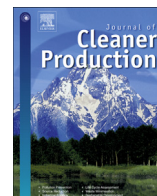




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## Screening of active solid catalysts for esterification of tall oil fatty acids with methanol

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### ABSTRACT

The paper is focused on the description of the activity/selectivity of mesoporous silica based materials loaded with various types of active species in the esterification of tall oil free fatty acids. The metals such as aluminium, molybdenum, gallium and zinc, including their combinations were impregnated on the mesoporous silica, which was tested in esterification reaction. All these catalysts preserved its tall oil free fatty conversion in the first and the second catalytic cycles. However, while only insignificant amount of gallium or molybdenum was lost from the solid catalyst into the liquid phases, zinc leached from every studied solid catalyst. In contrast to impregnated gallium on mesoporous silica, which exhibited higher acidity and higher tall oil free fatty acids conversion in the first catalytic cycle, but its value was not preserved in the second catalytic test.

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### 1. Introduction

Biodiesel (mixture of methyl esters of higher fatty acids) is usually prepared by transesterification of triglycerides, which are contained in vegetable or waste cooking oils and animal fats (Nair et al., 2012), with low molecular alcohol, the most often methanol (Math et al., 2010). The reaction is usually catalysed by alkoxide or homogeneous base (KOH, NaOH). The disadvantage is used of oil with low content of free fatty acids (FFAs) and moisture (Kwiecien et al., 2009, 2010), which is not cheap. This disadvantage can be tackled when using solid catalyst such as a solid acid supported catalyst (Bala et al., 2015), or bifunctional heterogeneous catalysts (Farooq et al., 2013). The price of vegetable oil accounts for 75%–85% of the biodiesel price (Narkhede et al., 2014), therefore new cheaper raw material resources are still being discovered. Biodiesel can also be produced via esterification of free fatty acids, which can be contained in low quality feedstock (Bala et al., in press). This reaction is usually catalysed by sulfuric acid but this

approach suffers from disadvantages such as corrosion, problems with separation and a lack of catalyst reusability.

Tall oil free fatty acids (TOFA) are an attractive raw material in biodiesel production. TOFA consists of approximately 97% free fatty acids. It is a side-product from the Kraft pulping process of (coniferous) wood. In principal, biodiesel can be prepared from TOFA without catalysts at high pressures and temperatures, if the alcohol (mostly methanol) is present in supercritical state (White et al., 2011). However, more attractive is the esterification of TOFA with methanol in the presence of a stable solid catalyst containing a high amount of strong Brønsted acid sites. Nevertheless, the catalyst stability and activity in the subsequent catalytic cycles represents the most important problem and has not been fully solved for any of the studied solid catalysts.

The aim of this paper was to describe various types of supported solid catalysts with a potential for esterification of TOFA. We selected for our study mesoporous silica SBA-15 (Santa Barbara Amorphous type material) loaded with zeolite ZSM-5 (Zeolite Socony Mobil-5), niobium (Nb) and cerium dioxide (CeO<sub>2</sub>). Next, we selected the aluminium SBA-15 loaded with zinc oxide (ZnO), gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) and their combination, molybdenum trioxide (MoO<sub>3</sub>) together with ZnO and Ga<sub>2</sub>O<sub>3</sub> together with zirconium

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dioxide (ZrO<sub>2</sub>) as catalysts. SBA-15 and Al-SBA-15 are highly ordered mesoporous supports not only for transesterification reaction. These materials are also tested as catalyst for other type of reaction such as isomerisation (Launay et al., 2009), Friedel–Crafts (El Berrichi et al., 2006) acylation and alkylation (Gracia et al., 2008). Previously, SBA-15 materials with various metals such as tungsten (Chen et al., 2015), zirconium (Melero et al., 2014) and niobium (Cruz et al., 2011) have been studied by other authors as catalysts in biodiesel production. In our work we used other attractive metal sites, with a potential to enhance the activity, selectivity and stability of the resulting materials in the esterification reaction. Zinc (Zn) based catalysts were also compared with zinc-aluminium (Zn-Al) mixed oxide.

## 2. Material and methods

The chemicals used upon preparation of the support Si-SBA-15 and Al-SBA-15, respectively, were tetraethyl orthosilicate and the polymeric template Pluronic 123 (poly-(ethylene glycol)-block-poly (propylene glycol)block poly (ethylene glycol)-copolymer, EO20-PO20-EO20, Mn ~5800) and were received from Sigma Aldrich ( $\geq 99\%$ ). The metal precursors gallium nitrate, niobium pentachloride, ammonium heptamolybdate. The cerium nitrate (hexahydrate) and zinc nitrate (hexahydrate) used in the preparation of impregnated catalysts were received from Sigma Aldrich and zirconyl chloride from Merck. The ammonium form of ZSM-5 (molar ratio between silicon and aluminium is 23) catalyst used in this study was received from Zeolyst International.

### 2.1. Preparation of catalysts

**Zn-Al mixed oxide.** Zn-Al hydrotalcite was synthesized by the coprecipitation method at constant pH 10 and temperature 65 °C. A solution of zinc and aluminium nitrates (1 mol/dm<sup>3</sup>) was continuously added (7.5 ml/min) to the reactor filled by 200 ml of distilled water. A constant pH of 10 was maintained with a 2 M solution of sodium carbonate. The reaction mixture was stirred at 1400 rpm for 18 h at 60 °C. Hydrotalcite was separated by filtration and washed until the pH of the solution was 7 and dried at 80 °C for 12 h in air and granulated to the particle size of 250–500 μm. The Zn-Al mixed oxide was prepared via a thermal pre-treatment at 400 °C.

**Al-SBA-15 (Si/Al=25).** 10 g of the structure directing agent Pluronic 123 was dissolved in 75 ml of deionized water and the solution was intensively stirred at 40 °C. The protonation of Pluronic 123 was carried out by 150 ml of hydrochloric acid (2 mol/dm<sup>3</sup>) for 3 h. Next, 0.833 g of aluminium isopropoxide was dissolved in 25 ml of hydrochloric acid (2 mol/dm<sup>3</sup>) and the solution was added dropwise to the solution of Pluronic 123. The amount of 21 g of tetraethyl orthosilicate was inserted dropwise and the reaction mixture was stirred for 24 h. Then the reaction mixture was aged for 48 h, at a temperature of 95 °C. The formed solid material was separated from the reaction mixture by filtration, washed and dried at 90 °C for 10 h. Finally, the material was calcined at 550 °C (1 °C/min) for 6 h in air. A similar procedure as described above was used for the preparation of pure SBA-15, excluding the addition of aluminium isopropoxide.

**Preparation of niobium (Nb) and cerium (Ce) containing Si-SBA-15.** 1.5 g of SBA-15 was dispersed in 20 ml of water in case of Ce-loaded catalyst and ethanol was used in case of the Nb-loaded catalyst. In fact, the required amount of Ce and Nb precursors were added to the suspension to yield 10 wt% of niobium and cerium in the final material. The above slurry was stirred for 8 h followed by vacuum drying and finally calcined at 500 °C for 4 h in air.

**Preparation of mono and bimetal containing Al-SBA-15 catalysts.** 1.5 g of Al-SBA-15 (Si/Al = 25) was dispersed in 20 ml of water. The

appropriate amount of different metal precursors such as zirconium (Zr), molybdenum (Mo), zinc (Zn) and gallium (Ga) pre-dissolved in distilled water were added to the above suspension to yield the final catalyst containing different amounts of a single or two metals (bimetal catalysts) as presented in Table 1. The above slurry was stirred for 8 h, followed by vacuum drying and finally calcined at 500 °C for 5 h in air.

The ZSM-5/SBA-15 material studied in this reaction was prepared as described in literature earlier (Vu et al., 2014).

### 2.2. Characterization

The physisorption of nitrogen was carried out on a Micromeritics TriStar porosimeter, CiAB Chemical Instruments AB. The adsorption-desorption isotherms were recorded at 77 K after degassing the samples at 473 K. The surface areas were calculated by the B.E.T. method and the pore volumes were calculated from the corresponding desorption isotherm. Further, the pore size distribution was estimated using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) available as built-in software from Micromeritics.

The powder X-ray diffraction patterns for the prepared materials were recorded on a Bruker D8 X-ray instrument using Cu Kα (k = 0.154 nm) radiation. In the case of SBA-15 based catalysts, the diffractograms were recorded in the small angle 2θ range of 0.5–10° and in the case of hydrotalcite catalysts, diffractograms were recorded in the high angle 2θ range of 10–80°, in steps of 0.02° with a count time of 15 s at each point.

The leaching of metals in different catalysts was monitored for each batch and analyzed by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP/OES) Optima 2000 DV (Perkin Elmer Instruments). In order to obtain the calibration curve, the blank and the standards (0.1, 1, 10 and 100 ppm) were prepared from 1000 ppm stock solutions and diluted with 2% nitric acid.

The acidic properties of the prepared catalysts were studied by using temperature programmed desorption (TPD). The acidic properties were measured by AutoChem 2920 (Micromeritics, USA) equipped with a TCD detector and quadrupole mass spectrometer (OmniStar GDS 300, Pfeiffer vacuum, Germany). 0.1 g of the sample was loaded in a U-shaped quartz reactor and pre-treated at 450 °C in helium (He) for 1 h. After that the catalyst was cooled to 100 °C under He flow and then treated with a flow of 5% ammonium in helium for 1 h at 100 °C. The physisorbed ammonia was removed by flushing with pure helium at 100 °C for 1 h. TPD analysis was carried out from 100 to 1000 °C with heating rate of 10 °C.min<sup>-1</sup>. Quantitative analysis of the desorbed ammonia was based on m/z = 15.

### 2.3. Esterification of TOFA with methanol

The esterification of TOFA (Tall oil fatty acid) with methanol was carried out in a stainless steel reactor (20 ml), which was placed in an oil bath. The TOFA sample was provided by company Forchem

**Table 1**  
The list of catalysts.

Catalysts	Metal loading (wt%)			
	Zn	Ga	Mo	Zr
Zn/Al-SBA-15	2			
Ga/Al-SBA-15		5		
Mo-Zn/Al-SBA-15	2		5	
Zr-Ga/Al-SBA-15		5		2
Ga-Zn/Al-SBA-15	2	5		

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