PHYSICAL CHEMISTRY 2016

13th International Conference on Fundamental and Applied Aspects of Physical Chemistry

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Volume I

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EFFECT OF BASICITY ON THE CATALYTIC PERFORMANCE OF HETEROGENEOUS CATALYSTS FOR BIODIESEL PRODUCTION

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ABSTRACT
In a heterogeneous base methanolysis of vegetable oils, among of the most important characteristics of the catalysts are the basicity and the availability of basic centers. The impact of these factors on the catalytic activity was investigated in the reaction of sunflower oil methanolysis by $CaO/\gamma\text{-}Al_2O_3$ catalyst. The particle morphology of CaO-dispersed onto $\gamma\text{-}Al_2O_3$ surface was analyzed by field emission scanning electron microscopy (FESEM), while basicity and basic strength of prepared catalysts were determined using Hammett indicators method. The results showed a strong dependance of catalytic activity on its basicity. The catalyst with the highest basicity was the most active, and decreasing basicity reduces activity of the catalyst. In addition, it was shown that the catalyst activity depends on the favorable spatial distribution of basic sites, i.e. of their availability.

INTRODUCTION
Fatty acid methyl esters (FAMEs) - biodiesel, produced from renewable resources such as vegetable oils or animal fats is expected to be one of the biomass-based alternative for fossil diesel fuel, due to its numerous advantages.

The usual method of biodiesel production is based on triacylglycerols methanolysis to FAMEs using homogeneous base catalysts. Heterogeneous solid base catalyzed processes are nowadays very promising alternatives for biodiesel production from vegetable oils [1]. Using the Ca-based catalysts for the biodiesel production is well known [2], particularly good results were obtained by loading of CaO on alumina carrier [3]. As this is a heterogeneous solid base catalyzed reaction, one of the most important factors affecting the reaction yield is catalyst basicity and the availability of basic sites on its surface.

The aim of this study was to examine the effect of basicity and basic sites distribution on the catalyst activity in the methanolysis of sunflower oil over the $CaO/\gamma\text{-}Al_2O_3$ catalyst.

EXPERIMENTAL

Catalyst preparation

$CaO/\gamma-Al_2O_3$ catalysts were prepared according to the modified wet impregnation (MWI) method [4], using $Ca(CH_3COO)_2$ as precursor salt, $\gamma-Al_2O_3$ (spherical shape) as support, and deionized water as medium. The sample designation, CaO content and preparation procedure are shown in Table 1.

Table 1. CaO content and preparation procedure for $CaO/\gamma-Al_2O_3$ samples

Sample		Preparation procedure			
		MWI		Calcination conditions	
Designation	CaO* (wt%)	C_{CaAc}[a] (wt%)	t_{WI}[b] (h)	t_C[c] (h)	T_C[d] (°C)
$Ca-500/\gamma-Al_2O_3$	4.2	25	2	4	500
$Ca-550/\gamma-Al_2O_3$	4.4	25	2	4	550
$Ca-600/\gamma-Al_2O_3$	4.1	25	2	4	600
$Ca-650/\gamma-Al_2O_3$	4.2	25	2	4	650
$Ca-700/\gamma-Al_2O_3$	5.5	25	2	4	700
$Ca-750/\gamma-Al_2O_3$	5.3	25	2	4	750

*Determined gravimetrically as $CaC_2O_4 \cdot H_2O$;[a]CaAc - $Ca(CH_3COO)_2$; [b]Impregnation time; [c] Calcination time; [d]Calcination temperature.

Catalyst characterization - FESEM was carried out on a Tescan MIRA3 XMU with accelerating voltage of 10 kV. Samples were placed over an aluminum drum and covered with an Au and Pt film. Basic strength and basicity ($H\_$) were determined using volumetric titration with the Hammett indicators. The following Hammett indicators were used: neutral red ($H\_$=6.8), phenolphthalein ($H\_$=9.3), **thymolphthalein**($H\_$=9.9) andthymol violet($H\_$=11.0).

Methanolysis procedure - The activity of the prepared catalysts was examined in the methanolysis of sunflower oil. All methanolysis reactions 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, at temperature of 60 °C and reaction time of 5 h.

RESULTS AND DISCUSSION

Loading CaO to $\gamma-Al_2O_3$carrier and subsequent calcination leads to the formation of cluster structure on the catalyst surface(Fig. 1). Scattered large rod-shaped crystals are present mainly on the surface of the catalyst calcined at the lowest temperature. By increasing the calcination temperature, the granular particles on the surface of catalyst become bigger. Also, it leads to the occurrence of agglomeration and clustering of particles. Evidently, on the $Ca-500/\gamma-Al_2O_3$only some cluster of irregular shape can be seen, on the

Ca-650/γ-Al_2O_3catalyst the entire surface is covered with clusters of spherical shapes, while on the catalyst calcined at the highest temperature (Ca-750/γ-Al_2O_3) spherical clusters are not visible due to massive agglomeration and sintering.

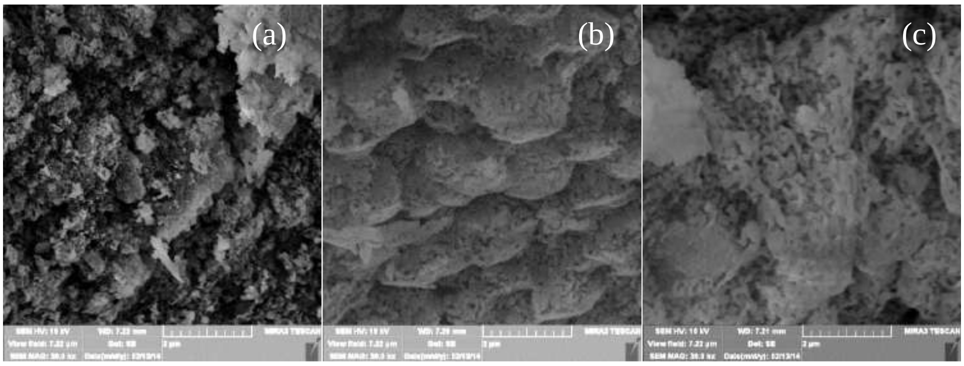

Figure 1. FESEM micrograph of the catalysts surface: (a) Ca-500/γ-Al_2O_3, (b) Ca-650/γ-Al_2O_3 and (c) Ca-750/γ-Al_2O_3

The base strength of CaO loaded onto γ-Al_2O_3 and thermally activated at different temperatures was measured by using Hammett indicators. As evident in Table 2, all catalysts arewithin the same range of the base strength, $9.3<H\_<9.9$.Therefore, these catalysts can be classified as materials with a medium base strength. Although belonging to the same base strength group, their basicity is not equal. Basicity of the samples increases with calcination temperature up to 700 °C at which reaches the maximum value (Table 2, Ca-700/γ-Al_2O_3). The basicity of the catalyst obtained by calcination at the highest temperature (Ca-750/γ-Al_2O_3) is lower, which is in accordance with the results of FESEM (Fig. 1). On the surface of Ca-750/γ-Al_2O_3catalystit was observed the massive sintering of particles. With the appearance of larger particles on the catalyst surface, the number and the availability of base catalytically active sites are reduced, despite the same concentration level of catalytically active compound - CaO (Table 1).

Table 2. Basicity and basic strength ($H\_$) of the CaO/γ-Al_2O_3 catalysts

Sample designation	Basic strength ($H\_$)	Basicity (mmol g^{-1})
Ca-500/γ-Al_2O_3	$9.3<H\_<9.9$	0.036
Ca-550/γ-Al_2O_3	$9.3<H\_<9.9$	0.102
Ca-600/γ-Al_2O_3	$9.3<H\_<9.9$	0.120
Ca-650/γ-Al_2O_3	$9.3<H\_<9.9$	0.157
Ca-700/γ-Al_2O_3	$9.3<H\_<9.9$	0.298
Ca-750/γ-Al_2O_3	$9.3<H\_<9.9$	0.228

Activity of the catalyst samples was evaluated by analysing the FAMEsyield after 5 h. As can be seen, the Fig. 2 reveals a clear correlation betweenFAMEs content after 5 h of the reaction and the basicity of the catalysts. The catalyst sample with the highest

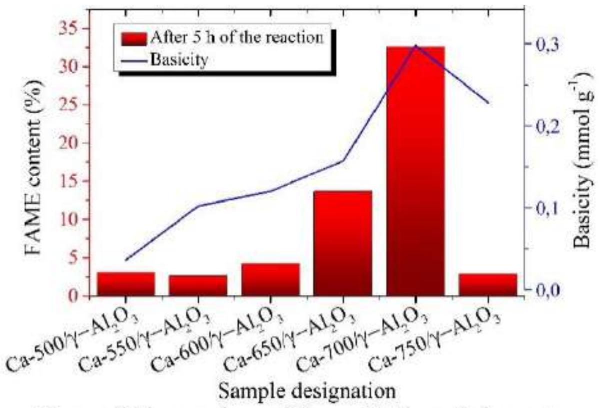

Figure 2 Comparison of the catalytic activity and the basicity of the CaO/γ-Al_2O_3 catalyst

basicity(Ca-700/γ-Al_2O_3) showed the highest activity, and the samples with the lowest basicity (Ca-500/γ-Al_2O_3 and Ca-550/γ-Al_2O_3)showed the lowest activity. Despite the relatively high basicityCa-750/γ-Al_2O_3 catalyst did not show adequate activity, probably due to reduction of base sites space availability.

CONCLUSION

Heterogeneous CaO/γ-Al_2O_3 catalyst samples were synthesized by modified wet impregnation method and thermally activated under inert atmosphere. The analysis of the catalyst activity in the reaction of sunflower oil methanolysis and basicity of synthesized catalysts a correlation between basicity and catalyst activity was observed. The catalyst with higher basicity had higher activity. The exception was the catalyst thermally activated at the highest temperature in which, probably due to sintering effect that leads to agglomeration of active sites on surface causes a reduction in its activity.

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