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A catalytic and mechanistic study of the Friedel–Crafts benzoylation of anisole using zeolites in ionic liquids

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Abstract

The Friedel–Crafts benzoylation of anisole with benzoic anhydride to yield 4-methoxybenzophenone has been carried out in a range of ionic liquids using zeolite catalysts. The rates of reaction were found to be significantly higher using ionic liquids compared with organic solvents. Continuous-flow studies of successful ionic liquid systems indicate that the bulk of the catalysis is due to the formation of an acid via the ion exchange of the cation with the protons of the zeolite. The acid liberated was quantified using both titration experiments and ion-exchange experiments using sodium-exchanged zeolites.

Keywords: Zeolite; Ionic liquids; Friedel–Crafts; Benzoylation; Anisole; Continuous flow; Ion exchange; Deactivation

1. Introduction

Friedel–Crafts acylation reactions are of great importance in the industrial manufacture of aryl ketones, and are used extensively in the production of pharmaceuticals such as the nonsteroidal anti-inflammatory drugs Ibuprofen and Naproxen. Conventionally, these reactions are catalysed by aluminum trichloride, using an acylating agent such as an acid chloride in a volatile organic solvent [1]. Due to the complexation of the ketone product with aluminum trichloride a stoichiometric excess must be used, which is then destroyed in the hydrolysis step required for product isolation. The large quantities of metal salt waste formed, as well as the production of HCl, have aroused much research in the development of new cleaner technologies, which generate minimal waste.

A major step toward waste minimisation would be to develop a truly catalytic process, using an acid anhydride, where the catalyst does not form a strong complex with the product and is recyclable. A number of Lewis acid catalysts have been found to facilitate Friedel–Crafts acylations, for example, metal triflate [2] and metal triflamide [3] salts as well as solid acid catalysts such as nafion [4] and zeolites [5]. For reasons including high costs of the metal salts, low yield, particularly with unactivated aromatic substrates, and poor recyclability the application of homogeneous catalysts has remained mainly of academic interest. In contrast, zeolites are currently used on a large industrial scale, for example, within the Rhodia process for the acylation of anisole [6]. Zeolites have been shown to facilitate the acetylation and benzoylation of both activated aromatic substrates such as anisole [7], veratrole [8], and 2-methoxynaphthalene [9] and unactivated aromatics such as toluene with acid anhydrides [10]. In these reactions, the activity and regioselectivity of the zeolite catalyst are dependent on the Si:Al ratio, crystallite size, and pore size [10,11]. Friedel–Crafts acylation reactions have also been carried out using zeolites which have been cation-exchanged with iron, zinc, indium, aluminum, and lanthanum [12] and more recently zeolites have been used to support chlorometallate ionic liquids in alkylation reactions [13].

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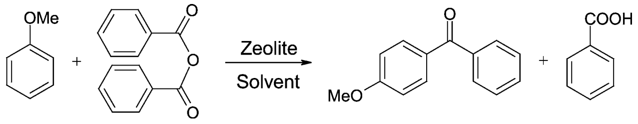


Scheme 1.

Ionic liquids represent a class of solvent, which has the potential to reduce the use of organic solvents and lower VOC's. Friedel–Crafts reactions have been studied extensively in ionic liquids and were one of the first synthetic reactions to be carried out in this media. Acidic organochloroaluminate systems were shown to be very efficient catalysts for the acylation of toluene, benzene, and chlorobenzene [14]; however, as with $AlCl_3$ the complexation of the keto-product to the ionic liquid necessitated its destruction in the product isolation step. The development of water and air-stable ionic liquids has led to a substantial increase in the number of reactions possible in these solvents. Here the ability of ionic liquids to dissolve both the catalyst and the substrate can be effectively utilised. For example, both Gmouh et al. and Ross et al. have demonstrated that using metal triflate salts in ionic liquids allows efficient Friedel–Crafts acylation of various aromatic substrates [15]. Furthermore, the ionic liquid allowed extraction of substrates and subsequent recycle of the catalyst-ionic liquid system, albeit with decreasing conversions.

Many of the reactions performed in ionic liquids have used homogeneous catalysts and these have been reviewed extensively [16]. In contrast, heterogeneous catalysts have been much less studied. Recently, a number of investigations using heterogeneous catalysts in ionic liquids have been reported. Both supported and unsupported transition metal (colloidal) catalysts have been used for a range of reactions including the Heck reaction [17], selective hydrogenations [18], and selective oxidations [19]. Katdare et al. have shown that zeolites can catalyse Friedel–Crafts acylation reactions in ionic liquids [20] and more recently microporous solids have been used for the Prins cyclisation of aldehydes and homoallylic alcohols [21], the alkylation of phenol [22], and the selective oxidation of thioethers [23]. However, the catalytic reaction mechanism for these reactions has not been elucidated to date.

This paper reports on a study of the interaction of zeolites with ionic liquids using the formation of 4-methoxybenzophenone by the benzoylation of anisole with benzoic anhydride as an exemplar reaction, Scheme 1, and the mechanism by which the catalyst operates.

2. Experimental

All zeolites used in the reactions were supplied by BP-Amoco, Quest, and Chevron-Texaco and calcined in air at 500 °C overnight before use. The characterisation of the catalysts used is summarised in Table 1. The sodium-exchanged zeolites were supplied by Catal International. Anisole (99%) and benzoic anhydride (98%) were obtained from Lancaster and used as received. Trifluoromethanesulphonic acid (HOTf) and bis-trifluoromethanesulphonimide ($HNTf_2$) were both obtained from Aldrich and used as received.

Table 1
The chemical composition and the textural parameters of the zeolites used

Zeolite	Si:Al ratio	BET surface area ($m^2\ g^{-1}$)	BET pore volume ($cm^3\ g^{-1}$)
H-USY-29	29	625.79	0.396
H-USY-42	42	669.11	0.436
H-USY-80	80	618.07	0.444
H-Beta	26	539.87	0.532
Mordenite	87	293.28	0.184
H-ZSM-5	52	283.17	0.184

Ionic liquids composed of either 1-alkyl-3-methylimidazolium ($[C_n mim]^+$), 1-ethyl-2,3-dimethylimidazolium ($[C_2dmim]^+$), N-butyl-N-methylpiperidinium ($[C_4mpip]^+$), N-octylpyridinium ($[C_8py]^+$), methyltrioctylammonium ($[N_{8881}]^+$), or trihexyltetradecylphosphonium ($[P_{66614}]^+$) cations with tetrafluoroborate ($[BF_4]^-$), hexafluorophosphate ($[PF_6]^-$), trifluoromethanesulphonate ($[OTf]^-$) or bis-trifluoromethanesulphonimide ($[NTf_2]^-$) anions were synthesized from the appropriate organic chloride or bromide salt using standard literature preparative procedures [24]. All ionic liquids were dried in vacuo at 60 °C for more than 4 h before use and contained < 0.01 wt% water, determined by Karl–Fischer analysis. The densities of the ionic liquid and reagent mixtures, used to calculate concentrations, were obtained using an Anton Parr DMA4500 densitometer.

The batch experiments were carried out in a 10-pot reactor (Stemblock) at 80 °C with magnetic stirring at 600 rpm. To the calcined zeolite (0.1 g), ionic liquid (2 g) and anisole (4.6 mmol) were added. The reaction mixtures were heated to the appropriate temperature, while stirring, before benzoic anhydride (5.0 mmol) was added. Analogous procedures were used for experiments using HOTf and $HNTf_2$.

The spinning basket reactor consisted of a baffled glass vessel (150 cm^3) in which was suspended a mesh (35 mesh) basket containing 2.2 g H-USY-29 (650 μm $<$ particle size $<$ 800 μm). The basket was rotated through 60 g of the stock solution consisting of $[C_2mim][NTf_2]$ (0.15 mol), anisole (0.46 mol), and benzoic anhydride (0.53 mol) using an overhead stirrer at 200 rpm.

Continuous-flow experiments (Fig. 4) were carried out using a fixed-bed reactor (4.57 mm i.d. × 76 mm) containing ~ 0.5 g zeolite (650 μm $<$ particle size $<$ 800 μm) connected to a pipe (1.40 mm i.d. ×1300 mm) acting as a heat exchanger suspended in a silicone oil bath. The feedstock made from $[C_2mim][NTf_2]$ (0.23 mol), anisole (0.37 mol), and benzoic anhydride (0.77 mol) was pumped through the reactor bed using a BHS Labotron LDP-4 piston pump at 156 $cm^3\ h^{-1}$ to achieve a 10 s residence time over the catalyst bed.

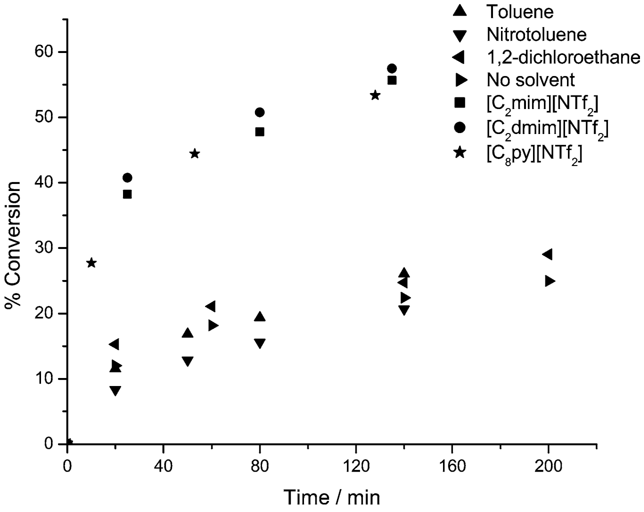


Fig. 1. Comparison of the percentage conversion for the benzoylation of anisole using benzoic anhydride using H-USY-29 in a range of ionic liquids and molecular organic solvents and in the absence of a solvent.

For all the reactions, samples of known mass ($\sim$ 30 mg) were removed over time and dissolved in acetonitrile (10 cm^3) for analysis by HPLC.

For the catalyst recycle experiments, the zeolite was calcined at 500 °C in air overnight between reactions before recharging the reaction solution and repeating the experimental procedure as described above.

Offline analysis was carried out using an Agilent HPLC system with a diode array detector set at 224 nm. An Eclipse XDB C8 column with an eluent of methanol/water (60/40) at a flow rate of 1.0 $cm^3\ min^{-1}$ was used. Yields with respect to the limiting reagent, anisole, were calculated using a calibration curve of known standards and mass balances $> 95\%$ were obtained. Titrations were carried out using an Orion 420A pH meter, calibrated using buffer tablets from BDH. Atomic absorption (AAS) measurements were made using a Perkin–Elmer AA Analyst 100 following digestion of the zeolite in aqua regia and dilution of the ionic liquid in water. For the aqueous extractions, titrations, and AAS dilutions, double-distilled deionised water was used.

3. Results and discussion

Fig. 1 compares the variation of conversion with time in a standard batch reactor for a range of $[NTf_2]^-$-based ionic liquids with conventional solvents using H-USY-29, for the benzoylation of anisole with benzoic anhydride. Clearly, higher activity is observed in the ionic liquids compared with either the molecular solvents or in the absence of a solvent. In each reaction the *para* selectivity was $> 94\%$. Not all the ionic liquids screened showed this variation. No reaction was observed in the water-miscible $[C_4mim][BF_4]$, $[C_6mim]Cl$, or $[C_4mim][OTf]$ ionic liquids. Therefore to test whether the poor reactivity was due to water adsorption from the atmosphere, reactions were also performed in a dry box. Even under these strictly "dry" conditions no reaction occurred. Furthermore, using a water-immiscible ionic liquid, $[C_8py][BF_4]$, no activity was observed, implying that the anion has a strong effect on the activity of the catalyst. It should be noted that the lack of activity found in the water-miscible ionic liquids, which are more difficult to obtain halide free, is not due to chloride impurities remaining after preparation. Addition of 100 ppm Cl^- to $[C_2mim][NTf_2]$ had little effect on the reaction rate. Although benzoylation was found to proceed in $[C_4mim][PF_6]$, the zeolite partly dissolved in the reaction mixture, indicating the presence of HF, itself an active catalyst for the reaction. The hydrolysis of $[PF_6]^-$-based ionic liquids to yield HF is well known [25] and therefore no further study was carried out on this system. The effect of the cation was investigated using $[NTf_2]^-$-based ionic liquids. The reaction rates were found to be similar in $[C_n mim][NTf_2]$ ($n = 2, 4, 6, 10$), $[C_2dmim][NTf_2]$, $[C_8py][NTf_2]$, and $[C_4mpip][NTf_2]$; however, the reaction proceeded only slowly in $[N_{8881}][NTf_2]$ and no reaction was observed in $[P_{66614}][NTf_2]$.

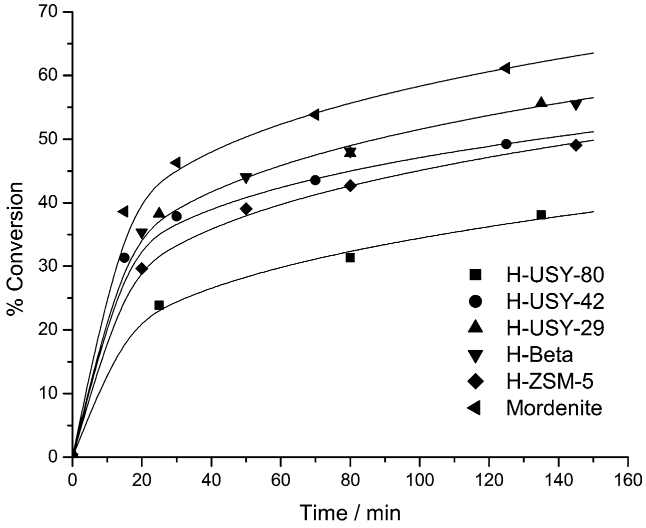


Fig. 2. Comparison of the percentage conversion for the benzoylation of anisole using benzoic anhydride as a function of time using a range of zeolites in $[C_2mim][NTf_2]$ at 80 °C.

Based on these observations $[C_2mim][NTf_2]$ was used as the solvent with a range of zeolites of varying Si:Al ratios, surface areas, and pore size. With the exception of amorphous silica, the sodium forms of ZSM-5 and zeolite Y, all the zeolites tested facilitated the reaction (Fig. 2). It can be observed that in the case of the H-USY zeolites the conversion appears to be dependent on the Si:Al ratio: i.e., as the ratio increased the conversion decreased. To determine the effect of internal diffusion and external mass transfer, particles of H-USY-29 of various sizes ranging from less than 106 µm to greater than 500 µm were used in $[C_2mim][NTf_2]$ at different stirring speeds from 300 to 1200 rpm. However, neither aggregate size nor stirring speed had any effect on the rate of reaction.

It can be observed from Figs. 1 and 2 that many reactions show a similar kinetic profile regardless of the ionic liquid or zeolite used. For each combination, the reaction rate is initially high but quickly decreases to a much lower rate. This profile is similar to that reported for other zeolite-catalysed acylation reactions. For example, Rohan et al. [26] observed a fast reaction on the fresh catalyst which was then followed by rapid deactivation. The deactivation was attributed to the adsorption of product in the mesopores of the zeolites and the subsequent polyacetylation to form di- and tri-acetylated products which blocked the micropores of the zeolite. Using an excess of anisole reduced this deactivation by reducing the adsorption of product on the surface of the zeolite. This not only increased the number of catalyst sites available but also reduced the formation of polyacetylated products. Derouane et al. [27] also found a similar kinetic profile for the acetylation of anisole using H-Beta with excess substrate as the solvent. In addition, they reported that, during the experiments, the zeolite changed colour from white to orange, which was attributed to the adsorption of product onto the surface of the zeolite. Similar visual changes were observed in the present study in the absence of solvent and using organic solvents; i.e., the zeolite became orange in colour while the liquid phase remained colourless. Contrastingly, when the reaction was carried out in ionic liquids, the catalyst barely changed in colour while the ionic liquid phase became dark orange.

In agreement with the findings of Rohan et al. [26] and Derouane et al. [27], the use of a 10-fold molar excess of anisole increased the reaction rate. In addition, when using ionic liquids, a 10-fold excess of benzoic anhydride also resulted in a similar increase in rate, indicating that in the case of ionic liquids adsorption of the product and further reaction may not be the main source of deactivation.

To study the deactivation a spinning basket reactor was initially used. This was run in batch mode for the first 30 min of operation, before being changed to continuous mode by pumping the reagents in and out at a flow rate of 0.5 $cm^3\ min^{-1}$ for a further 260 min. Fig. 3 shows the change in product concentration with respect to time when the system was run as a CSTR. Clearly, the reaction did not achieve steady state in the time studied; however, as product was still being formed over the duration of the experiment, as shown by comparison with the calculated dilution curve (i.e., the expected outlet concentration due to dilution of the bulk liquid by the incoming feed), the catalyst was still active. It was also observed that the catalyst deactivation was reversible and similar activity was found both for the fresh catalyst and after recycle, provided the catalyst had been calcined at 500 °C between reactions. It should be noted that recycles performed without precalcination of the catalyst showed little reaction.

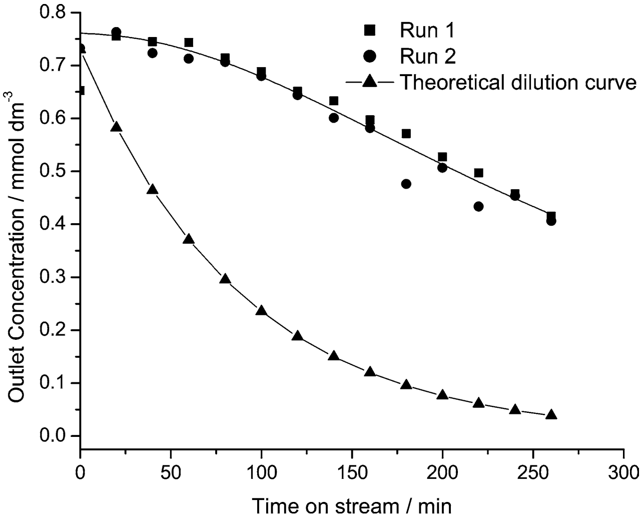


Fig. 3. Concentration of 4-methoxybenzophenone at the outlet of the spinning basket reactor as a function of time on stream using freshly calcined and recycled H-USY-29 in [C_2mim][NTf_2] at 80 °C.

The reaction was also run as a continuous plug flow system over a fixed bed of zeolite, shown schematically in Fig. 4. A comparison of product concentration at the outlet with respect to time on stream is shown in Fig. 5 for reactions performed in [C_2mim][NTf_2] and 1,2-dichloroethane (DCE). As expected from the batch experiments, a lower initial conversion was observed when the reaction was carried out in DCE than in [C_2mim][NTf_2]. In DCE the conversion remained constant with respect to time, indicating continued active sites on the surface; however, in the ionic liquid, a rapid decrease in conversion was observed with time on stream. A similar profile was observed when the ionic liquid reaction was carried out at 150 °C; as expected a higher level of activity was observed when compared to 90 °C. The dependence of the ionic liquid concentration present in the feed was also tested using the plug-flow reactor. Here it was observed that at high [C_2mim][NTf_2] concentrations (ranging from 835 to 13.6 mM), the previously observed conversion profile was obtained indicating that the concentration of the ionic liquid had little effect. However, at lower concentrations of [C_2mim][NTf_2] (1.420 mM) a much lower initial ac-

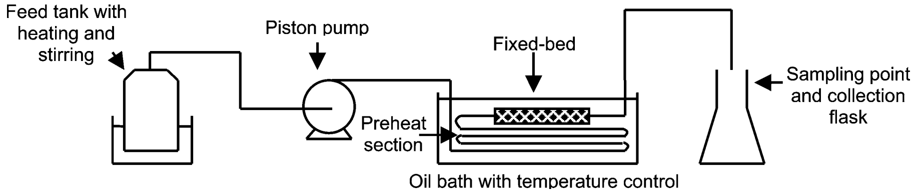


Fig. 4. Schematic diagram of the fixed-bed reactor.

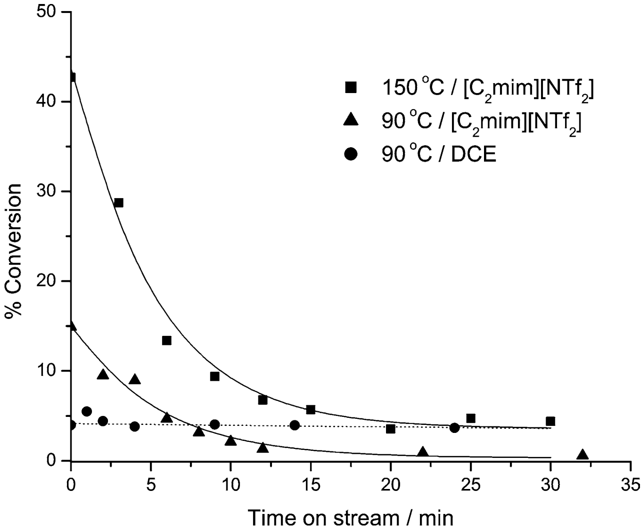
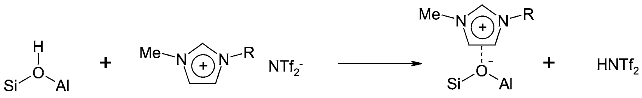


Fig. 5. Continuous-flow study using the fixed-bed reactor containing H-USY-29 at 90 °C in $[C_2mim][NTf_2]$ and 1,2-dichloroethane and at 150 °C in $[C_2mim][NTf_2]$.



Scheme 2.

tivity was observed which decreased at a significantly slower rate.

This type of rapid deactivation indicates a change in the zeolite catalyst to facilitate a homogeneous catalytic mechanism. No gross changes were observed on the zeolite, for example, neither XRD of the catalyst nor ICP analysis of the ionic liquid solution following the reactions showed any significant structural breakdown of the catalyst or removal of framework aluminum. This is consistent with the good recyclability of the zeolite, albeit after calcinations, and indicated that the reaction was taking place via an ion-exchange mechanism whereby the ionic liquid cation exchanges with the acidic proton on the zeolite releasing H^+ into the ionic liquid, as shown in Scheme 2. Similar effects have been observed with water whereby strong Brønsted acids are formed following the hydrolysis of the surface Lewis acid sites [28].

In a further experiment different fractions of pure ionic liquid feed were collected (3-min intervals) from the outlet stream of the plug-flow reactor operating at 80 °C and 40 $cm^3\,h^{-1}$. These fractions were then used in standard batch reactions without any additional catalyst present (Fig. 6). The activity of each subsequent fraction decreased, although the shape of the conversion profile remained the same. It should be noted that analogous experiments performed using samples of the zeolite removed from the fixed bed after washing with ionic liquid showed no residual activity. These results from the continuous experiments support the hypothesis that ion exchange is occurring and the resulting acid is the active catalytic species.

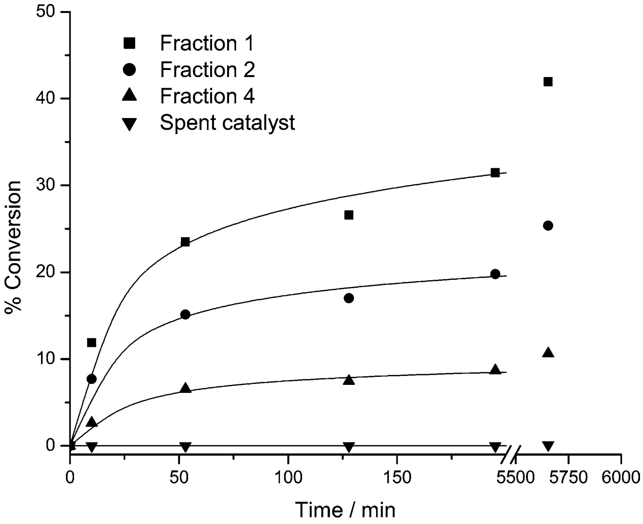


Fig. 6. Variation of the anisole conversion with respect to time for outlet fractions of $[C_2mim][NTf_2]$ collected after contact with H-USY-29 at 80 °C.

To prove that ion exchange had occurred, acid–base titrations and exchange experiments with Na zeolites were carried out in an attempt to quantify the acid liberated. Fig. 7 shows a series of titration curves from $HNTf_2$ in water; the aqueous extract of $HNTf_2$ dissolved in $[C_2mim][NTf_2]$, the aqueous extract of $[C_2mim][NTf_2]$ contacted with H-USY-29, and the aqueous extract of $[C_2dmim][NTf_2]$ contacted with H-USY-29 at 80 °C using NaOH (2.3 mM) as the titrant. The reference titration of $HNTf_2$ in water showed a typical strong acid-strong base titration curve; however, when $[C_2mim][NTf_2]$ was pumped through a fixed bed of H-USY-29 at 80 °C and the $[C_2mim][NTf_2]$ washed with water the resulting titration curve was ill-defined, with two points of inflection. In these cases the resulting data were fitted using cubic spline interpolation and the points of inflection found by finding the maximum of the first derivatives. A similar titration curve was obtained following the aqueous extraction of 1.55 mM $HNTf_2$ dissolved in $[C_2mim][NTf_2]$ with water, showing that the second inflection point corresponds to the neutralisation of $HNTf_2$. The first titration point is due to the dissolution of $[C_2mim][NTf_2]$ in the aqueous phase, albeit only a relatively small amount due to its low water miscibility. Washing $[C_2mim][NTf_2]$ with D_2O and analysing the solution with ^1H NMR confirmed the presence of the $[C_2mim]^+$ cation. It is well known that the C(2) proton is acidic, as shown by the disappearance of the ^1H NMR signal on the addition of base, and therefore the presence of the $[C_2mim]^+$ cation results in a diprotic acid titration curve [29]. To confirm this, $HNTf_2$ was dissolved in $[C_2dmim][NTf_2]$, where the C(2) position is protected by a methyl group, extracted into water, and titrated against sodium hydroxide. In this case the titration curve was well defined with a single inflection point. From the titration data it can be calculated that 76.6 mg of $HNTf_2$ is produced per gram of zeolite used. This corresponds to a concentration

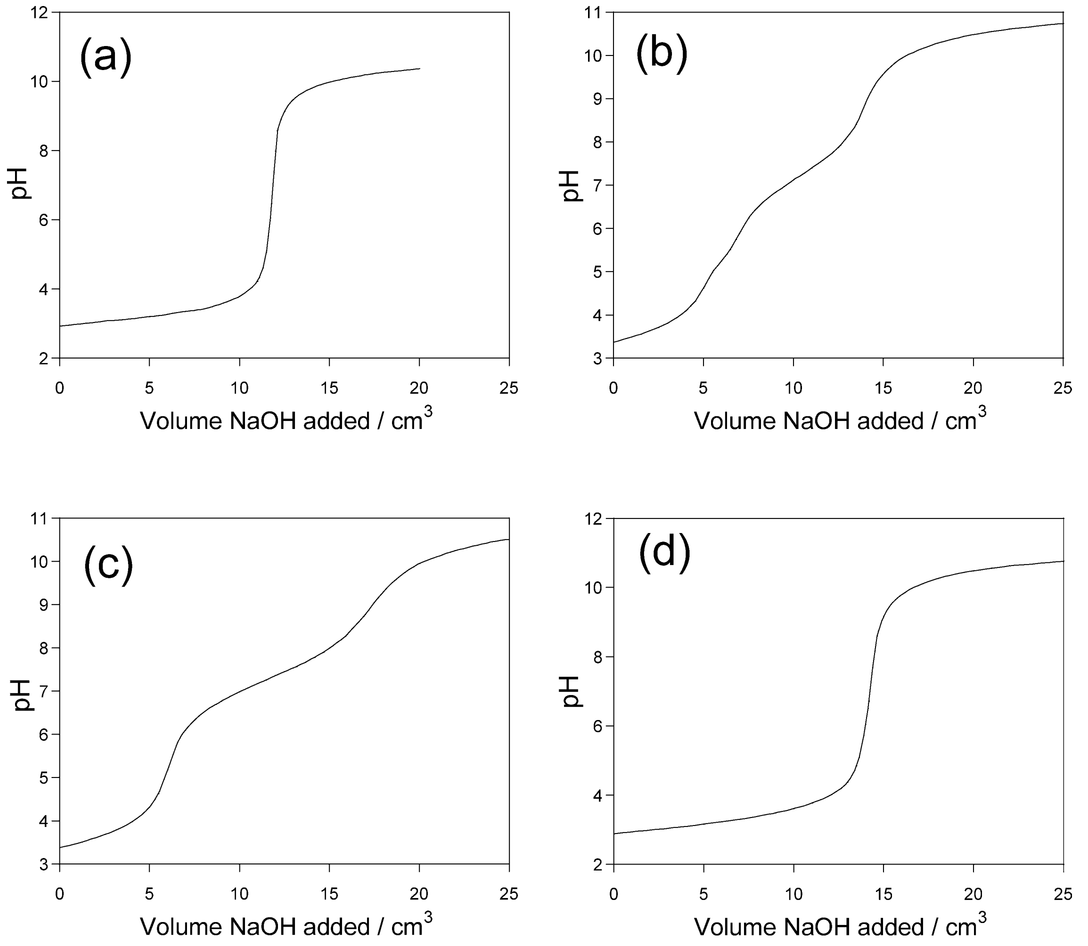


Fig. 7. Titration of (a) $HNTf_2$ in water, (b) aqueous extract from $[C_2mim][NTf_2]$ contacted with H-USY-29 at 80 °C, (c) aqueous extract of $HNTf_2$ from $[C_2mim][NTf_2]$, and (d) aqueous extract of $HNTf_2$ from $[C_2dmim][NTf_2]$ with 2.3 mM NaOH.

of 9.46 mM of acid in a typical reaction mixture, 10.68 mg $[C_2mim][NTf_2]$ consumed, i.e., only ∼ 0.5% ionic liquid loss corresponding to approximately 49% of the acid sites on the zeolite exchanged by $[C_2mim]^+$.

To further quantify the amount of ion exchange and to probe why no reaction occurred in either $[OTf]^-$- or $[BF_4]^-$-based ionic liquids, the extent of ion exchange from a series of Na-exchanged zeolites with a range of ionic liquids was determined. In each case, the zeolites were stirred in the ionic liquid at 80 °C, the zeolite and ionic liquid were separated by filtration, and the sodium content of both the ionic liquid and zeolite was determined by AAS; the results are summarised in Table 2. From the data it is clear that the anion does not affect the ion exchange significantly, similar sodium ion exchange was observed for equivalent $[NTf_2]^-$-, $[OTf]^-$-, and $[BF_4]^-$-based ionic liquids. It should be noted that while the anion has little effect on the extent of exchange, there are marked differences in the reactivity of the resulting catalytic species. Conversely, the cation does effect the exchange as seen by the level of exchange observed with the bulkier cations $[N_{8881}]^+$ and $[P_{66614}]^+$. The latter explains why the tetraalkylammonium and tetraalkylphosphonium-based ionic liquids show very low or no activity for the Friedel–Crafts reaction using the zeolite catalysts. Since these cations do not readily facilitate the exchange, little acid is formed and therefore an insignificant reaction occurs when using these ionic liquids. The lack of exchange with the tetraalkylammonium and tetraalkylphosphonium cations is probably due to the shape and size of the cations compared with the imidazolium, pyridinium, and piperidinium ions. The tetraalkylammonium and tetraalkylphosphonium cations are much more bulky than the corresponding heterocyclic ring systems studied which may prevent them from entering the pores of the zeolites. In addition, the charge distribution in these cations is

Table 2
Extent of cation exchange from sodium-exchange zeolites with 1,3-dialkylimidazolium, tetraalkylammonium, and tetraalkylphosphonium ionic liquids

	H-USY-5	H-USY-29	H-ZSM-5[a]
$[C_4mim][NTf_2]$	42 ± 4%	19 ± 1%	47 ± 1%
$[C_4mim][BF_4]$	31 ± 3%	34 ± 4%	42 ± 2%
$[C_4mim][OTf]$	42 ± 1%	48 ± 1%	41 ± 1%
$[N_{8881}][NTf_2]$	0 ± 1%	7 ± 1%	8 ± 2%
$[P_{66614}][NTf_2]$	0 ± 2%	0 ± 3%	0 ± 3%

[a] Si:Al = 52.

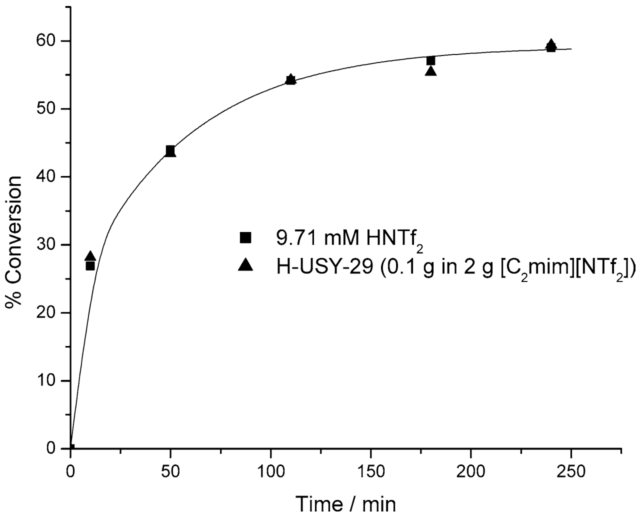


Fig. 8. Comparison of the percentage conversion as a function of time observed with H-USY-29 with that from the calculated equivalent concentration of $HNTf_2$ using $[C_2mim][NTf_2]$ at 80 °C.

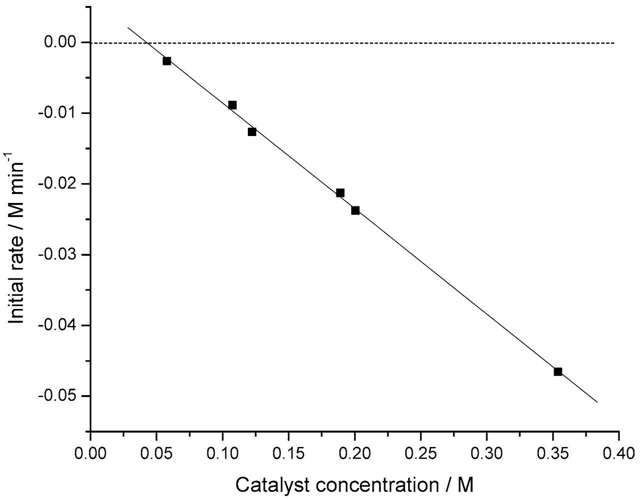


Fig. 9. Effect of triflic acid catalyst concentration on the initial rate of reaction. Initial rate is given as the initial rate of consumption of anisole.

highly localized on the central nitrogen/phosphorus and, due to the surrounding alkyl chains, this prevents a strong interaction between the positive charge on the cation and the surface sites. This may be compared with the more delocalised charge on the imidazolium-, pyridinium-, and piperidinium-based ionic liquids where the charge is easily accessible from either face of the heterocyclic ring. This exchange is also found to be temperature dependent. At higher temperatures the Na-exchange experiments do show an increase in the percentage of sodium exchanged, 7% exchange of sodium from USY-29 in $[N_{8881}][NTf_2]$ at 80 °C was found compared with 64% exchange at 150 °C. Interestingly, the Na-exchange results indicate that the amount of acid formed from USY-29 in $[C_4mim][NTf_2]$ was 83.7 $mg\,g^{-1}$ zeolite which is equivalent to 10.34 mM in a typical reaction. This value correlates well with the values obtained from the titration experiments and was further confirmed by comparing the reaction profiles generated from 0.1 g of H-USY-29 and a 9.71 mM acid concentration (Fig. 8). In agreement with the activity data, the close correlation shown between the $[C_2mim][NTf_2]$ titration results and the sodium-exchange results from $[C_4mim][NTf_2]$ also indicates the weak dependence on alkyl chain length for $[C_nmim]^+$-based ionic liquids.

The fact that not all the acid sites are exchanged by the ionic liquid despite the large excess of cation present indicates that the activity is dependent on the accessibility of the exchangeable sites as well as the number of sites. This is consistent with the results from the continuous-plug-flow study whereby increasing the temperature increased the activity due to increased availability of the exchangeable surface sites and no further increase in activity was observed above a certain concentration of ionic liquid.

The sodium ion exchange results do not explain the lack of activity in $[OTf]^-$- and $[BF_4]^-$-based ionic liquids. Triflic acid (HOTf), formed from the exchange of the zeolite proton in the triflate ionic liquid, is known to be a highly active Friedel–Crafts catalyst [30]. However, despite the concentration of acid generated in situ being greater in the $[OTf]^-$-based ionic liquid than in the $[NTf_2]^-$-based ionic liquid, no reaction occurred. To assess the relative activity of $HNTf_2$ and HOTf as Friedel–Crafts catalysts in the corresponding ionic liquid, reactions were performed as a function of the acid concentration. Fig. 9 shows the initial rate of change in anisole concentration as a function of triflic acid concentration (determined from the differential of the best fit third-order polynomial). Although there is a linear correlation between the concentration and initial rate data, the regression line does not intersect with the origin and shows that a threshold acid concentration is required before activity is observed. This type of threshold is typical of reactions which undergo catalyst poisoning and the cause is currently under further investigation. Comparison of the threshold concentration (42.4 mM) with the concentration estimated from the ion exchange with the H-USY-29 zeolite (116 mg HOTf g^{-1} zeolite which is equivalent to 26.8 mM in a typical reaction mixture) shows that there is an insufficient amount of acid generated using 0.1 g of zeolite in 2 g of triflate ionic liquid to facilitate reaction. In the analogous experiments using $HNTf_2$ no threshold value for concentration was observed.

If the hypothesis outlined above is correct then it should be possible to generate a known, controlled concentration of $HNTf_2$ in situ in an organic solvent by ion exchange using a source of $[NTf_2]^-$ with a zeolite. Fig. 10 shows a comparison of the benzoylation kinetics of H-USY-29 in $[C_2mim][NTf_2]$ and H-USY-29 in DCE in the presence of $LiNTf_2$. Similar rates of reaction were observed in each case whereas no reaction was observed in the absence of H-USY-29. This indicates that a similar mechanism is occurring in both media, where the acidic proton on the zeolite exchanges with the cation, either lithium or $[C_2mim]^+$, producing the active $HNTf_2$.

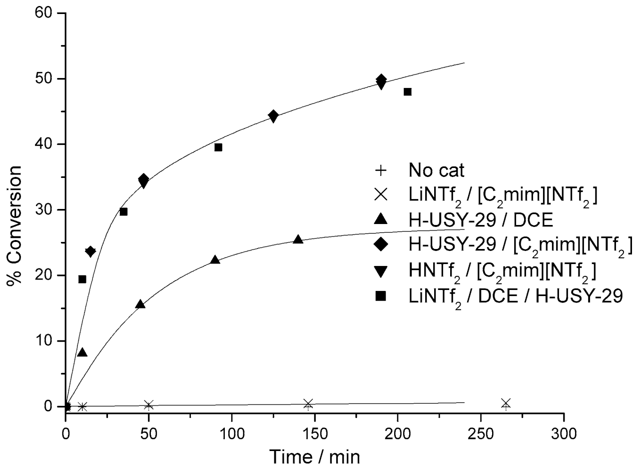


Fig. 10. Comparison of anisole conversion as a function of time in the absence of catalyst, addition of $LiNTf_2$ in $[C_2mim][NTf_2]$, H-USY-29 in DCE, H-USY-29 in $[C_2mim][NTf_2]$, $HNTf_2$ in $[C_2mim][NTf_2]$, and H-USY-29 in DCE in the presence of $LiNTf_2$ at 80 °C.

The exchange mechanism proposed is consistent with the rapid deactivation observed in the fixed-bed experiments. Once all the exchangeable sites were exhausted in the zeolite, at the temperature of the reaction, the catalyst is essentially inactive and the conversion decreases rapidly, as shown in Fig. 5. From the data presented in Fig. 5, it would appear that steady-state reaction is observed at 150 °C; however, longer experiments indicate that the conversion does continue to drop. In the case of the semicontinuous experiment carried out in the spinning basket reactor, the homogeneous acid catalyst would be diluted over time but some would still be present throughout the reaction, thus allowing continued reaction after switching to CSTR operation.

This mechanism is consistent with that proposed by Shen et al. [22]. Using $H_3PW_{12}O_{40}$ supported on MCM-41 increased conversion was found for the alkylation of phenol using ionic liquids compared with hexane. A similar ion-exchange mechanism to that described herein was postulated to explain the results obtained. Although this mechanism is consistent with the results presented, it cannot be ruled out that some heterogeneous activity contributes. However, under the conditions used in this study, there does not appear to be a significant contribution from the zeolite.

4. Conclusions

The benzoylation of anisole has been successfully carried out in $[NTf_2]^-$-based ionic liquids using a range of zeolites. The reaction is thought to proceed via a homogeneous mechanism, catalysed by $HNTf_2$, generated in situ by the exchange of the cation from the ionic liquid with the acid proton on the zeolite. The efficiency of this exchange is shown to be temperature dependent. With $[C_8py][BF_4]$, $[C_4mim][BF_4]$, and $[C_4mim][OTf]$ no reaction occurs, indicating that insufficient concentrations of acids are generated in these cases to facilitate the reaction. Whereas $[P_{66614}][NTf_2]$ does not support sodium exchange and $[N_{8881}][NTf_2]$ will exchange at low levels and do not therefore facilitate the reaction. The amount of acid generated at the reaction temperature (80 °C) has been quantified using titration and sodium-exchange experiments with both methods giving comparable results which correlate well with kinetic data.

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