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

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September 22-26, 2014
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PREPARATION OF $CaO/\gamma-Al_2O_3$ CATALYST FOR BIODIESEL FUELS. THE CATALYTIC ACTIVITY IN RELATION TO THERMAL TREATMENT

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ABSTRACT

A heterogeneous base catalyst ($CaO/\gamma-Al_2O_3$) 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 $CaO/\gamma-Al_2O_3$ 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 $CaCO_3$ 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-Al_2O_3 catalyst.

EXPERIMENTAL

Catalyst preparation

CaO/γ-Al_2O_3 samples were prepared according to the wet impregnation (WI) method [3], using $Ca(NO_3)_2{\cdot}4H_2O$ as precursor salt, γ-Al_2O_3 (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 (N_2 flow: 10 dm^3/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 CO_2 contact with the samples.

Table 1. CaO content and preparation procedure for CaO/-γAl_2O_3 samples

Sample		Preparation procedure					
		WI				Calcinations	
Designation	CaO* /wt%	$C_{Ca(NO_3)_2}$[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_2O_3	10.2	50	2	30	120	4	425
Ca-450/γ-Al_2O_3	10.9	50	2	30	120	4	450
Ca-475/γ-Al_2O_3	10.1	50	2	30	120	4	475
Ca-500/γ-Al_2O_3	9.6	50	2	30	120	4	500

[a]Impregnation salt concentration; [b]WI time; [c]WI temperature; [d]Drying temperature [e]Calcination time; [f]Calcination temperature; *Gravimetric determination of calcium as $CaC_2O_4{\cdot}H_2O$.

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 Kα 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 increase in calcination temperature.

Table 2. Summary of MIP data

Sample	V_{cum} [a] /cm^{3}g^{-1}	S_{Hg} [b] / m^{2}g^{-1}	$D_{av.}$ [c] /nm	P [d] /%
Ca-425/γ-Al_2O_3	0.322	59	20	50
Ca-450/γ-Al_2O_3	0.350	65	20	53
Ca-475/γ-Al_2O_3	0.455	89	20	59
Ca-500/γ-Al_2O_3	0.482	97	16	63
γ-Al_2O_3 [e]	0.620	125	16	69

[a] Cumulative pore volume; [b] Surface area; [c] Average pore diameter; [d] Total porosity; [e] Commercial-Rhone Poulenc.

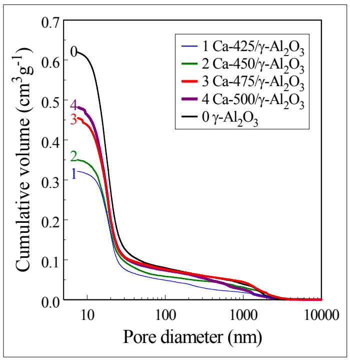
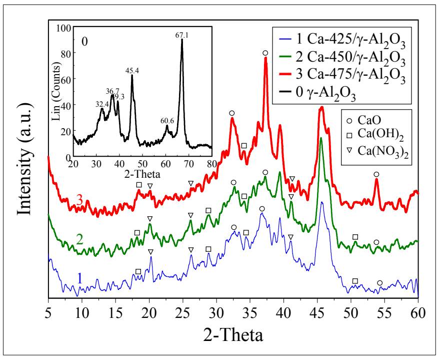


Figure. 1. Pore size

The XRD patterns of CaO/γ-Al_2O_3 catalyst samples calcined at different temperatures and γ-Al_2O_3 support are shown in Fig. 2. Commercial support showed XRD reflections at 2-theta corresponding to the γ-Al_2O_3 in cubic phase (JCPDS 50-0741). XRD patterns of the calcined samples (Ca-500/γ-Al_2O_3 not shown) were pronounced at similar 2-theta due to the γ-Al_2O_3 support. As indicated in Fig. 2, the typical XRD reflections indexed to $Ca(NO_3)_2$ 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 $Ca(NO_3)_2$ 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



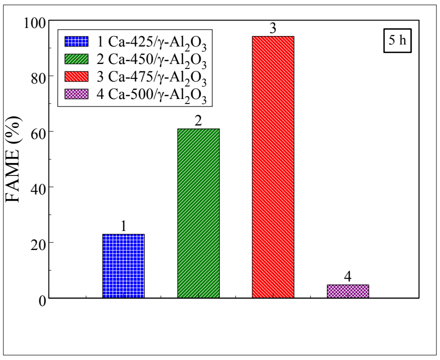


Fig. 2. XRD patterns of $CaO/\gamma\text{-}Al_2O_3$ samples and $\gamma\text{-}Al_2O_3$ support

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 ($Ca\text{-}500/\gamma\text{-}Al_2O_3$). 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 $CaO/\gamma\text{-}Al_2O_3$ catalyst was discussed in terms of the characteristics and activity of the catalysts. The results indicated that the catalyst sample calcined at 475 °C ($Ca\text{-}475/\gamma\text{-}Al_2O_3$) 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:

$$Ca\text{-}475/\gamma\text{-}Al_2O_3 > Ca\text{-}450/\gamma\text{-}Al_2O_3 > Ca\text{-}425/\gamma\text{-}Al_2O_3 >> Ca\text{-}500/\gamma\text{-}Al_2O_3$$

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