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Lewis acid solid catalysts for the synthesis of methylenedianiline from aniline and formaldehyde



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1. Introduction

Methylenedianiline (MDA, or diaminodiphenylmethane) is an important organic compound predominantly used in the production of methylene diphenyl diisocyanate (MDI), a precursor to polyurethane, a polymer class with sales of over 20 million tons globally and a market estimated at USD 65.5 billion in 2018 [1,2]. MDA is industrially synthesised in high yields by condensation of aniline and formaldehyde in a homogeneously catalysed process. The catalyst employed, hydrochloric acid, presents several drawbacks. Large quantities of a base, typically sodium hydroxide, are used to neutralise the resulting hydrochloride salt. Furthermore, the generated waste water has to be treated to remove organic contaminants prior to discharge. In light of this, there has been a strong incentive to search for solid acid catalysts to replace HCl whilst still fulfilling the following requirements: (i) enable reasonable vields to be reached with minimal intermediates and byproducts formation. (ii) offer control in the product composition. (iii) have a long lifetime, and (iv) be regenerated in a feasible way [3–5]. The heterogeneous process is generally split into two steps: a non-catalysed condensation reaction first takes place between aniline and formaldehyde, followed by phase separation to isolate the organic phase which contains the condensate N,N'-

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ABSTRACT

A catalyst containing Hf⁴⁺ and Zn²⁺ supported on silica has been found to be highly effective for the synthesis of methylenedianiline (MDA), an indispensable precursor in the polyurethane industry. Its performance was further improved when the silica support was replaced by silica-alumina, which resulted in a catalyst that was both active and selective, as indicated by the high MDA yield and high 4.4'-MDA/(2.2'-MDA + 2,4'-MDA) isomer ratio obtained. Furthermore, the catalyst also gave an appreciable oligomeric MDA (OMDA) yield and was noticeably more stable than the zeolites that were used in comparative tests: it could be used in at least five consecutive runs without any significant loss in activity. The combination of Brønsted and Lewis acidity strongly increases the overall activity and yields a catalyst that represents a remarkably stable and reusable alternative to the commonly studied systems for this reaction.

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diphenylmethylenediamine (also called aminal) and aniline, hereafter referred to as aminal solution. In the second step, the aminal is consumed in a series of acid-catalysed rearrangement reactions to form the MDA products via two N-(aminobenzyl)aniline intermediates (o- and p-ABA). The product mixture consists of MDA isomers (4,4'-, 2,4'-, and 2,2'-MDA), an oligomeric fraction (oligomers of \geq 3 aryl rings bridged by methylene groups), and byproducts (N-methyl-MDA, N-formyl-MDA, and quinazolines), out of which 4,4'-MDA, 2,4'-MDA, and the oligomeric fraction are of value. The reaction conditions of the two steps can be adjusted separately to tailor the product distribution to needs (Scheme 1)[3–5].

A wide array of materials and their modified versions have been probed over the years as potential catalyst substitutes: ionexchange resins were found to be selective to the 4,4'-isomer but lacked sufficient catalytic activity [6]; some clays showed good stability but were not selective to the 4,4'-isomer [7], and while silicaaluminas did show an increase in activity and a slower rate of catalvst deactivation compared with other materials, the 4.4'-isomer yield was low and eventual catalyst deactivation by fouling was inevitable [8,9]. Zeolites with their unique properties such as shape-selectivity and flexible acid strength, also emerged as candidates, but the bulky nature of the aminal reactant and the products implies that molecular diffusion limitations in the micropores of the zeolite crystals would severely decrease the overall activity and longevity of even large pore zeolites such as Beta and Mordenite [10–13]. To counteract this, access to the acid sites in zeolites





Scheme 1. Simplified reaction scheme for MDA synthesis.

has been improved by swelling and delaminating precursors of layered zeolites such as MCM-22 to obtain 2D zeolites like ITQ-2, ITQ-6, and ITQ-18, which performed better compared with the corresponding zeolites. However, a sizeable quantity of catalyst was required to achieve moderate 4,4'-isomer yields [14,15]. Since all of the catalytic systems studied so far have their downsides, there is still much interest in exploring solid materials with a different set of properties. One option that, to the best of our knowledge, has not been addressed so far in MDA synthesis is Lewis acid catalysis. Lewis acids can be supported on inorganic solids with high surface areas such as clays, silicas, silica-aluminas, and zeolites, in order to facilitate dispersion and accessibility of the active sites [16]. We expect that catalysts with Lewis acidic character could be viable candidates in the synthesis of MDA. To this end, various Lewis acid catalysts were investigated and characterised in the acid-catalysed synthesis of MDA.

2. Experimental

2.1. Catalyst preparation

Commercial zeolites were used in their proton form without further modification. Zeolite H-Y was obtained from Zeolyst International (CBV 720, Si/Al = 15), H-MCM-22 from China Catalyst Group (Si/Al = 14), and H-Beta from PQ Corporation (CP811 BL-25, Si/Al = 12.5) and from ZeoCat (Si/Al = 33). The silica used as a support was acquired from Cabot (CAB-O-SIL[®] M-5), the alumina from Condea Chemie (PURALOX NGa-150), the magnesium aluminate spinel (nanopowder, < 50 nm particle size) and hydroxyapatite (HAP, nanopowder, < 200 nm particle size) from Sigma-Aldrich, the titanium(IV) oxide (anatase) and zirconium oxide from Alfa Aesar, and the silica-alumina from Grace (MS 13/110, 13% Al₂O₃). For the metal-loaded catalysts, target amounts of the metal precursor salts were first dissolved in ultrapure water at room temperature (unless stated otherwise); then the required amounts of the supports were added and the mixture was left stirring until the water evaporated. The resulting powder was dried at 60 °C, then calcined in air at 500 °C for 2 h at a heating rate of 2 °C/min to obtain the samples presented in Table 1.

2.2. Catalyst characterisation

Powder X-ray diffractograms were recorded on a Malvern Panalytical Empyrean diffractometer in Transmission/Debye-Scherrer geometry ($1.3 - 45^{\circ} 2\theta$ range, 0.013° step size) with a PIXcel3D solid state detector. The metal content was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES)

Table 1

Metal-loaded catalysts tested in MDA synthesis.

Metal-loaded silica samples (precursor salts)	Hafnium-loaded samples ^a
$\begin{array}{c} La_{1.5}/SiO_2 \ (La(NO_3)_3\cdot 6H_2O) \\ Ce_{1.7}/SiO_2 \ (Ce(NO_3)_3\cdot 6H_2O) \\ Sc_{1.5}/SiO_2 \ (Sc(NO_3)_3\cdot xH_2O) \\ Ta_{1.3}/SiO_2 \ (TaCl_5)^{b} \\ Sn_{1.5}/SiO_2 \ (Sn(CH_3CO_2)_2) \\ Cr_{1.9}/SiO_2 \ (Cr(acac)_3)^c \\ Fe_{1.3}/SiO_2 \ (Cr(acac)_3)^c \\ Fe_{1.3}/SiO_2 \ (Cu(NO_3)_2\cdot 6H_2O) \\ Cu_{1.4}/SiO_2 \ (Xi(NO_3)_2\cdot 6H_2O) \\ Cu_{1.4}/SiO_2 \ (Cu(NO_3)_2\cdot 6H_2O) \\ Zn_{1.7}/SiO_2 \ (ZrCl_4) \\ Hf_{1.5}/SiO_2 \ (HfCl_4) \\ Hf_{2.6}/SiO_3/SiO_2 \ (HfCl_4) \\ Hf_{2.6}/SiO_3/Si$	Hf _{3.0} /Al ₂ O ₃ Hf _{1.5} /SiO ₂ ·Al ₂ O ₃ Hf _{3.0} /SiO ₂ ·Al ₂ O ₃ Hf _{2.7} Zn _{0.5} /SiO ₂ ·Al ₂ O ₃ Hf _{3.0} /Al ₂ MgO ₄ Hf _{3.0} /HAP Hf _{3.0} /TiO ₂ Hf _{3.0} /ZrO ₂ Hf _{3.0} /MCM-22 Hf _{3.0} /Y
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The subscripts indicate the metal content (wt%) as determined by ICP-OES.

^a HfCl₄ was used as the metal precursor salt.

^b Toluene was used to dissolve TaCl₅ in the sample preparation.

^c Ethanol was used to dissolve Cr(acac)₃ in the sample preparation.

using a Varian 720-ES equipped with a double-pass glass cyclonic spray chamber, a SeaSpray concentric glass nebuliser and a high solids torch. The textural properties of the solids were derived from N_2 physisorption isotherms, which were collected at -196 °C on a Micromeritics 3Flex surface characterisation analyser. Samples were outgassed under vacuum at 150 °C for 4 h prior to data collection. The specific surface areas (S_{BET}) were determined using the BET method, the specific external surface areas (S_{EXT}) and micropore volumes (V_{micro}) were obtained using the *t*-plot method, and the mesopore volumes (V_{meso}) were estimated by the BJH method. Temperature programmed desorption of ammonia (NH₃-TPD) was used to determine the number of acid sites in the catalysts. Measurements were conducted using a Gasmet DX4000 Fourier-Transform infrared (FTIR) gas analyser with Calcmet software for converting the collected spectral data into ammonia concentrations. The sample was activated at 200 °C for 2 h under nitrogen, then cooled to 100 °C and dosed with an ammonia/nitrogen gas mixture until saturation at this temperature. Non-adsorbed ammonia was then flushed away with nitrogen at 100 °C. The sample was subsequently heated at 5 °C/min under nitrogen and the amount of desorbed ammonia was monitored with a downstream Peltier cooled mercury cadmium telluride (MCT) detector. The nature of the acid sites and the acid site density were determined by pyridine adsorption followed by FTIR spectroscopy. To this end, a self-supported wafer was placed in a cell under vacuum and activated at 400 °C for 1 h. The cell was subsequently

cooled and a reference spectrum was recorded at 150 °C. After this, the cell was further cooled and pyridine (25 mbar) was contacted with the wafer at 50 °C until the sample material was saturated. Weakly coordinated pyridine was removed by evacuation for 30 min at 50 °C, prior to collection of the IR spectrum at 150 °C. Using the difference spectrum generated from the measurements and using Emeis' integrated molar extinction coefficients [17], the Lewis acidity was calculated from the area of the pyridine absorption band at 1450 cm⁻¹ and the Brønsted acidity from the area of the band at 1545 cm⁻¹. Samples were imaged by transmission electron microscopy (TEM) using a Tecnai Osiris machine operated at 200 keV in High-Angle Annular Dark-field Scanning (TEM) (HAADF-STEM) mode. Chemical composition maps were acquired by energy-dispersive x-ray spectroscopy (EDXS) using a Thermo-Fisher SuperX G1 detector. Prior to imaging, the powder samples were dispersed in ethanol and applied on an ultra-thin carbon TEM-grid.

2.3. Synthesis of aminal

Aminal was the product of the non-catalysed condensation reaction between aniline and formaldehyde. It was prepared following a modification of a previously reported procedure [15]. Briefly, in a 2 L two-necked round bottom flask, aniline (980 mL, Acros Organics, 99.8% purity) was stirred and heated at 50 °C. Formaldehyde (274 mL, VWR Chemicals, 36% aqueous solution, stabilised with methanol) was added dropwise until the mixture reached an aniline/formaldehyde (A/F) molar ratio of 3. The mixture was stirred for a further 1 h at 50 °C. The formed aminal and the residual aniline (generalised as aminal solution) was collected in the organic layer, and the aqueous layer was discarded after phase separation of the mixture. The remaining water content in the organic layer was determined by Karl Fischer titration. The A/F ratio was determined by proton nuclear magnetic resonance spectroscopy (¹H NMR). The NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz Spectrometer and CDCl₃ (Sigma-Aldrich, 99.8 atom % D) was used as the solvent.

2.4. Catalytic reactions

Catalysts were dried overnight at 200 °C before use. The aminal solution was added to the dried catalyst in a sealed vial, later purged with nitrogen. Typically, 200 mg of dried catalyst was used in the experiments, representing 5 wt% with respect to the aminal solution. The mixture was stirred and maintained at 150 °C (unless stated otherwise) for the required reaction time. Aliquots of \leq 100 µL were taken at different time points, and the spent catalyst was separated from the crude product solution by centrifugation. The crude product was then analysed by gas chromatography (GC). Tetrahydrofuran (Acros Organics, 99+% extra pure) was used to dilute the crude product solution and nitrobenzene (Fluka, > 99.5% purity) was added as an external standard. Reaction samples were analysed in a Shimadzu 2010 gas chromatograph equipped with a 60 m CP-Sil 5 CB column and an FID detector. Compounds were identified with known compounds and gas chromatography-mass spectrometry (GC-MS). For the recycling tests, after a reaction cycle of 24 h at 150 °C, the crude product was extracted for analysis, and the catalysts were used in subsequent reaction cycles without intermediate calcination.

2.5. Strength of aniline-catalyst interaction (temperature programmed desorption of aniline)

The strength of the aniline-catalyst interaction was probed by dosing the sample with aniline and using Thermogravimetric Analysis–Mass Spectrometry (TGA-MS). The MS signal at m/z 93 was

monitored as a function of increasing temperature; therefore, peaks appearing at higher temperatures indicate a stronger aniline-catalyst interaction. Aniline in THF (0.0025 $g_{aniline}/mL_{THF}$) was added (5 wt% solution with respect to the catalyst) to a predried sample (dried overnight at 200 °C). The mixture was then stirred at room temperature until it was dry. The measurements were carried out at a heating rate of 5 °C/min to 600 °C under a nitrogen atmosphere. TGA-MS data were collected on a NETZSCH STA 449 F3 Jupiter[®] thermal analyser and a Hiden HPR-20 EGA gas analysis system.

3. Results and discussion

3.1. Catalytic reactions using commercial zeolites

As mentioned in Section 1, the reaction was carried out in two steps; the first step being a non-catalysed condensation reaction between aniline and formaldehyde to form a biphasic mixture of the aminal condensate and water. The aminal solution was isolated (water content <1 wt%, Fig. S1) and used in the second step which involves a series of acid-catalysed rearrangement and condensation reactions to form the products. The first intermediates formed are aminobenzylanilines (ABA), which further react to form the methylenedianiline isomers (MDA) and their higher homologues, oligomeric MDAs containing at least three aryl rings (OMDA). Typically, MDA is produced with a sizeable oligomeric fraction and an excess of para- isomers compared to ortho- isomers, with the 2,2'isomer being undesired [13]. A profile of how the reaction proceeds over time is shown in Fig. S2. The 4,4'-MDA/(2,2'-MDA + 2,4'-MDA) isomer ratio drops as the reaction progresses, since the MDA products are formed from two ABA precursor isomers which differ in reactivity. The product 4,4'-MDA is derived from the rearrangement of the p-ABA intermediate, 2,2'-MDA from the o-ABA intermediate, whilst both the *p*- and *o*-ABA intermediates contribute to the formation of the 2,4'-MDA product isomer. As can be observed in Fig. S3, the *p*-ABA intermediate reacts considerably faster than the o-ABA, which prompts the decrease in the eventual 4,4'-MD A/(2,2'-MDA + 2,4'-MDA) isomer ratio.

A series of H-form zeolites were preliminarily tested to serve as a benchmark for this work. The yields of o-ABA and p-ABA were combined into a single ABA value (ABA), whereas the MDA yield represented the summed yields of the three MDA isomers. The catalytic activity results in the conversion of the ABA intermediates (Fig. 1). Zeolites H-Y and H-Beta with comparable Si/Al ratios showed similar catalytic activity but zeolite H-Y was more



Fig. 1. Yields of products obtained in MDA synthesis using various zeolites as catalysts. A/F = 3.0 M, 5 wt% catalyst, 150 °C, reaction time of 1 h, 5 h, and 24 h. Isomer ratio indicated by the crosses (\times).

selective towards 4,4'-MDA, as indicated by the much higher 4,4'-MDA/(2,2'-MDA + 2,4'-MDA) isomer ratio. Salzinger et al. reported that the catalytic activity of materials with the same zeolite topology can be directly correlated to the total number of Brønsted acid sites, and pore diffusion effects can be disregarded in this case [11]. This is confirmed by the comparison of two Beta zeolites with different Si/Al ratios. Upon increasing the Si/Al ratio from 12.5 to 33, the number of acid sites decreased and the catalytic activity dropped. Zeolite H-MCM-22 was the most active catalyst of the series, as reflected by the complete absence of the ABA intermediates after 5 h of reaction. However, the selectivity to 4,4'-MDA was very low. These results contradict previous studies that reported H-MCM-22 to be almost inactive [11]. Nevertheless, it is important to note that our reactions were carried out at a higher temperature. Zeolite H-MCM-22 has both 10-MR and 12-MR micropores, which restrict the diffusion of the bulky reactant and intermediates. As a result, the reaction is believed to mainly take place on the external surface of the catalyst and at the pore openings, which not only results in a suboptimal use of available acid sites, but also reduces the advantageous shape selectivity effect normally brought about by zeolites [11,18,19]. N₂ physisorption studies revealed that both the H-Y and the H-MCM-22 samples exhibit a type I isotherm, characteristic of microporous materials (Figs. S4 and S5) [20], this means they would be more prone to pore blockage by the bulky molecules and thus to fast deactivation. Nevertheless, these samples also possess a relatively high external surface area, as observed in Table S1, which contributes to the moderate catalytic activity exhibited by the zeolites. Furthermore, as explained earlier, for almost every studied zeolite, the 4,4'-MD A/(2,2'-MDA + 2,4'-MDA) isomer ratio drops as the reaction proceeds.

3.2. Catalytic reactions using Lewis acid catalysts

A series of metal loaded SiO₂ catalysts was evaluated to test the hypothesis that Lewis acid solids can catalyse the formation of MDA. The results are presented in Table 2 and Table S2. Blank experiments did not form detectable amounts of any products, not even ABA intermediates; unloaded SiO₂ only produced MDA in a 10% yield after 24 h reaction time (entries 1 and 2 respectively). Three rare-earth elements were studied; La, Ce, and Sc. La_{1.5}/SiO₂ and Ce_{1.7}/SiO₂ only showed a moderate activity (30% and 25% MDA yield, entries 3 and 4), this activity was improved with Sc_{1.5}/SiO₂ (entry 5). A transition metal like Ta and a post-transition metal like Sn, which are often used in other Lewis

acid-catalysed transformations [21–23], were only able to form MDA in modest yields (37% MDA yield with $Sn_{1.5}/SiO_2$, entry 7). In contrast, some of the studied first-row transition metals performed better. Although Cr_{1.9}/SiO₂, Ni_{1.4}/SiO₂, and Cu_{1.4}/SiO₂ showed poor activity, this was noticeably improved when $Zn_{1.7}$ SiO₂ was used as catalyst (27% MDA yield and a 4.8 4,4'-MDA/(2, 2'-MDA + 2,4'-MDA) isomer ratio, entry 12) and further enhanced with Fe_{1.3}/SiO₂ (55% MDA yield and a 4.3 4,4'-MDA/(2,2'-MDA + 2 ,4'-MDA) isomer ratio, entry 9). In fact, given the availability and low cost of Fe, this catalyst already emerges as an interesting candidate for the synthesis of MDA. Nonetheless, the best results were attained when other Lewis acids were employed. Both Zr_{1.4}/SiO₂ and $Hf_{1,5}/SiO_2$ (entries 13 and 14) were found to be outstanding potential catalysts for the synthesis of MDA, achieving high MDA and OMDA yields and a respectable 4,4'-MDA/(2,2'-MDA + 2,4'-M DA) isomer ratio. Moreover, the activity of such catalysts can be further improved by increasing the metal loading from 1.5 to \sim 3 wt%, as indicated by the results obtained with the sample Hf_{2 7}/SiO₂ (entry 15). A further increase in metal loading, however, did not lead to a noticeable surge in product yields (Fig. S6). In order to confirm that catalysts with exclusively Lewis acid sites are capable of catalysing the ABA to MDA rearrangement, a small amount of Zn was added in the preparation of the Hf- and Zrloaded samples. Previous research indeed showed that any residual Brønsted acidity on Hf/SiO₂ can be suppressed by the addition of Zn, likely because the formed ZnO particles have basic properties [24]. The acidity characteristics of the catalysts will be studied in detail in Section 3.3. Remarkably, upon testing the $Hf_{2.6}Zn_{0.5}/SiO_2$ catalyst, both the OMDA yield and the isomer ratio increased, with only a minor drop in MDA yield (entry 16). A bimetallic catalyst with double the amount of Zn showed very similar catalytic activity (Fig. S7). Due to the superior overall MDA and OMDA yields, the attractive 4,4'-MDA/(2,2'-MDA + 2,4'-MDA) isomer ratio, and the purely Lewis acidic nature of the material (see also Fig. 8 and Table 5), the bimetallic system $Hf_{2.6}Zn_{0.5}/SiO_2$ was selected for further study.

Using $H_{2.6}Zn_{0.5}/SiO_2$ as catalyst, the reaction temperature was varied to evaluate its influence on the product distribution; the results are plotted in Fig. 2. At 125 °C, the ABA intermediates fraction remained large at short reaction times; it was still present even after 24 h (13%) (Fig. 2a). The 4,4'-MDA yield increased over time to 38% after 24 h, which was comparable to values reached at higher reaction temperatures. Although the yield of the undesired 2,2'-MDA was favourably low (<0.2%, 5 h) at 125 °C compared to all the temperatures tested, and the 4,4'-MDA/(2,2'-MDA + 2,4'-

Table 2

Yields and isomer ratios of the MDA synthesis products over	er various metal-loaded silica catalysts (5 wt% catalyst, 24 h, 150 °C).
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		Yield (%)			
Entry	Catalyst	ABA	MDA	OMDA	4,4'/(2,2'+2,4')
1	Blank	1	1	/	/
2	SiO ₂	22.8	10.0	1	3.6
3	La _{1.5} /SiO ₂	13.7	30.1	3.6	4.6
4	Ce _{1.7} /SiO ₂	16.5	25.0	1	3.8
5	Sc _{1.5} /SiO ₂	3.8	48.8	10.8	4.0
6	Ta _{1.3} /SiO ₂	17.7	21.3	1	4.2
7	Sn _{1.5} /SiO ₂	4.7	37.3	5.1	4.1
8	Cr _{1.9} /SiO ₂	25.2	11.2	1	3.6
9	Fe _{1.3} /SiO ₂	6.1	55.4	10.8	4.3
10	Ni _{1.4} /SiO ₂	34.3	5.5	1	3.5
11	Cu _{1.4} /SiO ₂	36.2	3.3	1	1.9
12	Zn _{1.7} /SiO ₂	27.0	26.7	1	4.8
13	$Zr_{1.4}/SiO_2$	2.1	53.8	12.9	3.4
14	Hf _{1.5} /SiO ₂	5.9	46.5	15.1	4.0
15	Hf _{2.7} /SiO ₂	3.1	52.7	14.6	3.4
16	$Hf_{2.6}Zn_{0.5}/SiO_2$	3.8	51.5	16.5	4.0
17	Zr _{1.9} Zn _{0.3} /SiO ₂	3.6	52.3	15.4	3.0



Fig. 2. Temperature profiles of MDA synthesis using 5 wt% Hf_{2.6}Zn_{0.5}/SiO₂ as catalyst; values at zero were omitted for clarity. (a) ABA yield, (b) 4,4'-MDA and 2,2'-MDA yields, (c) OMDA yield, and (d) 4,4'-MDA/(2,2'-MDA + 2,4'-MDA) isomer ratio.

MDA) isomer ratio was at a high average of 5.5, the OMDA yield was only at a low 7%. At higher temperatures of 175 °C and 200 °C, ABAs were swiftly converted (Fig. 2a). The highest 4,4'-MDA and OMDA yields (Fig. 2b and c) were reached at 175 °C, but the increased 2,2'-MDA formation and decreased 4,4'-MDA/(2,2'-MDA + 2,4'-MDA) isomer ratio indicate that 175 °C may be suboptimal for this reaction. At 200 °C, the 4,4'-MDA yield was significant (36%) after 1 h, but it dropped over time, contrary to the positive trends observed at lower temperatures. Furthermore, both 2,4'-MDA and OMDA yields plateaued after 5 h. These trends suggest that the catalyst is more prone to deactivation at 200 °C, while also the higher 2,2'-MDA yield is undesired. The 4,4'-MDA/(2,2'-MDA + 2,4'-MDA) isomer ratio also dropped as the reaction proceeded at 175 °C and 200 °C, unlike the more stable ratio seen at

125 °C and 150 °C. In fact, after 24 h at 150 °C, the 2,2'-MDA yield remained low (<0.7%), the 4,4'-MDA and OMDA yields reached appreciable values of 41% and 17%, and the 4,4'-MDA/(2,2'-MDA + 2,4'-MDA) isomer ratio stayed at a satisfactory average of 4.1. Consequently, 150 °C was chosen as the reaction temperature for subsequent reactions. Similar effects of increased temperature, *e.g.* higher OMDA yields, and decreased 4,4'-MDA/(2,2'-MDA + 2,4'-M DA) isomer ratios, have been reported by others using zeolite catalysts [15,25].

To improve the catalytic activity, alternative supports were tested (Fig. 3). First, a magnesium aluminate spinel ($MgAl_2O_4$) was studied as a potential basic support [26]. However, no significant activity was observed with Hf on spinel, and not even the ABA intermediates were obtained after 1 h. This is likely due to the



Fig. 3. Product yields obtained in MDA synthesis using Hf loaded at 3 wt% on various supports; 150 °C, 5 wt% catalyst. 4,4'-MDA/(2,2'-MDA + 2,4'-MDA) isomer ratio indicated by the crosses (×).



Fig. 4. Yields of products obtained in MDA synthesis using Hf_{2.6}Zn_{0.5}/SiO₂, SiO₂·Al₂O₃, and Hf_{2.7}Zn_{0.5}/SiO₂·Al₂O₃. 1 wt% catalyst with respect to starting aminal solution, 150 °C. Isomer ratio indicated by the crosses (×).

Table 3

Initial rates of MDA formation using 1 wt% catalyst with respect to starting aminal solution (conditions same as in Fig. 4).

Catalyst	Initial rate of MDA formation $(mmol_{MDA}/g_{catalyst}/h)$
Hf _{2.6} Zn _{0.5} /SiO ₂	5.7
$SiO_2 \cdot Al_2O_3$	22
$Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$	153

basic behaviour of the spinel, suppressing the Lewis acidity. Similar results were obtained using hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$), which has more weakly basic properties [27]. With Hf_{3.0}/HAP as catalyst, the aminal conversion was incomplete, with an insignificant amount of MDA produced (<13%) even after 16 h. Next, two Lewis acidic metal oxides were tested, TiO₂ and ZrO₂ [28]. With TiO₂ as the support, a high isomer ratio was obtained after 5 h. However, the MDA yield was low even after 16 h (<17%). The results obtained over Hf_{3.0}/ZrO₂ were similar to those obtained with Hf_{3.0}/TiO₂, but with a lower 4,4'-MDA/ (2,2'-MDA + 2,4'-MDA) isomer ratio. However, a significant improvement was seen when supports with some Brønsted acid character such as alumina (Al₂O₃) and silica-alumina (SiO₂·Al₂O₃) were employed. Particularly silica-alumina produced a marked increase in the catalytic activity, with much higher MDA and OMDA yields obtained after just 1 h of reaction. Complete conversion was achieved as indicated by the absence of the ABA intermediates. Lastly, since zeolites like H-MCM-22 and H-Y showed promising activity (Section 3.1), they were also tested as supports. For Hf_{3.0}/MCM-22, this resulted in slightly higher ABA and OMDA contents, similar MDA yields, and a slightly higher 4,4'-MDA/(2,2' -MDA + 2,4'-MDA) isomer ratio, as opposed to values reached by the unloaded H-MCM-22 zeolite. For Hf_{3.0}/Y, all values were very similar to those obtained with the metal-free parent zeolite, suggesting that metal addition, at least in the case of Hf, does not change the catalytic behaviour of zeolite H-Y. Based on these results, silica-alumina appears to be the best potential support for the Lewis acid-catalysed synthesis of MDA.

Temperature variation for the $H_{f_2,7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$ catalyst showed similar trends as for $H_{f_2,6}Zn_{0.5}/SiO_2$, with the best 4,4'-MDA and OMDA yields obtained at 150 °C, together with a satisfactory high product isomer ratio (Fig. S8).



Fig. 5. NH₃-TPD profiles, normalised to the mass of sample (left) and difference IR spectra of adsorbed pyridine, normalised to 10 mg of sample/cm² (right) of (a) zeolite H-Y, Si/Al = 15, (b) Hf_{2.7}Zn_{0.5}/SiO₂·Al₂O₃, and (c) Hf_{2.6}Zn_{0.5}/SiO₂. Absorption bands corresponding to Brønsted (B) and Lewis (L) acid sites are marked.

Table 4

Acidity measurements of selected samples by $\rm NH_3\text{-}TPD$ and FTIR spectroscopy using pyridine as probe molecule.

Sample	NH3 desorbed ^a (mmol/g)	Acidity (µmol/g) ^b	
		Brønsted	Lewis
H-Y (Si/Al = 15)	0.43	200	57
Hf _{2.6} Zn _{0.5} /SiO ₂	0.16	n.d ^c	62
Hf _{2.7} Zn _{0.5} /SiO ₂ ·Al ₂ O ₃	0.46	22	62

^a Number of acid sites determined using NH₃-TPD.

^b Acidity determined by FTIR spectroscopy using pyridine as probe molecule after evacuation at 150 °C.

 $^{\rm c}\,$ Not detected, detection limit <2 $\mu mol/g.$

Table 5

Textural properties of fresh and spent zeolite H-Y (Si/Al = 15) and Hf_{2.7}Zn_{0.5}/SiO₂- Al_2O_3 determined by N₂ physisorption at -196 °C. Spent catalysts underwent a 24 h reaction.

Sample	S _{BET} (m ² /g) ^a	V _{micro} (cm ³ /g) ^b	V _{meso} (cm ³ /g) ^c
H-Y (Si/Al = 15)	870	0.262	0.27
H-Y (Si/Al = 15), spent, washed	61	0.011	0.12
Hf _{2.7} Zn _{0.5} /SiO ₂ ·Al ₂ O ₃	303	0.0086	0.94
Hf _{2.7} Zn _{0.5} /SiO ₂ ·Al ₂ O ₃ , spent, washed	226	negligible	0.68

 a BET p/p_0 range 0.001 – 0.07 for H-Y, 0.001 – 0.10 for washed H-Y, 0.001 – 0.20 for Hf_{2.7}Zn_{0.5}/SiO_2\cdot Al_2O_3, and 0.001 – 0.30 for spent Hf_{2.7}Zn_{0.5}/SiO_2\cdot Al_2O_3.

^b Micropore volume obtained using the *t*-plot method.

^c Mesopore volume estimated from BJH desorption.

To study in more detail the catalysts combining both Brønsted and Lewis acid sites, reactions were repeated with reduced catalyst amounts, and the results are presented as the initial rates of MDA formation (Fig. 4 and Table 3). The $Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$ catalyst produces MDA at a rate which is significantly higher than that of the individual $Hf_{2.6}Zn_{0.5}/SiO_2$ or $SiO_2 \cdot Al_2O_3$ catalysts. Moreover, the rate with $Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$ is also much higher than the sum of the rates obtained with the Lewis acidic $Hf_{2.6}Zn_{0.5}/SiO_2$ and with the Brønsted acidic $SiO_2 \cdot Al_2O_3$. Evidently, the combined presence of Brønsted acidity provided by the silica-alumina support, and of Lewis acidity provided by Hf is beneficial for creating an active catalyst for MDA synthesis.

3.3. Relation of catalytic activity with acidity characteristics and mechanistic implications

Two materials were selected for detailed characterisation, *viz.* $Hf_{2.6}Zn_{0.5}/SiO_2$ and $Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$. FTIR monitoring of adsorbed pyridine probe molecules shows that $Hf_{2.6}Zn_{0.5}/SiO_2$ indeed exclusively contains Lewis acid sites (Fig. 5, right; Table 4) [24]. In the NH₃-TPD profile (Fig. 5, left), this corresponds to a desorption of ammonia at rather low temperatures. In contrast, both Lewis and Brønsted acid sites are found on the $Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2 - O_3$ catalyst. Comparison of the latter material with H-Y in the NH₃-TPD data (Fig. 5, left) proves that $Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$ contains a larger number of weakly acid Brønsted sites than H-Y.

The activity of the purely Lewis acidic Hf_{2.6}Zn_{0.5}/SiO₂ for MDA formation is unusual, considering that the search for solid alternatives for HCl in MDA formation has strongly focused on Brønsted acid zeolites [10–15]. Clearly, Lewis acids are also capable of catalysing the rearrangement of the ABA intermediates to MDA. Such rearrangements, bringing an alkyl substituent from the N-atom of an aniline to the aromatic ring, are known as Hofmann-Martius rearrangements [10]. Notably, using $N-\alpha$ -phenethylaniline as a reactant, it has been shown that not only HCl, but also ZnCl₂ can effectively promote the rearrangement to ortho- and *para-* α -phenethylaniline. In fact, higher *para*-selectivities were even observed with ZnCl₂ than with HCl. Based on the mechanism by Hart and Kosak [29], a proposal for the mechanism of ABA rearrangement on the Hf Lewis acid sites in Hf_{2.6}Zn_{0.5}/SiO₂ is shown in Scheme 2. The first step is coordination of the ABA reactant on the Lewis acid site (I in Scheme 2), followed by formation of a wellstabilised benzylic carbenium ion, together with a Hf-coordinated anilide (II). Subsequently, an electrophilic aromatic substitution takes place to form complex **IV**. Aniline-TPD data is used to prove that Hf_{2.6}Zn_{0.5}/SiO₂ is capable of activating anilines, e.g. complex I in Scheme 2 (Fig. 6). The profile for $Hf_{2.6}Zn_{0.5}/SiO_2$ shows the same fast desorption of weakly physisorbed aniline as the SiO₂ support, but additionally, a distinct desorption of aniline is seen between



Scheme 2. Proposed mechanism for the formation of MDA from *p*-ABA, using a catalyst with Hf-centred Lewis acidity.



Fig. 6. Temperature programmed desorption of aniline for $Hf_{2,6}Zn_{0.5}/SiO_2$, $Hf_{2,7}-Zn_{0.5}/SiO_2$, Al_2O_3 , SiO_2 , SiO_2 , Al_2O_3 , and zeolite H–Y, investigated by monitoring the m/z value of 93 (corresponding to aniline, $C_6H_5NH_2$). MS peak intensity normalised to the sample mass.

150 and 300 $^{\circ}$ C, evidencing the interaction of anilines with the Lewis acid sites.

The mechanism as proposed in Scheme 2 also suggests how the additional presence of Brønsted acid sites could be beneficial for the strongly increased activity of $Hf_{2.7}Zn_{0.5}/SiO_2\cdot Al_2O_3$. Indeed, the desorption of the ring-alkylated product requires a reprotonation of intermediates **IV/V**, and the availability of mild proton acidity can enhance this step, leading to the formation of MDA and regeneration of the LAS.

3.4. Catalyst recycling and stability

The stability and reusability of selected samples were then investigated by recycling tests (Fig. 7). The product yields were obtained without intermediate regeneration of the catalyst after each cycle. Using zeolite H-Y, the catalytic activity plummeted after just one 24 h cycle; also the high isomer ratio obtained in the first run was lost in following runs. This is due to the microporous nature of the zeolite, together with the strong adsorption of the weakly basic $-NH_2$ groups on the strong acid sites of the zeolite. Physicochemical proof for the strong binding of anilines on H-Y was already provided by the aniline-TPD experiments in Fig. 6. Pore blocking is the major factor contributing to zeolite deactivation, as proven by the physisorption measurements of Fig. 8 and Table 5: the N₂ isotherm shows that the microporosity is largely lost, with a reduction of the micropore volume from 0.262 cm³/g to 0.011 cm³/g after reaction.

In contrast with zeolite H–Y, Hf_{2.6}Zn_{0.5}/SiO₂ was significantly more stable in consecutive runs (Fig. 7). Despite a gradual drop in catalytic activity after each run, the extent of deactivation was far less significant; the isomer ratio hovered around 4.2 during all five runs. Catalyst stability and recyclability were further improved when the silica support was replaced by silica-alumina (sample Hf_{2.7}Zn_{0.5}/SiO₂·Al₂O₃) (Fig. 7). The initial activity was maintained for five cycles and the isomer ratio remained around 3.4 throughout all five cycles. Complete conversion was obtained and the OMDA fraction remained high (around 20%) in all cycles. The isotherm and mesopore volume derived from N₂ physisorption of a solvent-washed, spent Hf_{2.7}Zn_{0.5}/SiO₂·Al₂O₃ catalyst after one 24 h reaction showed retention of the porosity, suggesting that the mesoporous sample was less prone to catalyst deactivation (Fig. 8, Table 5). Notably, in the aniline-TPD profile recorded for $Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$, the desorption occurs at the highest rates between 150 and 260 °C. This temperature range is much lower than that observed for H-Y, which displays maxima in the desorption profile at 220 and 390 °C (Fig. 6). Thus, in comparison with H-Y, both the larger pore diameters and the weaker interaction with anilines contribute to the lower susceptibility of Hf_{2.7}Zn_{0.5}/SiO₂-·Al₂O₃ to deactivation.

Finally, the metal contents of fresh and spent $Hf_{2.6}Zn_{0.5}/SiO_2$ and $Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$ catalysts were compared by ICP-OES. The metal contents were unchanged after a 48 h reaction, implying that there is no undesired metal leaching. For the most active catalyst, *viz*. $Hf_{2.7}Zn_{0.5}/SiO_2 \cdot Al_2O_3$, EDXS elemental maps were recorded, both on a fresh and a spent catalyst. These maps showed homogeneous dispersions of Hf and Zn on the silica–alumina support. After 24 h of reaction at 150 °C and subsequent calcination at 500 °C, the two metals remained in close contact with each other and also with the support, without apparent aggregation of metal particles. This stable dispersion is believed to contribute to the stability of this catalyst (Fig. 9).



Fig. 7. Catalyst recycling experiments for acid-catalysed MDA synthesis at 150 °C (24 h reaction time).



Fig. 8. Nitrogen physisorption isotherms of (left) zeolite H–Y (Si/Al = 15) (\blacksquare/\square), spent H–Y (Si/Al = 15) (\blacktriangle/\triangle), (right) Hf_{2.7}Zn_{0.5}/SiO₂·Al₂O₃ (\bullet/\bigcirc), spent Hf_{2.7}Zn_{0.5}/SiO₂·Al₂O₃ (\bullet/\bigcirc).



Fig. 9. HAADF–STEM image (a) and EDXS maps (b), (c), (d) of Hf_{2.7}Zn_{0.5}/SiO₂·Al₂O₃. HAADF–STEM image (e) and EDXS maps (f), (g), (h) of calcined, spent Hf_{2.7}Zn_{0.5}/SiO₂·Al₂O₃ after 24 h reaction of MDA synthesis at 150 °C. Green spots are Hf and blue spots are Zn. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

In the search for a viable heterogeneous alternative to hydrochloric acid in the industrial synthesis of MDA, various Lewis acid catalysts were tested. Among others, catalysts containing Hf on silica display satisfactory activity. Addition of a small amount of Zn to Hf resulted in a catalyst with exclusively Lewis acid sites, proving that purely Lewis acidic materials also catalyse MDA formation. Rates were strongly increased when SiO₂ as a support was replaced by SiO₂.Al₂O₃. Catalyst stability tests showed that the Hf, Zn on silica-alumina catalyst could be used in five consecutive runs without any significant drop in performance, while an H-Y zeolite readily loses its activity under identical reaction conditions. Both the mesoporosity and the moderately strong acidity of Hf, Zn on silica-alumina contribute to its resistance to deactivation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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