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AN ATTEMPT ON THE VOC OXIDATION USING MECHANICALLY ACTIVATED CATALYST

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Abstract

A catalytic action of the mechanochemical products of copper hydroxocarbonate with calcium carbonate was investigated in *n*-butyl alcohol oxidation tests. The solid products of high-energy milling were identified using thermogravimetry supplemented by X-ray diffraction method. It was shown that the mechanical activation induces more effective tested catalyst because it promotes the alcohol conversion at lower temperatures than that unmilled one.

Keywords: catalyst, Cu-hydroxocarbonate, mechanical activation, oxidation, thermal analysis, volatile organic compounds (VOC)

Introduction

Catalysis offers the possibility of fast and selective production of the desired chemical products. Therefore, the progress of catalysis, both science and technology depends on the new method of synthesis of catalytic materials.

Mechanical activation of solids by high-energy milling could be effective and harmless for the environment way for catalyst preparation.

Moreover this method has long been known as a technique which allows production of homogenous alloys starting from elemental powder mixtures. Such treatment can drive reactions which have a potential barrier and which cannot take place even at high temperatures [1–5].

The changes in the properties of solids during milling depend on the energy transferred into the materials. The type of a mill governs it. Mechanical activation is usually carried out in high-energy devices, such as planetary, vibrational and attritor mills where the phenomena of plastic deformation, fracture and friction occur. The impact energy is converted into different forms of energy. The increase of specific surface area and local growth of temperature and pressure are observed. Mechanical impulse also involves broken bonds, the structural and textural changes in milled ma-

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terials. High density of defects appearing during milling facilitates the diffusion processes. These carriers of excess energy are accumulated and mainly they cause activity of solids [6–10].

The catalysts obtained by processing, e.g. in a planetary ball mill, could be applied for combustion of hydrocarbons in flue gases. From the practical point of view the most important objective of catalytic combustion is the reduction of pollutant level in air.

The aim of this study is the general illustration of the action of mechanically activated products of $Cu_2(OH)_2CO_3{\cdot}CaCO_3$ system during the combustion of *n*-butyl alcohol, which was chosen as representative of volatile organic compounds (VOC).

Experimental

Stages of preparation catalysts

In the work three catalysts (I–III) were tested. They were prepared as a physical mixture of $Cu_2(OH)_2CO_3$–$CaCO_3$ at equimolar ratio of CuO:CaO. Copper hydroxocarbonate (malachite) and calcium carbonate (calcite) were obtained in a powder form by precipitation from aqueous solutions [11].

The catalysts II and III were mechanically treated in a laboratory planetary mill with balls made of steel [12]. Ball to material mass ratio was 14:1. The velocity of the ball was 3.20 m s^{-1}. The two vials were rotated at 1130 rpm. Milling was carried out in air, at ambient temperature and atmospheric pressure for 3 and 15 min. Catalyst I was not subjected to milling.

After mechanical treatment, each catalyst, i.e. samples I–III, was activated by heating at 673 K for 2 h, in air atmosphere.

The mesh fraction of 0.25–0.5 mm was used.

Phase identification of catalyst materials

Thermogravimetric analyses of the samples were carried out on a Mettler thermobalance TG-50 in a Mettler TA-4000 System. Records were obtained with samples heated up to 1223 K at a rate of 24 K min^{-1}, in an open platinum crucible. The sample size was about 20 mg.

X-ray powder diffraction patterns were obtained using a Philips X' Pert Diffractometer (CuK_{α}) in the 2θ range of 10–60°.

Catalytic tests

Catalysts were tested in deep oxidation of *n*-butyl alcohol. The catalytic test was conducted in a stainless steel microreactor loaded with 0.1 g of catalyst, at atmospheric pressure. Gases were analysed on-line with gas chromatograph, equipped with TCD detectors. Content of alcohol used in the test was 1.4% vol.

Results and discussion

The phase composition of the tested catalysts was estimated on the basis of thermogravimetric analysis (Fig. 1) and X-ray powder diffraction measurements (Fig. 2). The results are in the Table 1. As one can see, calcium carbonate, $CaCO_3$, is stable during milling, however malachite, $Cu_2(OH)_2CO_3$, decomposes partially forming CuO according to the reaction (1)

$$Cu_2(OH)_2CO_3 = 2CuO+CO_2+H_2O \tag{1}$$

Table 1 Phase composition of the $Cu_2(OH)_2CO_3$ – $CaCO_3$ system – sample I and its products after milling for 3 min sample II and for 15 min sample III

Sample	Phase composition/%		
	$Cu_2(OH)_2CO_3$	CuO	$CaCO_3$
I	52	0	48
II	23	24	53
III	6	39	55

The amount of copper oxide increases with milling time from 24 to 39% in the interval of 3–15 min.

For normal catalytic reason all samples were calcinated at 673 K involving only decomposition of $Cu_2(OH)_2CO_3$. $CaCO_3$ was thermally stable (as it was expected because of the calcination condition). It is important to note that after this operation all applied catalysts consist of 44% of CuO and 56% of $CaCO_3$. Although they differ in

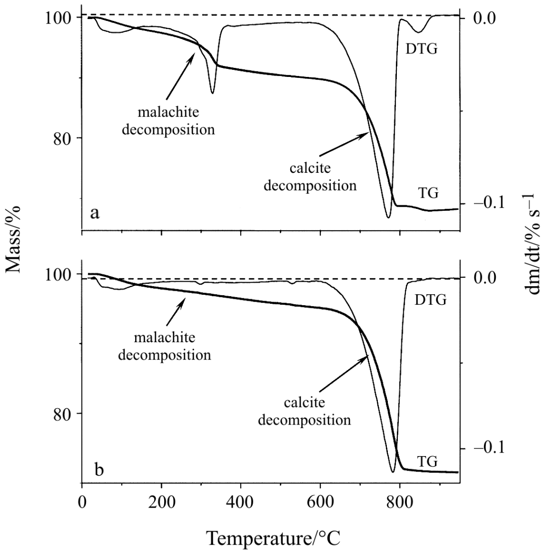

Fig. 1 TG/DTG curves for $Cu_2(OH)_2CO_3$ – $CaCO_3$ mixture after milling for: a – 3 min, b – 15 min

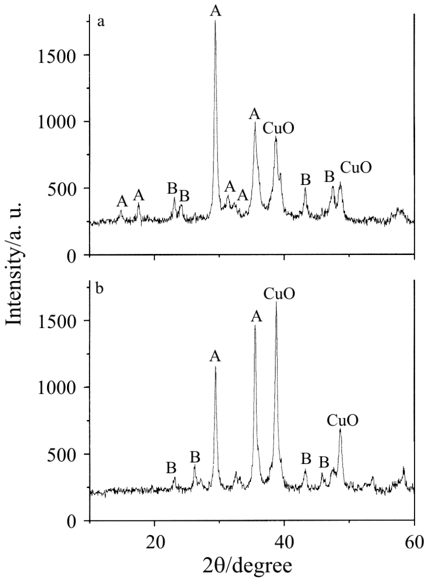

Fig. 2 X-ray diffraction patterns for $Cu_2(OH)_2CO_3$ (A) – $CaCO_3$ (B) mixture after milling for: a – 3 min, b – 15 min

the amount of CuO induced by the mechanical treatment (Table 1). It means that catalyst II includes 59% and III – 90% of CuO from the malachite decomposition in mill.

The reaction of *n*-butyl alcohol oxidation in which catalysts I–III were tested was as follows:

$$C_4H_9OH+6O_2=4CO_2+5H_2O \tag{2}$$

Catalyst activity was estimated on the basis of the temperatures needed to get 50 and 90% conversion levels of alcohol. Content of alcohol in the products was measured. The diagram showing the work of catalysts is given in Fig. 3. One can see that alcohol combustion temperature decreases in the presence of the mechanically activated catalysts, i.e. samples II and III (Table 2). Thus, the sample II leads to decrease of T_{50} from 540 to 505 K and T_{90} from 560 to 511 K in comparison with sample I which was without milling.

Table 2 Comparison of the temperatures for 50 and 90% conversion levels by using I–III catalysts in *n*-butyl alcohol oxidation

Sample	Milling time/ min	Temperature/K	
		T_{50}	T_{90}
I	0	540	560
II	3	505	511
III	15	508	515

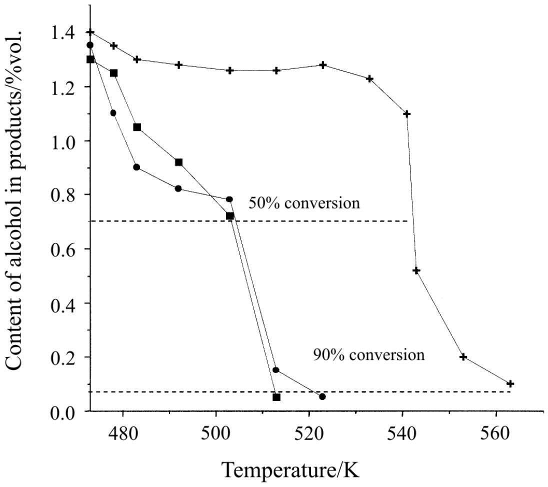

Fig. 3 Dependence of *n*-butyl alcohol conversion on temperature by using catalysts: + – I, ■ – II, ● – III

How could be explained the differences between mechanically treated catalysts (samples II and III) and untreated (sample I)? The probable answer is that two different origin of copper oxide are present in II and III samples. Thus the systems after mechanical activation contain CuO both after 'mechanical' decomposition of copper hydroxocarbonate and after calcination of undecomposed $Cu_2(OH)_2CO_3$ during milling. Whereas sample I which was not activated by milling includes CuO formed during calcination.

Moreover, it can be assumed that $CaCO_3$ is a support for both copper oxides being active catalytic phases.

Conclusions

The presented results indicate that the mechanical impulses in a high-energy mill improve the catalytic properties of solids.

The nature of copper oxide formed during the decomposition of hydroxocarbonate in mechanical treatment is probably responsible for higher catalytic activity. It should state that this positive effect is due to the increase in oxygen vacancy concentration, which favours the adsorption of gaseous oxygen and its transformation into lattice oxygen.

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