuO–Al and $Cu_2(OH)_2CO_3$–Al, using a high-energy ball mill (Pulverissette 6 Fritsch GmbH):

Final product in both systems was composite consisted of Cu(Al) solid solution and alumina (Al_2O_3). However, the kinetics of its formation was different. In the first system, final products appear after 10 h of milling while in the second one after 20 h (Fig. 2). This is because presence of CuO, required for aluminothermic reaction ($CuO+Al \rightarrow Cu+Al_2O_3$), should be preceded by decomposition of $Cu_2(OH)_2CO_3$ to CuO by mechanical treatment. However when CuO and Al directly react, the reaction may have combustive character leading to formation of coarse and separated particles of each composite phase. In order to produce Cu–Al matrix composite with fine dispersion of alumina particles, the combustive reaction must be suppressed. To achieve this effect the using less reactive initial reagents, e.g. salt, is needed. Figure 3 shows the microstructure with high degree of homogeneity of synthesized composites mentioned above.

Although our experiments demonstrate the formation of composite consisted of Cu(Al) solid solution and alumina, mechanical treatment permits to synthesize other intermetallic phases from Cu–Al binary phase system. However, it depends on the possible difficulties in their nucleation. It follows from

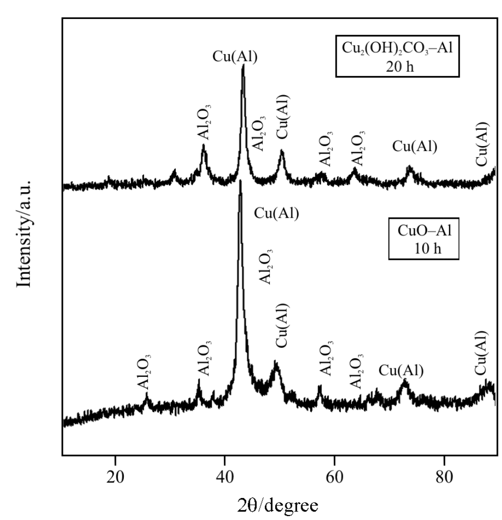

Fig. 2 X-ray diffraction patterns for composite synthesized mechanochemically from mixtures CuO–Al and $Cu_2(OH)_2CO_3$–Al, respectively

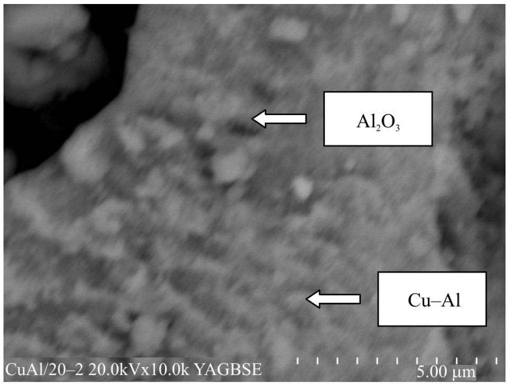

Fig. 3 Microstructure of Cu–Al/Al_2O_3 composite mechanochemically synthesized

the experiments that intermetallic compounds with complex or large unit cells are difficult to nucleate. At the same time, metallic electron phases form particularly easily during solid state reactions, even when their unit cells are rather complex and energy of formation is not very negative. Therefore, in both tested systems mechanochemical treatment causes the formation of Cu_9Al_4 intermetallics in spite of its unit cell is relatively large and complicated.

Biomaterials synthesis

Among the numerous biomaterials, ceramics made from hydroxyapatite has successfully used in orthopaedic and dentistry. Generally, it is prepared at high temperatures either by solid-state reaction between calcium and phosphate salts or by heating of a poorly crystallized hydroxyapatite. Mechanochemical treatment has been receiving particular attention recently as an alternative route to prepare materials characterized by better formability and biocompatibility with natural bone [29, 30]. For example, hydroxyapatite was synthesized in the two-step reaction process. First, a mechanochemical treatment of calcium pyrophosphate ($Ca_2P_2O_7$) and calcium carbonate ($CaCO_3$) mixture was realized in a mill operated at 170 rpm, then the product was calcined at 1100°C for 1 h. Obtained results indicated that the formation of the single phase of hydroxyapatite is critically dependent on the amount of the absorbed water formed during milling operation.

Our exploratory experiments dealing with the mechanochemical direct synthesis of hydroxyapatite starting from CaO and $CaHPO_4$ show that crystalline product appears in the system after 8 h of milling (Pulverissette 6 Fritsch GmbH) (Fig. 4). However, elongation of mechanical treatment time is required for increasing the yield of hydroxyapatite synthesis.

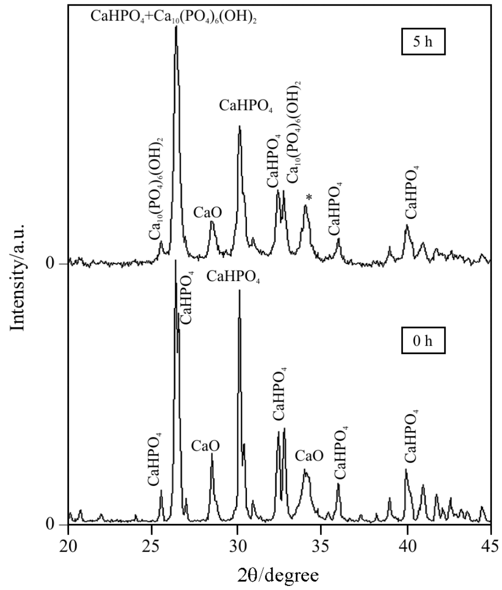

Fig. 4 X-ray diffraction patterns for CaO–$CaHPO_4$ system before and after its mechanochemical treatment; *WC – contamination from milling device

Catalysts synthesis

Traditional methods of catalyst preparation, which are based on precipitation and/or impregnation, are multistep processes. Mechanical treatment realized by high-energy ball milling of solid catalytic precursors in single step reduces this disadvantage. In our study [31] the possibility of supporting of vanadia nanolayer on chromia support during milling under different conditions was tested. It has proved that such operation is effective and involves spreading of vanadium oxide on chromia surface. Enrichment of surface catalyst with vanadium is a probable reason of higher catalytic activity of tested materials in oxidative dehydrogenation of propane [32].

Versatilities of thermal analysis methods for identifying and characterization the materials synthesized mechanochemically

A comprehensive study of physical and chemical processes, which occur during mechanical treatment by means of high-energy ball milling, is only possible if reliable identification of solids and the quantitative phase analysis of activated products is performed. Difficulties arise from the fact that the reactions are composed of many successive stages, which are very different in different cases. The experimental methods required for identifying and characterizing materials synthesized mechanochemically involve not only those techniques which are applicable to solids, but also others, more particularly adapted to the nanostructured character of the milling products. The universal method is the thermal analysis. Such techniques as thermogravimetry and the differential thermal analysis are very useful for describing mechanically activated substances because they make it possible to identify highly defected, finely crystalline, nanocrystalline materials or even amorphous phases formed during milling which might be difficult to achieve using other methods. Moreover, the thermal analysis allows the estimation of the quantitative phase composition of the activated mixture that enables for example, estimating the consumption of the initial components of the tested mixtures. Moreover, in some cases, thermoanalytical experiments may be used for simulating reactions, transformations that occur during reactive ball milling [33–35].

Final remarks

Presented examples of using mechanochemistry as a green technology describe the practical process in which wastes formed in classically realized synthesis are utilised mechanochemically. However, it seems to be more interesting the innovative applying of mechanical activation for direct synthesis of different kind of materials such as pigments, catalysts, composites and biomaterials. Although the effective mechanical activation of solids needs choosing the optimum conditions by systematic studies of progress the mechanochemical synthesis. The final effect strongly depends on the type of mills and various internal and external factors of operation.

It is worthwhile to underline that mechanochemical processes enable not only mixing of components at the atomic level, but also allow to synthesis the materials with controlled homogeneity and with nanocrystalline form. Nanometer-sized materials have generated great interest in the past decade, due to their specific properties, significantly different from those of materials with dimensions larger than 100 nm. Nanocrystalline products are exceptionally hard, ductile at high temperatures, wear-resistant, erosion-resistant and chemically very active, therefore are also much more formable than the conventional, commercially available counterparts are.

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References

1 D. L. Hjeresen, M. M. Kirchoff and R. L. Lankey, Corporate Environmental Strategy, 9 (2002) 259.
2 P. T. Anastas, M. M. Kirchoff and T. C. Williamson, Appl. Catal., A: General, 221 (2001) 3.
3 T. J. Nameroff, R. J. Garant and M. B. Albert, Research Policy, 33 (2004) 959.
4 D. Mooney, Chemical Health Safety, (2004) 24.
5 P. T. Anastas and J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York 1998.
6 E. Avvakumov, M. Senna and N. Kosova, Soft Mechanochemical Synthesis, Kluwer Acad. Publ., Boston, 2001.
7 L. Takacs, Prog. Mater. Sci., 47 (2002) 355.
8 B. Murty and S. Ranganathan, Int. Mater. Rev., 43 (1998) 101.
9 C. Suryanarayana, Prog. Mater. Sci., 46 (2001) 1.
10 F. H. Froes and B. Trindade, J. Mater. Process. Technol., 153–154 (2004) 472.
11 V. V. Boldyrev and K. Tkačova, J. Mater. Synth. Process., 8 (2000) 121.
12 K. Tkačova, Mechanical Activation of Minerals, Elsevier, Amsterdam 1989.
13 M. Monagheddu, G. Mulas, S. Doppiu, C. Deidda and G. Cocco, J. Phys. D. Appl. Phys., 36 (2003) 1917.
14 W. N. Rowlands, R. W. O'brien, R. J. Hunter and V. Patrick, J. Colloid Interf., 188 (1997) 325.
15 M. Monagheddu, G. Mulas, S. Doppiu, G. Cocco and S. Raccanelli, Environ. Sci. Technol., 33 (1999) 2485.
16 J. Ryou, Mater. Lett., 58 (2004) 903.
17 P. Plescia, D. Gizzi, S. Benedetti, L. Canilucci, C. Fanizza, P. De Simone and F. Paglietti, Waste Manage., 23 (2003) 209.
18 E. Ozel and S. Turan, J. Eur. Ceram. Soc., 23 (2003) 2097.
19 S. M. Naga, I. S. Ahmed Farag and D. M. Ibrahim, Ceram. Int., 21 (1995) 51.
20 P. Šulcová and M. Trojan, Dyes and Pigments, 4 (1998) 83.
21 R. Munoz, N. Masó, B. Julián, F. Marquez, H. Beltran, P. Escribano and E. Cordoncillo, J. Eur. Ceram. Soc., 24 (2004) 2087.
22 T. F. Grigor'eva, A. P. Barinova and N. Z Lyakhov, J. Nanopart. Res., 5 (2003) 439.
23 C. C. Koch, Nanostruct. Mater., 9 (1997) 13.
24 D. L. Zhang, Prog. Mater. Sci., 49 (2004) 537.
25 D. Y. Ying and D. L. Zhang, Mater. Sci. Eng., A361 (2003) 321.
26 J. M. Wu and Z. Z. Li, J. Alloys Compd., 299 (2000) 9.
27 K.Wieczorek-Ciurowa, K. Gamrat and K. Fela, Solid State Ionics, 164 (2003) 193.
28 K. Wieczorek–Ciurowa, K Gamrat and Z. Sawłowicz, J. Therm. Anal. Cal., 80 (2005) 619.
29 S. Rhee, Biomaterials, 23 (2002) 1147.
30 C. Mochales, H. El Briak-BenAbdelsam, M. P. Ginebra, Biomaterials, 25 (2004) 1151.
31 K. Wieczorek-Ciurowa, A. Gomułczak, J. Rakoczy, K. Gamrat, J. Stoch and Zb. Sawłovicz, Polish J. Appl. Chem., 49 (2005) 253.
32 A. Gomułczak, K. Wieczorek-Ciurowa, K. Gamrat and V. A. Zazhigalov, Ogólnopolskie Kolokwium Katalityczne, Kraków 15–18 marca 2006, Materiały (Ed. Ł. Mokrzycki), IKiFP PAN Kraków Poland) 2006 (ISBN 83-60514-00-3).
33 K. Wieczorek-Ciurowa, K. Gamrat, M. Paryło and Ju.G. Shirokov, J. Therm. Anal. Cal., 70 (2002) 165.
34 K.Wieczorek-Ciurowa, K. Gamrat, M. Paryło and Ju.G. Shirokov, J. Therm. Anal. Cal., 69 (2002) 237.
35 K. Wieczorek-Ciurowa, Ju. G. Shirokov and M. Paryło, J. Therm. Anal. Cal., 60 (2000) 59.

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