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Effect of the kinds of alcohols on the structure and stability of calcium oxide catalyst in triolein transesterification reaction

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ABSTRACT

Transesterification of triolein with various alcohols like methanol, ethanol, 1-propanol, 2-propanol and 1-butanol over CaO catalyst was performed at atmospheric pressure and the temperature near to the boiling point of each alcohol with various catalyst dosages. High transesterification reaction rate was obtained by the reaction with methanol over CaO catalyst. However some amounts of the catalyst dissolved into the products during the transesterification reaction and the crystalline phase of catalyst changed to $Ca(C_3H_7O_3)_2$ at the early stage of reaction. On the other hand, the moderate transesterification reaction rates were obtained by the reaction with higher alcohols like ethanol, 1-propanol and 1-butanol over CaO catalyst. Calcium was hardly dissolved into the product and the structure of catalyst was not changed until the triolein conversion reached to 100%. After all of the raw triolein converted to products, both calcium leaching and the formation of $Ca(C_3H_7O_3)_2$ started. Some experiments and characterization implied that triolein suppressed the formation of $Ca(C_3H_7O_3)_2$ by inhibiting the contact of glycerol with CaO in the absence of methanol and methanol seems to eliminate such inhibitory effect of triolein.

1. Introduction

Last decade has seen significant research in the area of alternative fuels especially on biodiesel due to an increase in the demand for transportation fuels, depletion of fossil fuel resources and stringent environmental regulation with respect to pollution. As vegetable oils and animal fats cannot be used as such for fuel application due to undesirable properties like high viscosity, poor volatility and atomization, polymerization in combustion chamber leading fuel line and filter clogging and injection fouling, conversion of them into fuels with desirable properties is required. Considering the disadvantages like catalyst separation and corrosiveness faced by homogeneous catalyzed transesterification for biodiesel production, considerable work has been reported for transesterification for biodiesel using various heterogeneous catalysts under various reaction conditions. Recent reviews [1,2] on transesterification using heterogeneous catalysts provide extensive works carried out by many researchers around the world.

CaO catalyst is one of the most studied systems for biodiesel production due to high activity, availability and low cost of the catalyst. Transesterification of tributyrin with methanol has been studied using CaO prepared from various precursors like calcium acetate, carbonate, hydroxide, nitrate and oxalate [3]. High activity was obtained for CaO prepared by calcining $Ca(OH)_2$ due to nano-sized pores and strong basicity. One of the problems reported for CaO as a solid base catalyst for transesterification reaction is the solubility of CaO in methanol and formation of Ca-glyceroxide [4]. Though Ca-glyceroxide is stable in air and can be reused for further transesterification reaction, it is less effective compared to original CaO. Kouzu et al. studied the transesterification of soybean oil for the production of biodiesel using calcium based catalysts like CaO, $Ca(OH)_2$ and $CaCO_3$ and compared their activities with that of homogenous NaOH catalyst [5]. Extension of their study with waste cooking oil showed the formation of soap, glyceroxide and methoxide with calcium due to the presence of polar species and moisture.

CaO catalysts supported on various metal oxides have been studied by some researchers. Yan et al. carried out transesterification of rapeseed oil with methanol over CaO catalysts supported on MgO, SiO_2, Al_2O_3 and H-Y zeolite to study their influence on the activity of CaO and to overcome the separation problem of catalyst due to the formation of suspensoids [6]. CaO/MgO catalyst was found to be effective but contaminated by gaseous poisons in air like CO_2 and moisture and required thermal treatment to activate. Alba-Rubio et al. have stabilized CaO by filling the mesoporous network of ZnO, which avoids the lixiviation of the active phase in the reaction medium [7]. Similarly lixiviation of the active phase was not observed by Albuquerque et al. for transesterification of

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