

# METHANOLYSIS OF SOYBEAN OIL OVER CALCINED Mg-Al HYDROTALCITES MODIFIED WITH CERIUM

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The biodiesel production by methanolysis of soybean oil over heterogeneous catalysts was studied. Catalysts were prepared by calcination of cerium modified Mg-Al layered double hydroxides (Mg/Al=3 atomic ratio). Hydrotalcites were prepared by precipitation from aqueous solutions of nitrate salts of magnesium, cerium and aluminum in presence of sodium carbonate (pH≈8). Fresh and post reaction catalysts samples were extensively characterized by physic-chemical techniques. Catalytic tests showed that prepared catalysts are active for the transesterification of soybean oil but present low stability since surface composition change during reaction. For some samples, unexpected increase of catalytic activity was obtained for the second batch with the same catalyst sample.

**Keywords:** *Biodiesel, Hydrotalcites, soybean oil, methanolysis, transesterification, FAME*

## Introduction

The scarcity of conventional fuel, the high price of crude and the concern of environmental protection have increased the research effort in the field of *green fuels or ecofriendly fuels* [1-4]. Some researchers have shown that triglycerides hold assure a alternative diesel engine fuel [5]. However, the direct use of vegetable oils and/or oils blends is generally impracticable for both direct-injection and indirect-type diesel engines. The high viscosity of vegetable oils seems to be the major problem. Three main processes have been investigated in order to overcome the drawbacks and allow vegetable to be a viable alternative fuel: pyrolysis, micro-emulsification, and transesterification.

The biodiesel, resulting from transesterification of vegetable oil with low molecular weight alcohol, is pointed out as feasible replacing fuel of fossil fuel, for transportation applications [4].

There are many reasons, behind the worldwide enthusiasm for biodiesel [6]. Biodiesel is viewed as:

- A mechanism for reducing dependence on imported fossil oil and extends diesel fuel supplies. This is a major issue for many countries that are “net importers” of crude oil and/or fuel supplies.
- A environmentally friendly alternative to fossil diesel. It is completely biodegradable, non-carcinogenic, non-mutagenic, and non-allergenic.
- An alternative to reduce greenhouse gas (GHG) emissions such as CO<sub>2</sub>, as well as carbon monoxide (CO), particulate matter (PM) and hydrocarbon (HC) emissions. This is a major reason for Europe, which is subjected to the Kyoto protocol

- Able to be used in existing diesel engines with proper care and attention. It can be used in any diesel motor vehicle with minor adjustment, and mixed in any ratio with fossil diesel as a lubricity and emissions improver.
- Compatible with the existing fuel distribution infrastructure.
- Able to stimulate agricultural markets and reduce poverty in rural areas by providing jobs. In India jatropha (to produce biodiesel) is regarded as the “seed of hope”

The major disadvantages of biodiesel are higher viscosity, lower energy content, higher cloud point and pour point, higher NOx emission [7, lower engine speed and power, injector coking, engine compatibility, high price and high engine wear [2]. Large scale production of biodiesel requires intensive exploitation of large arable areas. The questions “fuel or food?” and “biodiesel equal to hungry?” are posed by ambient organizations.

The transesterification (alcoholysis) reaction occurs in the presence of acid or basic catalysts. Homogeneous catalysts, although effective, lead to serious contamination problems that make essential the implementation of good separation and product purification protocols increasing the production costs [8]. Many types of solid catalysts have been tested in transesterification reactions and it is possible to group them in three general categories: metal, base, and acid catalysts [9].

The hydrotalcites and the corresponding mixed oxides obtained by thermal treatment (calcination) can be used as basic solid

catalysts for many reactions [10,11], namely for methanolysis of vegetable oils [12].

## Experimental

### *Preparation of the catalysts*

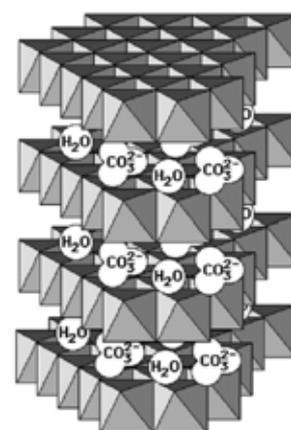


Fig.1 – Layered double hydroxides structure with brucite like layer interlayer and carbonate and water (adapted from [13]).

The incorporation of guest elements in the Mg-Al double layered hydroxides can be achieved by coprecipitation [14] The Mg-Al and Ce modified hydrotalcites were prepared according to the procedure schematized in Fig 2.

### *Characterization of the catalysts*

#### *Catalytic tests*

The transesterification reaction was carried out in a 500 mL three-neck round bottom flask equipped with a condenser and a mechanical stirrer. The reaction temperature was kept at 70°C by a water bath. Typical a mixture of 150 mL of soybean oil (refined from sharlau) with 9:1 (molar ratio) of methanol (Fluka, *pa*) was used as reaction mixture. The catalysts were dried at 120°C several hour before the catalytic tests in order to remove water and other adsorbed molecule such as

CO<sub>2</sub>. For each test 5% (w/w, oil basis) of catalyst was used.

The quality of the produced biodiesel and density was estimated by NIR [15].

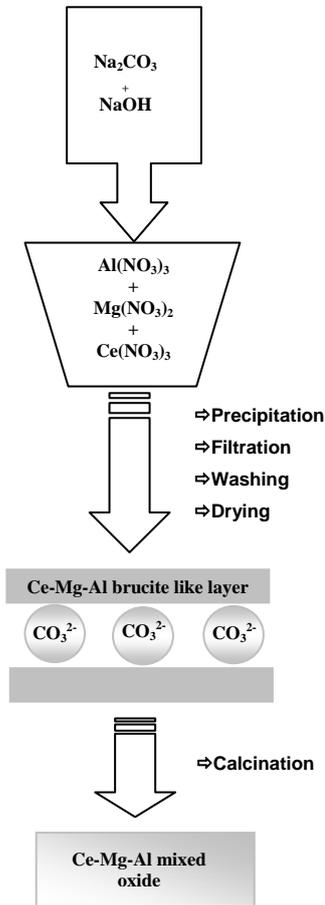


Fig. 2 – Scheme of the catalysts preparation procedure.

### Results and Discussion

The thermal behavior of Mg-Al and Ce modified hydrotalcites were assessed by TG-DTA under He. Typical behavior (Mg-Al LDH) is presented in Fig. 3 .

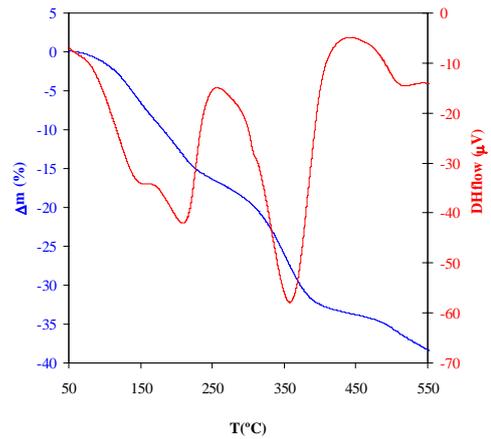


Fig. 3 – TG-DTA of Mg-Al hydrotalcites under He.

All the analyzed samples displayed four step decomposition, when heated under inert gas. Analogous thermal behaviour was referred by V. Rives [13]. According to A. Tsyganok and A. Sayari [14]. the first two processes that occurs for temperatures lower than 240°C are due to desorption of physisorbed water and CO<sub>2</sub> and structural water. The process around 300-500°C, account for the dehydroxilation of the sample. The highest temperature process is attributable to NO<sub>3</sub><sup>-</sup> decomposition.

The adsorbed species desorb for temperatures lower than 600°C. The referred processes were endothermic as referred in the literature [14,16,17]. The after reaction samples were characterized by thermogravimetry in order to quantify the adsorbed materials (Fig. 4). All the samples loose around 45% of the initial weight, However the DTG profile are different

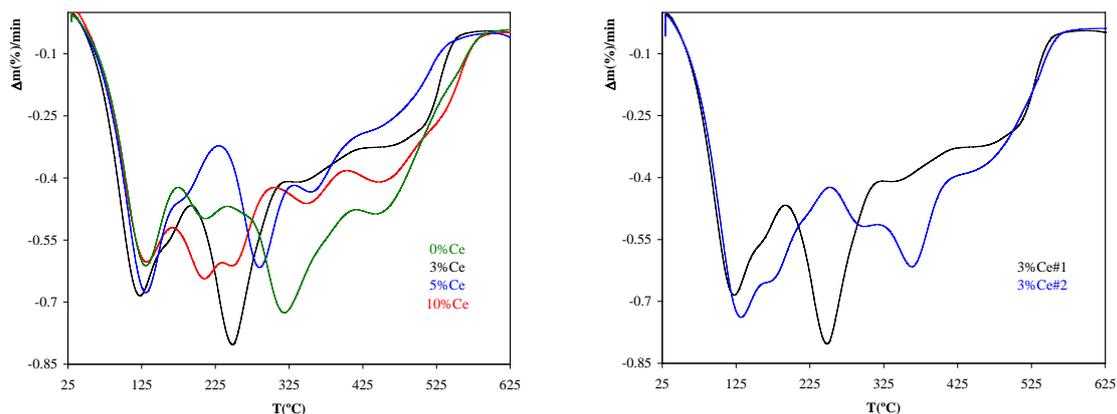


Fig. 4 – Thermogravimetry profiles of after reaction catalysts, under air.

The desorption process around 125°C is similar to all the analyzed samples and can be ascribable to physisorbed species such as soybean oil. Further characterization of after reaction samples, such as DRIFTS are needed in order to identify adsorbed species. The sample with 3% of Ce was characterized after each reaction test. Samples from reaction batch#1 and batch#2 display different profiles but the weight loss was almost the same.

Different DTG profiles signify different adsorbed species which can be due to dissimilar reaction mechanisms. This finding corroborates the deactivation of the catalysts during the first reaction batch. The presence of Ce also seems to change the reactions pathways. No data are available in the literature for the characterization of adsorbed species on the catalysts surface for the methanolysis of vegetable oils.

The layered double hydroxides and the mixed oxides obtained after calcination were characterized by FTIR. The obtained spectra are displayed in Fig.4. All the spectra exhibit a broad band around 3400-3500cm<sup>-1</sup> attributable to OH stretching vibration [18]. The shoulder around 3100 cm<sup>-1</sup> suggested

the presence of a second type of OH vibration possibly due to hydrogen bonds in the interlayer spacing [18]. The shoulder at 1600-1650 cm<sup>-1</sup> can be ascribable to the bending motion of interlayer water. The intense band around 1370 cm<sup>-1</sup> correspond to the vibrations of the interlayer CO<sub>3</sub><sup>2-</sup> and M-O (M=Mg, Al, Ce) [17]. The intensity of this band decreases for calcined samples due to the absence of carbonate species. The absence of 3500 cm<sup>-1</sup> band for calcined samples is due to dehydroxilation promoted by thermal treatment.

The morphology of the prepared catalysts and LDH samples was examined by SEM. Typical micrographs are displayed in Fig 5 .

The as prepared Mg-Al LDH shows agglomerates of nanoscopic spherical crystallites. Calcination of this sample promotes the formation of small plates instead spherical crystallites.

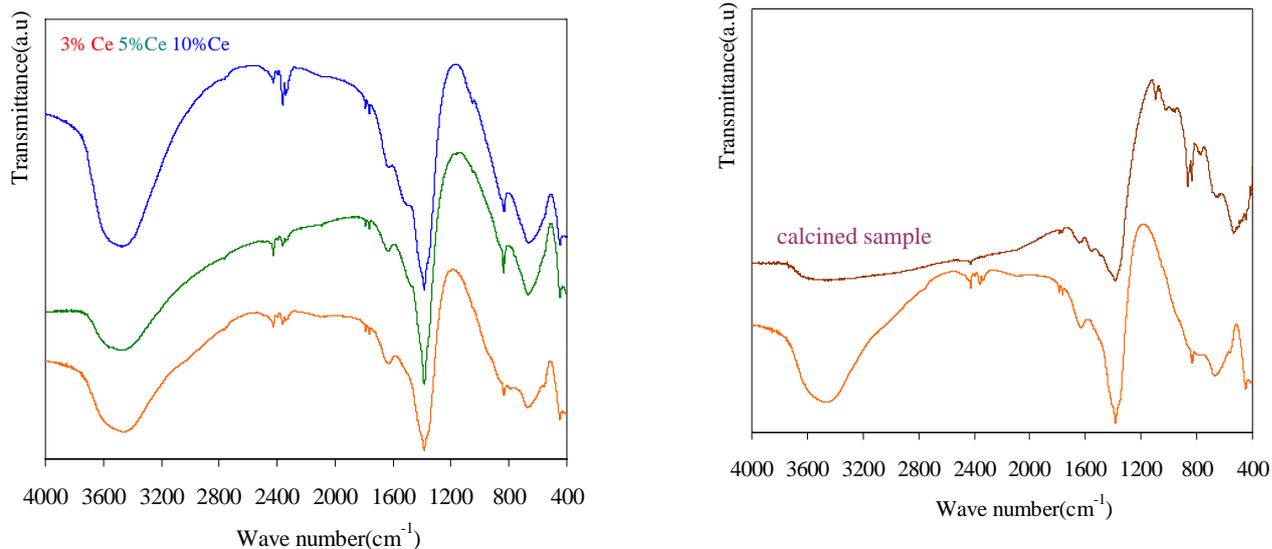


Fig 4– FTIR spectra of Ce modified LDH and 3%Ce-Mg-Al mixed oxide.

Calcination seems to promote a slight sinterization. The plate crystallites are clearly visible for the samples after the first reaction batch but the sample after the second reaction batch show remarkable sinterization. This is samples was subjected to a second calcination step, between the batch#1 and batch#2, in order to remove the adsorbed material during the first reaction batch. This could be responsible for the observed sinterization. Displayed morphologies are in accordance with those presented by M. J. Climent *et al.*[19].

The microanalysis performed during SEM micrographs acquisition show that sodium remains in the prepared samples. Data in Table 1 show that catalysts loose sodium and magnesium seems to migrate from the bulk to the surface.

The same fresh and post reaction catalyst, with 3%of Ce was examined by XPS.

The binding energies for Na, Mg, Al and Ce. Relevant data are resumed in Table 2.

Table 1– Microanalysis of fresh and post reaction 3% Ce sample by EDS.

atomic ratio	fresh	batch#1	batch#2
Mg/Al	1.81	2.29	2.33
Na/Mg	0.87	0.69	0.21
Ce/Mg	0.07	0.06	0.07

For magnesium sodium and aluminum elements, data from XPS and EDS are in conformity. Besides, due to the analysis depth, deep layers (EDS analysis) show depletion of of Na whereas surface (XPS) show Na enrichment. This result can due to the fact that catalyst loses Na to reactional medium.

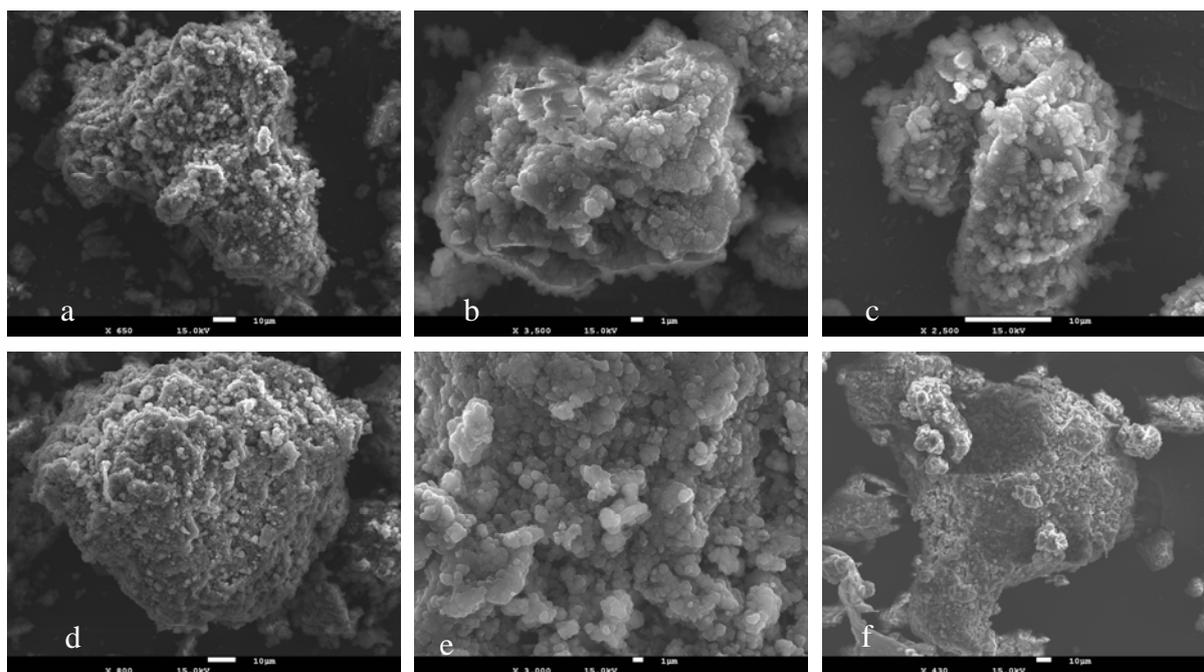


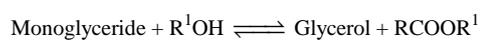
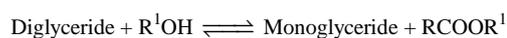
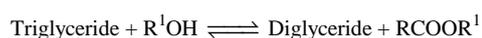
Fig. 5 - FTIR spectra of LDH and mixed oxides obtained by calcination.

Table 2 - XPS elemental analysis and binding energies for fresh and post reaction 3%Ce-Mg-Al catalyst.

3%Ce-Mg-Al			Fresh		Post reaction (batch#1)		
	BE (eV)	Atomic (%)	Atomic ratio		Atomic (%)	Atomic ratio	
Mg <sub>2p</sub>	49.9	17.3			22.77		
O <sub>1s</sub>	531.9	63.7	Mg/Al=	2.37	63.77	Mg/Al=	4.26
Al <sub>2p</sub>	69.5	6.5			8.11		
Al <sub>2p</sub> A	67.5	0.8	Na/Mg=	0.23		Na/Mg=	0.36
Na <sub>1s</sub>	1072.1	11.7			5.35		
Ce <sub>3d5</sub>	882.4	0.1	Ce/Mg=	0.005	not detected		

### Catalytic Tests

Transesterification of triglycerides produces fatty acid alkyl esters and glycerol. The glycerol settles down at the bottom of the reactor. Diglycerides and monoglycerides are intermediates in the process [20,21]:



All the prepared catalysts were tested for the transesterification of soybean oil with

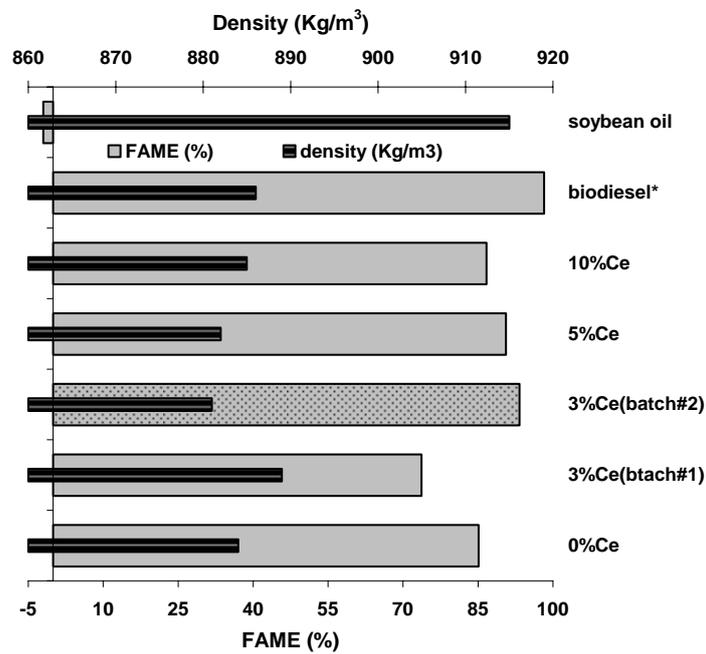
methanol. Results from catalytic tests are presented in Fig.6. Only the FAME content and the density were evaluated.

**Conclusions**

As reported by Lotero et al. [9] the application of heterogeneous catalysts to the production of biodiesel is only in its infancy.

The prepared catalysts by thermal treatment of hydrotalcites like materials showed good catalytic performances for the transesterification of biodiesel. However they loose sodium, from the surface, during reaction. Moreover the batch #2 performed with the 3% Ce–Mg–Al showed better catalytic performances than the same sample for the

batch #1. This allow to the conclusion that homogeneous process apparently performed by sodium (and others elements) washed down from the catalyst surface it is not the most important catalytic process. In fact catalyst used in batch #2 had less than ½ of Na than catalyst used in batch#1. The effect of the Cerium content can not be extracted from the presented data. More systematic studies must be performed in order reach a conclusion. A measure of the surface basicity (TPD of CO<sub>2</sub> and/or dehydration/dehydrogenation of isopropanol) seems to be key task for future work in order to well characterize the catalytic system.



\* obtained by homogeneous catalysis using NaOH as catalysts.

Fig. 6 – Biodiesel FAME content and density estimated by NIR.

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