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CsF and alumina: A mixed homogeneous–heterogeneous catalytic system for the transesterification of sunflower oil with methanol

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ABSTRACT

The activity and nature (i.e. heterogeneous and/or homogeneous) of catalysts based on CsF supported on α-Al_2O_3 were investigated for the transesterification of vegetable oil with methanol. The effect of the activation temperature, CsF loading and the reusability in a recirculating reactor were first studied. CsF/α-Al_2O_3 exhibited the highest activity for a CsF loading of 0.6 mmol/g and when activated at 120 °C. An important aspect of this study is the effect of CsF leaching into the reaction mixture, which is attributed to the high solubility of CsF in methanol, leading to a complete loss of activity after one run. It was identified that the activity of the catalyst resulted from a synergy between alumina and dissolved CsF, the presence of both compounds being absolutely necessary to observe any conversion. The use of an alumina with a higher surface area resulted in a far greater reaction rate, showing that the concentration of surface site on the oxide (probably surface hydroxyl) was rate-limiting in the case of the experiments using the low surface area α-Al_2O_3. This work emphasizes that combined homogeneous–heterogeneous catalytic systems made from the blending of the respective catalysts can be used to obtain high conversion of vegetable oil to biodiesel. Despite the homogeneous/heterogeneous dual character, such a catalytic system may prove valuable in developing a simple and cost-effective continuous catalytic process for biodiesel production.

1. Introduction

The use of heterogeneous catalysts in the transesterification of vegetable oils into biodiesel has been widely investigated [1–7] due to its merits such as easier separation of products and catalysts after reaction [8], no formation of soaps through free fatty acid neutralization by NaOH or triglyceride saponification, and high reaction yield (>95%) in systems with high molecular weight alcohols [9]. Among catalytic solids, supported fluorides exhibit a basicity higher than that of MgO, CaO or hydrotalcites [10] and have demonstrated high catalytic activities in a wide range of typically base-assisted reactions [11–13]. Fluorides in transesterification reactions increase the nucleophilicity of oxygen in alcohol molecules through strong hydrogen bonding [14] and also activate carbonyl groups in triglycerides [15], facilitating reaction completion.

However, the interaction between fluoride and γ-Al_2O_3 leads to fluoride compounds with a lower basicity than that of the parent alkaline fluoride precursor [10], thus higher loadings of fluorides can be necessary to compensate the basicity loss. These observations motivate the synthesis and utilisation of fluorides supported on a less reactive support, in particular α-Al_2O_3. Clacens et al. [16] have reported the benefit of using α-Al_2O_3 instead of γ-Al_2O_3 as a support for CsF for base-catalysed reactions such as the Michael addition of cyclohexene-2-one with nitroalkanes and in the synthesis of alkyl carbonates. Despite the much lower surface area of the catalyst based on α-Al_2O_3, the CsF/α-Al_2O_3 displayed far superior catalytic activity [16]. These authors also stressed the low activation temperature required (merely 120 °C) to activate the CsF/α-Al_2O_3.

Interestingly, no work on the use of CsF/α-Al_2O_3 has yet been reported for the transesterification of vegetable oils with methanol into biodiesel (i.e. fatty acid methyl ester, FAME). A high surface area mesostructured alumina was used in the case of the work carried out by Verziu et al. [10]. The CsF/alumina samples were also calcined at high temperature (i.e. 400 °C), which resulted in the formation of mixed compounds of CsF and alumina [10]. The effect of the activation temperature is here investigated using CsF supported over a commercial α-Al_2O_3. The possible role of CsF dissolution in the reaction mixture is also to be clarified, since fluorine leaching is sometimes reported [10] and that unsupported CsF is known to lead to active species [16]. The results obtained here will show that the most practical application of this catalytic system could rather be based on a process combining homogeneous (i.e. CsF dissolved in methanol) and heterogeneous (i.e. alumina) moieties.

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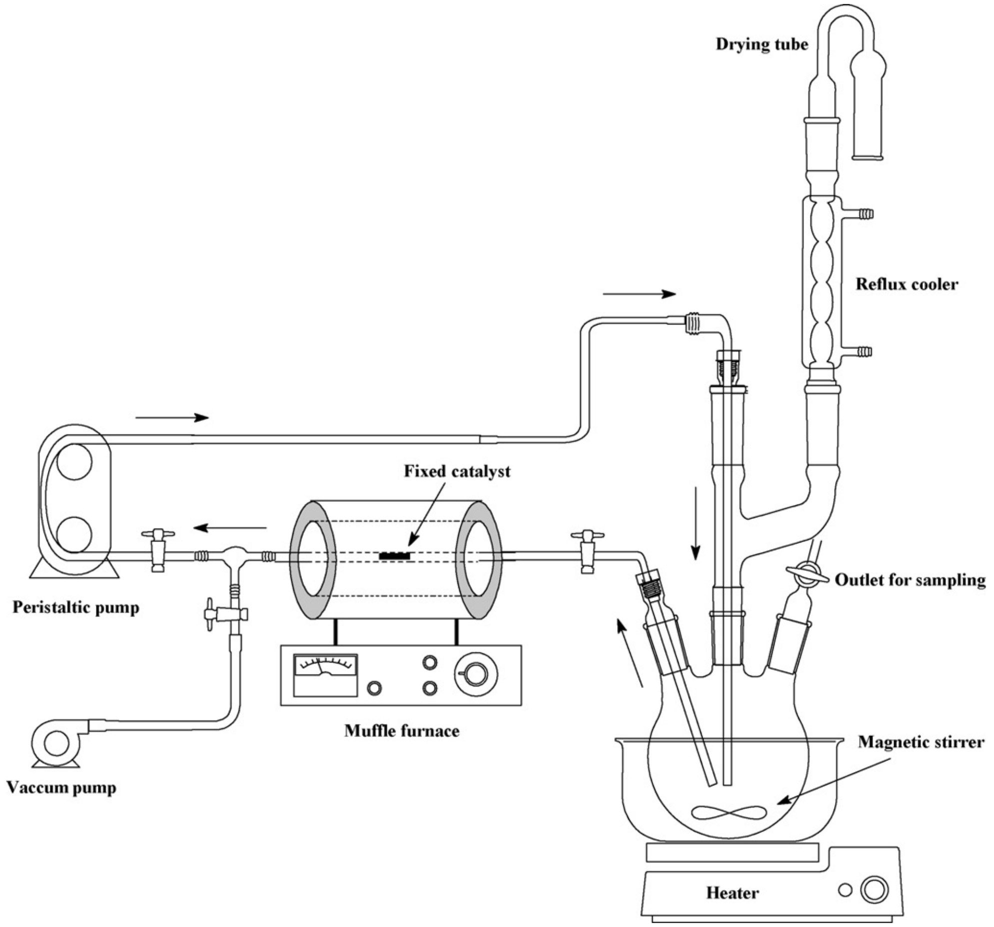

Fig. 1. Schematic layout of the reactor system used for the experiments involving the recirculation of the reaction mixture through a fixed catalytic bed.

2. Experimental

2.1. Catalyst and reagents

Commercial caesium fluoride (99.99%) from Aldrich and α-alumina (99.9% purity, 5.48 m^2/g) from Alfa Aesar were used as precursor for preparation of α-alumina-supported fluorides. The γ-alumina sample was obtained from BDH (26.0 m^2/g). The commercial grade sunflower oil was bought at Tesco supermarkets (density 0.91, fat composition: saturated 12.0 wt.%, mono-unsaturated 23.0 wt.%, polyunsaturates 65.0 wt.%, free fatty acid (FFA) content: 0.088 wt.%). The methanol (MeOH) (99.8% for HPLC) was purchased from VWR.

The catalyst, CsF supported on α-Al_2O_3, was prepared by an impregnation method using aqueous solutions of known concentrations of CsF as reported elsewhere [17]. The required amount of alumina was placed into a given quantity of deionised water containing the appropriate amount of CsF. Water was evaporated at 80 °C and the solid was then air-dried at 120 °C overnight. Prior to the catalytic tests, the catalysts were evacuated under 10^{-3} Pa at 120 °C for 6 h, unless otherwise stated

2.2. Catalytic experiments

30 ml of sunflower oil and the desired amount of methanol were placed into a stirred round bottom flask of 100 cm^3 volume fitted with a reflux condenser using a steady flow of water passing through to avoid methanol loss. The flask was immersed in an oil bath with a thermocouple to keep the bath temperature at 70 °C constantly throughout the reaction. The resulting flask temperature was monitored by an thermocouple plunging into the reaction mixture and remained at 65 ± 1 °C.

Two types of experiments were carried out, one of which was a simple batch reaction, for which a known mass of catalyst was simply added to the round bottom flask containing the reaction mixture and stirred at 1000 rpm. In the second type of experiments, the catalyst was placed in a quartz plug-flow tube reactor between a quartz filter and one layer of quartz wool (Fig. 1). The reaction mixture was stirred at the speed of 1000 rpm before being pumped into the quartz plug-flow tube using a peristaltic pump. The second mode, based on a fixed bed, was more appropriate to assess the catalyst reusability, by preventing any catalyst loss during the separation of the reaction products. In both cases 1 g of catalyst was used. The reaction medium was not a homogeneous solution, as it clearly separated into two phases (one alcohol-rich and one oil-rich) when the stirring was stopped.

For both reaction types, the catalyst was dried at 120 °C (unless otherwise stated) under vacuum for 6 h prior to the transesterification reaction before being contacted with the reaction mixture. The fresh catalyst was covered by the reactants, preventing exposure to water and CO_2. During the transesterification reaction, 50 μl of samples were drawn from one outlet of flask using a 1 ml syringe at certain intervals, then introduced immediately into samples bottles containing pre-weighed 5 μl of methyl pentadecanoate as an internal standard plus 20 μl of MSTFA (CAS no.: 24589-78-4) as derivatisation reagent. The weight of sample was obtained by comparing the weight of sample bottle before adding the samples and that afterwards. Then 80 μl of hexane was introduced into sample bottle as solvent. The samples were subjected to the GC analysis. The results are presented in the form of the FAME yield, which