

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

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17 Abstract

18 FAU-type zeolite was prepared using Irish shale rock and tested as a catalyst in the liquid-
19 phase esterification of oleic acid (a model test reaction for biodiesel production). A systematic
20 study was conducted (over the stated preparation ranges) by varying the water:shale ratio (4:1
21 to 15:1 by mass), and mixing (1-24 h), aging (6-48 h) and hydrothermal treatment times (6-72
22 h) to determine the optimal parameters. XRD confirmed that the product purity was highly
23 dependent on the experimental conditions used. The BET surface area of the calcined FAU-
24 type zeolite was 571 m²g⁻¹ and its crystal purity was comparable to that of a commercial zeolite
25 Y. The prepared zeolite was catalytically active in the esterification of oleic acid with ethanol
26 reaching a maximum of 78% conversion after 90 mins, which is practically identical to that
27 recorded for commercial zeolite Y.

28
29 **Keywords;** Biodiesel, esterification, Y zeolite, FAU, shale

31 1. Introduction

32 The need for a reliable supply of fuel is increasing due to growing human population and
33 expanding economies in both developing and developed countries. One innovation that
34 addresses this requirement is fracking, which allows previously unattainable oil and gas

35 reserves to be extracted from deep beneath the Earth's surface [1]. This typically occurs in
36 shale rock, which is a sedimentary rock composed of a mixture of clay minerals formed by
37 deposition of particulates and organic matter. Shale can be removed at shallower levels by open
38 pit mining and, thereafter, the oil is separated from the shale by pyrolysis at high temperature.
39 The vast majority of what remains is oil shale ash, which may be used for soil treatment and
40 cement production, but millions of tonnes are added to landfill annually with associated costs.
41 Efforts have been made, therefore, to use shale as a cheap and widely available starting material
42 to generate value-added products. Shale is also found in areas without containing fossil fuels.
43 Collectively, these regions contain huge reserves of shale rock that lie at/immediately below
44 the surface and are, therefore, easily accessible and an (almost) limitless supply of starting
45 materials for further synthesis.

46

47 Zeolite are high surface area materials that have been widely used in areas such as water
48 treatment and purification, humidity control, and heterogeneous catalysis [2]. To date, the
49 majority of established syntheses have used artificial reagents by heating a solution of some
50 form of silica, alumina and alkylammounium salts in water, which over time forms a solid
51 precipitated aluminosilicate zeolite [3]. Zeolites may also be prepared from naturally occurring
52 reagents. Clays, rocks and ash residues from combustion of solid fuels contain large amounts
53 of oxygen, silicon and aluminium that have similar chemical compositions to those of some
54 aluminosilicate zeolites. Fly-ash, for example, is produced in coal-fired power plants and has
55 been used to prepare zeolites, albeit initially with low crystal purity [4-10]; the purity was
56 improved by employing the alkali fusion method [11-14]. Kaolin, a naturally occurring
57 mineral, has been well studied as a starting material for zeolite synthesis and, to date, a wide
58 range of different zeolite types have been prepared [15-25]. [In a recent paper, fly ash-kaolinite
59 mixtures were used to synthesise zeolites at low temperature \[26\].](#) We recently reported the
60 successful preparation of zeolite Y from kaolin; the prepared material demonstrated structural
61 characteristics comparable to those of a commercial zeolite and was a highly active catalyst in
62 the esterification of oleic acid [27]. The (trans)esterification of natural oils to produce biodiesel
63 is well known, and a number of reviews have been published on the use of zeolite catalysts in
64 biodiesel production [28-33 and references therein]. Oil shale ash has been used to prepare
65 zeolite types in impure form; A, which was used to remove heavy metals from aqueous solution
66 [34,35], PI [36,37], hydroxysodalite [38] and a composite structure containing types A, X and
67 hydroxysodalite [39].

68

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

76

77 **2. Experimental**

78 **2.1 Materials**

79 The following is a list of the materials' source/supplier and purity; shale rock was collected
80 from the surface of a recently tilled field on a working farm in county Wexford, Ireland, washed
81 with water to remove all soil residue and dried at 120 °C for three hours; sodium hydroxide
82 (NaOH) pellets, extra pure, Scharlau; sodium silicate (Na₄SiO₄), 99% purity, BDH Chemicals
83 Ltd.; ammonium chloride (NH₄Cl), Sigma Aldrich; [absolute ethanol \(C₂H₅OH\) Sigma Aldrich](#);
84 phenolphthalein, 2% in ethanol, Sigma-Aldrich. Commercial zeolite Y was purchased from
85 Qingdao Wish Chemicals Co. Ltd.

86

87 **2.2 Zeolite preparation and optimisation**

88 The clean shale was crushed in a ball mill apparatus, sieved to <90 μm and calcined in air at
89 800 °C for 4 h to remove organic matter. 10 g of calcined shale was then refluxed with 40 cm³
90 of 5 M HCl at 85 °C for 4 h (to remove Fe) and the product recovered by filtration. 1 part (by
91 mass) of calcined shale was mixed with 1.5 parts (by mass) of 40 wt % aqueous NaOH solution
92 and the mixture was heated at 850 °C in air for 3 h in a furnace to get fused shale. The fused
93 shale was then crushed to powder form. Thereafter, varying amounts of fused shale and sodium
94 silicate were added to distilled water in polypropylene bottles, mixed (stirred) at room
95 temperature for 1 h, aged under static conditions at room temperature for 24 h, hydrothermally
96 treated at 100 °C for 24 h and the product recovered by filtration. Unless where stated
97 otherwise, this procedure was used to conduct a study to determine the influences of (in the
98 following order): (a) *water content*: 2 g fused shale and 1 g sodium silicate were added to 8,
99 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
100 and 15:1; (b) *mixing time*: 1 g fused shale and 0.5 g sodium silicate were added to 8 cm³ of
101 distilled water and mixed for 1, 3, 6, 12, 18 and 24 hrs; (c) *aging time (under static conditions)*:

102 1 g fused shale and 0.5 g sodium silicate were added to 8 cm³ of distilled water, mixed for 3
103 hrs and aged for 6, 12, 18, 24 and 48 hrs; (d) *hydrothermal treatment time*: 1 g fused shale and
104 0.5 g sodium silicate were added to 8 cm³ of distilled water, mixed for 3 h, aged for 18 h and
105 hydrothermally treated at 100 °C for 6, 12, 18, 24, 48 and 72 h.

106

107 To convert the prepared zeolite from Na⁺ to NH₄⁺ form, 90 g of zeolite were added to 250 cm³
108 of 2 N ammonium chloride and stirred in a round bottom flask at room temperature for 2 h.
109 The solid was recovered by filtration, washed with distilled water and the ion-exchange
110 procedure was repeated a further two times using 60 g and 30 g, respectively. The solid was
111 again recovered by filtration, washed with distilled water, dried for 12 hrs at 120 °C and
112 calcined in air at 500 °C for 4 h.

113

114 **2.3 Characterization**

115 X-Ray diffraction (XRD) was conducted in ambient conditions using a Panalytical X'Pert
116 Powder diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). All powder diffraction patterns
117 were recorded from 4 to 50° 2 Θ with step size 0.026 and step time 50 s, using an X-ray tube
118 operated at 40 kV and 30 mA with fixed 1/4° anti-scatter slit. Nitrogen adsorption/desorption
119 measurements were carried out using a Micromeritics ASAP 2020 Surface Analyser at -196
120 °C. Samples were degassed under vacuum ($p < 10^{-5}$ mbar) for 12 h at 350 °C prior to analysis.
121 BET-surface areas of the samples were calculated in the relative pressure range 0.05-0.30.
122 Microscopic images were recorded using a JEOL JSM-5600LV scanning electron microscope
123 (SEM). Semi-quantitative chemical analysis was performed by energy-dispersive X-ray
124 spectroscopy (EDAX) using a detector from Oxford Instruments.

125

126 **2.4 Catalyst testing**

127 The esterification reaction of oleic acid with ethanol was performed by reflux in a 500 ml batch
128 reactor placed in a thermostatic oil bath under stirring. The desired amount of catalyst was
129 dried before reaction at 130 °C for 2 h. The reactor was loaded with 50 ml (44.75 g) of oleic
130 acid and the desired amount of pre-heated ethanol was then added to give an ethanol to oleic
131 acid molar ratio of 6. Esterification was carried out at reaction temperatures 40, 50, 60 and 70
132 °C. 5 ml samples were withdrawn from the reaction mixture at 15 minute intervals, and
133 centrifuged for 10 min at 3000 rpm to separate the solid zeolite from the liquid phase. The
134 supernatant layer was analysed by titration with 0.1 N KOH, using phenolphthalein indicator,
135 to evaluate the acid value (AV) as shown in the following equation;

136
$$AV = \frac{\text{ml of KOH} \times N \times 56}{\text{Weight of Sample}} \quad (1)$$

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

139
$$\text{conversion\%} = \frac{AV_{t_0} - AV_t}{AV_{t_0}} \times 100\% \quad (2)$$

140 where:

141 AV_{t_0} (acid value of the reaction product at time 0)

142 AV_t (acid value of the reaction product at time t)

143

144 **3. Results and Discussion**

145 **3.1 Removal of Fe and alkaline fusion**

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

164

165 **3.2 Optimisation of zeolite preparation**

166 The next part of the study was to vary the experimental conditions in a systematic manner to
167 find the parameters that give the highest quality zeolite (as measured by most intense XRD
168 signal) from each experiment. The influence of water content was first determined, and its
169 optimal value was then used in all further preparation methods. Next the stirring time was
170 varied and its optimal value determined and used thereafter, and so on for aging time and
171 hydrothermal treatment times at 100 °C in that order. The XRD patterns in Fig 3 show that the
172 content of water has a profound effect on the degree of crystallinity. The zeolite was
173 progressively favoured up to water:fused shale ratios of 8:1 and thereafter decreased sharply
174 with only quartz present using a 15:1 ratio. For the sample prepared using ratio 8:1, the most
175 intense diffraction peaks confirm the presence of faujasite (FAU) zeolite according to the
176 International Zeolite Association (IZA) [40,41]. It makes sense that there is an optimum water
177 to shale ratio, as the water content alters both the amount and alkalinity of solution that can
178 dissolve reagents for nuclei formation and zeolite growth. To our knowledge, there are no
179 reports showing the influence of the water to shale ratio in the preparation of zeolite. Hu et al.
180 found that the ratio of water to sodium hydroxide had a profound effect on the crystals phases
181 prepared from shale; the framework type of the product changed from cancrinite to
182 hydroxysodalite sodalite when the water to Na₂O ratio was decreased from 25:1 to 5:1 [38]. In
183 the preparation of FAU-type zeolite from fly ash, the quantities of a dense sodium aluminium
184 silicate phase and quartz were reduced when the water to alkaline fused fly ash ratio was
185 increased from 4:1 to 10:1 [14].

186

187 Both the mixing and aging time (Figs. 4 and 5) experiments showed FAU zeolite was formed
188 over the full range of chosen conditions showing that FAU- zeolite forms readily from shale
189 but with large variations in crystal quality; the best conditions were 3 h mixing and 18 h aging
190 time. Mixing/aging the suspension at RT allows the formation of nuclei that increase the
191 eventual yield of zeolite. Fig 6 shows XRD patterns as a function of hydrothermal time; again
192 there was variation over the chosen range, with the highest FAU purity formed after 24 hours.
193 This finding matches well with Hu et al. who reported that the purity of hydroxysodalite
194 prepared from shale increased with hydrothermal treatment time with the best zeolite formed
195 after 24 hours (although longer times were not reported) [38]. Our findings also agree with that
196 reported by Fernandes Machado et al. which showed that zeolite X peaked over the range 12-
197 48 h at 100 °C and decreased substantially at longer times [39]. In the same synthesis, zeolites
198 A and hydroxysodalite peaked after 72 h and 96 h, respectively. The results suggest that there is
199 an evolution of crystal phases over time as follows: zeolite X → zeolite A → hydroxysodalite.

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

202

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

227

228 The total pore volume of the shale zeolite is $0.73 \text{ cm}^3 \text{ g}^{-1}$ and BET surface area is $571 \text{ m}^2 \text{ g}^{-1}$,
229 which is 8.6% lower than that for commercial zeolite Y, $625 \text{ m}^2 \text{ g}^{-1}$. This high surface area
230 provides further proof that the FAU zeolite prepared here is of high purity. SEM images, Fig
231 8, confirm the characteristic particle shape of FAU and agglomeration between particles in a
232 similar manner to that of commercial zeolite Y. Fig. 8 also shows that the particle size for both

233 samples was approximately 2 μm . The Si/Al ratio of the shale zeolite was estimated to be 1.98
234 based on EDAX, Fig. 8, which is in the range for zeolite Y.

235

236 **3.3 Esterification reactions**

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

248 As with any esterification reaction, the formation of water prevents complete conversion of
249 oleic acid by promoting the reverse reaction (hydrolysis) and driving the equilibrium to the left.
250 Oleic acid conversions between 60 and >99% were achieved for different montmorillonite-
251 based clay catalysts by running the reaction at 150 °C for six hours, which removed the water
252 produced during reaction by evaporation [43]. In another report, >99% oleic acid conversion
253 was found after 100 mins at 110 °C using sulfuric acid as catalyst whereby the water was
254 removed using a zeolite A adsorption column [44]. However, the temperatures used in these
255 methods also removes the ethanol required for esterification so is not ideal for real applications.
256 There are relatively few reports showing zeolite catalysed oleic acid esterification reactions,
257 and the majority use methanol where the following maximum conversion rates (of oleic acid)
258 were recorded; 86% for zeolite beta [45,46]; 81% for mordenite, 80% for ZSM-5, and 78% for
259 FAU-type zeolite [47]; and 83% for ZSM-5 modified with citric acid [48]. For oleic acid
260 esterification using ethanol, the maximum conversion over zeolite NaY was 27% [49]; the high
261 purity FAU-type zeolite prepared in this paper using shale shows significantly greater activity
262 (78%).

263

264 **4. Conclusions**

265 FAU-type zeolite was prepared from shale rock using a combination of acid leaching, alkaline
266 fusion and hydrothermal treatment. The quality of the FAU was progressively improved

267 through rigorous testing of the effects of preparation conditions on crystal purity. The FAU-
268 type zeolite with the highest purity was active in the catalysed esterification of oleic acid, a
269 model test reaction for biodiesel production, with conversions comparable to those of a
270 commercially sourced zeolite Y.

271

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273

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