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Towards an industrial synthesis of diamino diphenyl methane (DADPM) using novel delaminated materials: a breakthrough step in the production of isocyanates for polyurethanes

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Running title: Novel delaminated materials for synthesis of DADPM

Abstract

Delaminated materials ITQ-2, ITQ-6 and ITQ-18 are very efficient catalysts of zeolitic nature for the synthesis of diamino diphenyl methane (DADPM), the polyamine precursor in the production of MDI for polyurethanes. The exfoliation process results in excellent accessibility of their active sites to reactant molecules as well as fast desorption of products. These catalysts present higher activity and slower rates of deactivation than their corresponding zeolites. Moreover, the topology of the delaminated structure imposes a precise control of the isomer distribution, offering an additional flexibility in the synthesis of DADPM. By optimizing the process conditions it is possible to achieve final DADPM crude under industrial production specifications with ITQ-18. This catalyst represents a real chance for replacing HCl in the industrial production of DADPM.

1. Introduction

Diamino diphenyl methane (DADPM, also named methylendianiline, MDA) is the precursor of MDI (methylenediphenylenediisocyanate), an important monomer for the synthesis of polyurethanes and thermoplastics. Polyurethanes are used in the production of flexible and rigid foam products, coatings, adhesives, sealants, elastomers and binders, which have application in a wide variety of industries like automotive, footwear, refrigeration, construction and furniture [1]. In the USA alone, the 2003 production of polyurethanes and related products was 4.9 million tonnes, with a 2.8% growth increase over 2002 [2].

Commercially, DADPM is obtained by acid catalysed condensation of 2 molecules of aniline with 1 molecule of formaldehyde at 60-80 °C. The reaction mixture is then heated at 100-160 °C to complete the reaction. A sub-stoichiometric quantity of hydrochloric acid is normally used to catalyse the process, which after the condensation has to be neutralized with NaOH giving an equivalent amount of NaCl. The final mixture separates in two layers, organic and aqueous. The former phase is distilled to recover the unreacted aniline and crude DADPM is obtained [3,4]. This usually contains more than 60% of 4,4'-DADPM (the *para*-isomer) and small amounts (3-5%) of the other diamines, 2,4'-DADPM and 2,2'-DADPM (named *ortho*-isomers).. Besides DADPM, higher molecular weight species (basically triamines and tetramines) are also present in the product mixture (20-25%). The product distribution is strongly influenced by the process variables and a high quality 4,4'-DADPM crude is preferentially obtained by working at mild temperatures and a high aniline to formaldehyde (A/F) molar ratio. The recovered DADPM product may then be used to produce MDI by reaction with phosgene or conversion to isocyanate by non-phosgene routes.

The main drawback of the homogenous process is the disposal of the large amount of salt water liberated in the neutralization of HCl, that contains traces of aromatic amines which have to be removed by biological treatment before discharging the residual water.

Substitution of HCl by a suitable solid acid will minimize the generation of polluting water and it could allow the re-use of the catalyst, resulting in a simpler process [3]. Many solid acid catalysts have been evaluated over the past 30 years for the synthesis of DADPM, as recently revisited by De Angelis et al. [4]. Among them, ion-exchange resins have shown excellent selectivity to the *para*-isomer, although their specific activity is low and the final recovery and regeneration of the used catalyst has not been solved [5,6]. Very recently the researchers from Dow Global Technologies Inc. have obtained high yield in the production of 4,4'-DADPM and its polymeric derivatives over an ion exchange resin based in a styrene-divinylbenzene co-polymer but, unfortunately, this system presents the same serious limitations for the re-use of the expended catalyst [7].

Different salts of tungsten have also been tested (borides, silicides and sulfides) [8,9]. They present very mild acidity and their activities are low even at high reaction temperatures (200 ºC). Acidic clays [10-13] and diatomaceous earth [12] have also shown moderate activity for this process, which then requires high reaction temperatures, favouring *ortho*-substitution and the formation of polymeric DADPM. Silica-alumina has been claimed as an active catalyst for DADPM synthesis [14-16], but also with low yields of primary amines. However, recently Perego et al. have proposed the use of several amorphous aluminosilicates characterized by a narrow pore size distribution in the mesopore region [17-19]. These materials show high activity in the conversion of an aniline-formaldehyde condensate (aminal) to DADPM with a very

high ratio 4,4'-DADPM/(2,2'+2,4'-DADPM)(5.99-6.71). Unfortunately, they exhibit a relatively short catalyst life and some partial destruction of the pore structure during thermal regeneration.

Despite the results obtained with other inorganic solid acids, the best performance ever achieved in DADPM production used zeolitic materials. Zeolite Y pre-treated with a fluorinated agent [20], and Beta zeolite [17,21-25] in particular, have shown clear improvements in catalyzing the reaction. There are three main advantages of microporous materials as catalyst for this process: i) high acid site density, thus, improving catalytic activity and catalyst life; ii) a shape selectivity effect due to confined molecular diffusion. (The work of researchers from Eni Tecnologie is particularly relevant, as by modifying the pore aperture and channel diameter of Beta zeolite through a silylation treatment, they were able to increase the ratio 4,4'-DADPM/(2,2'+2,4'-DADPM) in the range 2.2 to 5.8 [4,23]. A similar effect was also observed upon treatment of the zeolite with boric acid (H_3BO_3) or with orthophosphoric acid (H_3PO_4) as free acids or as ammonia salts [24]; iii) a moderate water resistance is claimed for some zeolites, with a maximum tolerance of 3% H_2O in the feed.

The main drawback of zeolites is the strong limitation to molecular diffusion imposed by a structure built of narrow geometrical channels. Even in the case of a tri-dimensional zeolite with twelve-membered-ringtwelve-ring (12 MR12-ring) pores, e.g., Beta, the process is controlled by diffusion, which becomes evident as a reduction of the crystallite size gives a significant enhancement of the primary amines production [26]. Moreover, restrictions to diffusion of reactants and products can be even worse in the case of medium-pore size zeolites (e.g., ZSM-5, ERB-1) [21-22] or unidimensional structures (e.g., SSZ-59) [26].

As has been shown elsewhere, the accessibility of acid sites in zeolitic materials can be drastically enhanced by delamination of a given structure [27-30]. The exfoliation process can produce single layered structures with large external surface areas (≥ 300 m^2 g^{-1}) and very little, if any, microporosity. As a consequence, active sites are highly accessible through the external surface and, at the same time, reactant diffusion and product desorption are faster, as the process takes place basically on the outer shell [31]. This produces catalysts that are more active than their corresponding zeolites for reactions controlled by the diffusion into the micropores. On this basis, several delaminated zeolitic materials have been proposed as suitable catalysts for the synthesis of DADPM [26], with higher performance than large pore zeolites and with a much lower rate of deactivation and superior resistance to water content in the feed (up to 5%). Nevertheless, the amines distribution seems to be strongly affected both by the process conditions and the topology of the delaminated material. In the present contribution we explore the keys for the efficient preparation of DADPM with delaminated materials ITQ-2, ITQ-6 and ITQ-18. After presenting the reaction scheme corresponding to a process catalyzed by solid acids, the catalytic behavior of delaminated materials will be compared with their corresponding zeolite precursors. Furthermore, we provide optimized process conditions to accomplish the manufacture of crude DADPM to industrial production specifications, both in batch and continuous flow reactor systems.

2. Experimental

2.1. Catalysts

ITQ-2, ITQ-6 and ITQ-18 catalysts have been prepared by expansion and subsequent exfoliation of the corresponding laminar precursors, respectively, of the

MWW structure, Ferrierite (FER) and Nu-6 [27-29]. In the case of ITQ-18, two samples of this material were prepared with different levels of delamination. A further sample of ITQ18 was prepared as extrudates (1.6 mm diameter with 20% w/w alumina binder). For the purpose of comparison, the corresponding zeolitic materials MCM-22 [3231], FER [3332] and Nu-6 [3433] were also synthesized.

Al content in all samples was monitored by atomic absorption spectroscopy (Varian spectrAA-10 Plus). Powder X-ray diffraction patterns (not-shown) were collected using a Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA and employing nickel-filtered Cu-Kα radiation (λ=0.1542 nm). Materials crystallite size was estimated from TEM micrographs in a Philips CM-10 microscope operating at 100 kV. Acidity of samples was measured by the standard pyridine adsorption-desorption method [3435]. We are aware that this determination only can offer semi-quantitative data of the total acid sites distribution in some zeolites with narrow pores, like Nu-6 and FER. However, this situation does not happens in the case of delaminated materials, where most of their acid sites are fully accessible to the probe. Surface area of catalysts was calculated by the BET/BJH method with N_2 adsorption/desorption performed at 77 K in a Micromeritics ASAP 2000 instrument. The most relevant physicochemical properties of these catalysts are summarized in Table 1.

2.2. Reaction procedure

Synthesis of the aminal: to prepare the neutral A/F condensate 50.00 g of aniline (Aldrich, 99+% purity) were heated at 50°C at autogeneous pressure in a 100 ml two-necked flask with stirring. Formaldehyde (Aldrich, 37 wt% aqueous solution) was added with a syringe pump at 1.00 g min^{-1}, until the mixture achieved an A/F molar

ratio 3.0 (M). After complete condensation the mixture was distilled in a rotavapor until less than 2 wt% of water was left (Karl-Fisher test).

Batch testing: 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 reaction temperature in a silicon bath and then the appropriate amount of catalyst (typically 1.00 g) was added. After 60-120 min the reaction was stopped by cooling the mixture in an ice bath. Then the crude product was analysed by gas chromatography (GC) and ^{1}H-NMR analysis ($CDCl_3$, 300 MHz).

Fixed-bed testing: 3.20 g of catalyst pelletized to 0.42-0.59 mm were 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% H_2O) was fed at 2.7-9.4 g h^{-1} with a Gilson 306 HPLC pump. Reaction at 160 ℃ was followed with time on stream (TOS) by GC and ^{1}H-NMR.

In a second fixed bed test, 60 g of ITQ-18 extrudates were charged in a stainless-steel reactor (22 cm length, 25 mm ID). Neutral condensate (A/F = 4.0 M; ~1.5% H_2O) was fed at 1.0 g min^{-1} with a HPLC pump. Reaction at 125 ℃ was followed with TOS by GC and ^{1}H-NMR.

Product characterization: for GC analysis, reaction samples were diluted with methanol (1/10 v/v; Aldrich, 99.9+% purity). 1 μl of diluted sample was injected in a Varian 3900 GC apparatus, equipped with a 30 m HP-5 column and a FID detector. Nitrobenzene (Aldrich, 99+% purity) was used as internal standard to calculate the content in free aniline and the distribution of diamines and triamines. For ^{1}H-NMR analysis samples were exchanged several times with D_2O in order to remove all the labile protons (-NH_2 and HOH signals). Spectra were registered in a 300 MHz Varian Gemini spectrometer using $CDCl_3$ as solvent (Aldrich, 99.9 atom %D). Chemical shift

is expressed in δ (ppm) relative to the tetramethylsilane used as internal standard. Typically, four different groups of compounds can be quantified by this technique (see Figure 1): primary amines (^{1}H-NMR δ: 3.7, s, 2H, Ph-CH_2-Ph), secondary amines (^{1}H-NMR δ: 4.2, s, 2H, Ph-NH-CH_2-Ph), quinazolines (mainly 3-phenyl-3,4-dihydroquinazoline, ^{1}H-NMR δ: 4.8, s, 2H, Ph-CH_2-NR$_2$), and N-methylated derivatives (basically N-methyl-DADPM, ^{1}H-NMR δ: 2.7-2.6, s, 3H, Ph-NH-CH_3).

During the reaction, tar-like products were formed in the catalyst, and this became dark-brown. Used catalysts were extracted in a micro-soxhlet with CHCl$_3$ for 24 h [3635]. The solvent was evaporated and the remaining organic material was weighed, diluted with CDCl$_3$ and analysed by GC-MS and ^{1}H-NMR. These fractions were added to the amines content previously determined in the liquid phase. Residual carbon content was quantified by elemental analysis in order to estimate the non-extractable organic deposit.

3. Results and discussion

3.1. Production of DADPM with zeolitic materials

As commented before, the current industrial production of DADPM is carried out through a homogeneous process in a single step, where the aniline reacts with aqueous formaldehyde in an agitated tank in the presence of hydrochloric acid. After separation of the organic layer, this is distilled to recover the aniline and crude DADPM is obtained. However, when the process is catalyzed by zeolitic materials this single step reaction is not feasible. The main limitation comes from the organic/aqueous two-phase system (aniline-water) present, which strongly hinders mass transfer processes within the microstructure of the catalyst. As a consequence, incomplete conversion of the neutral aminal is achieved. In this sense, the preparation of DADPM over zeolites (in

general, over solid acids) works better through a two-step process [4,10-24], as shown in Scheme 1: i) synthesis of the aminal (**I**) under neutral conditions by condensation of 2 mols of aniline with 1 mol of formaldehyde (aqueous solution), followed by removal of the aqueous phase; here, an expensive distillation process can be avoided if catalyst used in the next step shows resistance to small amounts of water in the organic layer; ii) isomerization of the aminal into DADPM in the presence of a solid acid material. The second step comprises several sequential reactions. The acid catalyzed rearrangement of aminal takes place rapidly in the presence of an aniline excess, producing secondary amines, mainly aminobenzylanilines (ABAs) (**II**), by the electrophillic substitution on an aromatic ring with a strong *para-ortho* orientating amino group. The reaction is quantitative, even at low catalyst concentrations, and is followed by the dissociation of ABA to give a benzylic carbenium ion, which reacts with aniline to form DADPM (**III**). Besides aniline, the carbenium ion can also react with DADPM to give oligomeric amines (triamines and tetramines). The rearrangement takes place over Brønsted acid sites [19] and concerns the slower step of the reaction, thus, being limited by pore diffusion [3736]. A catalyst suitable for industrial purposes will be able to transform ABAs into the corresponding DADPMs with a final concentration of secondary amines in the crude below 5,000 ppm. However, depending on the process conditions (e.g., reaction temperature and A/F molar ratio) the product distribution can change. The higher the excess of aniline the higher the concentration of diamines in the product mixture. For steric reasons, 4,4'-DADPM will be favoured at low temperature. However, the *para*-isomer can also isomerize to 2,4' and 2,2'-DADPM at high reaction temperatures via an acid catalyzed protodealkylation. Moreover, in the presence of an excess of aniline, triamines and tetramines can follow a transalkylation process to give back DADPM enriched in the 2,4' fraction [3837]. The physico-chemical characteristics

of the solid acid catalyst (essentially the strength and distribution of acid sites), can bring about the formation of several by-products, which decrease the quality of the final crude. The most important ones are quinazolines (**IV**) and N-methylated products (**V**). These last are particularly undesirable because they cannot be transformed into isocyanate groups through reaction with phosgene. Although in the homogeneous process N-methylation takes place through the Plöchl reaction [3938], in our case, as the condensation step occurs in neutral conditions, this is not feasible. We hypothesize that N-methylated derivatives can be formed by rearrangement of the ABA intermediate by strong acid sites (see Scheme 1). Suitable DADPM crude will have less than 1% of N-methylated compounds, preferably, less than 0.5%.

3.2. Production of DADPM with ITQ-2 and ITQ-6

ITQ-2 comes from the exfoliation of the layered precursor of MCM-22 [26]. The delamination treatment makes accessible large cavities on the surface corresponding to twelve-membered-ringtwelve-ring (12 MR12-ring) pores of about 7 Å diameter, whereas in the original zeolite only the ten-membered-ringten-ring (10 MR10-ring) channels are accessible to the reactant molecules. As a consequence, a significant increase in the external surface area is achieved (Table 1). In the delaminated material better accessibility of the acid sites and lower limitations to molecular diffusion are expected. This is reflected by the superior activity of ITQ-2 versus MCM-22 (as determined by the content of primary amines in the reaction mixture), both with a Si/Al molar ratio of 15 (Table 2). Nevertheless, the selectivity to 4,4'-DADPM decreases significantly in the case of ITQ-2, with a 4,4'-DADPM/(2,2'+2,4'-DADPM) ratio about 1 (higher than 4 for MCM-22). The large dimensions (14.6 x 7.4 x 4.6 Å) of the aminal molecule gives rise to a strong steric hindrance to diffusion through the 10 MR10-ring

channels. Therefore a shape selectivity effect within the zeolitic structure is expected, which favors the production of the linear isomer 4,4-DADPM. Conversely, the aminal molecules can easily be accommodated in the large opened cavities of the external surface. In this sense, as the internal volume accessible is limited, the reaction takes place on the outer surface of the catalyst where no shape selectivity effect will be evident with ITQ-2. The reaction only takes place on the external surface, and the product distribution is controlled by the thermodynamics of the process (at 150 ºC the reaction in hydrochloric acid yields 56.0 % 4,4'-DADPM, 35.2 % 2,4'-DADPM and 8.8 % 2,2'-DADPM) [4039].

The effect of the exfoliation process on the catalytic behavior is also seen for ITQ-6 and its corresponding zeolitic precursor FER (both with a Si/Al molar ratio of 30). ITQ-6 presents a surface with opened cavities of 10 MR10-ring with a large increase of the external surface area (Table 1). Although ITQ-6 shows a somewhat lower concentration of Brønsted acid sites than FER due to some dealumination inherent to the delamination process, these are more accessible to bulky molecules. This was formerly demonstrated by our group by measuring the adsorption of 2,6-di-*tert*-butylpyridine (DTBPy) that certainly cannot penetrate in the 10-ring pores of FER [28]. The results showed that a much higher amount of DTBPy is adsorbed on ITQ-6 (90% accessibility) than on FER (~5% accessibility). Therefore, the superior catalytic activity offeredshown by the delaminated material in the synthesis of DADPM is not surprising (Table 2). Again the delamination process involves the loss of the shape selectivity effect inherent to the zeolitic structure, and ITQ-6 presents a 4,4'-DADPM/(2,2'+2,4'-DADPM) ratio of 1.4, whereas in FER this ratio is 5.0.

3.3. Production of DADPM with ITQ-18

Another delaminated zeolitic material developed by our group is ITQ-18, the exfoliated form of Nu-6 zeolite [29]. Its framework structure has been recently solved [30] and is characterized by the existence of 1D straight eight-membered-ring (8 MR) channels developing along the [010] direction and two non-equivalent sets of 8 MR channels alternating along the crystallographic *c* direction.

We have tested Nu-6 and ITQ-18 samples, both with a Si/Al molar ratio of 45, for the synthesis of DADPM in a batch reactor and the results are presented in Table 3. They show the exfoliation process leads to a significant increase in the production of primary amines and a lower production of N-methylated impurities, which is in agreement to that observed in ITQ-2 and ITQ-6 materials. However, ITQ-18 presents a catalytic behavior clearly different to the other delaminated samples. On one hand, ITQ-18 is less active than ITQ-2 and ITQ-6, and needs more severe process conditions (i.e., higher reaction temperature and/or higher catalyst loading) to achieve full conversion of secondary amines. According to the standard pyridine adsorption-desorption method (Table 1), ITQ-18 possesses a smaller population of medium strength Brønsted acid sites, which are those active in the isomerization reaction, as a consequence of its lower Si/Al molar ratio. The importance of the acid site density and strength in the catalytic performance has been reported for amorphous aluminosilicates [19]. Unfortunately, it has not been possible to synthesize the ITQ-18 structure with a higher framework Al content. On the other hand, it is surprising that ITQ-18 retains the selectivity to *para*-substitution of the parent zeolite Nu-6. This can be rationalised through consideration of the 8 MR channels of Nu-6 which are very narrow (4.,5 x 2.,6 Å). This precludes the internal diffusion of the aminal molecule, which means that the isomerization into

DADPM takes place mostly on the outer surface. A preliminary study of diffusion within the pore structure by Montecarlo Simulation and of adsorption within pores by Molecular Dynamics Simulation [4140], has reported that the large opened cavities present on the surface of ITQ-2 and ITQ-6 materials are deep enough to allow the *ortho*-substitution in the isomerization reaction. Conversely, the same study revealed that the interaction of 4-ABA and the substitution in the 4-position are favoured in the shallow cavities present on the surface of Nu-6 and ITQ-18.

As the exfoliation process involves a large increase in the accessibility to reactant molecules of the catalytically active hydroxyl bridging groups, and then an increase in the production of primary amines, one could think that the way to increase the specific activity of ITQ-18 could be to extend the process of delamination as much as possible. This has been done by synthesizing another sample through a prolonged treatment in the ultrasound bath (Table 1, ITQ-18B). This material presented an increase of about 50% in the external surface area and a similar distribution of acid sites as standard ITQ-18. However, no improvement in the catalytic performance was achieved (Table 3), showing that all catalytic sites are accessible in both samples.

Nonetheless, complete conversion of the aminal (as measured by the total disappearance of secondary amines in the mixture), can be achieved over ITQ-18 by moving to more severe process conditions. By increasing the catalyst loading in the range 16-24% at 150 ºC (Table 4, entries 1-3, Figure 2), the percentage of aminobenzylanilines decreases from 10.8 to 0.6% with no substantial change in neither the 4,4'-DADPM/(2,2'+2,4'-DADPM) ratio, nor in the triamines production. When increasing the reaction temperature in the range 110-160 ºC there is a dramatic reduction of the secondary amines content in the final crude (respectively, from 31.5 to less than 0.1%), although such temperature increases result in an increase in the degree

of *ortho*-substitution [4]. Therefore, an increase in the concentration of *ortho-para* and *ortho-ortho* isomers is observed and the 4,4'-DADPM/(2,2'+2,4'-DADPM) ratio drops from 6.9 to 3.6 (Table 4 entries 2,4-6, Figure 3). Furthermore, the higher reaction temperature favours DADPM oligomerization, which is reflected by an increase in the triamines fraction.

3.4. Catalytic deactivation of ITQ-18 in a continuous flow fixed-bed reactor

As commented before, the main limitation for the application of zeolites as catalysts in the synthesis of DADPM is their fast deactivation. During the reaction strongly basic compounds (e.g., quinazolines) can be irreversibly adsorbed on acid sites, leading to blocking of the micropores and rapid deactivation. To avoid this, researchers working with zeolites have carried out the reaction with very high aniline to formaldehyde ratios, which requires the use of large reactors and the distillation and recycling of a large volume of aniline. At the end of the reaction, the partially exhausted zeolite catalyst can be regenerated, which is usually performed by burning of the organic deposit in air or oxygen, although it can also be suggested that regeneration can be achieved by washing the catalyst with aniline [4241]. In the case of delaminated materials, one would expect that the large external surface area and the absence of microporosity will preclude a fast deposition of the reaction products on the catalyst surface. To demonstrate this, the rearrangement of aminal (A/F= 3.0 M; <1% H_2O) has been carried out in a continuous flow fixed-bed reactor working at 160 ºC, 4 bar and a contact time (W/F) of 0.34 h. The results presented in Figure 4 show that delaminated ITQ-18 material displays a slow decay over the 8 h duration of the experiment, after which it retains 94% of the initial activity. Under similar process conditions, Beta zeolite shows the same initial activity but a much higher rate of deactivation, and after 8

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h of TOS the catalyst barely achieves 30% of the initial activity [26]. Moreover, if the contact time is increased to 1 h, ITQ-18 shows no sign of catalytic decay over the same duration of the experiment, with no production of secondary amines and a constant 4,4'-DADPM/2,2'+2,4'-DADPM) ratio about 80% of the *para*-isomer (Figure 4). This is in agreement with former results published by our group on the stability of the catalytic behavior of ITQ-2 during the isomerization of the aminal, as a consequence of the improved molecular diffusion and faster desorption of products inherent to a process that takes place mainly on the outer shell of the catalyst [26].

Even if catalytic deactivation occurs slowly, sooner or later catalyst regeneration is needed. Here, ITQ-18 exhibits excellent performance after thermal regeneration in air (540 ºC, 24 h). Figure 5 shows the results obtained in the acid rearrangement of the aminal (A/F= 3.0 M; <1% H_2O) in a continuous flow fixed bed reactor (T=150 ºC, P= 4 bar, W/F= 0.34 h) with catalyst fresh and after 4 reaction-regeneration cycles. No significant change in amines production neither in the product distribution is observed. The complete burning of the organic deposit in the regenerated catalyst was confirmed by elemental analysis, with carbon content of about 0.1 wt%.

The benefits of using a delaminated material are also demonstrated at a significantly larger technical scale, where the rearrangement of aminal (A/F= 4.0 M; ~1.5% H_2O) has been carried out using ITQ-18 extrudates in a continuous flow fixed-bed reactor working at 125 ºC, 4 bar and a contact time (W/F) of 1 h. The results presented in Figure 5 show that delaminated ITQ-18 extrudates display little decay over the 72 h duration of the experiment. Over this same period the 4,4'-DADPM/(2,2'+2,4'-DADPM) ratio remains constant at ~ 4.3. Overall levels of N-methylated impurities were ~ 0.5%. Lower levels of N-methylated impurities (0.1-0.3%) can be obtained when the process is operated at lower temeratures for the intial conversion of aminal to ABAs.

4. Conclusions

Delaminated materials ITQ-2, ITQ-6 and ITQ-18 are active and selective for the synthesis of DADPM. The exfoliation process allows excellent accessibility of their acid sites to reactant molecules as well as fast desorption of products. As a consequence, these catalysts offer significant advantages over conventional zeolites for the synthesis of DADPM: i) higher activity; ii) Lower levels of impurities formation (basically, N-methylated products); iii) Ability to control product selectivity, as the amines distribution can be tuned according to the topology of the delaminated material. In the case of ITQ-18, the interaction of the intermediate 4-ABA with its surface and the 4-substitution are favoured, thus, resulting in the highest selectivity to the most desired isomer 4,4'-DADPM. This catalyst constitutes a real option for replacing HCl in the industrial production of DADPM by a non-salt producing catalytic system based in a solid silico-aluminate with zeolite type structure where the active sites are highly accessible through the external surface.

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Table 1

Physico-chemical characteristics of zeolites and delaminated materials tested in the present work.

Sample	Si/Al (M)^a	Crystal (μm)^b	$S_{EXT.}{}^c$ (m^2 g^{-1})	$S_{MICRO.}{}^d$ (m^2 g^{-1})	Acidity (μmol py)^e					
					Brønsted			Lewis		
					250	350	400	250	350	400
MCM-22	15	0.1	141	312	56	48	33	23	20	20
ITQ-2	15	0.1	234	367	69	60	31	33	22	14
FER	30	0.1	53	225	19	15	4	3	3	1
ITQ-6	30	0.1	413	79	15	9	7	10	9	6
Nu-6	45	0.1	34	44	5	5	3	3	2	2
ITQ-18	45	0.1	610	209	16	9	4	7	6	6
ITQ-18B	45	0.1	892	8	14	6	3	19	13	10

^{a} As-made ratio determined by atomic absorption spectrophotometry.
^{b} As-estimated from the TEM images.
^{c} External surface area.
^{d} Micropore area.
^{e} Determined from the infrared spectra of adsorbed pyridine after evacuation at 250, 350 and 400 °C.

Table 2

DADPM synthesis on ITQ-2 and ITQ-6 in a batch reactor and comparison with their corresponding zeolites.[a]

Catalyst	Amines (%)[b]	Diamines (%)[c]	Triamines (%)[c]	Sec. Amines (%)[b]	N-methylated (%)[b]	Quinazolines (%)[b]	DADPM distribution (%)[c]			DADPM- isomer ratio 4,4'/(2,2'+2,4')
							2,2'	2,4'	4,4'	
MCM-22	95.9	79.3	16.6	3.1	1.0	0	1.1	14.8	63.4	4.3
ITQ-2	98.4	83.8	14.6	0.3	1.1	0.2	3.8	37.7	42.3	1.0
FER	60.3	53.7	6.6	36.9	2.0	1.0	0	8.9	44.8	5.0
ITQ-6	98.1	79.9	18.2	0.8	0.8	0.3	2.8	30.8	46.3	1.4

[a] Experimental condition: A/F=3.0 M (<1% H_2O); T=150 ºC; 20 wt% catalyst; TOS=60 min.

[b] Determined by ^{1}H-NMR.

[c] Determined by GC.

Table 3

DADPM synthesis on ITQ-18 samples and comparison with the corresponding zeolite Nu-6.[a]

Catalyst	Amines (%)[b]	Diamines (%)[c]	Triamines (%)[c]	Sec. Amines (%)[b]	N-methylated (%)[b]	Quinazolines (%)[b]	DADPM distribution (%)[c]			DADPM- isomer ratio 4,4'/(2,2'+2,4')
							2,2'	2,4'	4,4'	
Nu-6	74.7	64.9	9.8	22.0	2.3	1.0	0	11.3	53.6	4.7
ITQ-18	90.7	71.8	18.9	7.7	1.3	0.3	0.6	12.8	58.3	4.4
ITQ-18B	89.3	71.3	18.0	8.6	1.8	0.3	0.6	12.9	57.8	4.3

[a] Experimental condition: A/F=3.0 M (<1% H_2O); T=150 ℃; 20 wt% catalyst; TOS=60 min.

[b] Determined by ^{1}H-NMR.

[c] Determined by GC.

Table 4

DADPM synthesis on ITQ-18 in a batch reactor: effect of the catalyst loading and the reaction temperature.[a]

T (°C)	Weight (%)	Amines (%)[b]	Diamines (%)[c]	Triamines (%)[c]	Sec. Amines (%)[b]	N-methylated (%)[b]	Quinazolines (%)[b]	DADPM distribution (%)[c]			DADPM- isomer ratio 4,4'/(2,2'+2,4')
								2,2'	2,4'	4,4'	
150	16	86.8	71.0	15.4	10.8	2.1	0.3	0.7	13.4	56.9	4.0
150	20	90.7	71.8	18.9	7.7	1.3	0.3	0.6	12.8	58.3	4.4
150	24	98.2	80.9	17.3	0.6	1.2	<0.1	1.6	14.9	64.3	3.9
110	20	67.4	60.0	7.4	31.5	0.8	0.3	0	7.6	52.4	6.9
130	20	86.3	72.6	13.7	12.4	1.0	0.3	0	10.7	61.9	5.8
160	20	99.5	73.7	26.3	<0.1	0.5	<0.1	1.1	15.0	57.6	3.6

[a] Experimental condition: A/F=3.0 M (<1% H_2O); TOS=120 min.

[b] Determined by ^{1}H-NMR.

[c] Determined by GC.

Caption to Schemes and Figures

Scheme 1. General reaction scheme for the isomerization of the neutral aminal to DADPM over zeolitic materials. Processes (1) and (2) involve several steps.

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

Fig. 2 Production of secondary amines and amine distribution over ITQ-18 sample *vs* the catalyst load in the rearrangement of the neutral condensate (A/F=3.0 M;< 1% H_2O) in a batch reactor. Symbols: Secondary amines (□); diamines/trimanes (wt/wt) ratio (○); 4,4'-DADPM/(2,2'+2,4'-DADPM) (wt/wt) ratio (Δ). Experimental conditions as in Table 4.

Fig. 3 Production of secondary amines and amine distribution over ITQ-18 samples *vs* the reaction temperature in the rearrangement of the neutral condensate (A/F=3.0 M;< 1% H_2O) in a batch reactor. Symbols: Secondary amines (□); diamines/trimanes (wt/wt) ratio (○); 4,4'-DADPM/(2,2'+2,4'-DADPM) (wt/wt) ratio (Δ). Other experimental conditions as in Table 4.

(Δ); (●); (○); (■).

Fig. 4 Rearrangement of the neutral condensate (A/F=3.0 M;< 1% H_2O) over ITQ-18 sample in a continouous flow fixed-bed reactor. (a) Production of primary and secondary amines; (b) 4,4'-DADPM/(2,2'+2,4'-DADPM) (wt/wt) ratio. Symbols: W/F=0.34 h (○,●); W/F=1.17 h (□,■). Other experimental conditions: T=160 ºC; P=4 bar.

Fig. 5 Rearrangement of the neutral condensate (A/F=4.0 M; ~1.5% H_2O) over ITQ-18 extrudates in a continuous flow fixed-bed reactor. (a) Production of primary (□) and

secondary amines (■); (b) 4,4'-DADPM/(2,2'+2,4'-DADPM) (wt/wt) ratio. Other

experimental conditions: T=125 ºC; P=4 bar; W/F = 1.00 h