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Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin

Aidan M. Doyle [a, *], Talib M. Albayati [b, **], Ammar S. Abbas [c], Ziad T. Alismaeel [d]

[a] Division of Chemistry and Environmental Science, Manchester Metropolitan University, Chester St., Manchester M1 5GD, United Kingdom
[b] Department of Chemical Engineering, University of Technology, 52 Alsinaa St., P.O. Box 35010, Baghdad, Iraq
[c] Department of Chemical Engineering, College of Engineering, University of Baghdad, Al-Jadryah, P.O. Box 47221, Baghdad, Iraq
[d] Department of Biochemical Engineering, Al-Khwarizmi College of Engineering, University of Baghdad, Al-Jadryah, P.O. Box 47008, Baghdad, Iraq

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ABSTRACT

Zeolite Y, with a Si/Al ratio 3.1, was prepared using Iraqi kaolin and tested as a catalyst in the liquid-phase esterification of oleic acid (a simulated free fatty acid frequently used as a model reaction for biodiesel production). XRD confirmed the presence of the characteristic faujasite structure of zeolite Y, and further analysis was conducted using BET adsorption, FTIR spectroscopy, XRF, DLS particle size and SEM. A range of experimental conditions were employed to study the reaction; alcohol/oleic acid molar ratio, temperature, and catalyst mass loading. The optimum conditions for the reaction were observed at 70 °C, 5 wt% catalyst loading and 6:1 ethanol to oleic acid molar ratio. The oleic acid conversion using the zeolite prepared from kaolin was 85% after 60 min, while the corresponding value for a commercial sample of HY zeolite was 76%. Our findings show that low Si/Al ratio zeolite Y is a suitable catalyst for esterification, which is in contrast to the widespread view of the unsuitability of zeolites, in general, for such applications.

1. Introduction

Biodiesel is an alternative fuel produced from natural sources such as vegetable oils and animal fats [1–4]. Vegetable oils were first used as fuels over a century ago by Rudolf Diesel but this source of fuel has been replaced by cheaper petroleum oil fractions that are reformed to diesel using heterogeneous catalysts. Despite the continuing widespread use of fossil fuels, and recent technologies that allow increasing amounts of extraction from previously unavailable sources, the total amount of petroleum oil that is available is limited and will someday expire. Vegetable oils are extracted from plants and are therefore an almost limitless means of storing solar energy. Natural oils typically comprise mostly glycerides/triglycerides and suffer from high viscosity and inappropriate burning rate (cetane number), both of which render them less than ideal as fuels for transportation.

The (trans)esterification of natural oils using heterogeneous catalysis overcomes these problems by generating alkyl esters that are much more suited to use as fuels, and a number of reviews have been published on the use of solid-acid catalysts in such applications [5–10 and references therein]. However, there appears to be a general consensus in such reports that microporous zeolites are unsuitable catalysts for fatty acid esterification. Some reports base this conclusion on a disproportionately small number of publications whereas others mistakenly exclude the field of microporous zeolites altogether. While Corma and co-workers accurately proved that pores with diameter <2 nm impose a diffusion limitation for reactant molecules above a crucial dimension [11] we find that certain zeolites are active in oleic acid esterification if sufficiently low Si/Al ratios are employed.

Kaolin clay is a cheap and plentiful raw material found in numerous geographical locations and has been used successfully in the synthesis of mesoporous aluminosilicates [12] and various microporous zeolite frameworks; ZSM-5, X/Y, β, and A [13–22]. A large part of these studies was the removal of impurities in the clays (typically quartz) via the thermal transformation of the untreated clay into metakaolin, which is itself catalytically active in the transesterification of waste cooking oil to alkyl esters [23]. The

* Corresponding author.
** Corresponding author.
E-mail addresses: a.m.doyle@mmu.ac.uk (A.M. Doyle), talib_albyati@yahoo.com (T.M. Albayati), dr_ammar19@yahoo.com (A.S. Abbas), ziadalismaeel@yahoo.com (Z.T. Alismaeel).

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