METHYL ESTER PRODUCTION FROM CANOLA OIL ON HETEREGENEOUS BASE CATALYSTS

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Introduction

Biodiesel, monoalkyl esters of long chain fatty acids, is generally derived from a lipid feedstock using either homogeneous alkali catalysts but it is challenging on heterogeneous base catalysts. Although it is well known that base catalysts are very active in transesterification of vegetable oils [1], it is not clear how the basic strength and/or basicity and crystallite sizes are controlling to achieve high biodiesel yield at low temperature and methanol amount. In this study, we investigated the effect of basicity, basic strength and crystallite size on the biodiesel yield over sol-gel made heterogeneous base catalysts.

Materials and Methods

Four mixed oxide catalysts; CaO/SiO_2, CaO/Al_2O_3, MgO/Al_2O_3 and MgO/SiO_2 (for loadings of 5, 20, 50 and 80 wt%) were synthesized using a modified single step sol-gel method [2]. All catalysts were tested using a batch reactor at the reaction condition: methanol/oil ratio of 3.6; catalyst amount of 6 wt% and reaction temperature of 50 ºC for 4 h. Three replicate tests were done for each catalyst during catalyst activity evaluation. Biodiesel content was measured by using a Shimadzu GC-17A gas chromatograph equipped with a FID detector and DB-WAX capillary column (30 m long, 0.25 mm in diameter and 0.25 µm).

Results and Discussion

The catalyst screening tests show that CaO/Al_2O_3 with 50% and 80% CaO loadings have the highest biodiesel yield without leaching out of CaO within 4 h of operation under the unfavorable reaction conditions used in this study, such as low Methanol/Oil molar ratio of 3.6 and the low reaction temperature, 50 ºC, as compared to studies conducted with high temperature and alcohol/oil ratios as reported in the literature [2, 3]. Over 80% CaO/Al_2O_3 and 50% CaO/Al_2O_3 catalysts, biodiesel yields are ~100% and ~87%, respectively. Other mixed oxide catalysts regardless of support type and active phase loading shows biodiesel yield less than 10%, as seen in Table 1.

XRD patterns seen in Fig. 1 indicate that CaO could highly be dispersed upto 50% loading but at 80% CaO loading, we observed small diffraction peaks corresponding to $CaCO_3$ crystallite phase. Similar trend is also observed on SiO_2 supported CaO. In contrast, for MgO catalysts, MgO peaks were seen at 50 and 80% loadings regardless of support type. The interaction between support and active phase may be responsible for the variation in the observed biodiesel yield through either directly with the changes in the number of the active sites and/or the creation of new "basic" sites.

From CO_2 TPD reported in Table 1, it is seen that 80%CaO has uniform basic site distribution centered at ~407 ºC as compared with other catalysts and TOFs calculated at low biodiesel yields, such as ≤12%, show that 80%CaO/Al_2O_3 catalyst is the most active catalyst. As a conclusion, not only the basicity but also moderate basic strength is necessary to obtain high biodiesel yield on heterogeneous base catalysts.

Table 1. Basicity, basic strength and biodiesel yield for selected catalysts

Catalyst	Total Basicity (µmole CO_2/m^2)	Basic strength (Peak Temperature, ºC)	Biodiesel Yield %	TOF (h^{-1})
Pure CaO	7.28	453	11.2	$3.18x10^5$
50% CaO/Al_2O_3	78.6 35.7	300 488	86.7	$1.70x10^5$
80% CaO/ Al_2O_3	126.0	407	100	$5.91x10^5$
50% MgO/ Al_2O_3	79.8	147	1.9	$2.58x10^2$
80% MgO/ Al_2O_3	34.5 1.0 30.3	180 394 472	3.5	$6.74x10^2$

Significance

In this study, we show that moderate basic strength is necessary for a solid base catalyst to be highly active for transesterification of canola oil at low Methanol/Oil molar ratio and 50 ºC of reaction temperature and this could be achieved using sol-gel preparation and appropriate support material for CaO.

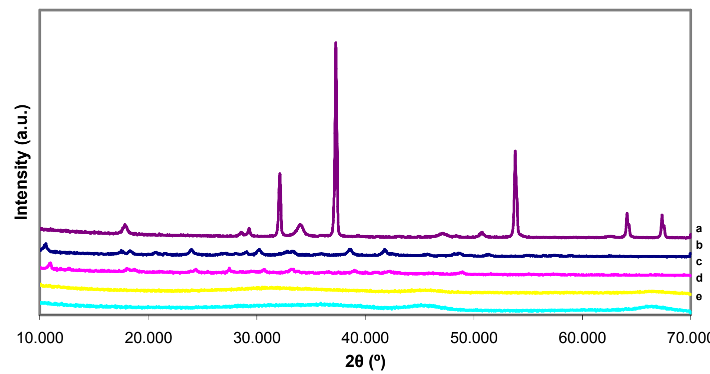

Figure 1. XRD patterns of fresh CaO/Al_2O_3 as a function of CaO loadings. ; **a)** pure CaO, **b)** 80% CaO/Al_2O_3, **c)** 50% CaO/Al_2O_3, **d)** 20% CaO/Al_2O_3, **e)** 5% CaO/Al_2O_3

References

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