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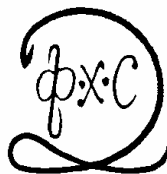
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# PHYSICAL CHEMISTRY 2018

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*Organized by*

*The Society of Physical Chemists of  
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*in co-operation with*

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*and*

*Boriskov Institute of Catalysis Siberian Branch of  
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*and*

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## SYNTHESIS OF CALCIUM OXIDE BASED CATALYSTS FOR BIODIESEL PRODUCTION

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### ABSTRACT

In this work, synthesis of several types of calcium oxide based catalysts by mechanochemical treatment and subsequent calcination is presented. Prepared nanocomposite CaO·ZnO, calcium containing perovskites CaTiO<sub>3</sub>, CaMnO<sub>3</sub>, CaZrO<sub>3</sub> and Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, a series of CaO·SiO<sub>2</sub> mixed oxides and calcium diglyceroxide (CaDG) were characterized and tested in the methanolysis of sunflower oil under different working conditions: catalyst amount, agitation speed, temperature and methanol to oil molar ratio.

### INTRODUCTION

Biodiesel, a mixture of fatty acid methyl esters (FAME), due to its environmental benefits such as non-toxicity and biodegradability and the fact that it might be synthesized from renewable resources, has gained significant attention as a promising alternative substitute to diesel fuels. Commonly, biodiesel is produced by alcoholysis of different triacylglycerols in the presence of homogeneous or heterogeneous catalysts. Calcium oxide due to the high activity, availability and low cost is one of the most studied heterogeneous catalysts [1]. However, since leaching into the reaction medium was observed for this catalyst, it is important to improve CaO properties by supporting it on different carriers or mixing with other oxides. Mechanochemical synthesis is a simple and waste-free technique for the preparation of different materials, including catalysts.

Milling of CaO and ZnO with water was carried out to obtain calcium zinc hydroxide hydrate (CaZn<sub>2</sub>(OH)<sub>6</sub>·2H<sub>2</sub>O), which was subsequently transformed to CaO·ZnO catalyst by calcination at 700 °C for 3h [2]. Calcium diglyceroxide (Ca(C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>)<sub>2</sub>) was synthesized by mechanochemical treatment of CaO dispersed in glycerol [3]. Calcium-containing perovskites CaTiO<sub>3</sub>, CaMnO<sub>3</sub>, CaZrO<sub>3</sub> and Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> were synthesized by calcination of mechanochemically treated stoichiometric mixtures of CaCO<sub>3</sub> and either TiO<sub>2</sub>, MnO<sub>2</sub>, ZrO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub> powders [4]. Mixtures of CaO and SiO<sub>2</sub> in a molar

ratio in the range of 1 to 3 with addition of water have been mechanochemically treated and calcined to prepare a series of  $\text{CaO}\cdot\text{SiO}_2$  mixed oxides.

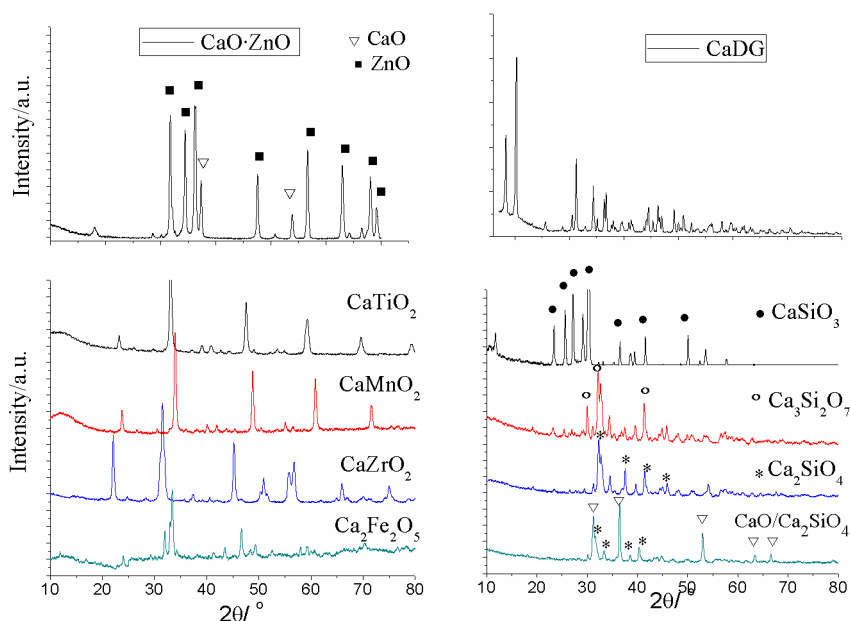
## EXPERIMENTAL

Mechanochemical treatment of different starting materials was carried out in the planetary ball mill Fritsch Pulverisette 5, in air atmosphere. The prepared catalysts were characterized by XRD, TGA/DSC, FTIR, SEM/EDX, and base strength using Hammett indicator method. The detailed preparation of catalysts and the used instruments for their characterization are described elsewhere [2-4].

The methanolysis of sunflower was carried out in  $300\text{ cm}^3$  batch autoclave or in a 250 ml three-necked thermostated glass flask with a condenser and magnetic stirrer under different working conditions: catalyst amount, agitation speed, temperature and methanol to oil molar ratio.

## RESULTS AND DISCUSSION

The X-ray diffraction patterns of prepared catalysts are shown in Fig. 1.



**Figure 1.** XRD patterns of synthesized catalysts

Mechanochemical treatment of  $\text{CaO}$  and  $\text{ZnO}$  powder mixture with water and subsequent calcination led to the formation of fine composite powder composed of  $\text{CaO}$  and  $\text{ZnO}$ . The formation of  $\text{CaDG}$  by mechanochemical

treatment of CaO and glycerol was confirmed with all the peaks well indexed to the calcium diglyceroxide phase  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$ . XRD patterns revealed that  $\text{CaTiO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{CaZrO}_3$  and  $\text{Ca}_2\text{Fe}_2\text{O}_5$  perovskites consist dominantly of one phase. Milling of  $\text{CaO} + \text{SiO}_2$  powder mixtures with molar ratio in the range of 1–2 followed by calcination at 900 °C for 48 h, produced single-phase calcium silicate compounds, while starting from the  $3\text{CaO} + \text{SiO}_2$  powder mixture, two phase  $\text{CaO}/\text{Ca}_2\text{SiO}_4$  was obtained.

**Table 1.** Catalytic activity of synthesized catalysts

Catalyst	Starting material and calcination temperature	Basic strength	Reaction conditions <sup>a</sup>	FAME yield, %
$\text{CaO}\cdot\text{ZnO}$	$\text{CaO} + \text{ZnO} + \text{H}_2\text{O}$ $T_{\text{calc}}=700\text{ °C}, 3\text{h}$	$11 < H_- < 18.4$	$T = 60\text{ °C};$ $\text{MR} = 10:1;$ $\text{Cat} = 2\%;$ $t = 4\text{h}$	98.2
$\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$ (CaDG)	$\text{CaO} + \text{Glycerol}$ /	$11 < H_- < 15.0$	$T = 60\text{ °C};$ $\text{MR} = 10:1;$ $\text{Cat} = 0.5\%;$ $t = 2\text{h}$	97.9
$\text{CaTiO}_3$	$\text{CaCO}_3 + \text{TiO}_2$	$6.8 < H_- < 9.3$		0.1
$\text{CaZrO}_3$	$\text{CaCO}_3 + \text{ZrO}_2$	$6.8 < H_- < 9.3$	$T = 60\text{ °C};$	0.0
$\text{CaMnO}_3$	$\text{CaCO}_3 + \text{MnO}_2$	$6.8 < H_- < 9.3$	$\text{MR} = 6:1;$	0.0
$\text{Ca}_2\text{Fe}_2\text{O}_5$	$\text{CaCO}_3 + \text{Fe}_2\text{O}_3$ $T_{\text{calc}}=700\text{ °C}; 24$	$6.8 < H_- < 9.3$	$\text{Cat} = 10\%;$ $t = 10\text{h}$	0.0
<sup>b</sup> $\text{CaO}/\text{CaTiO}_3$	<sup>b</sup> $\text{CaCO}_3 + \text{TiO}_2$ $T_{\text{calc}}=1050\text{ °C}, 2\text{ h}$	<sup>b</sup> $9.3 < H_- < 10$		<sup>b</sup> 98.1
$\text{CaSiO}_3$	$\text{CaO} + \text{SiO}_2$	$H_- < 9.3$	$T = 60\text{ °C};$	0.31
$\text{Ca}_3\text{Si}_2\text{O}_7$	$3\text{CaO} + 2\text{SiO}_2$	$H_- < 9.3$	$\text{MR} = 10:1;$	0.52
$\text{Ca}_2\text{SiO}_4$	$2\text{CaO} + \text{SiO}_2$	$H_- < 9.3$	$\text{Cat} = 2\%;$	0.81
$\text{CaO}/\text{Ca}_2\text{SiO}_4$	$3\text{CaO} + \text{SiO}_2$ $T_{\text{calc}} = 900\text{ °C}, 48\text{h}$	$11 < H_- < 15$	$t = 5\text{h}$	96.03

<sup>a</sup> $T$  = temperature; MR = molar ratio methanol to oil; Cat = catalyst loading;  $t$  = time.

<sup>b</sup>Mixed using agate mortar and pestle (but without subsequent mechanochemical treatment)



The results of catalytic activity of the prepared catalysts in methanolysis of sunflower oil, along with their basic strength ( $H_-$ ), reaction conditions, and preparation procedure are given in Table 1.

The high FAME yields were achieved when CaO·ZnO and CaDG were used as catalysts, as well as two-phase samples containing CaO, while pure perovskites and calcium silicates showed no activity in methanolysis at 60 °C. High catalytic activity of prepared catalysts is related to high basic strength, which is considered as one of the most significant factor that affects the activity of different catalysts for biodiesel production. With the exception of CaDG, which has different structure, in all other cases the high basicity of samples, accompanied with their high catalytic activities, arises from the existence of CaO phase. The perovskites possess different structure compared to the rock salt structure of CaO and from that reason they are not active in transesterification of sunflower oil at lower temperature.

## CONCLUSION

Mechanochemical treatment was successfully used for the synthesis of various CaO based heterogeneous catalysts. Prepared CaO·ZnO and CaDG showed a high catalytic activity in methanolysis of sunflower oil at 60 °C resulting in FAME yield over 96%. Under these conditions, pure perovskites (CaTiO<sub>3</sub>, MnO<sub>3</sub>, CaZrO<sub>3</sub> and Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>) and pure calcium silicates (CaSiO<sub>3</sub>, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> and Ca<sub>2</sub>SiO<sub>4</sub>) phases exhibited no catalytic activity, while two-phase samples containing CaO (CaTiO<sub>3</sub>/CaO and Ca<sub>2</sub>SiO<sub>4</sub>/CaO) were active.

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