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

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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.

Keywords; Biodiesel, esterification, Y zeolite, kaolin, Si/Al ratio.

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 Vegetable oils were first used as fuels over a century ago by Rudolf Diesel but this source of fuel has been replaced by cheaper petroleum oil fractions that are reformed to diesel using heterogeneous catalysts.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 same transesterification reactions were conducted using metakaolin that was transformed to zeolite A by hydrothermal activation with NaOH [24]. The liquid-phase acid catalysed esterification of free fatty acids is another important reaction to produce biodiesel. Li et al. reported a lanthanide ion-containing ZSM-5/MCM-41 composite material, prepared from kaolin, that was active in the esterification of ethanoic acid with n-butyl alcohol [25]. Da RochaFilho and co-workers investigated the esterification of oleic acid using a catalyst prepared from Amazon flint kaolin, which was converted to metakaolin and subsequently treated with sulphuric acid. The as-prepared materials were catalytically active but, to our knowledge, no studies were reported to investigate whether the acid content is leached during reaction so it is unclear how stable the catalyst is and whether the system is truly heterogeneous [26-29].

Kaolin from Iraq has been used to prepare zeolite A for desulfurization of liquified petroleum gas (LPG) and zeolite Y for catalytic cracking (FCC) of cumene [30-32]. Here we prepare zeolite Y from Iraqi kaolin and test its catalytic activity in the liquid-phase esterification of oleic acid over a range of experimental conditions; ethanol to oleic acid ratio, catalyst loading and temperature. The acidic groups are generated by the charge imbalance of Al bonded to the framework of the zeolite and is therefore more stable than those attached using the relatively simple loading method for the Amazon flint kaolin [26-29]. Our findings demonstrate that the activity of the prepared catalyst in oleic acid esterification compares favourably with that of a commercially available Y zeolite.

2. Experimental

2.1 Materials

The following is a list of the materials' purity and source/supplier; kaolin clay, State Company of Geological Surveying and Mining, Iraq; oleic acid ($C_{17}H_{33}COOH$), Thomas Baker; sodium hydroxide ($NaOH$) pellets, extra pure, Scharlau; absolute ethanol (C_2H_6O), >99.8% GC, Sigma Aldrich; sodium silicate (Na_4SiO_4), 99% purity, BDH Chemicals Ltd.; ammonium nitrate (NH_4NO_3), Hopkin & Williams; oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$), >99% purity, Fluka Chemika; phenolphthalein, 2% in ethanol, Sigma-Aldrich. HY-commercial zeolite was purchased from Qingdao Wish Chemicals Co. Ltd.

2.2 Catalyst preparation

Zeolite Y was prepared using the method described in Abbas and Abbas whereby NaY was first prepared and then converted to HY zeolite (HY-kaolin) by ion exchange [33].

2.3 Preparation of NaY zeolite

1 part (by mass) 45-75 µm (by sieve fraction) kaolin clay was mixed with 1.5 parts (by mass) of 40 wt % aqueous NaOH solution and the mixture was heated at 850 °C for 3 hours in a furnace to get fused kaolin. The fused kaolin was then milled to get fused kaolin in powder form. 50 g of the prepared kaolin and 63 g of sodium silicate were dispersed in 500 ml of deionized water by stirring at 50 °C for 1 hour giving a slurry of approximate pH 13.3. The slurry was aged at 50 °C for 24 h under static conditions in a polypropylene bottle, and then crystallized at 100 °C for 48 h. The solid was recovered by filtration, washed with deionized water and dried in an oven at 100 °C for 16 h. Finally, the dried powder was calcined in air at 500 °C for 1 h.

2.4 Preparation of HY zeolite

100 g of prepared NaY zeolite were mixed with 600 ml of 1 M ammonium nitrate at 100 °C for 4 h and stirred in a round bottom flask fitted with a reflux condenser. NH_4Y zeolite was recovered by filtration, washed with deionized water and dried at 100 °C for 6 h. HY zeolite was prepared by stirring 40 g of the prepared NH_4Y zeolite with 800 ml of 0.5 N oxalic acid at room temperature for 8 h. HY zeolite was recovered by filtration, washed with deionized water, dried at 100 °C and calcined in air at 550 °C for 5 h.

2.5 Catalyst characterization

X-Ray diffraction (XRD) was conducted in ambient conditions using a Panalytical X'Pert Powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). All powder diffraction patterns were recorded from 4-50˚ 2θ with step size 0.026 and step time 50 s, using an X-ray tube operated at 40 kV and 30 mA with fixed 1/4˚ anti-scatter slit. Nitrogen adsorption/desorption measurements were carried out using a Micromeritics ASAP 2020 Surface Analyser where samples were degassed under vacuum ($p < 10^{-5}$ mbar) for 12 h at 350 ˚C prior to analysis. BET-surface areas of the samples were calculated in the relative pressure range 0.05–0.30 and total pore volume was determined from the adsorption branch of the N_2 isotherm as the quantity of liquid nitrogen adsorbed at $p/p_0 = 0.995$. Microscopic images were recorded using a Jeol JSM-5600LV scanning electron microscope (SEM). Chemical compositions were determined by X-Ray Fluorescence (XRF) using a Spectro XEPOS instrument with X-LAB Pro software; all measurements were done in He.

2.6 Catalytic test

The esterification reaction of oleic acid with ethanol was performed by reflux in a 500 ml batch reactor placed in a thermostatic oil bath under stirring. The desired amount of catalyst was dried before reaction at 130 °C for 2 h. The reactor was loaded with 50 ml (44.75 g) of oleic acid and the desired amount of pre-heated ethanol (3/1, 6/1 or 9/1 ethanol to oleic acid by molar ratio) was then added. Esterification was carried out over a range of catalyst loadings (2, 5 and 10 wt% with respect to oleic acid) and reaction temperatures (40, 50, 60 and 70 °C). 5 ml samples were withdrawn from the reaction mixture at 15 minute intervals, and centrifuged for 10 min at 3000 rpm to separate the solid zeolite from the liquid phase. The supernatant layer was analysed by titration with 0.1 N KOH, using phenolphthalein indicator, to evaluate the acid value (AV) as shown in the following equation;

$$AV = \frac{\text{ml of KOH} \times N \times 56}{\text{Weigth of Sample}} \qquad (1)$$

From the acid value, the conversion of oleic acid can be calculated for each amount of the catalyst as shown in the following equation;

$$\text{conversion} = \frac{AV_{t0} - AV_{t}}{AV_{t0}} \qquad (2)$$

where:

AV_{t0} (acid value of the reaction product at time 0)

AV_{t} (acid value of the reaction product at time t)

The esterification of oleic acid was conducted in the absence of zeolite to determine the extent of any homogeneous reaction. The conversion after 90 minutes was 12% for an ethanol/oleic acid molar ratio 6:1 at 70 °C, showing that while there is some homogeneous contribution the reaction is predominantly due to heterogeneous catalysis by zeolite.

3. Results and Discussion

3.1 Catalyst characterization

The XRD powder pattern of HY-kaolin is shown in Fig. 1. The three most intense peaks of the prepared HY-kaolin, located at angles 6.34°, 15.76° and 23.77° 2-theta, confirm the presence of the characteristic faujasite structure of zeolite Y according to the Commission of the International Zeolite Association (IZA) [34, 35]. Additional comparison with the corresponding pattern of commercial HY clearly supports the presence of zeolite Y in the prepared sample, while the absence of additional peaks in the HY-kaolin pattern confirms that the prepared sample did not contain any detectable quantity of non-zeolitic crystal phases.

Nitrogen adsorption porosimetry results are summarised in Table 1. The BET surface area of the HY-kaolin, 390 m^2/g, was lower than that for HY-commercial zeolite, 625 m^2/g. Similar differences were observed for the micropore surface areas, A_{μ}, and micropore volumes, $V_{\mu P}$, of both samples. When combined with the XRD findings in Fig. 1, the porosimetry results confirm the presence of micropores in HY-kaolin, whereby the reduced surface area/micropoore volume complements the reduced intensities of the characteristic diffraction peaks. Based on micropore surface areas, the HY-kaolin contains approximately 65% zeolite Y. The remainder is attributed to the presence of impurities in the kaolin source, which are not transformed into zeolite and, thus, contribute to the final product as amorphous, non-zeolitic impurities. The total pore volumes, V_P, of both samples are shown for clarity; readings taken close to p_0 will inevitably include intra-particular condensation, so the higher value attributed to the HY-kaolin (0.853 vs. 0.783 cm^3/g), while numerically accurate, is not indicative of the faujasite structure.

Table 1: BET adsorption analysis of HY-kaolin and HY-commercial.

Sample	A_{BET} (m^2/g)	A_{μ} (m^2/g)	V_P (cm^3/g)	$V_{\mu P}$ (cm^3/g)
HY-kaolin	390	235	0.853	0.113
HY-commercial	625	355	0.783	0.258

A_{BET} and $A\mu$ are the BET and micropore surface areas, respectively. V_P and $V_{\mu P}$ are the total pore volume (at relative pressure 0.995) and micropore volume, respectively.

Elemental compositions were determined by XRF, Table 2. HY-kaolin contains somewhat similar amounts of SiO_2 and Al_2O_3 to that in zeolite Y; this is not surprising given that the prepared sample is predominantly aluminosilicate zeolite Y. The Si/Al ratio of the HY-kaolin was found to be 3.1, which is similar to the value of 2.8 in a similar study using Nigerian Ahoko kaolin [16]. Zeolite X has a Si/Al ratio < 1.5, which means that the more catalytically active and stable form of faujasite, zeolite Y, is formed here [36]. Major differences in the elemental makeup of the samples were seen in the relative concentrations of Fe, Na, K, Mg and Ca oxides, which were all vastly greater in HY-kaolin. These oxides, or various combinations thereof, are hereby assigned to be the non-zeolitic impurities that are either X-ray amorphous or too dilute to be seen with XRD.

Table 2: Elemental compositions determined by XRF.

Mass/wt%	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	MgO	K_2O	CaO	P_2O_5
HY-kaolin	15.92	58.11	3.191	0.147	1.222	0.067	4.112	0.6448
HY-commercial	13.66	69.74	0.051	0.032	< 0.0034	< 0.0012	0.151	0.5853

SEM images, Fig. 2, confirm the characteristic micron sized particles of the faujasite structure in the HY-commercial and the corresponding agglomeration between such particles for the HY-kaolin samples. It is possible that the impurities in the HY-kaolin have contributed to the agglomeration in a similar manner to how binders e.g. alumina, are used in the stabilization of bulk zeolite powders.

3.2 Esterification reactions

The esterification of oleic acid with ethanol is a reversible reaction so an excess quantity of ethanol is commonly used to enhance conversion. Three ethanol/oleic acid molar ratios were employed; 3/1, 6/1 and 9/1. The fractional conversion of oleic acid, Fig. 3, increases, as expected, with reaction time and decreases slightly due to catalyst deactivation after 45 min. The conversion is also found to increase with increasing molar ratio of ethanol to oleic acid; conversions after one hour were 69% and 85% for ratios 3/1 and 6/1, respectively. There was only a minimal further increase in conversion for the reaction at 9/1 molar ratio. These results agree with those reported by SathyaSelvabala et al. who also determined an identical optimum molar ratio of 6:1 in the esterification of Neem oil using H-mordenite modified with phosphoric acid [37].

The influence of catalyst loading at oleic acid/ethanol molar ratio of 6/1, Fig. 4, shows an increase in maximum conversion from 70 to 85% after 60 min going from 2 to 5 wt% but only a small improvement thereafter. A progressive, although slight, decrease in conversion was seen for all catalyst loadings during the second hour of reaction.

Fig. 5 shows the oleic acid conversion over the temperature range 40-70 ˚C. The conversion of oleic acid is highly dependent on reaction temperature whereby the maximum conversion increases from approximately 40% at 40 °C to 85% at 70 °C.

The recyclability of HY-kaolin was examined. Briefly, when the reaction was finished, the catalyst was recovered by filtration, dried at 100 °C, calcined in air at 550 °C for 5 h, and used in a new identical reaction for one hour reaction time. The conversion decreased from 85% to 77%, possibly due to adsorption of water released during esterification, but still retains catalytic activity.

3.3 Comparison between HY-kaolin and HY-commercial in esterification reaction

Fig. 6 compares the oleic acid conversion of HY-kaolin with that of the commercially sourced HY zeolite. The difference in activity between zeolites is interesting; the HY-kaolin is somewhat more active in the early stages of reaction, but reduces to the same conversion as the commercial sample after two hours. The difference may be due to impurities in the HY kaolin zeolite which initially enhance the esterification reaction; however, it is difficult to assign such causation with certainty without further exploration and, therefore, this will not be considered further here. Alternatively the effect may be due to the different Si/Al ratios of the sample; 3.1 for HY kaolin versus 4.5 for HY commercial. It is well known that an increase in Si/Al ratio for zeolite Y over the range 2.5-10 causes increases in Bronsted acid strength and catalyst hydrophobicity and a decrease in the acid site density/number [36]. Chung and Park showed that the activities of oleic acid esterification on ZSM-5 and mordenite improved as the number of acid sites increased i.e. with lower Si/Al ratio [38]. A similar increase in activity is observed in this paper for HY-kaolin, which contains a greater number of acid sites than HY commercial, during the early stages of reaction. Chung and Park also reported a conversion of 57% for the same reaction using Y zeolite, Si/Al ratio 3, but did not present any results regarding changes in this ratio. Overall, the findings presented here are in contrast to the claims made in many review papers that microporous zeolites are universally unsuited to the esterification reactions used in biodiesel production, certainly so in the case of oleic acid [5-10].

4. Conclusion

Iraqi kaolin was used to prepare Y zeolite in H form. This material was found to be an active catalyst in the esterification of oleic acid with conversion 85% obtained after 60 min reaction time using a 6/1 molar ratio of ethanol/oleic acid at 70 °C. The activity, which was comparable to a commercially sourced zeolite Y, was attributed to a high density of acid sites provided by the low Si/Al ratio (3.1).

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