Heterogeneous catalytic aziridination of styrene using transition-metal-exchanged zeolite Y

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Transition-metal-exchanged zeolite Y (Cr, Mn, Fe, Co, Ni, Cu, Zn) are compared as catalysts for the aziridination of styrene using (*N*-(*p*-tolylsulfonyl)imino)phenyliodinane (PhI=NTs) as the nitrene precursor. The Cu-exchanged zeolite shows high levels of aziridine formation, but significant yields of aziridine are also obtained with the Cr-, Mn-, Fe- and Co-exchanged zeolite Y. In contrast, these cations produce much lower yields of aziridine in the corresponding homogeneously catalysed reactions. Addition of a chiral bis-oxazoline ligand leads to a significant decrease in the yield of aziridine for all the ion-exchanged zeolites, with the exception of the Cu-exchanged zeolite Y. Further experiments with (*N*-(*p*-nitrophenylsulfonyl)imino)phenyliodinane (PhI=NNs) as nitrene donor indicate that, in addition to Cu-exchanged zeolite Y, significant yields of the aziridine can be formed for Zn-, Mn-, Fe- and Co-exchanged zeolite Y. The major by-product was benzaldehyde, probably formed by oxidation of styrene. These data confirm that Cu-exchanged zeolite Y is the best aziridination catalyst but it is shown that other metal-exchanged zeolites are also catalytically active.

KEY WORDS: aziridination; alkenes; asymmetric catalysis; bis(oxazoline)-modified zeolite Y

1. Introduction

The catalytic transfer of atoms to alkenes remains a class of reactions of immense interest and a number of homogeneous and heterogeneously catalysed reactions have been investigated to date. In particular, the epoxidation and cyclopropanation of alkenes has been extensively studied using homogeneous catalysts [1,2]. In contrast, the analogous reaction of a nitrene donor with an alkene to yield an aziridine has been much less studied. The first metal-catalysed nitrogen atom transfer process observed [3] involved the reaction of benzenesulfonyl azide with cyclohexene and the observed products were considered to be consistent with the involvement of a nitrene intermediate. Subsequently, Mansuy and co-workers [4–6] showed that styrene could react with a nitrene precursor (*N*-(*p*-tolylsulfonyl)imino)phenyliodinane, PhI=NTs [7], to form the aziridine in 80% yield with Mn(III)-derived porphyrin catalysts. In 1994, Evans *et al*. [8] showed that Cu^{2+} cations in solution could act as an efficient catalyst for the aziridination of alkenes using the same nitrene donor. Recently, we have shown that Cu-exchanged zeolite Y can be used as a wholly heterogeneous catalyst for this reaction and that, following modification with a chiral bis(oxazoline) ligand, asymmetric heterogeneous aziridination of alkenes is possible [9,10]. In the earlier study, Evans *et al*. [8] compared a number of transition metal triflates (Cu, Mn, Fe, Co, Ni) and found that Cu^{2+} was by far the best homogeneous catalyst for this reaction. In this paper, in an extension to our earlier initial study [10], we compare the catalytic activity of ion-exchanged zeolite Y (containing Cr, Mn, Fe, Co, Ni, Cu, Zn) in the aziridination of styrene with the soluble acetates as homogeneous catalysts.

2. Experimental

Cation-exchanged zeolites were prepared by ion-exchange of zeolite H-Y (Union Carbide L2Y 84) with the appropriate metal acetate (0.1 mol/l in water) at 70 °C for 24 h. Catalysts with metal loadings of 4 wt% were obtained by this method. Following ion-exchange, the zeolites were washed with deionised water and dried (120 °C, 16 h), calcined in static air (550 °C, 8 h) and stored under desiccation prior to use.

The aziridination of styrene was carried out using the following procedure. Metal-exchanged zeolite (0.3 g) was stirred in acetonitrile (2.5 ml) together with molecular sieve (0.3 g, 5 Å, Aldrich), styrene (0.505 g) and PhI=NTs (0.362 g) (styrene : PhI=NTs mol ratio $= 5:1$) at 25 °C. In experiments where the chiral bis(oxazoline), (S)-(−)-2,2′-isopropylidene-bis(4-phenyl-2-oxazoline) was added, the zeolite was stirred with the bis(oxazoline) (0.024 g) for 15 min prior to the addition of the styrene and the PhI=NTs. Comparable homogeneously catalysed reactions were carried out as follows. The metal acetates (4.13×10^{-5} mol)

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were dissolved in acetonitrile (2.5 ml), reacted with styrene (0.505 g) and PhI=NTs (0.362 g) at 25 °C for 24 h. The reaction products were analysed using HPLC as described previously [10].

3. Results and discussion

The results for the homogeneously and heterogeneously catalysed aziridination of styrene (acetonitrile as solvent, 25 °C, styrene : PhI=NTs = 5 : 1 mol ratio) are shown in figures 1 and 2. For the heterogeneously catalysed aziridination, the metal-exchanged zeolite Y catalysts were compared with the non-exchanged zeolite H-Y and the fully-exchanged zeolite Na-Y as blank reactions. It is apparent that the non-exchanged zeolite Y led to some formation of the aziridine and, indeed, higher yields of the aziridine were obtained with zeolite H-Y than with Na-Y, Ni-H-Y and Zn-H-Y. The copper-exchanged zeolite, as expected, gave a very high yield of the aziridine. However, the Cr-, Mn-, Fe- and Co-exchanged zeolites all show yields of the aziridine in excess of that expected for the blank reaction with the non-exchanged zeolite. In solution, Cr^{3+} and Mn^{2+} do not exhibit any catalytic activity in this reaction. In addition, Co^{2+} and Fe^{2+} in solution are less effective for the formation of the aziridine than with the ion-exchanged zeolites containing the same concentration of the metal cation. Analysis of the reaction mixture following the reaction of the metal-exchanged zeolites showed that only minimal levels of the cation (*ca.* <10 ppm, compared with a maximum concentration of 3600 ppm if all the metal had leached) had leached into solution. These concentrations of metal cations in the solution are too low to increase the azirdine yield significantly over that of the overall blank reaction in the absence of any catalyst (figure 2). These results show that immobilisation of the cation within the zeolite pore structure enhances the reactivity of the cation. Hence, this represents a further example of a reaction for which the immobilised catalyst gives a superior catalyst performance to the equivalent non-immobilised homogeneous catalyst. Recently, Raynor *et al.* [11] showed a similar effect for an enantioselective amination reaction, and we have shown that immobilised chiral Co-salen complexes give higher enantioselection for the epoxidation of *cis*-stilbene than does the homogeneous catalyst process [12].

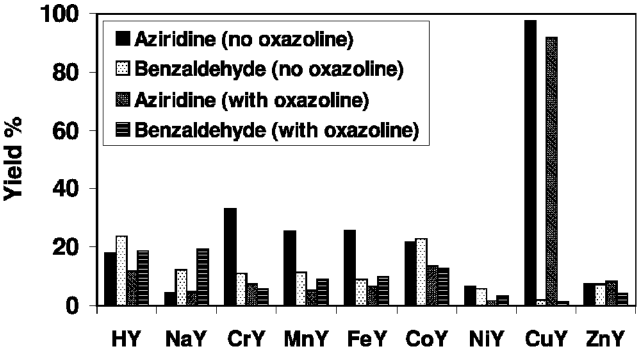

Figure 1. Aziridination of styrene using metal-exchanged zeolites at 25 °C for 30 h with and without the presence of a chiral oxazoline.

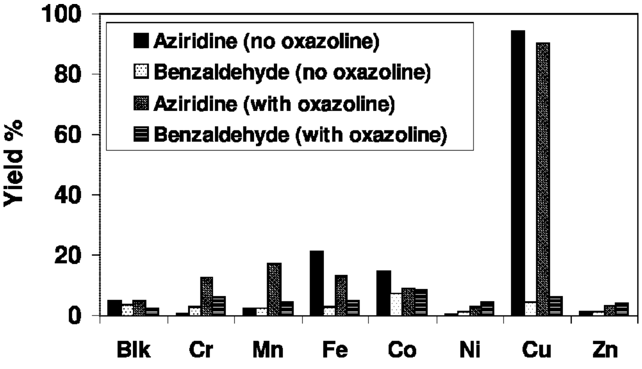

Figure 2. Homogeneous aziridination of styrene using metal acetates at 25 °C for 24 h with and without the presence of a chiral oxazoline; Blk indicates no metal acetate added to the reaction mixture.

Addition of the chiral bis(oxazoline) ligand, (S)-(−)-2,2′-isopropylidene-bis(4-phenyl-2-oxazoline), to the metal-exchanged zeolite resulted in a marked decrease in the yield of the aziridine, although the PhI=NTs conversion remained 100%. This is possibly due either to pore diffusion effects for the zeolite catalyst or to the oxazoline ligand being more tightly bound at the metal cation so that the nitrene donor cannot compete effectively due to steric hindrance. In contrast, for the homogeneously catalysed reactions, a small increase in the yield of the aziridine is observed for the manganese and chromium acetate catalysts in the presence of the bis(oxazoline). When the bis(oxazoline) was present, the enantioselectivities for the heterogeneously and homogeneously Cu^{2+}-catalysed reactions were in excess of 80% ee. However, for the other reactions, insufficient product could be isolated to permit analysis of the enantioselectivity.

For all the homogeneously and heterogeneously catalysed reactions studied, with the exception of the Cu^{2+}-catalysed reactions, significant levels of benzaldehyde, relative to the yield of aziridine, were formed as a by-product. There are several possibilities for the route by which benzaldehyde is formed, either directly from styrene [13–18] or from styrene oxide [19]. It is barely feasible that benzaldehyde could be formed from the aziridine. Indeed, in a standard experiment, where styrene was replaced by the corresponding aziridine, no benzaldehyde was formed. Hence, this pathway is not considered to be possible in the experiments described in this study. The formation of benzaldehyde *via* styrene oxide is also considered unlikely as styrene oxide has been shown to be stable under the present oxidative conditions. It, therefore, seems most likely that benzaldehyde is formed from styrene directly.

Benzaldehyde can be formed from styrene *via* oxidative cleavage of the C–C double bond. Formaldehyde, which would also be a product, was not observed. Oxidative cleavage has been reported to occur directly with styrene and molecular oxygen in acetonitrile in the presence of Cu^{2+} [18], although these experiments were carried out

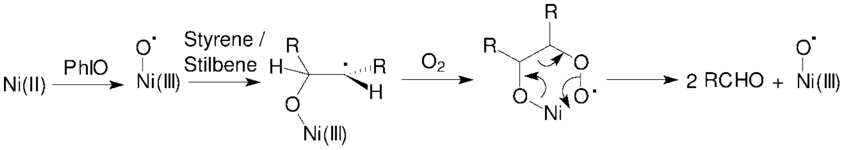

Figure 3. Formation of benzaldehyde from styrene using PhIO as oxidant.

Table 1
Metal-exchanged zeolite Y as catalyst for the aziridination of styrene.[a]

Cation-exchanged zeolite HY	PhI=NTs			PhI=NNs		
	Time[b] (h)	Aziridine yield (%)	Benzaldehyde yield (%)	Time[b] (h)	Aziridine yield (%)	Benzaldehyde yield (%)
None[c]	66	6	10	332	34	25
Zn^{2+}	66	3	10	332	56	6
Ni^{2+}	66	17	18	332	7	6
Fe^{3+}	66	12	24	332	45	25
Mn^{2+}	5	10	26	332	3	14
Co^{2+}	6	15	36	332	45	32
Cu^{2+}	3	86	12	5	93	5

[a] CH_3CN, 25 °C, nitrene donor : styrene = 1.5 : 1 mol ratio.
[b] Reaction time, followed by dissolution of the nitrene donor.
[c] No catalyst added.

Table 2
Reaction of styrene with iodosylbenzene.[a]

Experiment	Reaction mixture	Styrene conversion (%)	Benzaldehyde selectivity[b] (%)
1	CuHY/PhIO/bis(oxazoline)	28.6	100
2	CuHY/PhIO	16.8	100
3	CuHY/bis(oxazoline)	10.2	100
4	PhIO/bis(oxazoline)	11.3	100

[a] Reaction conditions: CH_2CN 2.5 ml, CuHY 0.3 g, bis(oxazoline) 0.029 g, styrene 0.101 g, iodosylbenzene 0.3024 g.
[b] Product analysed by HPLC.

under reflux in an oxygen-rich atmosphere. Hatjiapoglou *et al.* [13] reported the reaction between phenyliodonium bis(arylsulphonyl) methylides and alkenes in acetonitrile (analogous to the aziridination reaction where the NTs group in PhI=NTs is replaced with $C(Ts)_2$). Styrene and stilbenes were found to form benzaldehyde as well as the corresponding cyclopropanes. The oxidant was proposed to be iodosylbenzene, which was formed by the reaction of phenyliodonium bis(arylsulphonyl) methylide with residual water, a process which could also occur in the aziridination reaction mixture. Residual water within the reaction solvent can hydrolyse PhI=NTs to form iodosylbenzene and *p*-toluene sulphonamide, and it is the iodosylbenzene which acts as the oxidant to form benzaldehyde. Studies have been carried out into the oxidation of styrene and stilbenes with iodosylbenzene catalysed by transition metal ions [14–17] in acetonitrile, and all of these studies report the formation of benzaldehyde at yields of 10–30% alongside the corresponding epoxides. Kinneary *et al.* [16], using a homogeneous Ni catalyst, found that the amount of benzaldehyde formed increased when molecular oxygen was bubbled through the reaction mixture, but oxygen transfer to form the epoxide was exclusively from iodosylbenzene, as shown by ^{18}O labelling. No oxidation was observed if oxygen was bubbled through the reaction mixture when iodosylbenzene was absent. It was suggested that iodosylbenzene and styrene interacted with the nickel catalyst to form a benzylic intermediate which reacted with oxygen, and following an intramolecular rearrangement, produced benzaldehyde, as shown in figure 3. The requirement of oxygen for benzaldehyde formation was confirmed in Co^{2+}-containing reaction mixtures by Ozaki *et al.* [17]. Hence, in the aziridination reactions described in this paper, once iodosylbenzene is formed, the conversion of styrene to benzaldehyde is considered to proceed *via* a mechanism analogous to that shown in figure 3. To support this, we reacted styrene with iodosylbenzene (PhIO) with CuHY as catalyst modified by the bis(oxazoline) using standard reaction conditions in the presence of air. The results, shown in table 2, confirm that benzaldehyde is readily formed, particularly when the bis(oxazoline) is present (experiment 1). In particular, the results show that, even when CuHY is absent, benzaldehyde is still formed in a non-catalysed reaction (experiment 4). Also, benzaldehyde is formed when no iodosylbenzene is present (experiment 3). This indicates that a Cu–O$^{\bullet}$ oxidising species can be produced by the interaction of CuHY with dioxygen dissolved in the CH_3CN solvent.

In a final set of experiments (table 1) a much lower concentration of styrene was investigated (PhI=NTs : styrene = 1.5 : 1) and for acetate cations, with the exception of Cu^{2+}, very low yields of the aziridine and the benzaldehyde by-product were observed. However, using an alternative nitrene donor (N-(p-nitrophenylsulfonyl)imino)iodinane, PhI=NNs [20], higher yields of the aziridine are observed for the Zn-, Fe- and Co-exchanged zeolites than for the blank reaction in which non-exchanged zeolite H-Y is used (table 1).

In conclusion, the data presented in this paper confirms that, as noted by Evans *et al*. [8] for homogeneous conditions, the Cu^{2+} cation is the most effective catalyst for the aziridination of styrene with PhI=NTs as nitrene donor. However, it is shown that significant yields of the aziridine can be obtained with Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Zn^{2+}, above the levels observed for blank reactions, when these cations are immobilised by ion-exchange within the pores of zeolite Y. This demonstrates that significant differences exist between the homogeneously and heterogeneously catalysed reactions, which may be of mechanistic significance for the design of improved heterogeneous catalysts.

Acknowledgement

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