Zinc-ion exchanged zeolites for the intramolecular hydroamination of 6-aminohex-1-yne

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Zinc-ion exchanged BEA is an excellent catalyst for the intramolecular addition of an amine N–H to the CC triple bond in 6-aminohex-1-yne showing a much higher activity than the corresponding homogeneous catalysts, *e.g.* $Zn(CF_3SO_3)_2$.

The derivatisation of carbon–carbon double and triple bonds by catalytic addition of compounds, such as phosphines,[1] water[2] and amines[3] faces increasing attention as a fast and atom efficient catalytic transformation. Here, direct addition of an amine N–H bond to a carbon–carbon triple bond has been explored using the cyclisation of 6-aminohex-1-yne as specific example. The intramolecular addition first generates 2-methylene-piperidine with an exocyclic double bond which reacts *via* a subsequent 1,3-hydrogen-shift *in situ* to the more stable isomeric imine 2-methyl-1,2-dehydropiperidine. It has been demonstrated using homogeneous catalysts based on late transition metals that the reaction can also be applied to the cyclisation of other similar compounds.[4] Using *e.g.* $Zn(CF_3SO_3)_2$, in refluxing toluene, the cyclisation of 5-aminopent-1-yne, 5-amino-1-phenylpent-1-yne and 2-(phenylethynyl)aniline has been successfully performed.[3] in general, if the formation of two different ring sizes is possible, the smaller ring is formed with high regioselectivity (> 99%) which is consistent with classical, stereoelectronically controlled cyclisation processes.[5] The best homogeneous catalysts for this reaction are early transition metal complexes[1,6–8] or complexes of late transition metals containing Ru(0),[9] Rh(I),[4,10] Ir(I)[11] Cu(I), Pd(II) or Zn(II).[3] Zinc was chosen for the preparation of the heterogeneous catalyst systems as it has only one oxidation state available allowing for a straightforward mechanistic analysis.

Several zinc exchanged zeolites, *i.e.* BEA, MOR, FAU[12] and silica were prepared by repeated ion exchange of the corresponding H-zeolite in an aqueous solution of $Zn(CH_3CO_2)_2$.[13] The material obtained was dried, calcined and the metal loadings were determined by AAS (0.03–1.6 mmol Zn^{2+} per gram zeolite, Table 1). The activities of the zinc ion exchanged materials in the cyclisation of 6-aminohex-1-yne are compiled in Fig. 1.[14]

It is apparent that Zn-BEA (4.4 wt% Zn) exhibits an exceptional activity which is at least ten fold higher compared to the other materials. We speculate that this is related to the small crystal size of the BEA sample (0.1–0.3 μm) and the best fit between the molecules synthesised and the pores. For BEA the pore diameter of the interconnected channels (5.5 × 5.5 Å in the [001] direction and 6.4 × 7.6 Å in the [001] direction}[15] is just big enough to allow the 6-aminohex-1-yne molecules (stretched *ca.* 3.0 × 3.6 × 9.8 Å)[16] to enter the pores and the 2-methyl-1,2-dehydropyridine molecules (*ca.* 4.0 × 5.5 × 7.1 Å) to leave the pore system. In contrast, MOR and FAU have pores with a bigger diameter (6.5 × 7.0 Å and 7.4 × 7.4 Å, respectively). In order to achieve a maximum activity for different substrates the zeolite chosen requires a pore size for which an optimum interaction between the molecules to be synthesised and the pore system is achieved.

Table 1 Zinc loadings of the ion exchanged zeolites prepared as measured by AAS

Catalyst	Wt%	Mmol Zn^{2+}/g
Zn–BEA	0.22–4.41	0.03–0.67
Zn–MOR	4.01	0.61
Zn–FAU	10.6	1.62
$Zn–SiO_2$	4.77	0.73

The $Zn–SiO_2$ displayed higher activity than Zn–MOR or Zn–FAU. This agrees well with reports that zinc silicates are good catalysts for hydroamination reactions.[17] However, the activity of $Zn–SiO_2$ is much lower than that of Zn–BEA. The indicates that with Zn–BEA the reaction occurs inside the pores and that the high activity results either from the pore system (*via* an increased adsorption constant) or the special environment of zinc ions in the pore system. To test the latter hypothesis the zinc salt $Zn(CF_3SO_3)_2$ was tested as the corresponding homogeneous catalyst for its catalytic activity. We observed an activity intermediate between that of $Zn–SiO_2$ and Zn–BEA. This is contrary to expectation as porous catalysts are often assumed to be less active than the corresponding homogeneous catalysts as diffusion within the pores may slow down the overall reaction. In order to confirm that during the calcination process no significant amounts of ZnO were formed it was tested in the cyclisation of 6-aminohex-1-yne. In contrast to the Zn^{2+}-ion exchanged zeolites ZnO did not show catalytic activity.

On basis of the best catalyst Zn–BEA, materials with loadings ranging from 0.03 to 0.58 mmol Zn^{2+} per gram BEA (0.2 to 3.8 wt%) were prepared and tested for their catalytic activity in comparison to the parent H–BEA and Na–BEA (Fig. 2). The latter two materials show low, but not negligible activity. The activity of the material increases with the zinc loading up to 0.21 mmol Zn^{2+} per gram zeolite (1.4%). This loading corresponds to 91% ion exchange degree, where in average two acid sites of the parent H–BEA zeolite (acid site density 0.46 mmol H^+ per gram zeolite) are exchanged by one Zn^{2+} cation. Adsorption of NH_3 showed that for each zinc two

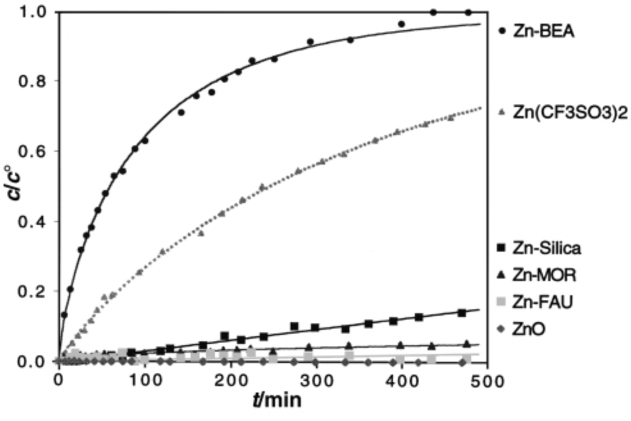

Fig. 1 Heterogeneous zinc catalysts for the cyclisation of 6-aminohex-1-yne in comparison to the homogeneous salt $Zn(CF_3SO_3)_2$.

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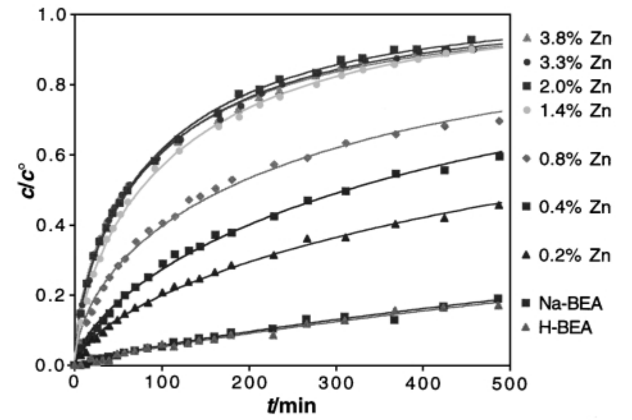

Fig. 2 The cyclisation of 6-aminohex-1-yne with Zn–BEA catalysts loaded with different amounts of Zn^{2+} cations.

NH_3 molecules are adsorbed. This suggests ion exchange of the protons by ZnOH$^+$ rather than Zn^{2+}. In the material with 0.21 mmol Zn^{2+} per gram zeolite 46% of the Brønsted sites are thus concluded to be exchanged with ZnOH$^+$.

A correlation between the activity and the zinc loading is observed as long as there is at least one proton associated with each zinc cation. For higher loadings the number of catalytically active zinc sites increases, however, the number of protons decreases. This suggests that the protons act as co-catalysts. For exchange degrees above 0.21 mmol Zn^{2+} per gram zeolite the additional zinc is balanced by a lower activity of each zinc centre and no further increase in activity is observed. This is in agreement with experiments where the cyclisation of 6-aminohex-1-yne by the homogeneous catalyst [Pd(Triphos)]$(CF_3SO_3)_2$ was accelerated by addition of CF_3SO_3H to the catalytic mixture.[18] The higher activity of Zn–BEA relative to the homogeneous catalyst $Zn(CF_3SO_3)_2$ is thus due to the higher pH in the solid sample compared to the homogeneous catalytic mixture. The complete lack of catalytic activity observed for ZnO is due to the basic nature of this material.

In summary, a series of ion exchanged zeolites was prepared which proved active as catalysts for the cyclisation of 6-aminohex-1-yne of which Zn–BEA was the most favourable. With varying the zinc loading, it was observed that the activity increases with the Zn^{2+} loading until a Zn^{2+}/H^+ ratio of 1 is reached. The higher activity of the Zn–BEA compared to the homogeneous catalysts is attributed to the simultaneous presence of Zn^{2+} and protons in the zeolite.

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12. The SiO_2/Al_2O_3 ratio of the zeolites used was 25 (BEA), 18 (MOR) and 5.1 (FAU).
13. In a typical experiment the corresponding H-zeolite (10 g) was stirred in an aqueous solution of $Zn(CH_3CO_2)_2$ (0.05 mol dm^{-3}) at 80 °C for 12 h. The zeolite was separated by centrifugation (5000 rpm, 20 min). To ensure complete ion exchange the procedure was repeated four times followed by calcination (5 °C min^{-1} to 500 °C, 1 h at 500 °C).
14. In a typical experiment the Zn^{II}-zeolite was activated at 200 °C in vacuum (10 mbar) for 12 h. Dry toluene (15 cm^3) was added, the mixture heated to reflux temperature (111 °C) and the catalytic reaction started by addition of 6-aminohex-1-yne (**1**, 60×10^{-3} cm^3, 0.53 mmol, [**1**]/[Zn^{2+}] = 100). During the reaction samples were taken for GC-analysis. For the experiments given in Fig. 1, 11 mg Zn–BEA, 1.9 mg $Zn(CF_3SO_3)_2$, 6.9 mg Zn–Silica, 9.4 mg Zn–MOR, 3.3 mg Zn–FAU and 8.3 mg ZnO and for the experiments in Fig. 2, 11 mg of the respective Zn–BEA zeolite were used.
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