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Stability, activity and selectivity study of a zinc aluminate heterogeneous catalyst for the transesterification of vegetable oil in batch reactor

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ABSTRACT

The transesterification reaction of rapeseed oil by methanol was studied using a zinc aluminate catalyst in order to develop an alternative to the currently used homogeneous processes. At first, the reaction parameters such as catalyst particle size, stirring rate and amount of catalyst required to perform the transesterification reaction under a kinetically controlled-regime were determined. Thorough study of the catalyst stability was performed, in particular leaching of active species. A peculiar activity of the reactor walls was observed and XPS analysis allowed to determine that it stemmed from adsorption on the reactor walls of zinc species coming from catalysts prone to leaching. A method was therefore proposed to free oneself from this phenomenon. The zinc aluminate catalyst was found to be particularly stable as compared to ZnO catalyst.

Optimization of the reaction parameters for achieving high yields and obtaining high quality products was performed. Indeed the influence on the activity, stability and selectivity of the temperature, the reactants ratio, and the presence of water in the reactants, was studied.

Finally a pseudo-homogeneous kinetic model was validated and used to determine the kinetic parameters of the reaction.

1. Introduction

Transesterification of vegetable oil attracts a lot of interests since it enables the production of alkyl esters known as biodiesel which can be used as a potentially sustainable substitute for petrol-based diesel [1,2].

In order to be economically viable, traditional processes for production of these esters use basic homogeneous catalysts (NaOH, KOH, etc.) to improve biodiesel yields [3,4]. Acid catalysts (H_2SO_4, etc.), while also able to catalyze these reactions, are less used because they are less active and more corrosive.

A lot of work has been carried out recently towards the development of new more eco-friendly processes involving heterogeneous catalysts [5–14] in order to suppress the neutralisation and separation steps. Moreover, the quality of co-produced glycerine is also greatly enhanced and this opens the doors to better potential co-valorisation of this byproduct.

The solid catalysts, used in these processes, need to be very stable as well as active in order to compete with the homogeneous processes. Standards are very strict on fuels quality and particularly the amount of impurities (especially metal impurities) has to be very low. A literature survey shows that it is hard to obtain fuels totally free of impurities coming from both homogeneous and heterogeneous catalysts. Studies of heterogeneous catalyst stability, when performed, generally shows that leaching of active species occurs in the effluent which is not acceptable for an industrial process [5,9,11]. However, IFP has developed an industrial process under the commercial name Esterfip-H which uses a zinc aluminate catalyst. This catalyst has proven to be stable and active in the transesterification reaction of oil by methanol in a continuous process. Moreover it enables to produce very high quality glycerine and ester without any further treatments such as distillation or washing [15].

Kinetics of the homogeneous reaction have been largely studied [4,16–18], in contrast to the heterogeneous reaction [19–21].

In this work, the transesterification reaction of rapeseed oil by methanol (MeOH) has been studied using a zinc aluminate catalyst. The experimental conditions of the reaction have been extensively studied. The leaching of active species from the catalysts as well as peculiar activity of the reactor walls were especially examined. A kinetic study has also been performed and a reaction model allows us to calculate the kinetic constants of the 3

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consecutive reactions taking place in the transesterification of triglycerides by methanol. This study showed that zinc aluminate catalysts operating at high temperature and pressure are very stable and unlike many other heterogeneous catalysts, neither deactivation nor leaching of active phase in the glycerine or ester is observed.

2. Experimental

2.1. Materials

The catalyst was prepared by treating 300 g of commercial pseudo-boehmite with 175 g of water containing 5 wt% nitric acid, 95 g of commercial zinc oxide powder (bought from Bayer) was then added, the mixture was kneaded for about 45 min, then it was extruded in order to form 3.2 mm diameter cylinders. The catalyst was then dried over night at 120 °C and calcined at 700 °C. The catalyst produced is a mesoporous zinc aluminate mixed oxide with a Zn/Al molar ratio of 0.3, a specific surface area of 160 m^2/g and mesopores ranging between 9 and 100 nm. The dry catalyst is composed of extrudates having the following dimensions: 2 mm of diameter and 3–5 mm of length. Powder catalysts were obtained by grinding and sifting of the extrudates. As comparison basis, gamma alumina extrudates and ZnO extrudates with specific surface area of 290 and 16 m^2/g, respectively, were also used.

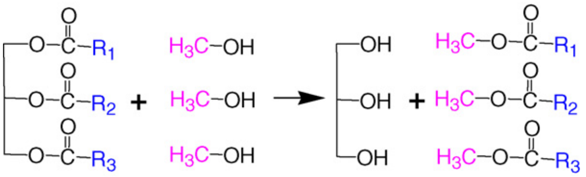
2.2. Transesterification batch tests

Experiments were performed in Hastelloy or stainless steel batch reactors of 500 and 100 mL, respectively. The reactors are equipped with a magnetic stirring system coupled with a dispersimax impeller system in order to avoid vortex formation in the reaction medium. Reactants were introduced in the reactor. Pellet catalysts are placed directly in a 316L stainless steel cylindrical basket, while powder catalysts are placed in a 316L stainless steel 60 μm mesh cigar like cylinders and then inside the basket. In the 500 mL Hastelloy batch reactor, the basket was hooked inside the reactor, above the reacting medium and was released when operating temperature (~200 °C) was reached. In the 100 mL stainless steel batch reactor the catalyst was immersed from the beginning into the reaction medium.

Commercial reactants used were MeOH and edible grade rapeseed oil both containing about 200 ppm of water and for the latter an acid number of 0.01 mg KOH/g. Triglycerides (TG) contained in the rapeseed oil, are successively transesterified by MeOH to yield diglycerides (DG), monoglycerides (MG), glycerol (GLY) and for each step 1 molecule of fatty acid methyl ester (FAME) (Scheme 1). The initial reaction medium as well as the reaction effluents form each a biphasic mixture, the polar phase containing mainly glycerol and unreacted MeOH and the apolar phase containing mainly FAME and glycerides. 2 cm^3 samples were collected manually from the reaction medium at different reaction times for analysis.

At the end of each test, reactors were thoroughly rinsed with water, acetone and then MeOH.

Two main side reactions are likely to occur during transesterification reaction in the chosen experimental conditions.



Scheme 1. Transesterification reaction.

$$R_1\text{–OH} + R_2\text{–OH} \rightleftharpoons R_1\text{–O–}R_2 + H_2O$$

Scheme 2. Ether formation.

Formation of ethers – dimethylether, methoxyglycerol, dimethoxy glycerol, diglycerol – may occur by methanol and/or glycerol dehydration (Scheme 2).

Ether is found in the polar phase of the reaction effluent. It is important that the amount of ethers found in the glycerine phase remains very low (beneath 1%) in order not to decrease the glycerine quality.

2.3. Analysis

2.3.1. Analysis of the composition of the apolar phase by gel permeation chromatography

The samples were washed with NaCl saturated water in order to remove glycerine and MeOH which were not analyzed. Then 8 drops of the apolar phase (containing glycerides and FAME) were diluted in 3 cm^3 analytical grade THF and the sample was analyzed by gel permeation chromatography.

Equipment used was a HPLC Waters apparatus equipped with 3 Waters Styragel columns (THF) with a molar mass range of 0–1000 g mol^{-1}. These columns were placed in a thermostated oven at 40 °C. Detection was made using a Waters 2414 refractive index detector.

The results gave a relative percentage composition of the apolar phase in triglycerides, diglycerides, monoglycerides and fatty acid methyl ester (FAME). Fig. 1 shows an example of the evolution of the composition of the apolar phase plotted against time. The relative percentage of FAME recovered in the organic phase is reported in this paper as FAME yield.

2.3.2. ICP analysis of metal species in the reaction medium

At the end of the reaction, the reaction medium was collected, filtered on a Teflon 0.1 μm filter and extra MeOH was evaporated. The apolar phase (containing ester and non-converted glycerides) and the polar phase (containing glycerine and ethers) were separated and analyzed by ICP-OES. Apparatus used was an ICP OES Thermo Jarrell Ash Iris Advantage. The apolar phase samples were diluted in xylene and directly injected while the polar phase samples were diluted in ethanol and injected via a cold (−10 °C) nebulisation chamber.

2.3.3. GC ether analysis in the polar phase

A small quantity of the collected polar phase, containing mainly glycerine but also ether components formed by the reaction between two alcohol molecules, was used to quantify the ether

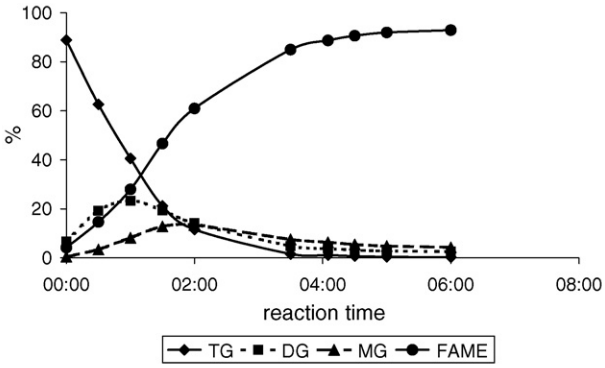


Fig. 1. Evolution of the composition of the apolar phase (triglycerides, diglycerides, monoglycerides, FAME) plotted against reaction time, $ZnAl_2O_4$ extrudates (200 °C, 4 wt% catalyst/oil, molar ratio MeOH/oil = 27/1, catalyst powder 315–125 μm).