Synthesis of Diaminodiphenylmethane (DADPM) and its Higher Homologues using Delaminated Zeolites

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Introduction

Diaminodiphenylmethane (DADPM), an intermediate for the production of polyurethanes, is obtained by condensation of aniline and formaldehyde in the presence of HCl [1,2]. This process gives a mixture of diamines and higher molecular weight species (triamines, tetramines, etc.), but also generates a large amount of waste [2]. Considerable efforts have been directed to replacing HCl by a suitable solid acid catalyst, and zeolites have been suggested as suitable alternatives owing to their strong acidity and the possibility to introduce shape selectivity effects [3-5].

Recently, delaminated zeolites have been proposed as suitable catalysts for the synthesis of DADPM [6,7]. These materials are expected to offer advantages for the production of DADPM, owing to the increased accessibility of the acid sites compared to conventional zeolites. In this work the catalytic performance of two delaminated materials, ITQ2 and ITQ18, are compared and contrasted with that of large pore zeolites, such as zeolite Beta.

Materials and Methods

Samples of ITQ2 and ITQ18 were prepared using reported procedures [8,9]. The sample of zeolite Beta (Si/Al = 15) was obtained from PQ Corp. Aminal was prepared by the reaction of aniline with aqueous formaldehyde solution (37%w/w) at 50°C, followed by phase separation of the water. Reaction of the aminal mixture with the different catalysts was carried out in a 50ml round bottom flask at a range of temperatures (90-150°C). The crude reaction product was analysed at intervals by gas chromatography and ^{1}H-NMR analysis (see [6] for full details).

Results and Discussion

Table 1 summarises the results obtained for different catalysts after a 4 hour reaction time at 150°C, 10%w/w catalyst concentration and an aniline to formaldehyde mole ratio = 3.0.

Table 1. Catalyst Performance at 150°C

Catalyst	Si/Al ratio (M)	Surface Area (m^2g^{-1})	Brønsted Acidity ($mmolg^{-1}$ Py)	Secondary amines (%)	N-methyl (%)	4,4' / (2,4'+2,2')
Beta	15	290	50	1.8	4.6	1.6
ITQ2	50	630	7	0.4	0.8	1.9
ITQ18	50	600	6	0.5	0.6	3.5

The delaminated materials show significantly higher levels of activity (lower secondary amines) when compared to zeolite Beta. This is consistent with high degree of accessibility of the active sites achieved through the exfoliation process, which favours molecular diffusion and faster desorption of the reaction products. The mild acidity of the delaminated materials also results in lower levels of impurities such as N-methylated species being formed. Unexpectedly, the choice of delaminated material has a dramatic influence on the levels of *ortho*- substituted products formed, offering additional flexibility for the synthesis of DADPM using these catalysts.

A reaction kinetics study revealed that the quantity and rate of disappearance of the 2-aminobenzylaniline intermediate varied markedly between the two delaminated zeolites – see Figure 1. These results are interpreted in terms of the different external surface topologies of the ITQ2 and ITQ18. Molecular dynamics simulations of adsorbed species have been used to offer insight into these differences.

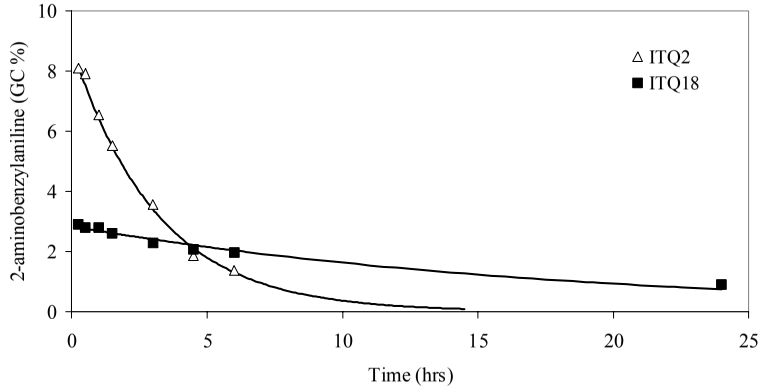

Figure 1. Disappearance of 2-aminobenzylaniline during reaction of aminal (aniline-formaldehyde mole ratio= 3.0) at 110°C using 10%w/w ITQ2 and ITQ18 catalysts.

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