High purity FAU-type zeolite catalysts from shale rock for biodiesel production

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Abstract

FAU-type zeolite was prepared using Irish shale rock and tested as a catalyst in the liquid-phase esterification of oleic acid (a model test reaction for biodiesel production). A systematic study was conducted (over the stated preparation ranges) by varying the water:shale ratio (4:1 to 15:1 by mass), and mixing (1-24 h), aging (6-48 h) and hydrothermal treatment times (6-72 h) to determine the optimal parameters. XRD confirmed that the product purity was highly dependent on the experimental conditions used. The BET surface area of the calcined FAU-type zeolite was 571 m^2g^{-1} and its crystal purity was comparable to that of a commercial zeolite Y. The prepared zeolite was catalytically active in the esterification of oleic acid with ethanol reaching a maximum of 78% conversion after 90 mins, which is practically identical to that recorded for commercial zeolite Y.

Keywords; Biodiesel, esterification, Y zeolite, FAU, shale

1. Introduction

The need for a reliable supply of fuel is increasing due to growing human population and expanding economies in both developing and developed countries. One innovation that addresses this requirement is fracking, which allows previously unattainable oil and gas reserves to be extracted from deep beneath the Earth's surface [1]. This typically occurs in shale rock, which is a sedimentary rock composed of a mixture of clay minerals formed by deposition of particulates and organic matter. Shale can be removed at shallower levels by open pit mining and, thereafter, the oil is separated from the shale by pyrolysis at high temperature. The vast majority of what remains is oil shale ash, which may be used for soil treatment and cement production, but millions of tonnes are added to landfill annually with associated costs. Efforts have been made, therefore, to use shale as a cheap and widely available starting material to generate value-added products. Shale is also found in areas without containing fossil fuels. Collectively, these regions contain huge reserves of shale rock that lie at/immediately below the surface and are, therefore, easily accessible and an (almost) limitless supply of starting materials for further synthesis.

Zeolite are high surface area materials that have been widely used in areas such as water treatment and purification, humidity control, and heterogeneous catalysis [2]. To date, the majority of established syntheses have used artificial reagents by heating a solution of some form of silica, alumina and alkylammounium salts in water, which over time forms a solid precipitated aluminosilicate zeolite [3]. Zeolites may also be prepared from naturally occurring reagents. Clays, rocks and ash residues from combustion of solid fuels contain large amounts of oxygen, silicon and aluminium that have similar chemical compositions to those of some aluminosilicate zeolites. Fly-ash, for example, is produced in coal-fired power plants and has been used to prepare zeolites, albeit initially with low crystal purity [4-10]; the purity was improved by employing the alkali fusion method [11-14]. Kaolin, a naturally occurring mineral, has been well studied as a starting material for zeolite synthesis and, to date, a wide range of different zeolite types have been prepared [15-25]. In a recent paper, fly ash-kaolinite mixtures were used to synthesise zeolites at low temperature [26]. We recently reported the successful preparation of zeolite Y from kaolin; the prepared material demonstrated structural characteristics comparable to those of a commercial zeolite and was a highly active catalyst in the esterification of oleic acid [27]. The (trans)esterification of natural oils to produce biodiesel is well known, and a number of reviews have been published on the use of zeolite catalysts in biodiesel production [28-33 and references therein]. Oil shale ash has been used to prepare zeolite types in impure form; A, which was used to remove heavy metals from aqueous solution [34,35], PI [36,37], hydroxysodalite [38] and a composite structure containing types A, X and hydroxysodalite [39].

Here, we show that surface shale rock from Ireland is an excellent reagent to prepare faujasite (FAU-type zeolite). The zeolite characteristics are found to be very dependent on the choice of experimental conditions. The method developed here gives FAU-type zeolite in pure form, which is an improvement on the mixed phase materials and high quantities of quartz impurity previously reported [34-39]. The prepared zeolite is an active catalyst in the esterification of oleic acid, an important model reaction for biodiesel production, with near identical catalytic properties to those of a commercial zeolite Y.

2. Experimental

2.1 Materials

The following is a list of the materials' source/supplier and purity; shale rock was collected from the surface of a recently tilled field on a working farm in county Wexford, Ireland, washed with water to remove all soil residue and dried at 120 °C for three hours; sodium hydroxide (NaOH) pellets, extra pure, Scharlau; sodium silicate (Na_4SiO_4), 99% purity, BDH Chemicals Ltd.; ammonium chloride (NH_4Cl), Sigma Aldrich; absolute ethanol (C_2H_5OH) Sigma Aldrich; phenolphthalein, 2% in ethanol, Sigma-Aldrich. Commercial zeolite Y was purchased from Qingdao Wish Chemicals Co. Ltd.

2.2 Zeolite preparation and optimisation

The clean shale was crushed in a ball mill apparatus, sieved to <90 µm and calcined in air at 800 °C for 4 h to remove organic matter. 10 g of calcined shale was then refluxed with 40 cm^3 of 5 M HCl at 85 °C for 4 h (to remove Fe) and the product recovered by filtration. 1 part (by mass) of calcined shale was mixed with 1.5 parts (by mass) of 40 wt % aqueous NaOH solution and the mixture was heated at 850 °C in air for 3 h in a furnace to get fused shale. The fused shale was then crushed to powder form. Thereafter, varying amounts of fused shale and sodium silicate were added to distilled water in polypropylene bottles, mixed (stirred) at room temperature for 1 h, aged under static conditions at room temperature for 24 h, hydrothermally treated at 100 °C for 24 h and the product recovered by filtration. Unless where stated otherwise, this procedure was used to conduct a study to determine the influences of (in the following order): (a) *water content*: 2 g fused shale and 1 g sodium silicate were added to 8, 12, 16, 20 and 30 g distilled water to give water:fused shale ratios of 4:1, 6:1, 8:1, 10:1, 12:1 and 15:1; (b) *mixing time*: 1 g fused shale and 0.5 g sodium silicate were added to 8 cm^3 of distilled water and mixed for 1, 3, 6, 12, 18 and 24 hrs; (c) *aging time (under static conditions)*:

1 g fused shale and 0.5 g sodium silicate were added to 8 cm^3 of distilled water, mixed for 3 hrs and aged for 6, 12, 18, 24 and 48 hrs; (d) *hydrothermal treatment time*: 1 g fused shale and 0.5 g sodium silicate were added to 8 cm^3 of distilled water, mixed for 3 h, aged for 18 h and hydrothermally treated at 100 °C for 6, 12, 18, 24, 48 and 72 h.

To convert the prepared zeolite from Na^+ to NH_4^+ form, 90 g of zeolite were added to 250 cm^3 of 2 N ammonium chloride and stirred in a round bottom flask at room temperature for 2 h. The solid was recovered by filtration, washed with distilled water and the ion-exchange procedure was repeated a further two times using 60 g and 30 g, respectively. The solid was again recovered by filtration, washed with distilled water, dried for 12 hrs at 120 °C and calcined in air at 500 ºC for 4 h.

2.3 Characterization

X-Ray diffraction (XRD) was conducted in ambient conditions using a Panalytical X'Pert Powder diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). All powder diffraction patterns were recorded from 4 to 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 at -196 °C. 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. Microscopic images were recorded using a JEOL JSM-5600LV scanning electron microscope (SEM). Semi-quantitative chemical analysis was performed by energy-dispersive X-ray spectroscopy (EDAX) using a detector from Oxford Instruments.

2.4 Catalyst testing

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 was then added to give an ethanol to oleic acid molar ratio of 6. Esterification was carried out at 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;

$$\mathrm{AV} = \frac{\text{ml of KOH} \times \mathrm{N} \times 56}{\text{Weight of Sample}} \quad (1)$$

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

$$\text{conversion}\% = \frac{\mathrm{AV_{t0}} - \mathrm{AV_t}}{\mathrm{AV_{t0}}} \text{x}100\% \quad (2)$$

where:

$\mathrm{AV_{to}}$ (acid value of the reaction product at time 0)

$\mathrm{AV_t}$ (acid value of the reaction product at time t)

3. Results and Discussion

3.1 Removal of Fe and alkaline fusion

The XRD patterns showing the effects of calcination, acid leaching and alkaline fusion are shown in Fig. 1. The untreated shale (dried at 120 °C) is composed primarily of chlorite, laumontite and quartz [34-39]. Calcination in air at 800 °C removes chlorite completely and causes partial decomposition of laumontite. Quartz remained after calcination and its diffraction peaks actually increased in intensity. Acid leaching was done to eliminate Fe from the shale as it competes with Al in the zeolite framework. The reduction in the orange-brown colour and Fe signal in EDAX, Fig. 2, confirm the removal of iron. Acid leaching also removed the remaining laumontite and caused a reduction in the peak intensity for quartz. The XRD pattern for NaOH fused shale confirms that quartz was removed completely by alkaline fusion and that sodium silicate and sodium aluminosilicate were the predominant phases remaining. These species are soluble in alkaline solution and provide the nutrients for the formation and eventual growth of zeolite crystals [3]. It is not possible to compare our findings directly with previous reports on the phases formed with shale (as opposed to kaolinite or fly-ash) after alkaline fusion, as no such results are reported [34-39]. However, it is well known that sodium silicate and sodium aluminosilicate are formed by the alkaline fusion of kaolinite, e.g. Belviso and Fiore have published widely on such preparations [15]. This finding, therefore, supports the formation of sodium silicate and sodium aluminosilicate in the present study, considering that kaolinite and shale have somewhat similar chemical compositions.

3.2 Optimisation of zeolite preparation

The next part of the study was to vary the experimental conditions in a systematic manner to find the parameters that give the highest quality zeolite (as measured by most intense XRD signal) from each experiment. The influence of water content was first determined, and its optimal value was then used in all further preparation methods. Next the stirring time was varied and its optimal value determined and used thereafter, and so on for aging time and hydrothermal treatment times at 100 °C in that order. The XRD patterns in Fig 3 show that the content of water has a profound effect on the degree of crystallinity. The zeolite was progressively favoured up to water:fused shale ratios of 8:1 and thereafter decreased sharply with only quartz present using a 15:1 ratio. For the sample prepared using ratio 8:1, the most intense diffraction peaks confirm the presence of faujasite (FAU) zeolite according to the International Zeolite Association (IZA) [40,41]. It makes sense that there is an optimum water to shale ratio, as the water content alters both the amount and alkalinity of solution that can dissolve reagents for nuclei formation and zeolite growth. To our knowledge, there are no reports showing the influence of the water to shale ratio in the preparation of zeolite. Hu et al. found that the ratio of water to sodium hydroxide had a profound effect on the crystals phases prepared from shale; the framework type of the product changed from cancrinite to hydroxysodalite sodalite when the water to Na_2O ratio was decreased from 25:1 to 5:1 [38]. In the preparation of FAU-type zeolite from fly ash, the quantities of a dense sodium aluminium silicate phase and quartz were reduced when the water to alkaline fused fly ash ratio was increased from 4:1 to 10:1 [14].

Both the mixing and aging time (Figs. 4 and 5) experiments showed FAU zeolite was formed over the full range of chosen conditions showing that FAU- zeolite forms readily from shale but with large variations in crystal quality; the best conditions were 3 h mixing and 18 h aging time. Mixing/aging the suspension at RT allows the formation of nuclei that increase the eventual yield of zeolite. Fig 6 shows XRD patterns as a function of hydrothermal time; again there was variation over the chosen range, with the highest FAU purity formed after 24 hours. This finding matches well with Hu et al. who reported that the purity of hydroxysodalite prepared from shale increased with hydrothermal treatment time with the best zeolite formed after 24 hours (although longer times were not reported) [38]. Our findings also agree with that reported by Fernandes Machado et al. which showed that zeolite X peaked over the range 12-48 h at 100 °C and decreased substantially at longer times [39]. In the same synthesis, zeolites A and hydroysodalite peaked after 72 h and 96 h, respectively. The results suggest that there is an evolution of crystal phases over time as follows: zeolite X → zeolite A→ hydroxysodalite.

Similar phase changes to progressively more stable structures were observed for mesoporous materials [42].

The results of water:shale ratio and mixing, aging and hydrothermal treatment times are quantified in Fig. 7 by plotting the d_{111} peak intensities. All four variables have a major influence on the FAU purity evidenced by the variation of peak intensity with changes in any given variable. The maximum peak intensities for each experiment confirm that the FAU zeolite with the highest intensity prepared by us (after optimising water:shale ratio and mixing, aging and hydrothermal treatment times) has comparable intensity to that of a commercial HY zeolite (dashed line). Overall, the results show that FAU zeolite can be prepared in pure form from shale rock using the method described here. This is a significant improvement on the procedure used by Fernandes Machado et al., which results in composite materials containing zeolites A, X and hydroxysodalite, all of which are contaminated by quartz [39]. Because of the large number of experimental variables (time, temperature, reagents) it is difficult to assign with certainty the exact cause(s) of the different results observed. While the general conditions of both syntheses are somewhat similar, the procedure used by Fernandes Machado et al. incorporated alumina and conducted alkaline fusion at 350 °C, while our method uses sodium silicate with alkaline fusion at 850 °C [39]. Unfortunately, no XRD results were provided to show the effect of alkaline fusion on the crystal phases present in shale, so based on the presence of quartz in all the final materials it is possible that quartz was not completely removed during the alkaline fusion step [39]. The variation may arise from the different minerals present: the shale contained illite, labradorite, quartz and chlorite, while our shale contains laumontite, quartz and chlorite. It is also interesting to note that the XRD patterns for the shale ash used in the syntheses of zeolites A [34,35] PI[37] and hydroxysodalite [38] showed that the relative amounts of quartz differed; for example the shale used to produce PI was reported to contain mainly feldspar while quartz was predominantly found in the shales used to prepare zeolite A and hydroxysodalite.

The total pore volume of the shale zeolite is 0.73 $cm^3\ g^{-1}$ and BET surface area is 571 m^2g^{-1}, which is 8.6% lower than that for commercial zeolite Y, 625 m^2g^{-1}. This high surface area provides further proof that the FAU zeolite prepared here is of high purity. SEM images, Fig 8, confirm the characteristic particle shape of FAU and agglomeration between particles in a similar manner to that of commercial zeolite Y. Fig. 8 also shows that the particle size for both samples was approximately 2 μm. The Si/Al ratio of the shale zeolite was estimated to be 1.98 based on EDAX, Fig. 8, which is in the range for zeolite Y.

3.3 Esterification reactions

The esterification of oleic acid with ethanol is used as a test reaction to assess the catalytic activity of the shale zeolite. This is a reversible reaction so an excess quantity of ethanol, 6:1 ethanol/oleic acid molar ratio, is used to enhance conversion. The fractional conversions of oleic acid, Fig 9, increase, as expected, with reaction time at all temperatures but decreases slightly after 90 mins at 70 °C. The conversion of oleic acid is highly dependent on reaction temperature where the maximum conversion increases from 45% at 40 °C to 78% at 70 °C. This conversion compares well to that found in our previous study, which showed maximum oleic acid conversion of 85% for identical reaction conditions at 70 °C [27]. Fig. 10 shows that zeolite prepared from shale has almost identical conversions as that for the commercially sourced zeolite Y, which strongly suggests that the shale zeolite has Bronsted acidity and catalytic properties practically identical to that of commercial zeolite Y.

As with any esterification reaction, the formation of water prevents complete conversion of oleic acid by promoting the reverse reaction (hydrolysis) and driving the equilibrium to the left. Oleic acid conversions between 60 and >99% were achieved for different montmorillonite-based clay catalysts by running the reaction at 150 °C for six hours, which removed the water produced during reaction by evaporation [43]. In another report, >99% oleic acid conversion was found after 100 mins at 110 °C using sulfuric acid as catalyst whereby the water was removed using a zeolite A adsorption column [44]. However, the temperatures used in these methods also removes the ethanol required for esterification so is not ideal for real applications. There are relatively few reports showing zeolite catalysed oleic acid esterification reactions, and the majority use methanol where the following maximum conversion rates (of oleic acid) were recorded; 86% for zeolite beta [45,46]; 81% for mordenite, 80% for ZSM-5, and 78% for FAU-type zeolite [47]; and 83% for ZSM-5 modified with citric acid [48]. For oleic acid esterification using ethanol, the maximum conversion over zeolite NaY was 27% [49]; the high purity FAU-type zeolite prepared in this paper using shale shows significantly greater activity (78%).

4. Conclusions

FAU-type zeolite was prepared from shale rock using a combination of acid leaching, alkaline fusion and hydrothermal treatment. The quality of the FAU was progressively improved through rigorous testing of the effects of preparation conditions on crystal purity. The FAU-type zeolite with the highest purity was active in the catalysed esterification of oleic acid, a model test reaction for biodiesel production, with conversions comparable to those of a commercially sourced zeolite Y.

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