Acid/Base Catalysis (Transesterification of vegetable oil to biodiesel over MgO-functionalized mesoporous catalysts)

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Introduction

Recently, there has been an increased research activity directed at the development of heterogeneous catalyst systems to produce biodiesel due to their environmental and economic advantages. Mesoporous catalyst is one of the most popular choices among all because their acidic/basic properties can be easily modified by varying their surface groups and composition, they have uniform structures and high surface areas, which are ideal as catalysts for large organic molecules and guest-host chemical supports. This study compares the catalytic activity of MgO-functionalized mesoporous materials, synthesized using different: (i) silica supports (MCM-41, KIT-6 and SBA-15); (ii) precursor salts (magnesium acetate and nitrate); and (iii) loading methods (impregnation and in-situ coating), in the transesterification of blended vegetable oil with ethanol to produce biodiesel.

Materials and Methods

SBA-15 and KIT-6 were prepared based on literatures [1, 2], and MCM-41 was taken from a batch of the material that was synthesized at the University of Queensland. They were each used as the support material for MgO impregnation [3]. Another batch of SBA-15 catalyst was loaded with MgO by in-situ coating [4], using $Mg(CH_3COO)_2{\cdot}4H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ as the precursor salt. The impregnated catalysts are denoted as X/MgO(Y) and the in-situ coated catalysts are denoted as MgO(Y)-X, where X designates the mesoporous material (i.e. M for MCM-41, K for KIT-6 and S for SBA-15) and Y represents the anion of the precursor salt used for impregnation (i.e. A for acetate and N for nitrate).The catalyst structure was characterized by XRD measurements performed on a Bruker D8 Advance X-Ray Diffractometer; whereas the surface area and porosity were determined by N_2 adsorption/desorption using Quantachrome NOVA 1200. Chemisorption of acidic CO_2 was performed at the set pressures of 5 and 760 mm Hg at 200°C using an Autosorb-1-C Chemisorption-Physisorption Analyzer (Quantachrome Instruments). The amount of CO_2 uptake per gram of solid at the manifold pressures indicates the quantity of strong basic sites as well as the total basic sites available in the catalysts, respectively.

The transesterification of blended vegetable oil was carried out in a 4560 Mini Bench Top Reactor for 5 hours under continuous stirring at 220°C, with an oil-to-ethanol molar ratio of 1:6, and a catalyst amount of ~2 wt %. The resulting product was prepared and analyzed by a Varian CP 3900 GC according to ASTM Method D6584 [5]. The yields of the selected esters, ethyl palmitate, oleate and stearate, which are most abundant in vegetable oils, were calculated in terms of grams of ester produced per gram of vegetable oil used.

Results and Discussion

The total yields of the selected esters were compared among the reactions catalyzed by the tested catalysts. As summarized in Figure 1, pure mesoporous silica showed little or no catalytic activity, but was found to be active catalysts once loaded with MgO. Their resulting yields ranged from 62% to 96% when compared to a complete homogeneous transesterification catalyzed by KOH using the same feedstock. Among all, S/MgO(A) was the most effective catalyst under the described experimental conditions.

The number of strong basic sites in a catalyst appeared to be a major contributing factor for its catalytic activity, demonstrating a strong correlation with the resulting ester yield as shown in Figure 2. The number of total basic sites present was found to be less relevant on the yield. The basicity, and thus the catalytic activity of a catalyst were found to be attributed to the type of supporting material used instead of the quantity of MgO loaded. The loading method also affects the overall catalytic activity of the catalysts because it determines the dispersion of MgO and accessibility of basic sites to the reactants. Impregnation, in this case, was a more effective loading method than in-situ coating. Analyses among the SBA-15 catalysts showed that the type of precursor salt used had insignificant effect on the resulting ester yield

Significance

This study finds SBA-15 to be the best support material for MgO impregnation, giving the highest basicity and ester yields. Future studies will involve varying the physical/chemical properties of this catalyst to further investigate how its catalytic activity may be improved.

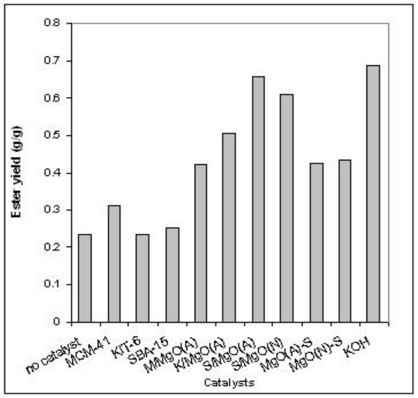

Figure 1. Ester yields of transesterification reactions catalyzed by pure and functionalized mesoporous silica.

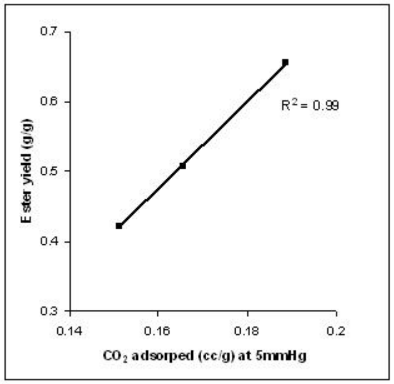

Figure 2. Correlation between basicity strength of catalyst and ester yield.

References

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