



PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
Belgrade, Serbia



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CONTENTS

Volume 1

Organizers	IV
Committees	V
Sponsors	VI
Plenary lectures	1
Chemical Thermodynamics	47
Spectroscopy, Molecular Structure, Physical Chemistry of Plasma	113
Kinetics, Catalysis	205
Nonlinear Dynamics	317
Electrochemistry	365

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Fundamental and Applied Aspects of
Physical Chemistry*

*Organized by
The Society of Physical Chemists of
Serbia*

*in co-operation
with_*

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**PREPARATION OF CaO/ γ -Al₂O₃ CATALYST FOR BIODIESEL
FUELS. THE CATALYTIC ACTIVITY IN RELATION TO
THERMAL TREATMENT**

D. Marinković^{1*}, M. Stanković^{1**}, B. Nedić Vasiljević², A.V. Veličković³
and J. Avramović³

¹*University of Belgrade, Institute of Chemistry, Technology and Metallurgy,
*Department of Ecology and Technoeconomics, **Department of Catalysis
and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia,*

²*University of Belgrade, Faculty of Physical Chemistry, Studentski trg
12-16, 11000 Belgrade, Serbia,*

³*University of Niš, Faculty of Technology, Bulevar oslobođenja 124, 16000
Leskovac, Serbia.*

ABSTRACT

A heterogeneous base catalyst (CaO/ γ -Al₂O₃) for biodiesel production from sunflower oil was prepared by the impregnation method. The catalyst was characterized by means of MIP and XRD methods. The catalytic activity of the nitrate-derived CaO/ γ -Al₂O₃ was determined in relation to the calcination temperature ranging from 425 to 500°C. The reaction was carried out in a batch type of reactor equipped with a reflux condenser. The maximum yield of biodiesel of almost 95% was achieved with the catalyst calcined at 475 °C under the following reaction conditions: reaction temperature of 60 °C, methanol to oil molar ratio of 12/1, reaction time of 5 h.

INTRODUCTION

Biodiesel, fatty acid methyl esters (FAMES) derived from renewable resources such as vegetable oils or animal fats is expected to be one of the biomass-base alternative fuel for diesel fuel due to its numerous advantages such as: renewability, high biodegradability, low SO_x particulate matter content and lack of aromatic compounds. The classical method of biodiesel production is based on triacylglycerols transesterification to FAMES. Homogeneous base catalysts are the most conventional catalyst used in the biodiesel production. Transesterification with heterogeneous base catalysts is one of the very promising alternatives for producing biodiesel from vegetable oils. Kouzu et al. [1] used Ca-based catalysts such as CaO, Ca(OH)₂ and CaCO₃ as solid catalysts in the production of biodiesel from soybean oil with the biodiesel yield of 93, 12 and 0%, respectively.

Alumina supported CaO-based catalyst has also been used for production of biodiesel from vegetable oils [2]. It should be noted that catalytic activities most of them are not as high as those of the homogeneous catalysts. In addition, information regarding the influence of the thermal treatment of the catalyst in the final step of its preparation such as temperature and time duration of the calcination on their activity is quite scarce. Therefore, the aim of this study was to examine the effect of calcination temperature on the yield of biodiesel in the methanolysis of sunflower oil over the CaO/ γ -Al₂O₃ catalyst.

EXPERIMENTAL

Catalyst preparation

CaO/ γ -Al₂O₃ samples were prepared according to the wet impregnation (WI) method [3], using Ca(NO₃)₂·4H₂O as precursor salt, γ -Al₂O₃ (spherical shape, 1-3 mm in diameter) as support, and water as medium. The sample designation, CaO content and preparation procedure are shown in Table 1.

The calcination was performed in the nitrogen atmosphere (N₂ flow: 10 dm³/h) using a tube vertical furnace (Carbolite Furnaces CTF 12/75, Eurotherm 818P). The calcined samples were kept in a desiccator in the presence of silica and KOH pellets to avoid water and CO₂ contact with the

Table 1. CaO content and preparation procedure for CaO/ γ -Al₂O₃ samples

Sample		Preparation procedure					
Designation	CaO* /wt%	WI	Calcinations				
		C _{Ca(NO₃)₂} ^a /wt.%	t _{WI} ^b /h	T _{WI} ^c /°C	T _D ^d /°C	t _C ^e /h	T _C ^f /°C
Ca-425/ γ -Al ₂ O ₃	10.2	50	2	30	120	4	425
Ca-450/ γ -Al ₂ O ₃	10.9	50	2	30	120	4	450
Ca-475/ γ -Al ₂ O ₃	10.1	50	2	30	120	4	475
Ca-500/ γ -Al ₂ O ₃	9.6	50	2	30	120	4	500

^aImpregnation salt concentration; ^bWI time; ^cWI temperature; ^dDrying temperature; ^eCalcination time; ^fCalcination temperature; *Gravimetric determination of calcium as CaC₂O₄·H₂O.

samples.

Catalyst characterization

Mercury intrusion porosimetry (MIP) was carried out on a Porosimeter 2000 series (Carlo Erba Strumentazione). Powder X-ray diffraction (XRD) patterns were collected by means of the Philips, PW 1710 diffractometer (Cu K α radiation).

Transesterification procedure

The activity of the prepared catalysts was examined in the methanolysis of sunflower oil. All transesterification runs were performed in a 250 ml three-neck glass flask equipped with a reflux condenser and a magnetic stirrer.

Experiments were conducted under the following conditions: catalyst loading of 0.5 wt.% CaO (relative to the amount of oil), methanol/oil molar ratio of 12/1, reaction temperature of 60 °C and reaction time of up to 5 h. After each interval, fractions of reaction mixture were captured for HPLC analysis. Reaction mixture was analyzed *off-line* by an Agilent 1100 Series HPLC (Zorbax® 5 µm Eclipse-XDB-C18 80 Å, LC Column 150 x 4.6 mm).

RESULTS AND DISCUSSION

Mercury porosimetry results are summarized in Table 2. The results indicated that the parameters of the porous structures such as pore volume, surface area and porosity of the samples were gradually increased with an

Table 2. Summary of MIP data

Sample	$V_{\text{cum}}^{\text{a}}$ /cm ³ g ⁻¹	S_{Hg}^{b} /m ² g ⁻¹	$D_{\text{av.}}^{\text{c}}$ /nm	P^{d} /%
Ca-425/ γ -Al ₂ O ₃	0.322	59	20	50
Ca-450/ γ -Al ₂ O ₃	0.350	65	20	53
Ca-475/ γ -Al ₂ O ₃	0.455	89	20	59
Ca-500/ γ -Al ₂ O ₃	0.482	97	16	63
γ -Al ₂ O ₃ ^e	0.620	125	16	69

^aCumulative pore volume; ^bSurface area; ^cAverage pore diameter; ^dTotal porosity; ^eCommercial-Rhone Poulenc.

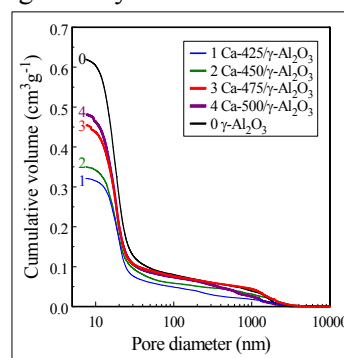


Figure 1. Pore size

increase in calcination temperature.

The XRD patterns of CaO/ γ -Al₂O₃ catalyst samples calcined at different temperatures and γ -Al₂O₃ support are shown in Fig. 2. Commercial support showed XRD reflections at 2-theta corresponding to the γ -Al₂O₃ in cubic phase (JCPDS 50-0741). XRD patterns of the calcined samples (Ca-500/ γ -Al₂O₃ not shown) were pronounced at similar 2-theta due to the γ -Al₂O₃ support. As indicated in Fig. 2, the typical XRD reflections indexed to Ca(NO₃)₂ for the samples which were calcined at lower temperatures (425 and 450 °C). This observation indicated that the impregnated precursor was not decomposed completely on the sample surface at temperatures below 450 °C. With increase in the calcination temperature from 450 to 475 °C, the characteristic reflections corresponding to Ca(NO₃)₂ disappeared and the well-defined diffraction reflections corresponding to CaO became more intensive in the XRD pattern.

Figure 3 shows the yield of FAME versus calcination temperatures after reaction time of 5 h. It was clearly seen that the activities of the samples were strongly influenced by the calcination temperatures. With respect to the yield to FAME, the calcination temperature of 475 °C appeared to be

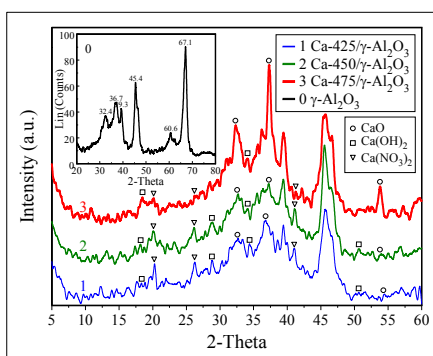


Fig. 2. XRD patterns of CaO/ γ -Al₂O₃ samples and γ -Al₂O₃ support

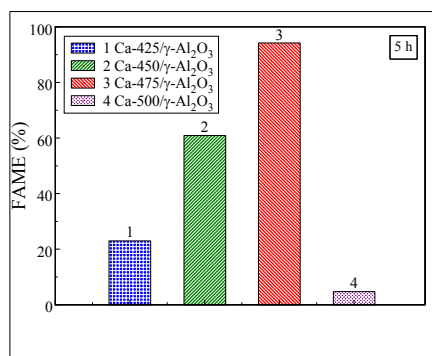
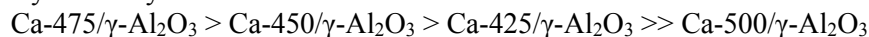


Fig. 3. Yields of FAME produced by the sunflower oil methanolysis

most beneficial. However, the very low FAME yield was observed with the sample calcined at temperatures above 475 °C (Ca-500/ γ -Al₂O₃). It might be because of the crystallite aggregation caused by the increased degree of sintering of the active metal particles and/or the lack of strong basic sites where the methanolysis occurs [2].

CONCLUSION

The effect of different calcination temperatures for the nitrate-based CaO/ γ -Al₂O₃ catalyst was discussed in terms of the characteristics and activity of the catalysts. The results indicated that the catalyst sample calcined at 475 °C (Ca-475/ γ -Al₂O₃) exhibited higher activity in the methanolysis of sunflower oil compared to the samples calcined at lower (425 °C and 450 °C) and higher (500 °C) temperatures. Consequently, the following order of catalyst activity was established:



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