Catalytic heterogeneous aziridination of styrene using CuHY catalyst: an assessment of catalyst stability

Sophia Taylor,[a] **John Gullick,**[a] **Paul McMorn,**[a] **Donald Bethell,**[b] **Philip C. Bulman Page,**[c] **Frederick E. Hancock,**[d] **Frank King**[d] **and Graham J. Hutchings** *[a]

[a] *Department of Chemistry, Cardiff University, PO Box 912, Cardiff, UK CF10 3TB.*
  E-mail: hutch@cardiff.ac.uk
[b] *Leverhulme Centre for Innovative Catalysis, Department of Chemistry,*
  University of Liverpool, UK L69 3BX
[c] *Department of Chemistry, Loughborough University, Loughborough, Leicestershire,*
  UK LE11 3TU
[d] *Synetix, PO Box 1, Billingham, Teesside, UK TS23 1LB*

The stability of the heterogeneous CuHY catalyst for the aziridination of styrene using nitrene donors, with and without the presence of chiral bis(oxazoline) modifiers, is described in detail. Cu^{2+} is found to leach from the CuHY and the rate of Cu-leaching is dependent on the reaction time, the nature of the nitrene donor, the structure of the bis(oxazoline), the presence of solvent and the breakdown products of the nitrene donor. It is found that between 0.08–6.8% by weight of the Cu present in CuHY can be leached during standard reaction conditions. However, using short reaction times it is shown that the amount of Cu removed can be limited readily to the lower value. Detailed studies show that for this reaction system the leached Cu^{2+} plays no significant role in the formation of the aziridine, and that the high enantioselectivities observed with CuHY are due to Cu^{2+} which is electrostatically bound within the pores of the zeolite and modified by a chiral bis(oxazoline) ligand.

Introduction

The synthesis of pure enantiomers is of current importance for the pharmaceutical and agrochemical industries. In particular, considerable attention[1,2] has been given to the design of heterogeneous catalysts that can be used in these complex syntheses. Often this is achieved by immobilisation of homogeneous catalysts and a number of methods have predominated. The first involves the use of a thin layer of solvent, dispersed over a high surface area support that contains and retains the homogeneous catalyst.[3] The second approach involves encapsulation of large complexes within the pore structure of a material using a *ship-in-a-bottle* technique, which was pioneered by Jacobs *et al.*[4,5] The third approach involves the tethering of the homogeneous catalyst to a support, *e.g.* Thomas *et al.*[6–8] have shown that titanium metallocenes grafted onto MCM-41 can act as a heterogeneous oxidation catalyst. In contrast to these methods, we have developed the use of zeolites and mesoporous aluminosilicates modified with chiral molecules and we have demonstrated that these can be used as effective heterogeneous asymmetric catalysts for three reactions: (a) the dehydration of butan-2-ol,[9,10] (b) the aziridination of alkenes[11,12] and (c) the epoxidation of alkenes.[13–15] In this method the cations, which act as the catalyst, are ion-exchanged into the material and are retained within the porous structure by electrostatic forces. The addition of chiral molecules such as dithiane l-oxide,[9,10] bis(oxazolines)[11,12] or salen[13,15] ligands leads to the formation of a chiral active site. When these catalysts are used for asymmetric synthesis in non-aqueous solvents we have shown that the catalysts are particularly stable. However, it is possible that the catalyst can degrade through leaching of the cations into the reaction mixture. The amount of leaching will be dependent on the nature of the solvent, chiral modifier, reaction conditions and the hydrophobicity of the zeolite. This effect has recently been highlighted by Sheldon *et al.*[16] who proposed that

three possibilities need to be considered when using metal-containing zeolite and mesoporous catalysts: (a) metal can be leached into solution but the leached cations are inactive as a homogeneous catalyst, (b) metal can be leached into solution and the leached cations can act as a homogeneous catalyst, and (c) the catalyst is stable and no leaching occurs. At the present time, most researchers consider that metal-containing zeolites are not stable under typical reaction conditions. For example, we have recently shown that Ti can be leached from the titanium silicalite TS-1 during the epoxidation of allylic alcohols due to the interaction of a triol by-product with framework Ti that degrades the structure.[17,18] It is recognised that low levels of leaching can be tolerated in a reaction since the low levels of impurities formed can readily be removed from the product in the subsequent work-up and purification stages. However, it is important that the catalyst stability is determined, so that the potential role of any homogeneously catalysed component of the reaction, due to the leached cations, can be recognised. In this paper, we report a detailed study of the stability of copper-exchanged zeolite Y which we have previously shown[11,12] to be an effective heterogeneous asymmetric aziridination catalyst.

Results and discussion

Catalytic activity of reaction filtrate

We have previously shown that copper-exchanged zeolite Y (CuHY) modified by chiral bis(oxazolines)† can act as a heterogeneous asymmetric catalyst for the aziridination of styrene using either [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane† (PhI=

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† The IUPAC name for 1,3-oxazoline is 4,5-dihydro-1,3-oxazole and for iodinane is λ^3-iodane.

Table 1 Catalytic activity of filtrate from CuHY catalysed aziridination of styrene[a]

Initial reaction period/h	Additional aziridine yield (%)	
	PhI=NTs	PhI=NNs
2	0	0
10	7	16
24	17	41

[a] Standard reaction carried out initially for 2, 10 or 24 h; bis(oxazoline) **1** (0.07 mmol), CH$_3$CN (2.5 cm^3), 25 °C, nitrene donor : styrene = 1.5 : 1 mol ratio. Following reaction, the CuHY catalyst was removed by filtration and fresh styrene and nitrene donor were added and allowed to react for a further 24 h.

NTs)[11,12] or [N-(p-nitrophenylsulfonyl)imino]phenyliodinane (PhI=NNs).[19] In the initial study[11,12] we showed that the catalyst could be reused several times and that the filtrate of the reaction mixture, i.e. after the CuHY zeolite had been removed by filtration, was inactive for further reaction when fresh reagents were added. In these initial studies an excess of the styrene was used, as this was considered necessary to achieve high yields. In the subsequent study[19] we have found that the yield and enantioselection can be significantly improved by using a slight excess of the nitrene donor relative to styrene. To extend these earlier studies, two sets of experiments were carried out using either PhI=NTs or PhI=NNs as nitrene donor. For each set, styrene was reacted with the nitrene donor (mol ratio nitrene donor : styrene = 1.5 : 1) in acetonitrile at 25 °C for 2, 10 or 24 h using CuHY catalyst modified with chiral bis(oxazoline) **1**.

After the reaction time, the reaction mixture was filtered through Celite to remove the CuHY catalyst. Styrene and nitrene donor (nitrene donor : styrene = 1.5 : 1 mol ratio) were then added to the filtrate and the reaction mixtures were stirred at 25 °C for an additional period of 24 h, without the addition of further bis(oxazoline). The results are shown in Table 1. The filtrate obtained from the aziridination reaction after 2 h was inactive for the formation of further aziridine with either PhI=NTs or PhI=NNs. These results confirm our earlier study that the filtrate is inactive.[11,12] However, the filtrates obtained after 10 and 24 h reaction both gave additional aziridine formation, and this is indicative that Cu^{2+} may have leached from the CuHY catalyst during these longer reaction times. The additional aziridine formation was more marked for PhI=NNs.

Determination of Cu-leaching from CuHY

The aziridination of styrene using both PhI=NTs and PhI=NNs as nitrene donors was investigated using CuHY modified by two chiral bis(oxazolines) **1** and **2** to determine the concentrations of Cu leached. The reactions were followed by the dissolution of the nitrene donor and, following complete dissolution, the reaction mixture was filtered to remove the CuHY catalyst and the copper concentration of the filtrate was measured. The results are shown in Table 2 for a range of reaction conditions. All the reaction mixtures were found to contain Cu^{2+} that had leached from CuHY; levels in the reaction mixture from 3–34 ppm (0.08–0.94% of total Cu in CuHY) were observed when PhI=NTs was used, and from 36–244 ppm (1.0–6.8% of total Cu in CuHY) when PhI=NNs was used. In general, higher levels of Cu-leaching were observed when using
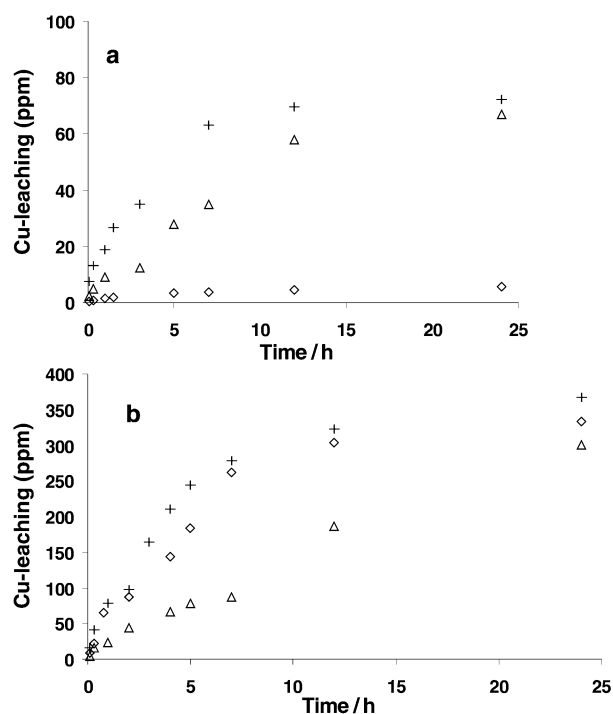

Fig. 1 Cu-leaching profiles from CuHY catalyst during the aziridination of styrene (CH$_3$CN, 25 °C, nitrene donor : styrene = 1.5 : 1 mol ratio). (a) PhI=NTs, (b) PhI=NNs. Key: ◇ no chiral modifier, + chiral modifier **1**, △ chiral modifier **2**.
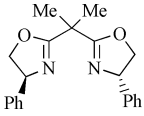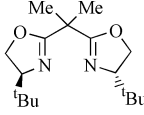
PhI=NNs. Cu-leaching increased with increasing concentration of the nitrene donor and reaction time. However, these two parameters are linked since the reaction time is determined by the rate of dissolution of the nitrene donor and this necessarily increases as the nitrene donor : styrene ratio is increased.

Effect of chiral modifier on Cu-leaching

The aziridination of styrene was carried out using either PhI=NTs or PhI=NNs both with and without the addition of the chiral bis(oxazoline) modifier under our standard conditions, and the reactions were stopped after a specified time. The reaction mixture was filtered to remove CuHY and the copper concentration remaining in the reaction mixture was determined. The results (Fig. 1) show that, for all reaction conditions, the leaching of copper is a function of the reaction time. With PhI=NTs as nitrene donor the leaching of copper in the absence of the chiral modifiers was negligible and only 0.16% of the copper present in CuHY was leached into solution. However, addition of the chiral modifier significantly enhanced the Cu-leaching, and higher rates of Cu-leaching were observed with modifier **1** compared to **2**. With PhI=NNs, Cu-leaching was observed for all conditions, and much higher levels of Cu-leaching were observed than with PhI=NTs. Interestingly, the rate of Cu-leaching was significantly decreased when the chiral modifier **2** was used. However, when PhI=NNs was used, the yield of aziridine and the enantioselection observed with bis(oxazoline) **2** are very similar to those observed with bis(oxazoline) **1** (Table 2) and this is indicative that the leached Cu^{2+} is not playing a significant role in the heterogeneously catalysed reactions. The decreased leaching with **2** may be due to a steric effect which decreases the effective interaction with Cu^{2+} electrostatically bound within the zeolite, compared with **1**.

To extend these studies, a series of experiments were carried out in which CuHY was stirred in acetonitrile at 25 °C for 24 h in the presence of additional reaction components. Following reaction, the mixture was filtered to remove the CuHY catalyst and the concentration of copper in the filtrate was determined. The results are shown in Table 3. It is apparent that the solvent and the substrate do not significantly contribute to the

Table 2 Determination of Cu leaching during the aziridination of styrene[a]

Bis(oxazoline)	Nitrene : styrene[b]	PhI=NTs				PhI=NNs			
		Time[c]/h	[Cu][d] (ppm)	Yield[e] (%)	Ee[e] (%)	Time[c]/h	[Cu][d] (ppm)	Yield[e] (%)	Ee[e] (%)
Me Me / O N N O / Ph Ph	1 : 5	0.75	8	86	29	1	60	83	78
	1 : 1	1.5	12	55	76	2.5	61	53	36
	1.5 : 1	3	34	78	76	5	244	78	85
Me Me / O N N O / tBu tBu	1 : 5	1.5	3	90	17	2	43	76	35
	1 : 1	2	7	89	13	3	36	94	61
	1.5 : 1	3	12	58	24	7	88	68	82

[a] CH$_3$CN, 25 °C, CuHY (0.3 g). [b] Molar ratio. [c] Time for total dissolution of the nitrene donor. [d] ppm Cu in final solution, if all Cu leached 3600 ppm Cu would be in solution. [e] Yield and ee of aziridine.

Table 3 Cu-leaching as a function of reaction conditions[a]

	[Cu] (ppm[b])	
Reactants	No chiral modifier	Chiral modifier 1
CH$_3$CN	0	7
CH$_3$CN–styrene	2	7
CH$_3$CN–PhI=NTs	2	52
CH$_3$CN–PhI=NTs–styrene	6	72
CH$_3$CN–PhI=NNs	208	246
CH$_3$CN–PhI=NNs–styrene	334	369
CH$_3$CN–TsNH$_2$[c]	6	9
CH$_3$CN–TsNH$_2$[c]–styrene	12	16
CH$_3$CN–NsNH$_2$[c]	62	32
CH$_3$CN–NsNH$_2$–styrene[c]	24	22
CH$_3$CN–NTs aziridine[d]	2	8
CH$_3$CN–NNs aziridine[d]	1	1

[a] Each compound was added to CuHY (0.3 g), 25 °C, 24 h. [b] ppm Cu in final solution following removal of CuHY by filtration; if all Cu leached 3600 ppm Cu would be in solution. [c] Sulfonamide. [d] Aziridine formed from PhI=NTs or PhI=NNs as nitrene donor.

Cu-leaching. In general, higher Cu-leaching is observed when the bis(oxazoline) is present. The highest leaching levels are observed when all components are present.

Model studies using Cu(OTf)$_2$

In previous studies using Cu(OTf)$_2$ as a homogeneous catalyst,[19] solutions containing 3600 ppm Cu^{2+} have been used, and these have been directly compared with the reaction data of the heterogeneous catalyst CuHY containing an equivalent amount of Cu^{2+}. However, the Cu-leaching data indicate that between 3–244 ppm Cu^{2+} leaches from CuHY under standard reaction conditions for the complete consumption of the nitrene donor. In view of this, the formation of aziridine over a 24 h reaction period, using either PhI=NTs or PhI=NNs, together with bis(oxazolines) **1** and **2**, was studied for Cu(OTf)$_2$ concentrations of 1–250 ppm. These are compared with the data for the standard homogeneously and heterogeneously catalysed reactions under comparable conditions and the results are shown in Fig. 2. In addition, experiments in which no catalyst was added to the reaction mixture are also included, and it is apparent that 3–4% aziridine formation is observed over the 24 h period. With the bis(oxazoline) **1**, the aziridine formation with 1 ppm Cu(OTf)$_2$ is marginally above the blank reaction, and with 250 ppm the aziridine yield is *ca.* 20% over a normal reaction period as used with the heterogeneous catalyst (*ca.* 3 h). With the bis(oxazoline) **2**, higher levels of aziridine formation are observed, particularly when PhI=NTs is used as the nitrene donor. The yield of aziridine at 3 h reaction time for the Cu(OTf)$_2$-catalysed reactions is shown in Fig. 3, and this confirms that the reaction rate is a function of both the nitrene

donor and the chiral modifier. The ee observed in the experiments using Cu(OTf)$_2$ as catalyst were the same as those observed previously for the homogeneously catalysed reaction (3600 ppm Cu) under the same reaction conditions.

Comments on the contribution of the leached Cu to the overall catalysed reaction

It is apparent that during the heterogeneously catalysed synthesis of the aziridine with CuHY, Cu is leached from the zeolite into solution and consequently this could act as a homogeneous catalyst. It is, therefore, important to consider what proportion of the overall reaction can be ascribed to a homogeneously catalysed process rather than a heterogeneously catalysed reaction. However, the filtrate from the reaction of styrene with PhI=NNs with bis(oxazoline) **1** is inactive for the subsequent synthesis of aziridine when fresh reagents are added (Table 1). The data in Fig. 1 show that this solution contains *ca.* 100 ppm Cu^{2+}, which according to the data presented in Figs. 2, 3 should be active for the formation of aziridine. In our previous studies[19] with the homogeneously catalysed reaction using Cu(OTf)$_2$ we have shown that PhI, the breakdown product from PhI=NNs and PhI=NTs, significantly decreases the rate of aziridine formation. The effect on the Cu(OTf)$_2$ catalyst by PhI is far more marked than on the heterogeneous catalyst CuHY. This is probably due to diffusion effects of PhI in the pores of the zeolite limiting the poisoning effect, and suggests that Cu leached into solution during reactions, when in the presence of PhI and traces of TsNH$_2$, will have very limited reactivity. Indeed, the model studies with 1–250 ppm Cu(OTf)$_2$ represent an upper limit to the potential contribution of a homogeneously catalysed reaction to the heterogeneous process. This is because Cu-leaching is time-dependent (Fig. 1) and the highest levels of Cu leaching are only observed at the end of the reaction. At short reaction times, the amount of Cu leached is low for all conditions, and consequently the contribution of the homogeneous reaction to the heterogeneously CuHY catalysed reaction is considered to be negligible. However, it is apparent that the reaction conditions for the heterogeneously catalysed reaction should be selected so that the reaction is completed within a few hours, since then (a) Cu-leaching is minimised, and (b) the leached Cu is known to be inactive for this short reaction period.

Two further pieces of experimental evidence demonstrate that the leached Cu^{2+} from CuHY has negligible activity in the catalysed reactions. First, in our earlier study[11,12] we showed that *trans*-stilbene was unreactive for the formation of the corresponding aziridine with CuHY as catalyst, but high yields were obtained with the homogeneous catalyst Cu(OTf)$_2$. However, in this experiment the combination of solvent and PhI=NTs would have leached Cu into solution, yet no reaction was observed. Molecular simulations indicated that the react-
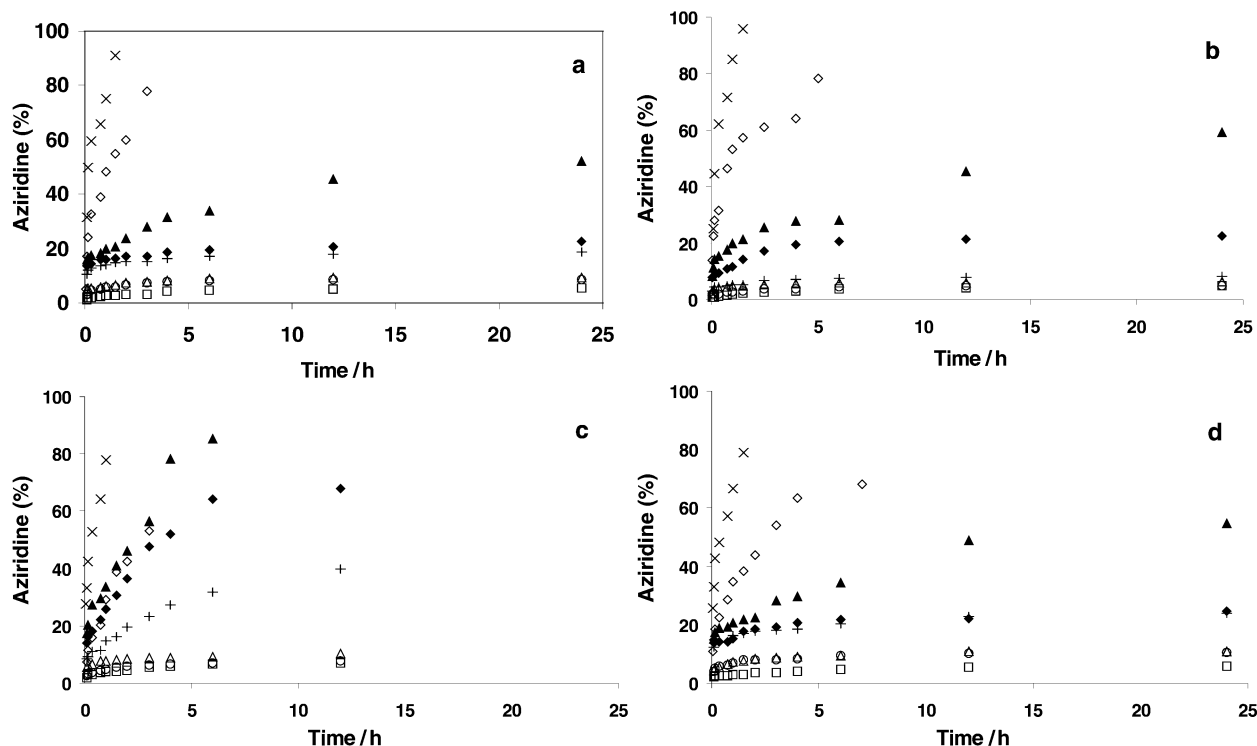
Fig. 2 Effect of [Cu(OTf)₂] on the aziridination of styrene (CH₃CN, 25 °C, nitrene donor : styrene = 1.5 : 1 mol ratio); (a) PhI=NTs with chiral modifier **1**, (b) PhI=NNs with chiral modifier **1**, (c) PhI=NTs with chiral modifier **2**, (d) PhI=NNs with chiral modifier **2**. Key ppm Cu: □ 0, ○ 1, △ 5, + 10, ◆ 50, ▲ 250, ◇ standard homogeneous catalysed reaction with Cu(OTf)₂ (3600 ppm Cu), × standard heterogeneous reaction with CuHY (3600 ppm Cu).

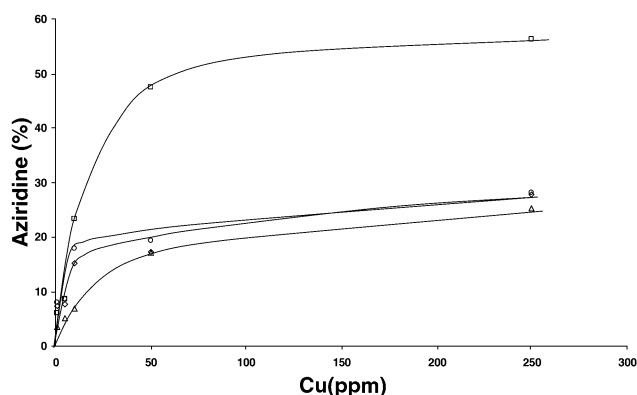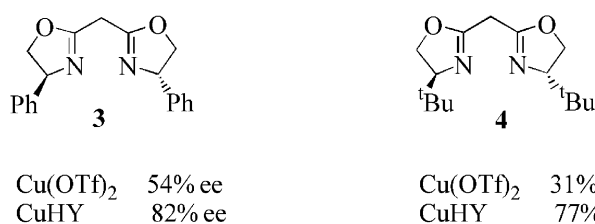**Fig. 3** Yield of aziridine at 3 h reaction time as a function of [Cu]. Reaction conditions as Fig. 2. Key: ◇ PhI=NTs with chiral modifier **1**, △ PhI=NNs with chiral modifier **1**, □ PhI=NTs with chiral modifier **2**, ○ PhI=NNs with chiral modifier **2**.

Cu(OTf)₂ 54% ee	Cu(OTf)₂ 31% ee
CuHY 82% ee	CuHY 77% ee

These results indicate that care must be taken with the interpretation of model leaching studies, since based on the studies with 1–250 ppm Cu(OTf)₂ in solution, high reactivities could be expected for the Cu leached from CuHY. However, due to the enhanced poisoning effect of PhI on Cu²⁺ in solution, relative to the immobilised Cu²⁺ in the zeolitic pores,[19] together with the slow time-dependent Cu-leaching observed, we conclude that the leached Cu does not play a significant role in the formation of the aziridine. In addition, the low levels of Cu leached from CuHY can readily be removed from the solution during the subsequent purification stages. However, the leaching of Cu will eventually limit the re-use of the CuHY catalyst and reaction conditions need to be selected to minimise Cu leaching.

Experimental

Apparatus

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

(b) Solution copper concentrations were determined using atomic absorption spectroscopy which was performed with a Perkin-Elmer 373 Atomic Absorption spectrometer.

(c) HPLC analysis was recorded using a Dynamax S D 200 pump equipped with Dynamax Al-3 autosampler, Dynamax injector and UV absorbance detector. An Apex ODs 5 μ column was used for analytical work. The eluent system was

ants and products could all freely diffuse though the pore structure of CuHY, but the transition state for the formation of the aziridine could not be accommodated. Hence, no heterogeneously catalysed reaction could be expected, and none was observed. The lack of any aziridine formation confirms that the homogeneously catalysed process related to leached Cu is negligible for these reaction conditions. Secondly, we have shown that CuHY modified by chiral ligand **2** can give 82% ee in the aziridination of styrene with PhI=NNs as the nitrene donor (Table 2). However, in our preceding study[19] we observed that under the same conditions Cu(OTf)₂, with an equivalent [Cu], gave an ee of only 43%. If the homogeneously catalysed reaction were significant when CuHY was used, then it could be expected that a lower ee would have been observed, since the reaction time for this experiment was 7 h. The higher ee for CuHY with bis(oxazoline) **2** with PhI=NNs as nitrene donor was also observed with two other bis(oxazolines) **3** and **4**.

The enhanced ee is considered to be due to enhanced steric constraints within the pore structure of the zeolite.

acetonitrile–water (85 : 15). Baseline separation was achieved for all reagents and products. For chiral HPLC analysis a 25 cm Chiracel OJ column was used. The eluent system was hexane–propan-2-ol (82 : 18). Baseline separation was achieved for both enantiomers.

Materials

Styrene, the bis(oxazolines) and copper(II) triflate were obtained from Aldrich. Ultrastabilised NH_4^+Y zeolite was obtained from Union Carbide and converted to CuHY as described previously.[19] The nitrene donors PhI=NTs and PhI=NNs were prepared as described previously.[19]

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

Styrene (0.101 g, 1.0 mmol), nitrene donor (1.5 mmol) and copper(II) triflate (trifluoromethanesulfonate) (1.4×10^{-8}–1.5×10^{-4} mol) were stirred in dry acetonitrile (2.5 cm³) at 25 °C. If a chiral bis(oxazoline) (0.07 mmol) was added, this was added together with the copper(II) triflate in dry acetonitrile prior to the addition of the styrene and nitrene donor. Reaction time varied according to 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 cm³) as eluent. Flash chromatography gave the aziridine as a white solid. For each point in Figs. 2 and 3 a separate experiment was carried out.

Heterogeneous aziridination reaction catalysed by CuHY

Styrene (0.101 g, 1.0 mmol), nitrene donor (1.5 mmol) and CuHY (0.3 g) were stirred together in dry acetonitrile (2.5 cm³) at 25 °C. If a chiral bis(oxazoline) (0.07 mmol) was added, this was stirred with the CuHY in the dry acetonitrile prior to the addition of the 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 cm³) as eluent and [Cu] was determined using atomic absorption spectroscopy. Flash chromatography gave the aziridine as a white solid. For each point in Figs. 1–3 a separate experiment was carried out.

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