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Replacing HCl by solid acids in industrial processes: synthesis of diamino diphenyl methane (DADPM) for producing polyurethanes†

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Delaminated zeolite catalysts allow replacement of HCl in the production of DADPM: they offer higher activity and catalyst life than conventional zeolites, and their structured external surface controls product selectivity.

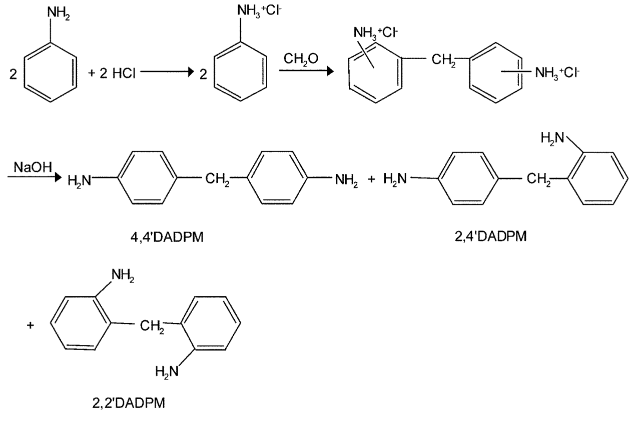
DADPM is a key intermediate for the production of polyurethanes. By the end of the last decade, the annual production in western Europe and USA was more than two million metric tonnes. Surprisingly the industrial production of DADPM is still totally performed by reacting formaldehyde with stoichiometric amounts of hydrochloric acid and aniline. The very large amount of HCl used in this process has to be neutralized with NaOH at the end of the reaction, giving a stoichiometric amount of NaCl. The reaction mixture separates into organic and aqueous phases. The aqueous phase not only contains the NaCl formed in the neutralization step, but also contains traces of aromatic amines that are present as contaminants which are removed before discharging the salt water.[1]

As can be deduced from above, the use of HCl as a catalyst in the synthesis process not only requires additional steps for neutralization and separation but also produces a large amount of residual salt water that needs to be treated before disposal.

The synthesis of DADPM involves the condensation of two molecules of aniline with one molecule of formaldehyde as presented in Scheme 1.

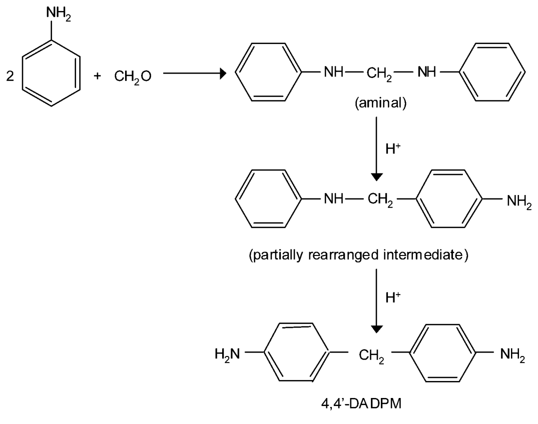
As well as forming diamines, higher molecular weight species (triamines, tetraamines, *etc.*) are also produced. By controlling the aniline : formaldehyde ratio, HCl content and reaction temperature, the final mixture of homologues and isomers can be carefully managed. Higher aniline : formaldehyde ratios and lower temperatures generally favour formation of the 4,4′-DADPM. Furthermore, *N*-methylated products and quinazolines can also be formed which are undesirable as they represent a yield loss from the intended primary amine groups required for conversion to isocyanate.

It is clear that finding a suitable solid catalyst for this reaction would be highly desirable, since not only would that simplify the process, but it would also decrease the amount of residual water. Along this line, the condensation of aniline and formaldehyde has been carried out using ion exchange resins.[2,3] They gave an excellent selectivity to the desired product, but their activity per gram of catalyst was low. Inorganic solid acids such as clays, amorphous silica–alumina and zeolites have been widely used as catalysts for the synthesis of DADPM. Amorphous silica–alumina[4] possesses too low an acidity and therefore requires high reaction temperatures to achieve high yield in primary amines, with the associated penalty of the lower selectivity to 4,4′-DADPM. Very recently it has been shown that a mesoporous amorphous silica–alumina can be a more efficient and selective catalyst for the process.[5] Zeolites have also been proposed as an alternative to amorphous silica–alumina, since the former possess higher acidity, and can introduce shape selectivity effects that may increase the yield of the 4,4′-DADPM (*para*) isomer, with respect to the *ortho* (2,2′-DADPM) and *ortho*–*para* (2,4′-DADPM) isomers. Thus, zeolites such as Y, ZSM-5, Beta, silylated Beta and ERB-1[6–9] have shown a clear improvement for catalyzing the reaction. The work of researchers from EniTecnologie is particularly relevant. They have shown the possibility for producing 4,4′-DADPM with a ratio of 4,4-DADPM/(2,4′+2,2′-DADPM) in the range 2.2 to 5.8 using Beta and silylated Beta zeolite as catalyst, the latter introducing shape selectivity effects due to product diffusion. However, it has to be said that the molar ratio of aniline to formaldehyde used in their work was very high (14.8) and relatively fast deactivation of the catalyst was observed when the process was carried out in a fixed bed reactor. Clays have also been found to be interesting catalysts from the activity–selectivity point of view but, unfortunately, their resistance to water was much lower than that of zeolites, which can tolerate up to 3 wt%.



Scheme 1 Current industrial process for DADPM synthesis.

It appeared to us that even with the most promising zeolite catalyst (Beta), the process could be controlled by diffusion, and consequently only a fraction of the acid sites will be accessible to the aminal (product of the neutral condensation of aniline with formaldehyde, A–F) that is converted into DADPM as shown in Scheme 2. We have checked this hypothesis by working with two Beta zeolites of Si/Al ratio of 15 (M): a Beta zeolite of crystallite size 400–500 nm and a commercial Beta sample (CP811, PQ-Zeolyst) of average crystallite size 100 nm.



Scheme 2 Synthesis of DADPM on solid acids.

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† Electronic supplementary information (ESI) available: detailed analytical procedures by GC and ^{1}H-NMR techniques. See http://www.rsc.org/suppdata/cc/b4/b406303a/

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The neutral A–F condensate was prepared as follows: in a 100 ml three-necked flask 50.00 g of aniline (Aldrich, 99% purity) was added and heated at 50 °C at autogeneous pressure, with stirring. Formaldehyde (Aldrich, 37 wt% aqueous solution, stabilized with 10–15 wt% of methanol) was added with a syringe pump at 1.00 g min^{-1}, until the mixture achieved an A/F ratio of 3.0 (M). After complete condensation the mixture was distilled in a rotavapor until less than 1 wt% of water was left. Methanol was also removed in that step. Optionally, the neutral A–F condensate was dried with a molecular sieve (0.3 nm) until less than 0.05 wt% of water was left. For studying the effect of water, up to 5 wt% of this was added to the condensate. 4.00 g of the A–F mixture was introduced in a 25 ml flask, with a reflux condenser and nitrogen inlet. The mixture was heated to 150 °C and then 1.00 g of the catalyst was added. The reaction was left for 60 min. After reaction, the crude was analysed by gas chromatography (GC) and ^{1}H-NMR analysis. GC was used to determine the free aniline and the distribution of diamines and triamines. ^{1}H-NMR let us quantify the different groups of compounds obtained in the reaction (Fig. 1): primary amines (Ph–CH_2-Ph), secondary amines (Ph–NH–CH_2–Ph), quinazolines (mainly 3-phenyl-3,4-dihydroquinazoline, Ph–CH_2–NR_2), and *N*-methylated derivatives (basically *N*-methyl-DADPM, Ph–NH–CH_3).

The results presented in Table 1 show that the commercial Beta sample (Beta-2) with smaller crystallite size gives higher activity than the larger crystallize size Beta-1, confirming that even with the large pore Beta zeolite (pore diameter 0.67 nm), the process is controlled by diffusion. It is noticeable that despite the small crystallite size of the commercial Beta zeolite the reaction is still controlled by diffusion. Indeed, when a third sample of a Beta zeolite is prepared with a smaller crystallite size than the commercial one (Beta-3, average crystallite size 50 nm), the former gives a higher yield in primary amines (see Table 1). Taking this into account, and in order to design a better catalyst for producing DADPM, one would like to preserve the acidity of the zeolites and their resistance to water, but at the same time to increase acid site accessibility. This could be done conventionally by increasing the pore diameter of the microporous zeolite or, as we saw above, by reducing the crystallite size of the zeolite. To check the first option we have used as a catalyst a 14 membered ring zeolite with pore diameter of 0.66 × 0.88 nm and Si/Al = 50 (M) (SSZ-59). This sample was synthesized following a literature procedure.[10] The results presented in Table 1 show that the activity of this zeolite is lower than that of Beta, probably due to the unidimensionality of the pore system, which becomes rapidly blocked by strongly adsorbed products. Nevertheless, and in order to separate the effect of the higher Si/Al ratio of SSZ-59 from the effect of the unidimensionality on deactivation, we have performed the reaction with a Beta and an ITQ-2 sample both with Si/Al = 50 (M). The results obtained show a yield in primary amines of 87.6 wt% and 98.5 wt% respectively, that are higher than for SSZ-59. It should also be taken into account that the Si/Al ratio for ITQ-18 is already 45 (M) and the activity is much higher than for SSZ-59. Therefore, it appears that the unidimensionality of SSZ-59 has a negative effect on the activity/life of the catalyst, despite of its larger pore diameter.

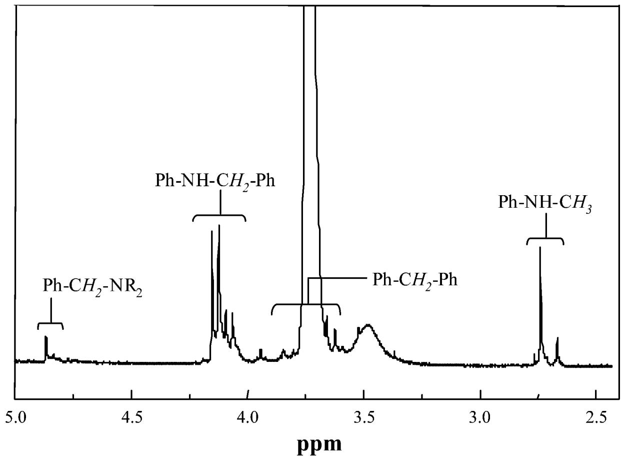

Fig. 1 ^{1}H-NMR characterization of a reaction sample showing the different groups of products determined. Chemical shift is expressed in δ (ppm) relative to the tetramethylsilane used as an internal standard.

The accessibility of acid sites in zeolites could also be drastically enhanced by delamination of a given zeolite, as has been shown previously.[11] For instance, in the case of the laminar precursor of the MWW structure (ERB-1, MCM-22 or SSZ-25),[12] Ferrierite[13] or Nu-6[14] the layered precursors can be expanded and delaminated producing structured single layers with large external surface areas (≥600 $m^2 g^{-1}$) and very little, if any, microporous surface area.[11,15,16] In these materials, named as ITQ-2, ITQ-6 and ITQ-18 respectively, the acid sites should be accessible through the external surface, producing catalysts more active than the corresponding zeolites for reactions controlled by the diffusion in the micropores. We have prepared these delaminated materials[11,15–17] and the characteristics are given in Table 2. When used as catalysts for the synthesis of DADPM, the results presented in Table 1, working in a batch reactor, show that the delaminated materials are more active than the corresponding zeolites, and even more active than the nanocrystalline Beta zeolite. On the other hand, the formation of *N*-

Table 2 Chemical and textural properties of delaminated zeolites

Catalyst	Si/Al[a]/M	Area[b]/$m^2 g^{-1}$	Acidity[c]/μmol Py	
			Brønsted	Lewis
ITQ-2	15	601	68	27
ITQ-6	30	492	15	10
ITQ-18	45	900	14	19

[a] As-made ratio. [b] BET surface area (N_2 adsorption). [c] Calculated from the infrared spectrum of adsorbed pyridine after evacuation at 250 °C.

Table 1 Condensation of aniline with formaldehyde in a batch reactor on tested catalysts at 150 °C after 60 min reaction time[a]

Sample	Amines (%)[b]	Diamines (%)[c]	Triamines (%)[c]	Sec. Amines (%)[b]	*N*-methylation (%)[b]	Quinazolines (%)[b]	Diamine distribution (%)[c]		
							2,2′-DADPM	2,4′-DADPM	4,4′-DADPM
ITQ-2									
< 0.05% H_2O	98.6	81.5	17.1	0.8	0.6	< 0.1	3.3	35.7	42.5
< 1% H_2O	98.4	83.8	14.6	0.3	1.1	0.2	3.8	37.7	42.3
5% H_2O	98.8	84.1	14.7	0.4	0.8	< 0.1	3.5	35.1	45.5
ITQ-6	98.1	79.9	18.2	0.8	0.8	0.3	2.8	30.8	46.3
ITQ-18[d]	99.5	73.4	26.1	< 0.1	0.5	< 0.1	1.1	14.9	57.4
Beta-1	88.9	78.6	10.3	2.1	9.0	< 0.1	4.5	28.8	45.3
Beta-2	93.7	82.3	11.4	0.5	5.8	< 0.1	3.7	30.0	48.6
Beta-3	94.8	74.8	20.0	0.6	4.6	< 0.1	5.2	24.5	45.1
SSZ-59	79.8	78.0	1.8	15.1	3.7	1.4	1.5	12.7	63.8

[a] Results for the rearrangement of the aminal obtained in the neutral condensation of aniline with formaldehyde (A/F = 3.0 (M); < 1% H_2O except where indicated; 20 wt% of catalyst). [b] Determined by ^{1}H-NMR. [c] Determined by GC. [d] T = 160 °C.

methylated and quinazoline products is very low. Furthermore, the yield of trimers plus tetramers is below 30%. It is remarkable that the 4,4′/(2,4′+2,2′) DADPM isomer ratio depends on the external surface structure of the delaminated zeolite, being close to 4 for ITQ-18. Meanwhile, these materials can also tolerate an amount of water in the reaction mixture of, at least, 5% under the reaction conditions studied. In any case, ITQ-2 tolerates better than Beta the presence of water in the feed.

At this point, we can see delaminated materials show higher activities, with selectivities as good as those of the best zeolite catalysts. However, there is another factor such as the catalyst life that can be determinant for this process. In principle, one would expect that the micropores of the zeolites could be blocked by products, and this will lead to a rapid deactivation of the catalyst. To avoid this, researchers working with zeolites have carried out the reaction with very high aniline to formaldehyde ratios which requires the use of larger reactors and the distillation and recycling of large volumes of aniline. In the case of delaminated zeolites, the absence of microporosity could, in principle, decrease the rate of deactivation. Then, in order to study catalyst deactivation, experiments have been performed in a fixed bed continuous flow reactor at 150 °C in the following way: 1.20 g of catalyst pelletized to 0.42–0.59 mm was charged in a stainless-steel reactor (160 mm length, 10.5 mm ID), and the system was pressurized at 4 bar with nitrogen. The neutral condensate (A/F = 3.0 (M); < 1 wt% H_2O) was fed at 3.20 g h^{-1} (W/F = 0.38 h). Reaction was followed with time on stream by GC and ^{1}H-NMR and the results obtained with Beta-2 and ITQ-2 are given in Fig. 2. It can be seen that while the delaminated ITQ-2 material maintains the initial activity after the 8 h duration of the experiment, Beta zeolite has lost more than 50% of the initial activity. The longer catalyst life of ITQ-2 is attributed to the improved molecular diffusion and faster desorption of products inherent to a process that takes place basically in the outer shell of the catalyst. Moreover, the 4,4′/(2,4′+2,2′) DADPM isomer ratio is very similar for both catalysts, whilst the ITQ-2 catalyst produces less undesired *N*-methylated species.

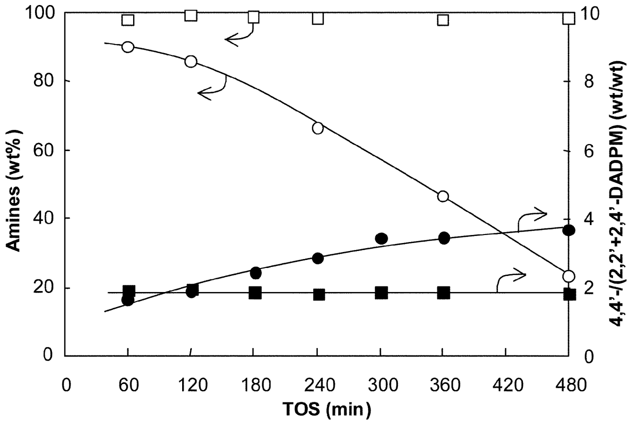

Fig. 2 Production of primary amines and amines distribution *vs.* time on stream (TOS) in the continuous rearrangement of the neutral condensate (A/F = 3.0 M; < 1% H_2O) in a fixed-bed reactor. Symbols: ITQ-2 (□, ■); Beta-2 (○, ●). Experimental conditions: T = 150 °C; P = 4bar; W/F = 0.38 h.

In conclusion, we have shown that it is possible to replace HCl by a solid silico-aluminate catalyst with a zeolite type structure where the acid sites are accessible through the external surface. This is achieved by means of delaminated zeolites. It has been found that depending on the form of the structured external surface the product distribution can be changed, offering an additional flexibility to this type of material for the synthesis of DADPM. Delaminated zeolites show a much lower rate of deactivation than large pore zeolites.

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