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# Catalytic asymmetric heterogeneous aziridination of styrene using $Cu^{2+}$-exchanged zeolite Y: effect of the counter-cation on enantioselectivity and on the reaction profile†

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Effective catalysts have $Cu^{2+}$-exchange levels of *ca.* 40–60% of the maximum concentration for electroneutrality and, consequently, Cu-zeolite Y catalysts contain an additional counter-cation ($H^+$, $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$) whose effect is explored. With $Li^+$, $Na^+$, $K^+$ counter-cations, the zeolite structure is not markedly affected but, with $Rb^+$ and $Cs^+$, there is some loss of crystallinity. Replacement of $H^+$ by group I cations does not markedly influence the overall ee observed for aziridine indicating that the presence of protons in the Cu-HY catalysts are not detrimental to the reaction. Catalysts containing group I cations typically give decreased leaching of $Cu^{2+}$ during the reaction. At low nitrene donor to styrene molar ratios (1 : 1), replacement of $H^+$ by group I cations leads to a small enhancement in the ee of aziridine, although the yield of aziridine formed is decreased under all reaction condition. At higher molar ratios of nitrene donor to styrene, the ee is suppressed, particularly with Rb and Cs. The effect of reaction time on aziridine yield reveals a reaction profile in which the reaction initially proceeds rapidly, then slows down prior to accelerating again in the latter part of the reaction. This effect is accentuated by increasing the size of the counter-cation. This reaction profile is also observed for the homogeneously catalysed pathway and, consequently, it cannot be due solely to a confinement effect within the zeolite pores. Over addition of reaction by-products ($NsNH_2$, PhI) accentuates the shape of this reaction profile and the effect is discussed in terms of the interactions of such molecules at the active site.

## Introduction

The synthesis of pure enantiomers using catalytic processes continues to receive considerable research attention. The significant success achieved with homogeneous catalysts has been recognised with the recent award of the Nobel prize in chemistry to Sharpless, Noyori and Knowles.[1] Recently, attention has started to be focussed on the immobilisation of homogeneous catalysts,[2] particularly using chiral bis(oxazoline) ligands.‡ [3] This is particularly important as many homogeneous catalysts utilise relatively expensive chiral ligands and their recovery and re-use are of immense importance. Immobilisation can avoid the necessity of ligand recovery and hence will improve asymmetric catalysts potential in commercial processes applications.

We have previously shown that $Cu^{2+}$ immobilised within microporous and mesoporous materials prepared by ion-exchange and modified by chiral bis(oxazoline) is effective in the asymmetric aziridination of alkenes.[4–7] In particular, higher enantioselection can be observed with these immobilised catalysts when compared with non-immobilised catalysts investigated under identical conditions.[6] More recently, we have extended the use of these immobilised catalysts to asymmetric Diels Alder reactions[8] and carbonyl- and imino-ene reactions.[9] To date, we have found that the optimum catalysts are prepared by exchanging 40–60% of protons present within the intracrystalline space of zeolite HY with $Cu^{2+}$. This means that the catalytically active $Cu^{2+}$ cations also have protons present within the microporous structure. In this study, we investigate the effect of introducing alternative counter-cations from group I ($Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$) to replace protons and, in particular, we investigate their effect on the formation of aziridine in the early stages of the reaction. Recently, we have shown that the ee increases with conversion in the aziridination reaction[10] and this study also extends our investigation on the reaction profile of aziridination of styrene.

## Results and discussion

### Catalyst characterisation

A series of $Cu^{2+}$-exchanged zeolite Y catalysts were prepared, containing *ca.* 4.0% $Cu^{2+}$ from zeolite Y that had been previously ion-exchanged with group I cations (see Table 1). Ion-exchange is known to affect the stability of the zeolite framework and, consequently, to investigate this, the catalysts were characterised using powder X-ray diffraction and $^{27}Al$ MAS NMR spectroscopy (see electronic supplementary information, ESI) following calcination at 550 °C for 3 h. The X-ray diffraction patterns of Cu-LiY, Cu-NaY, Cu-KY are very similar to Cu-HY but there is some loss of crystallinity for the zeolites containing the larger group I cations, Cu-RbY and

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† Electronic supplementary information (ESI) available: powder X-ray diffraction patterns, $^{27}Al$ MAS NMR spectra and thermogravimetric analyses of Cu-Y catalysts with group I counter-cations $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$. See http://www.rsc.org/suppdata/nj/b4/b410932p/
‡ The IUPAC name for 1,3-oxazoline is 4,5-dihydro-1,3-oxazole.

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**Table 1** Effect of group I cations on the heterogeneously catalysed aziridination of styrene using copper-exchanged zeolite Y[a]

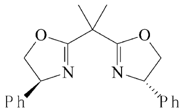
| | | PhI=NNs : styrene mol ratio | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1.1 | | 1.3 | | 1.5 | | |
| Catalyst | [Cu]/wt % | Yield | ee | Yield | ee | Yield | ee | % Cu leached [b] |
| Cu-HY | 3.7 | 85 | 81 | 80 | 92 | 85 | 91 | 1.9 |
| Cu-LiY | 3.5 | 85 | 92 | 80 | 87 | 66 | 77 | 1.6 |
| Cu-NaY | 4.0 | 68 | 88 | 72 | 91 | 67 | 85 | 1.5 |
| Cu-KY | 3.6 | 76 | 91 | 75 | 93 | 56 | 72 | 1.6 |
| Cu-RbY | 4.0 | 74 | 89 | 75 | 90 | 75 | 74 | 1.6 |
| Cu-CsY | 3.8 | 66 | 90 | 60 | 90 | 60 | 77 | 1.3 |

[a] Reaction conditions: $CH_3CN$, 25 °C, 4 h [b] % leached over 4 h reaction period from fresh catalyst using PhI=NNs : styrene mol ratio = 1.5 as this leads to the highest rate of Cu leaching

Cu-CsY. $^{27}$Al MAS NMR confirmed an increase in intensity of the signal associated with octahedrally coordinated extra-framework Al for the Cu-RbY and Cu-CsY due to de-alumination of the tetrahedrally coordinated framework alumina. However, de-alumination is not extensive and it is considered that the zeolite framework remains largely intact in these comparative experiments. Thermal gravimetric analysis (TGA, see ESI) of the samples showed a single feature at *ca.* 150 °C associated with loss of water from the catalysts. In general, group I cation-exchanged Cu-Y zeolites exhibited 9% weight loss, which is attributed to the additional water associated with the group I counter-cation. All catalysts were calcined (550 °C, 3 h) immediately prior to use and, consequently, the materials were essentially anhydrous at the beginning of the reaction.

## Effect of group I counter-cation on the aziridination of styrene

Aziridination of styrene using [*N*-(*p*-nitrophenylsulfonyl)imino]phenyliodinane§ (PhI=NNs) as the nitrene donor with Cu-exchanged zeolites modified by (*S*,*S*)-2-2′-isopropylidene-bis (4-phenyl-2-oxazoline), **1**, was investigated and the results, after a reaction time of 4 h, are shown in Table 1. When a 10% molar excess of nitrene donor relative to styrene was used, the ee was enhanced slightly for group I ion-exchanged zeolites, but, this was associated with lower yields of aziridine.



**1**

This effect is considered to be due to the stability of the nitrene donor under the reaction conditions employed. At low PhI=NNs concentration, the presence of protons in Cu-HY can lead to enhanced decomposition of the nitrene donor to form sulfonamide. At higher PhI=NNs concentration, it is possible that the small amount of residual water associated with group I cations or introduced with the solvent leads to enhanced formation of PhIO which subsequently reacts with styrene to form benzaldehyde, thereby decreasing the aziridine yield.[11] However, the key result is that the protons present within the Cu-HY zeolite, which has been extensively studied to date,[2,4–7] do not markedly influence the function of the aziridine. Indeed, their replacement does not affect the reaction markedly indicating that the protons are not central to the reaction mechanism. There are two possible explanations for this observation. First, the counter-cation replacing the proton will have a different electrostatic affinity towards the zeolite[12] and this may be crucial in retaining the copper within the zeolite, this effect binge further influenced by the size of the cation. Second, the effect may be due to the diffusion limitations introduced, perhaps, as a result of the larger size of the group I cations compared to proton.

The effect of group I counter-cations on catalyst stability during the reaction was also investigated and $Cu^{2+}$ leaching, observed during the reaction, was determined (Table 1). We have previously made a detailed study of $Cu^{2+}$ leaching in this reaction system[7] and we found that, although up to *ca.* 7% of the $Cu^{2+}$ initially present in Cu-HY can leach under standard reaction conditions (PhI=NNs : styrene molar ratio = 1.5, **1**, 25 °C, $CH_3CN$), nevertheless, the reaction was due to the heterogeneously catalysed process. Indeed, the leached $Cu^{2+}$ was ineffective as a catalyst since the homogeneously catalysed aziridination reaction is poisoned preferentially by the presence of PhI, a by-product issued from the decomposition of the nitrene donor. Interestingly, in the present study, the leaching of $Cu^{2+}$ was decreased by *ca.* 15–20% in group I ion-exchanged Cu-Y zeolites. Again, the two possible explanations stated before may apply here. Confinement effects have been observed to play a role in microporous and mesoporous heterogeneous asymmetric catalysts. In the present case, the larger cations may restrict access to $Cu^{2+}$ by N-containing materials, that is, the excess PhI=NNs and $CH_3CN$ solvents that potentially lead to leaching. The enhancement in ee at low molar excesses of PhI=NNs and decreased $Cu^{2+}$ leaching indicate that group I ion-exchanged zeolites may be preferable catalysts to the standard $Cu^{2+}$-exchanged zeolite Y used in previous studies in terms of the enhanced ee outweighing the slight decrease in aziridine yield.

## Effect of reaction time on aziridine yield with group I ion-exchanged zeolite Y

The effect of the reaction time on the conversion of styrene and the yield of aziridine was investigated for the group I ion-exchanged zeolite as a function of the PhI=NNs : styrene molar ratio (Figs. 1–3). In general, increasing the PhI=NNs : styrene molar ratio enhances the yield in the early stages of the reaction and this is particularly marked for the Cu-CsY catalyst. With a 10% molar excess of nitrene donor, the rate of styrene conversion and the yield of aziridine in the early reaction stages (0–100 min) are suppressed with the increasing size of group I cations (Fig. 1). These results are a further evidence that the counter-cation present in the zeolite intracrystalline space can play a significant role in the course of the reaction. Overall, replacement of protons with small group I cations can be beneficial at low molar excesses of nitrene donor and may, therefore, be useful in other catalytic applications. However, larger cations are deleterious as they lead to lower rates of reaction, probably due to steric effects.

An interesting observation with these reaction time studies concern the nature of the reaction profile for both styrene conversion and aziridine yield. This is also apparent for Cu-HY catalyst in data we have previously published[6] but we have

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§ The IUPAC name for iodinane is $\lambda^3$-iodane.

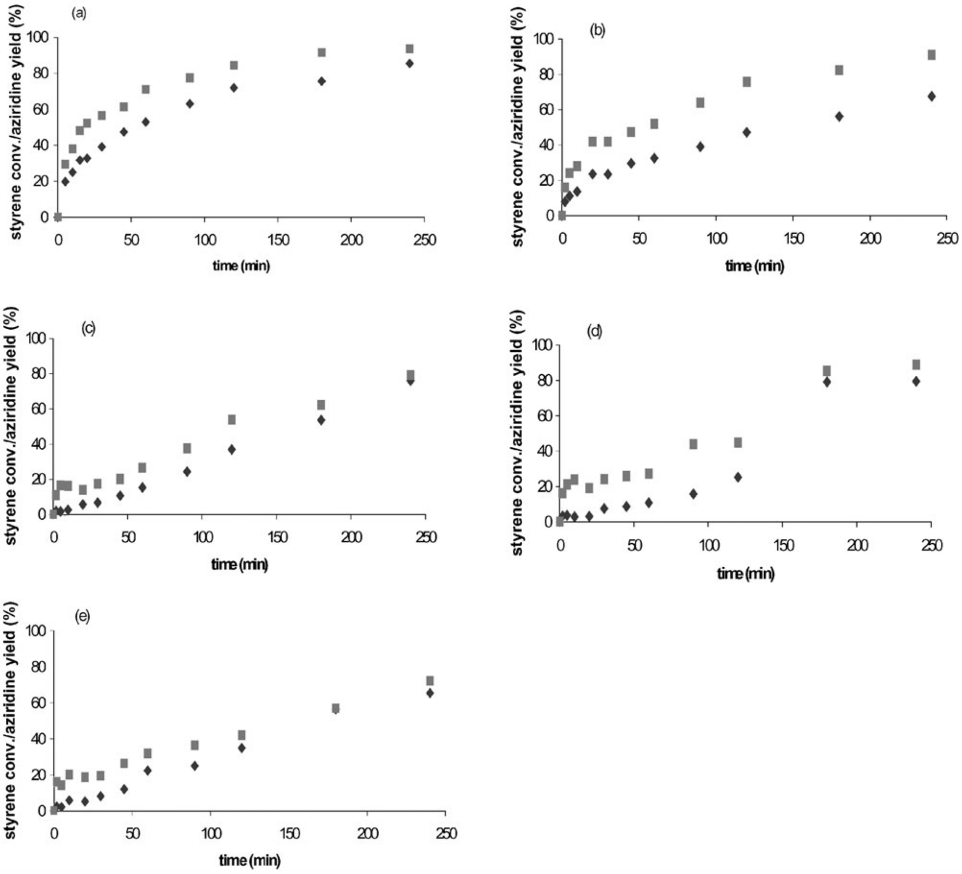


**Fig. 1** Effect of group I cations on the aziridination of styrene using Cu-exchanged zeolite Y, bis(oxazoline) **1**, $CH_3CN$, 25 °C, PhI=NNs : styrene mol ratio = 1.1. (◆) Aziridine yield; (■) styrene conversion. (a) Cu-LiY; (b) Cu-NaY; (c) Cu-KY; (d) Cu-RbY; (e) Cu-CsY.

not, to date, commented on this effect. The aziridination reaction is characterised by an initial rapid conversion of styrene and formation of aziridine; however, after the initial period, the rates of styrene conversion and aziridine formation slow down before subsequently accelerating again as the reaction proceeds. It is apparent that there is a marked difference in the yield of aziridine and styrene conversion, and plots of styrene conversion minus aziridine yield are useful in quantifying this effect since it varies with reaction time and clearly shows the key characteristic of the reaction profile (Fig. 4).[6] It is observed that, the larger the size of the counter-cation, the more apparent the effect. In the heterogeneously catalysed reaction, the active site within the supercage of the zeolite is highly confined. As noted previously,[6] this leads to an enhancement in the ee observed with these catalysts. It is also apparent that the active site can also interact with reaction by-products (*e.g.* PhI, $NsNH_2$), as well as the resulting aziridine and the starting nitrene donor. In our preceding communication,[10] we showed that aziridine could interact with $NsNH_2$ and the nitrene donor and these interactions played a role in the observed enhancement in ee with styrene conversion. This observation shows that the coordination sphere of $Cu^{2+}$, although highly confined within the zeolite, changes in its nature during the reaction. We believe that this also manifests itself in the observation of the S-shaped reaction profile (Figs. 1–3) and that the size of the cation would, therefore, play a significant role by enhancing steric confinement of the active centre.

## Effect of by-products on reaction profile

In our previous study,[6] we investigated the effect of adding significant amounts (10 mol%) of $NsNH_2$ and PhI in the formation of aziridine using PhI=NNs as the nitrene donor (PhI=NNs : styrene, 1 : 1.5). At these levels, the addition of $NsNH_2$ and PhI significantly affected the rate of aziridine formation. When a lower PhI=NNs : styrene molar ratio is used, the reaction profile of aziridine formation with reaction time is particularly marked for the heterogeneous Cu-HY catalyst (Fig. 5). It is still apparent, although not as marked, in the homogeneously catalysed reaction with $Cu(OTf)_2$ (Fig. 6). This is an important observation since, although it is apparent that the steric confinement of the active site within the zeolite pore accentuates this effect, it demonstrates that confinement is not the sole cause of this interesting phenomenon concerning the reaction profile of aziridine formation. In addition, in the homogeneously catalysed reaction, there is no counter-cation in the system (*i.e.* $H^+$, $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$), and no solid/liquid interface. Hence, we consider that it is easier to study the origin of the reaction profile in the homogeneously catalysed reaction system. The initial decrease in rate following the initial rapid reaction is observed at *ca.* 20–40% conversion and, at this time, the reaction mixture comprises styrene, PhI=NNs, PhI, and aziridine, with a smaller amount of $NsNH_2$. To indicate the possible effect of low levels of $NsNH_2$ and PhI on the formation of aziridine, experiments were conducted in which 2 mol% of these compounds were added at the start of the reaction for the homogeneously catalysed reaction (Fig. 7). Addition of $NsNH_2$ exaggerates the shape of the reaction profile, while addition of PhI at this low level does not have such a marked effect.

In a final set of experiments, the homogeneously catalysed reaction was carried out at 10 °C and 0 °C to investigate whether the effect could be more readily studied at lower temperature. Compared with yields of ≥ 80% in aziridine for the reaction at 25 °C for 3 h, the yields were 65% and 15% at 10 °C and 0 °C, respectively. Reaction at 10 °C proceeded slowly. However, for reactions at 0 °C, only the

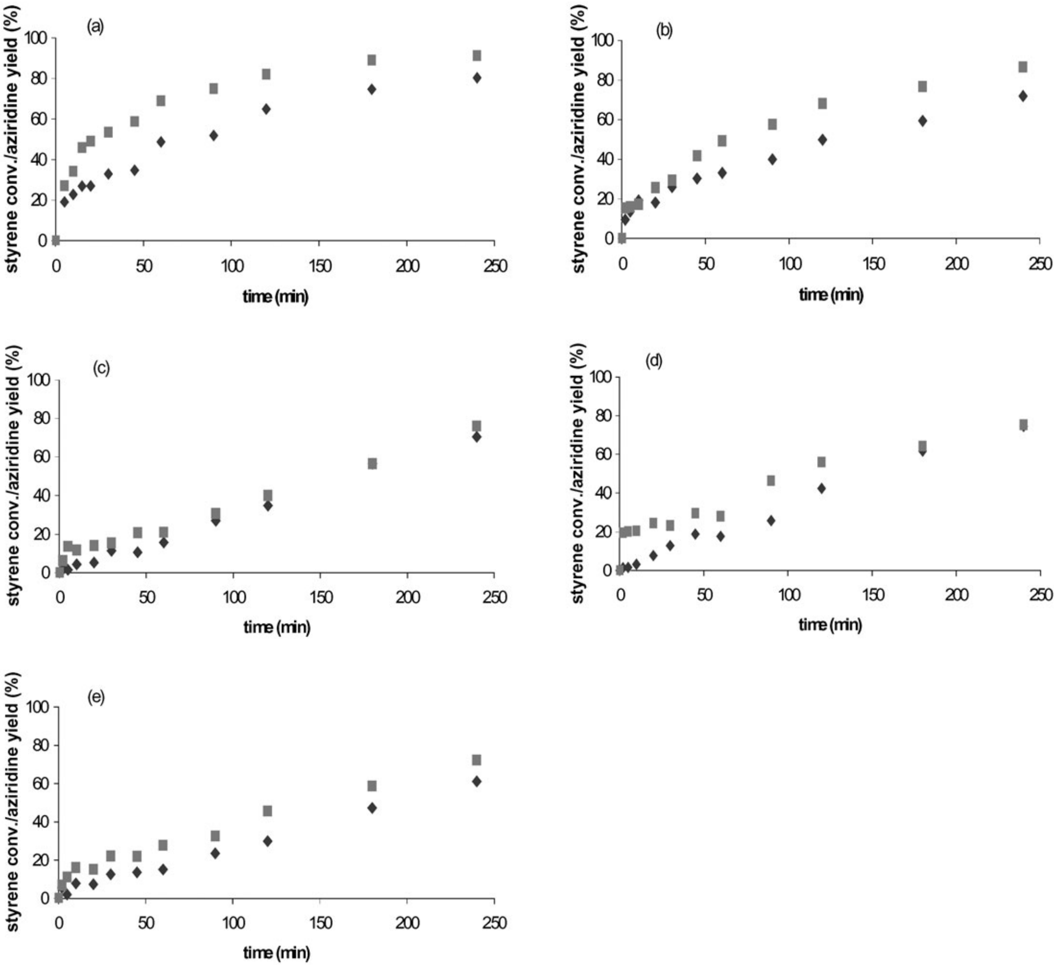


**Fig. 2** Effect of group I cations on the aziridination of styrene using Cu-exchanged zeolite Y, bis(oxazoline) **1**, $CH_3CN$, 25 °C, PhI=NNs : styrene mol ratio = 13. (◆) Aziridine yield; (■) styrene conversion. (a) Cu-LiY; (b) Cu-NaY; (c) Cu-KY; (d) Cu-RbY; (e) Cu-CsY.

initial rapid formation of aziridine was observed and no subsequent aziridine formation was noted during the 3 h reaction (Fig. 8). This indicates that there may be a two-stage process. First, there is a rapid, initial reaction leading to the formation of aziridine and by-products. The product and by-products subsequently interact with the copper-active centre and modify the course of the reaction. During this second period, the ee is enhanced[6,10] due to the complex interactions occurring at the active centre. This is a central feature for both homogeneous and heterogeneous catalysis reactions.

## Comments on the origin of the reaction profile

The shape of the conversion *versus* time curves indicates a two-stage process for the consumption of alkene: (i) an initial phase, the extent of which appears to be determined roughly by the initial ratio of catalyst to alkene and which is complete after about one hour under the conditions used here; and (ii) a second phase, which starts slowly but then accelerates before slowing down as the reaction reaches completion, resulting in the characteristic reaction profiles observed for both heterogeneous and homogeneous catalysts.

The mechanism of aziridination catalysed by copper cations is known to be a very complex process, but it has yet to be fully elucidated. Previous studies[13,14] have suggested the possible co-existence of two mechanisms, involving singlet and triplet nitrene intermediates. Clearly these two processes could lie at the heart of the observed reaction profile, particularly as it is still apparent in the homogeneously catalysed process. However, it is clear that many factors affect the rate of the aziridination reaction and the extent of enantioselectivity. In particular, the presence of by-products together with aziridine can influence the process as shown in the present study when the reaction profile is shown to be very sensitive to the introduction of the sulfonamide by-product.

Given this complexity, we wish to consider the nature of the reaction pathway that would lead to the generation of a reaction profile in which an initial rapid reaction is followed by a period of relatively slow reaction, before once again observing a relative reaction profile. This type of behaviour is not immediately apparent for the operation of two pathways involving different nitrene intermediate, but is more likely to result from competitive interaction at the active centre of the many competing reaction components. Leaving aside the complicating role exerted by the sulfonamide by-product and of the iodobenzene produced in the reaction, a possible interpretation of the initial phase is that it arises from a simple competitive formation of enantiomeric aziridines by reaction of the alkene with the bis(oxazoline) complexed copper(II)-nitrene, the product aziridines then acting as competitive inhibitors of the catalytic copper centres. The rate of conversion of alkene then approaches zero when all the copper is complexed with aziridine. At this stage a second route, slow up to this point begins to become apparent and its form suggests the occurrence of a co-operative effect, which could be autocatalysis. Our interpretation is speculative at this time since our attempts to simulate the kinetics are not yet complete, but we can make some preliminary remarks.

Our recent observation of the enhancement of enantioselectivity with conversion in the aziridination of styrene using copper bis(oxazoline) complexes was interpreted in terms of interconversion of (*R*) and (*S*) aziridines by reaction with the

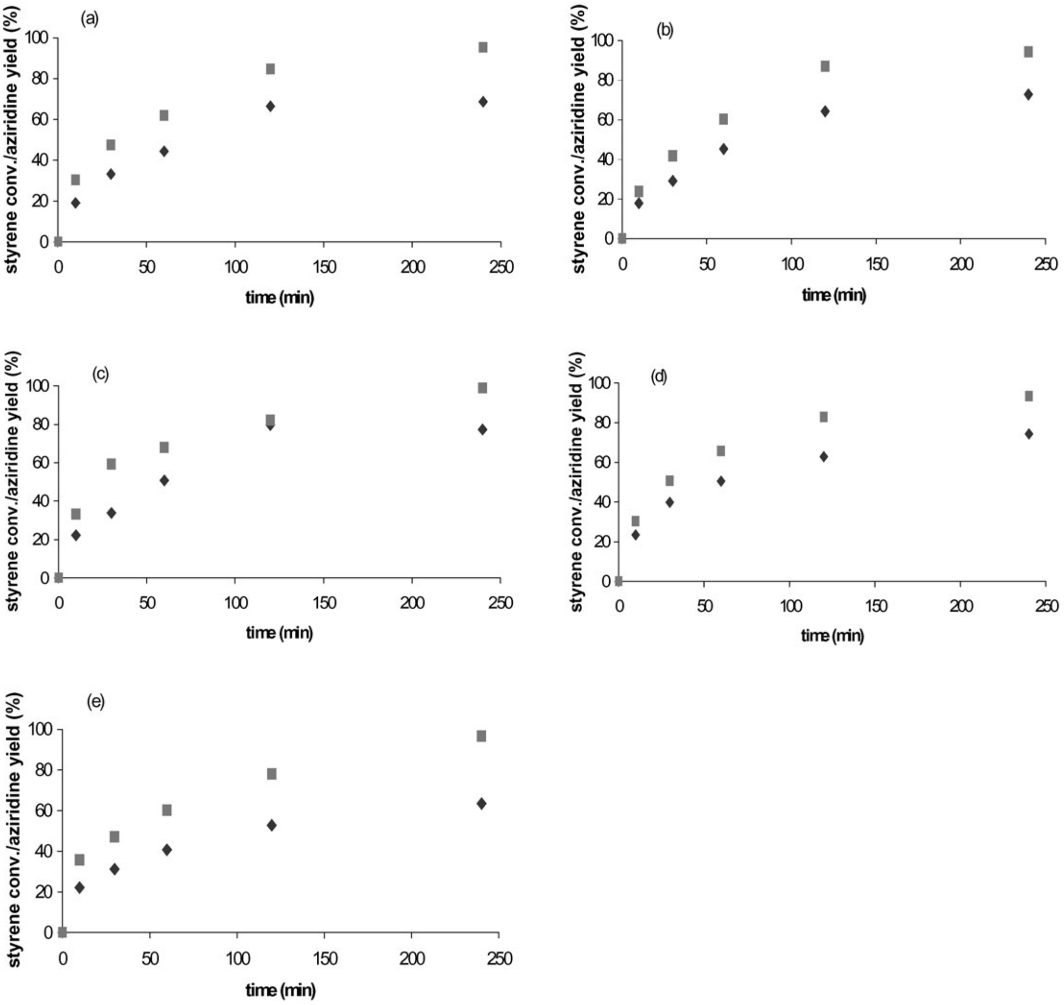


**Fig. 3** Effect of group I cations on the aziridination of styrene using Cu-exchanged zeolite Y, bis(oxazoline) **1**, $CH_3CN$, 25 °C, PhI=NNs : styrene mol ratio = 1.5. (◆) Aziridine yield; (■) styrene conversion. (a) Cu-LiY; (b) Cu-NaY; (c) Cu-KY; (d) Cu-RbY; (e) Cu-CsY.

copper nitrene species perhaps by way of an intermediate ring-opened diamine.

Scheme 1 [in which *S* represents the *S*-enantiomer of the bis(oxazoline) used] incorporates this process. Attempts to simulate the scheme, led us to a two phase conversion *versus* time curve, but did not reproduce the plateau that is observed after an hour, as well as the sigmoidal shape thereafter. We ascribe this to the absence in Scheme 1 of an autocatalytic process. We are currently carrying out further studies in this area to attempt to eludicate the mechanism further.

## Conclusions

In the heterogeneously catalysed aziridination of styrene with PhI=NNs using $Cu^{2+}$-exchanged zeolites modified by bis(oxazoline), the counter-cation can be an important component of the system at low PhI=NNs : styrene molar ratios. Replacement of $H^+$ by $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$ does not have a marked effect in the reaction but at low nitrene donor to styrene molar ratios replacement of $H^+$ by group I metal cations can lead to a slight enhancement in ee with a loss of yield due to increased formation of $NsNH_2$ as a nitrogen-containing by-product. The formation of aziridine with reaction time demonstrates a complex profile which, although more pronounced in the heterogeneously catalysed reaction, particularly when large group I cations are present, is still observed in the homogeneously catalysed reaction using $Cu(OTf)_2$ as catalyst. This effect is considered to be caused in part by the interaction of the product, aziridine, and the by-products, $NsNH_2$ and PhI, with the active copper site during the course of the reaction. In our preceding communication,[10] we showed that this significantly affected the ee. Other contributing factors may arise from product inhibition of the catalytic centres as the reaction proceeds. The nature of the active site is, therefore, more complex than a bis(oxazoline)-modified copper cation interacting with the PhI=NNs nitrene donor, since the products and by-products also play a role in generating the enantioselective active site.

## Experimental

### Methods

$^1H$ NMR spectra were obtained using a Bruker Avance 400 MHz DPX spectrometer, equipped with Silicon Graphics workstation. The chemical shifts of $^1H$ NMR spectra are recorded in $CDCl_3$ and $d_6$-DMSO. Spectra were recorded on the d scale and signals quoted in the form: chemical shift in ppm (number. of protons, multiplicity, assignment).

$^{27}Al$ magic-angle spinning (MAS) NMR spectra were recorded at 9.4 T using a Chemagnetics CMX Infinity 400 spectrometer with zirconia rotors 4 mm in diameter spun at 6 KHz. The spectra were measured at a frequency of 104.3 MHz with a 1.0 s pulse delay. All spectra were referenced to an external kaolin $[Al(H_2O)_6{}^{3+}]$ standard.

Powder X-ray diffraction patterns were obtained using an Enraf Nonius FR 590 instrument with a monochromatic CuKα radiation. The X-ray generator was set at 1.2 kW (30 mA

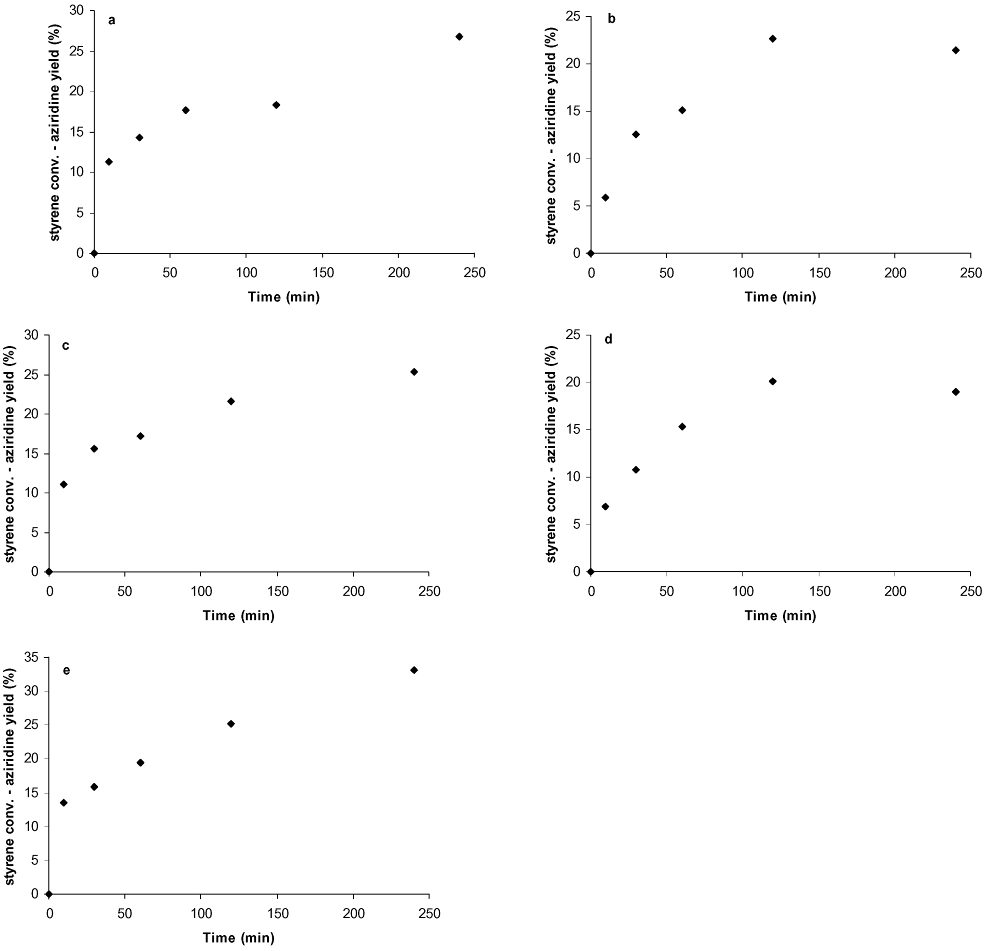


**Fig. 4** Plots of styrene conversion and aziridine yield to demonstrate the nature of the reaction profile. (a) Cu-LiY; (b) Cu-NaY; (c) Cu-KY; (d) Cu-RbY; (e) Cu-CsY.

and 40 Kv). Each sample was measured from $2\theta = 4.4$ to 124.6 for 30 min. The diffraction pattern was collected using a semi spherical position sensitive detector (Inel PSD120). The ionisation gas in the detector was a mixture of 15% ethane in argon. To permit the phase identification of the unknown samples, the pattern collected was corrected against a standard Si pattern, followed by background subtraction and removal of $K_{\alpha 2}$ peaks to provide the d-spacings. Phase identification was carried out by comparison with data from the IZA website (http://www.iza-structure.org/).

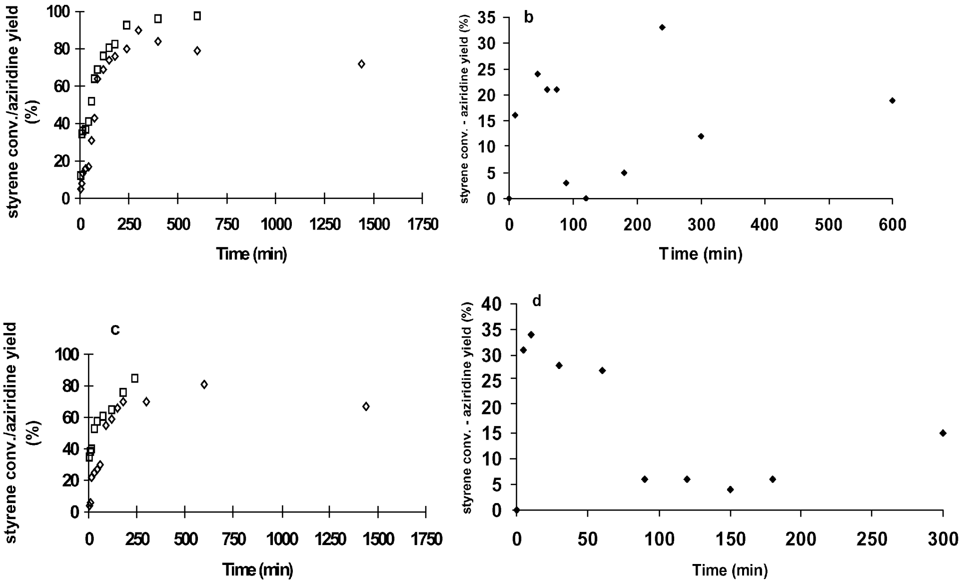


**Fig. 5** Effect of reaction time on the formation of aziridine and conversion of styrene, in the presence of excess by-products, under heterogeneous catalysis. Reaction conditions: Cu-exchanged zeolite HY, bis(oxazoline) **1**, $CH_3CN$, 25 °C. (a) 1 : 1.1 styrene : PhI=NNs; (b) plot of (a) as styrene conversion – aziridine yield; (c) 1 : 1.3 styrene : PhI=NNs. (d) plot of (c) as styrene conversion – aziridine yield. (◇) Aziridine yield, (□) styrene conversion.

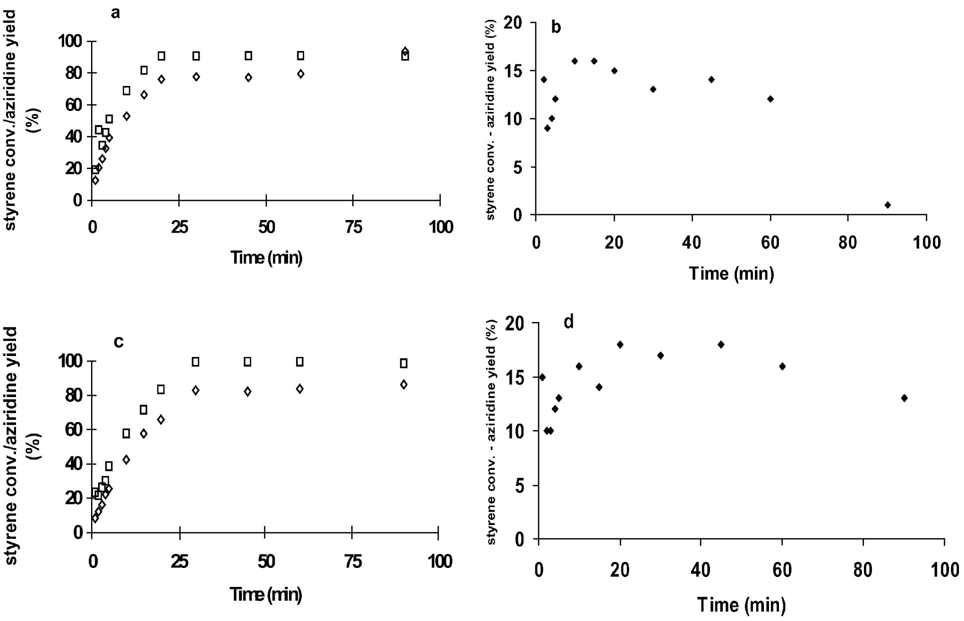


**Fig. 6** Effect of reaction time on the formation of aziridine and conversion of styrene in the presence of excess by-products, under homogeneous catalysis. Reaction conditions: $Cu(OTf)_2$, bis(oxazoline) **1**, $CH_3CN$, 25 °C. (a) 1 : 1.1 styrene : PhI=NNs; (b) styrene conversion – aziridine yield plot from (a); (c) 1 : 1.3 styrene : PhI=NNs ratio; (d) styrene conversion – aziridine yield plot from (c). (◇) Aziridine yield, (□) styrene conversion.

Thermal gravimetric analysis was carried out using a Perkin Elmer TG7 instrument. Each sample (2–3 mg) was placed in the platinum sample pan and heated from 40 °C to 900 °C at 25 °C $min^{-1}$ under a flow of $N_2$ (20 ml $min^{-1}$).

Flash column chromatography was performed on Merck Kieselgel 60 (230–400 mesh) and analytical TLC on silica gel 60 F-254 plates.

Atomic absorption spectroscopy was performed on a Perkin-Elmer 373 Atomic Absorption spectrometer using an air-acetylene flame.

HPLC analysis was recorded using a Dynamax SD200 pump equipped with Dynamax Al-3 autosampler, Dynamax injector and UV absorbance detector. An Apex ODS 5μ column was used for analytical work. The eluent system was acetonitrile–water

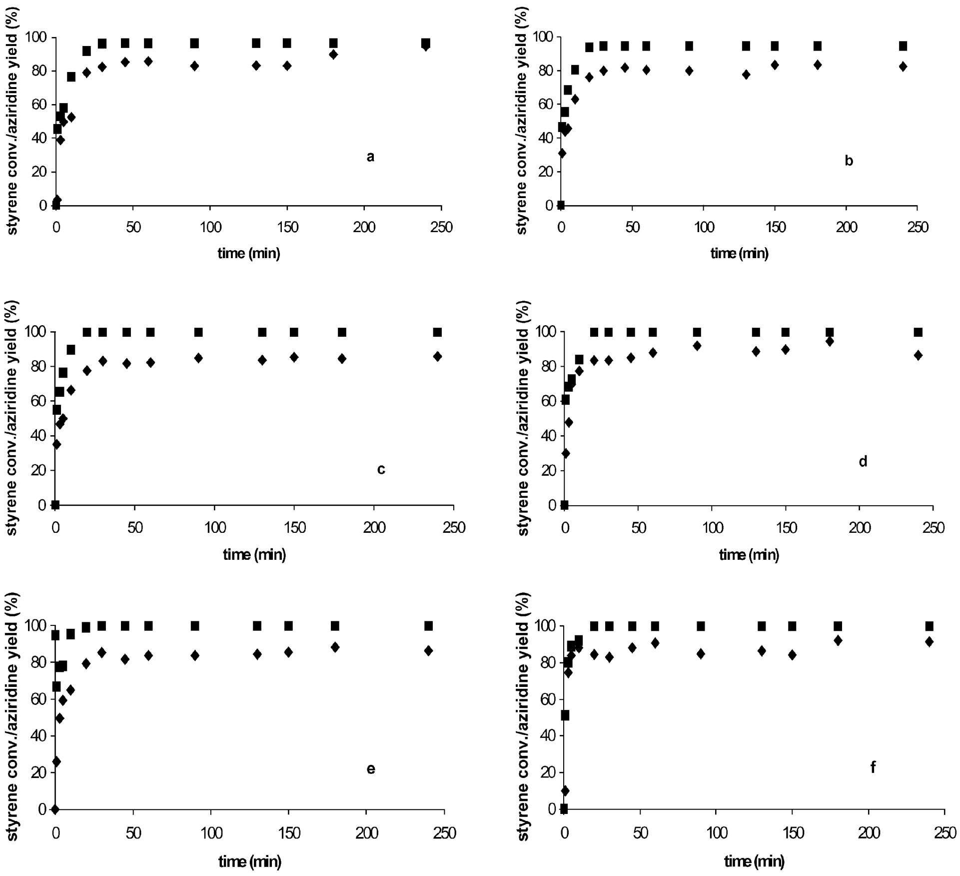


**Fig. 7** Effect of reaction time on the formation of aziridine and the conversion of styrene with $Cu(OTf)_2$ as catalyst, bis(oxazoline) **1**, $CH_3CN$, 25 °C, and in the presence of 2 mol % $NsNH_2$ (a, d), 2 mol % PhI (b, e) and 2 mol % $NsNH_2$ + PhI (c, f). PhI=NNs : styrene molar ratio is 1.1 for (a, b, c) and 1.3 for (d, e, f) . (◆) Aziridine yield; (■) styrene conversion.

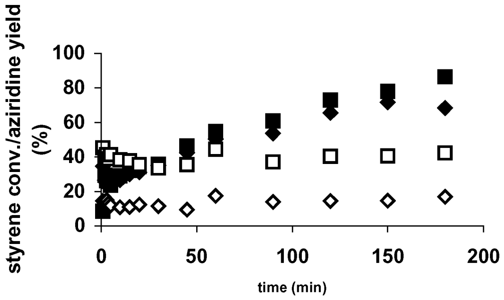


**Fig. 8** Effect of temperature on aziridination of styrene using $Cu(OTf)_2$ as catalyst, bis(oxazoline), $CH_3CN$, PhI=NNs : styrene mol ratio = 1.1. (◆) Aziridine yield at 10 °C; (■) styrene conversion at 10 °C; (◇) aziridine yield at 0 °C; (□) styrene conversion at 0 °C.

85 : 15. Baseline separation was achieved for all reagents and products. For chiral HPLC analysis, a 25 cm Chiralcel OJ column was used. The eluent system was hexane–propan-2-ol 82 : 18. Baseline separation was achieved for both enantiomers. Absolute configuration was confirmed by optical polarimetry and comparison with the literature.[6]

## Materials

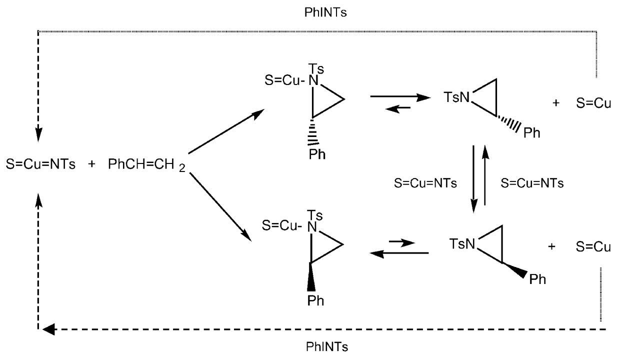
Styrene (99 + %) and the bis(oxazolines) (98%) were obtained from Aldrich and Fluka respectively. Acetonitrile (>99% purity) was obtained from Fisher scientific. Ultrastabilised $NH_4^+$ Y zeolite (Union Carbide, LZY84, 5.0 g) was calcined at 550 °C for 5 h, then stirred in 0.5 mol solution of copper(II) acetate solution (100 ml) for 24 h at room temperature. The mixture was then centrifuged and washed with distilled water. This was repeated a twice. The Cu-HY zeolite was then dried at 100 °C for 24 h, then recalcined (550 °C) for 5 h. Cu content 3.7% by weight. $Cu^{2+}$-exchanged zeolites containing group I cations were prepared in a similar manner. Zeolite HY (4.0 g) was refluxed with group I metal nitrate (0.1 mol $l^{-1}$, 100 ml) for 24 h and then recovered by hot filtration, washed with water and the process repeated twice, each time using a fresh solution of the metal nitrate. After the third treatment, the metal-exchanged zeolite was dried before exchange with $Cu^{2+}$. The metal-exchanged zeolite was stirred with copper sulfate (0.1 mol $l^{-1}$, 100 ml) at 25 °C for 24 h. The zeolite was recovered by filtration, dried and calcined as described above.

## Preparation of PhI=NNs

Iodobenzene diacetate (3.22 g; 1.0 mmol) was added to a stirred mixture of potassium hydroxide (1.4 g; 0.025 mmol) and *p*-nitrobenzenesulfonamide (2.02 g; 1.0 mmol) in HPLC grade methanol (40 ml), keeping the temperature at 0 °C during the addition. The solution was stirred at room temperature and over a 4 h period a cream precipitate formed. The precipitate was then filtered, washed with distilled water and dried at room temperature in a vacuum desiccator (3.23 g, 80.6%). $\delta_H$ (d6-DMSO, 400 MHz) 8.2 (doublet, 2H), 7.95 (multiplet, 4H), 7.56 (multiplet, 1H), 7.4 (multiplet, 2H). Anal. calcd. C 35.69, H 2.27, N 6.93%; found C 35.56, H 2.29, N 6.62%.

## Homogeneous aziridination reactions catalysed by $Cu(OTf)_2$

Styrene (0.101 g, 1.0 mmol), nitrene donor (1.5 mmol), and copper(II) triflate (0.15 mmol) were stirred in acetonitrile (2.5 ml) at 25 °C. If a chiral bis(oxazoline) (0.07 mmol, Aldrich, 98%) was added, it was done together with the copper(II) triflate in dry acetonitrile prior to the addition of styrene and nitrene donor. Reaction times varied depending on the different nitrene precursors. The reaction was stirred in air at 25 °C until complete dissolution of the nitrene donor. The reaction mixture was then filtered through a plug of silica with ethyl acetate (50 ml) as eluent. Flash chromatography gave the aziridine as a white solid. Experiments were carried out in triplicate and reproducible results were obtained; the experimental error associated with the styrene conversion and aziridine yield are ≤ ±1%.



**Scheme 1**

## Heterogeneous aziridine reaction catalysed by Cu-exchanged zeolite Y

Styrene (0.101 g, 1.0 mmol), nitrene donor (1.5 mmol), Cu-HY (0.3 g) were stirred together in dry acetonitrile (2.5 ml) at 25 °C. If a chiral bis(oxazoline) (0.07 mmol, Aldrich, 98%) was added, it was stirred with Cu-HY in acetonitrile prior to the addition of styrene and nitrene donor. Reaction times varied depending on the nitrene donor. The reaction mixture was stirred in air at 25 °C until complete dissolution of the nitrene donor. The reaction mixture was then filtered through a plug of silica with ethyl acetate (50 ml) as eluent. Flash chromatography gave the aziridine as a white solid. Experiments were carried out in triplicate and reproducible results were obtained; the experimental error associated with the styrene conversion and aziridine yield are ≤ ±1%.

## Determination of leached $Cu^{2+}$ for the heterogeneously catalysed reaction

Following the reaction described above, the mixture was filtered through a celite plug to remove the zeolite catalyst. The filtrate was then analysed for its $Cu^{2+}$ content using atomic absorption spectroscopy.

## Kinetic simulation

Simulations were carried out using the program "Kinetics" (Chemistry Courseware Consortium, University of Liverpool).

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