

Effect of temperature, pressure, and acidity of zirconia on catalytic cracking of methyl stearate via ketonic decarboxylation

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Abstract

The transformation of fatty acids and derivatives into fuels and other useful chemicals is growing interested in recent years. Ketonic decarboxylation is one of the most reaction to convert carboxylic acids or carboxylic esters into ketones, carbon dioxide, and water. Generally, the ketonic decarboxylation of fatty acids is carried out in the gas phase at high temperatures from 400 to 550 °C at atmospheric pressure. However, the cracking reaction usually occurs as the side reaction that resulting to decrease the selectivity and restrict the yield of the desired ketone product. Methyl stearate (C18:0) is one of the key fatty acid methyl ester (FAME) component of biodiesel fuel and it becomes more attention in Thailand as an alternative and renewable diesel fuel. Therefore, Methyl stearate was selected as a substrate for ketonic decarboxylation. Moreover, various factors such as temperature, pressure, acidity, etc. were reported as the effects which promote catalytic cracking side reaction during ketonic decarboxylation. Therefore, this work is focused to investigate the optimum condition that suppressed the catalytic cracking of methyl stearate. The ketonic decarboxylation of methyl stearate has proceeded in a tubular fixed bed reactor containing commercial monoclinic zirconia (m-ZrO₂) catalyst. The effect of temperature, pressure, and acidity of zirconia will be investigated to optimize for minimizing the cracking ratio. The degree of factors was considered in term of the relative cracking ratio which provides high conversion and high selectivity.

Four sulphated zirconia catalysts were synthesized via conventional wet-precipitation and solvent-free methods with different molar ratios of the sulphating agent. Their activity for direct and unsaturated methyl esters. The solvent-free catalysts were more active with a conversion thermocatalytic cracking of rapeseed oil was evaluated at temperature of 270oC and atmospheric pressure. The nature and concentration of the active Brønsted and Lewis acid sites on the catalysts were examined. Brønsted acid sites were found to be important in the catalytic reaction. The catalysts at this temperature exhibited different selectivities towards formation of saturated of 78% in 21/2 hours, while the wet-precipitated catalysts had a maximum of 66% conversion after two hours. The catalysts prepared by the solvent-free method had 59% yield for methyl ester, with

75% of these being unsaturated. The wet-precipitated catalysts exhibited a lower yield for methyl esters (maximum: 32%), but within this a greater proportion (68%) were saturated. After regeneration, the solvent-free catalysts regained their catalytic properties, whereas the conventional catalysts did not. Three of the catalysts exhibited substantial leaching, with one of the conventional catalysts losing 100% of the sulphate responsible for its activity. Thus, to improve their properties the catalysts were

supported with meta-kaolin which resulted in higher Brønsted acidity and better stability.

In some cases a mixture of different types of these catalysts are used to enhance product selectivity. Dupain et al. (2007) studied the catalytic cracking of rapeseed oil using a commercial equilibrium FCC catalyst (silica–alumina matrix with zeolite crystals). The catalysts were found to be effective. The presence of double bonds in the molecular structure of the feedstock enhanced the formation of aromatics in gasoline and light cycle oil (LCO). Modified transition metal oxides have been found to be potentially active catalysts that could allow the same hydrocarbon conversion at lower temperatures than zeolites, when other operating conditions are similar (Charusiri et al., 2006; Idem et al., 1997). Despite this, current challenges include maximizing their efficiency by improving the pore size and stability. The surface area of a catalyst is the only physical property which determines the extent of adsorption and catalytic reaction (Thomas and Thomas, 2005). The rate of product formation is a function of the available surface area of the catalyst. Support or promoter may be used to increase the surface area. The larger the surface area of a catalyst that is accessible to the reactants the greater the throughput. That is the amount of reactant converted to product per unit time per unit catalyst mass. If, on continuous use, the activity of a catalyst declines rapidly than any decrease in the surface area the catalyst is said to be poisoned (i. e. blockage of active sites). On the contrary, if the surface area reduces with reduced activity, then the catalyst is thermally deactivated. The pore structure is also important because it contributes to the total surface area; however, narrow pore structure limits reaction rate. The surface and pores of a catalyst are responsible for the catalytic reactions, and they must not be blocked so that the catalytic sites will be accessible to reactants.

Series of models have been postulated in order to resolve the controversy surrounding how sulphation enhances the surface acidity and the nature of the active sites. The first model of sulphated zirconia was proposed by Yamaguchi et al. (1986), where they claimed that only Lewis sites existed on the surface of the catalyst. Clearfield et al. (1994) proposed a dual Brønsted and Lewis model. Their model suggested that the uncalcined sulphated zirconia contains protons as bisulphate and a hydroxyl groups bridging the two zirconium ions. According to them, during calcination the water lost could result into two species (I and II), as shown in Figure 2.12. The Brønsted acid sites are formed as a result of the reaction of two adjacent hydroxyl groups. In both cases Lewis acid sites are formed as indicated by the asterisks. However in model I, the bisulphate remains intact.