Towards a Sustainable Manufacture of Hierarchical Zeolites

Journal Article

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Hierarchical zeolites have been established as a superior type of aluminosilicate catalysts compared to their conventional (purely microporous) counterparts. An impressive array of bottom-up and top-down approaches has been developed during the last decade to design and subsequently catalytically exploit these exciting materials. However, the sustainability of the developed synthetic methods has rarely been addressed. This paper highlights important criteria to ensure the ecologic and economic viability of the manufacture of hierarchical zeolites. Moreover, using base leaching as a promising case study, we verify a variety of approaches to increase reactor productivity, recycle waste streams, prevent the combustion of hydrocarbons, and minimize separation efforts. By reducing their synthetic footprint, we aim to position hierarchical zeolites as an integral part of sustainable chemistry.

Introduction

The development of novel heterogeneous catalysts represents a field of tremendous impact, rendering existing conversions more efficient and enabling unprecedented transformations.[1,2] An important driving force in the design of these catalysts is the ability to produce targeted chemicals in a more sustainable fashion, for example by making use of renewable feedstocks[3,4] and greener solvents.[5] However, besides the ecologic impact of a particular catalytic conversion, the sustainability of the employed catalyst should be considered as well (**Figure 1a**).[6] State-of-the-art catalysts should ideally attain a superior performance, while comprising non-toxic earth-abundant elements[7-9] and being prepared in an affordable, energy-efficient, safe, and scalable fashion.[6]

Zeolites are a class of crystalline microporous aluminosilicate catalysts of paramount industrial importance and have been synthesized commercially for several decades. Zeolites have become the catalyst of choice in many (petro)chemical conversions like cracking, alkylation, and isomerization, due to their high surface area, high hydrothermal stability, strong acidity, and shape-selective behavior.[10-12] Nevertheless, the preparation of zeolites is not a very ecologically friendly process. The latter is mostly due to that, in addition to bulk chemicals as NaOH, silica, and alumina, often organic templates (known as structure-directing agents, SDAs) are required to yield the desired framework topology. SDAs, typically in the form of tetraalkylammonium cations (TAAs) or amines, cannot be recycled as they need to be removed thermally, forming CO_2 and hazardous nitrous oxides.[13-15]

Surprisingly, although the micropores give rise to the above-mentioned exceptional features, they can also render the zeolite's active sites sub-optimally exploited in catalyzed reactions. The latter is implied by the stringent access and diffusion limitations that many molecules experience due to the (limited) size of the micropores (0.3-1 nm). In addition, the low external surface of the zeolite crystals renders them prone to deactivation, due to blocking of the micropores
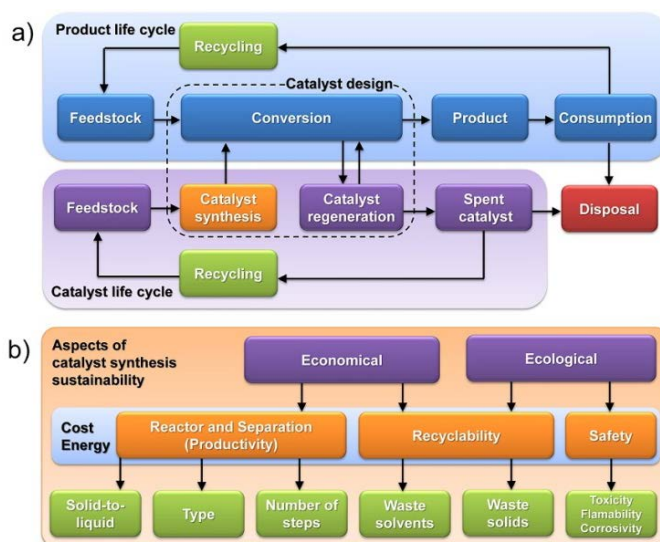

Figure 1. (a) The focus in catalysts design (dashed box) is often placed on the product life cycle (top), while the catalysts life cycle (bottom) represents an integral part of sustainable chemistry. In the product and the catalyst life cycle, preferably non-toxic renewable feedstocks are used, that can be recycled at the end of their lifetime. (b) Aspects that govern the sustainability of catalysts manufacture. In this contribution, the opportunities regarding the green themes are addressed to make the manufacture of hierarchical zeolite catalysts more ecologically and ecologically attractive. Cost and energy concerns represent general underlying aspects.

by coke deposition. To address this complication, the class of hierarchical zeolites was developed, coupling a secondary network of mesopores to the intrinsic micropores, aimed at reducing access and diffusion limitations.[16-20] Hierarchical zeolites have yielded strongly enhanced catalytic performances in numerous established[21,22] and emerging applications, such as biomass conversions.[23-25]

Nowadays, a wide variety of bottom-up and top-down synthesis routes are available to prepare hierarchically-structured zeolites.[16-20] While bottom-up approaches require adjustment of the hydrothermal synthesis protocol, top-down approaches involve post-synthetic modifications of conventional zeolite crystals. Although being superior catalysts, the sustainability of hierarchical zeolites can be considered inferior to that of conventional zeolites. For example, bottom-up

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Table 1. Properties of ZSM-5 zeolites prepared by base treatment.

Sample[a]	[Zeolite] [g L^{-1}]	[NaOH] [M]	Yield[b] [%]	Si/Al[c] [mol mol^{-1}]	Crystallinity[d] [%]	V_{micro}[e] [cm^3 g^{-1}]	V_{pore}[f] [cm^3 g^{-1}]	S_{meso}[e] [m^2 g^{-1}]
Z40-P	-	-	-	-	-	0.21	0.27	30
Z40-B1	33	0.2	63	-	-	0.12	0.53	262
Z40-B1+NaCl	33	0.2	58	-	-	0.14	0.60	323
Z40-B2	300	1.8	46	-	-	0.13	0.81	247
Z40-B3	300	1.0	71	-	-	0.14	0.37	186
Z40-(Z15-B1f)	33	n.d.[g]	43	-	-	0.09	0.85	313
Z15-P	-	-	-	14.1	100	0.15	0.23	52
Z15-B4	33	0.6	67	10.3	73	0.16	0.45	138
Z15-B4+NaCl	33	0.6	43	5.4	30	0.13	0.78	262
Z15-B4-A1	33	0.6	90	14.5	45	0.15	0.45	257
Z15-B5	300	5.4	0	-	-	-	-	-
Z15-B6	300	1.8	67	-	-	0.12	0.38	134

[a] Base (suffix '-B*x*') and acid (suffix '-A*x*') treatments were performed on conventional ZSM-5 zeolites with Si/Al = 40 (Z40-P) or Si/Al = 15 (Z15-P). The '*x*' represents integers for further specification. In the case 1 M NaCl was included in the alkaline solution, the suffix '+NaCl' was used. Reference to filtrates is made by adding the letter 'f' to the sample code. Treatments performed using the filtrates are labeled using the zeolite code followed by the code of the applied filtrate between brackets. [b] Solid yield after treatment. [c] ICP-OES. [d] XRD. [e] *t*-plot method. [f] N$_2$ volume adsorbed at p/p_0 = 0.99. [g] Not determined.

approaches make use of exotic ingredients, like germanium,[26] or feature even larger amounts of hydrocarbon templates compared to their purely-microporous counterparts.[27,28] Other bottom-up protocols are less attractive due to low yields and/or poorly filterable materials, like in the case of nano-sized crystals.[19,29,30] Top-down methods have received critique as they often imply a leaching (hence loss) of costly zeolite, like in the case of desilication,[31] and give rise to additional wastewater streams. However, while for conventional zeolites[15] and other types of catalysts[6] substantial efforts are directed towards rendering the synthetic pathways more environmentally attractive, the sustainability of hierarchical zeolites has remained systematically neglected.

We herein address the need for a more sustainable manufacture of hierarchical zeolites. We discuss aspects to drive catalyst synthesis to a more industrially-relevant and ecological modus operandi, and substantiate these opportunities in a case study on post-synthetic modification. Using a holistic experimental strategy covering various distinct areas (**Figure 1b**), it is demonstrated how to (i) recycle leached species, organics, and wastewater streams, (ii) increase reactor productivity, and (iii) minimize separation efforts. The presented experimental examples are focused on base leaching, or desilication, as it represents a highly versatile and tunable pathway,[31] that can be easily extrapolated to an industrial context.[32] Our results emphasize the bright prospects of hierarchical zeolites manufactured by post-synthetic design, and contribute to extrapolating the

sustainability concept from chemical conversion to the manufacture of novel catalysts.

Results and Discussion

In order to keep our contribution concise, the physico-chemical properties of the synthesized samples are described only briefly. The principle features of the hierarchical zeolites are the developed external surface area (S_{meso}) and the preserved of the intrinsic zeolitic properties, *i.e.* the crystallinity and the microporosity (V_{micro}). In addition, some structural, morphological, and elemental analyses are provided.

Reducing Wastewater by Increased Zeolite Content

Low reactor productivity is often encountered in the preparation of hierarchical zeolites. Typical syntheses of commercial zeolites are performed batch-wise and yield about 100-250 g of solid product per liter of reagents.[13,33] In the case of nanocrystals, yields can be substantially lower due to a more dilute synthesis gel[34] or an incomplete conversion of the alumina and (predominately) silica precursors to the crystalline phase.[35] In the case of desilication, low productivity is common as typically 33 g of zeolite per liter of alkaline media (typically 0.2 M NaOH) is used, yielding about 23 g L^{-1} of hierarchical zeolite.[31] Nevertheless, Groen *et al.*[36] proved that the zeolite content can be increased by a factor of 4, assuming that the base concentration is concurrently increased by a

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factor of 4 (to 0.8 M NaOH). However, this was studied for only a single zeolite (ZSM-5, Si/Al = 25), leaving it unclear if the obtained linear extrapolation holds for different hierarchical zeolites prepared using a variation of conditions.

In order to get more insights in the influence of the zeolite content, we performed the desilication of ZSM-5 with Si/Al = 40 using the typical 33 g of zeolite per liter (Z40-B1) and a zeolite content of 300 g L^{-1} and corresponding alkalinity of 1.8 M NaOH (Z40-B2, **Table 1**). The resulting samples possess the typical isotherms of mesoporous zeolites (**Figure 2a**). Nevertheless, in the case of Z40-B2, the leaching proved more severe judging by the lower yield, larger pore volume and larger mesopore size. The latter was tuned by lowering the alkalinity to 1.0 M NaOH (Z40-B3). Using standard conditions (65°C, 30 min, 33 g L^{-1}), the more aluminum-rich ZSM-5 with Si/Al = 15 demonstrated more resistant to alkaline leaching and required an enhanced alkalinity (0.6 M NaOH) to introduce mesoporosity (Z15-B4).[37] The treatment performed at 300 g L^{-1} (Z15-B5), involving a 5.4 M solution of NaOH, resulted in a complete dissolution. The latter result, like for sample Z40-B2, demonstrates that upon increasing the alkalinity linearly with the zeolite content, the dissolution increases. To reduce the degree of dissolution the concentration of NaOH was reduced to 1.8 M (Z15-B6). This treatment resulted into a yield (67%) and a mesopore surface area similar to the Z15-B4 (134 m^2 g^{-1}).

While for ZSM-5 the use of NaOH suffices to desilicate, all-silica zeolites and fragile zeolites, e.g. USY and beta, may require additional hydrocarbon additives, e.g. tetrapropylammonium (TPA$^+$) cations and amines, to ensure an efficient mesopore formation, working as organic 'pore-directing agents' (PDAs).[31,38] The latter pose a complication as the applied concentration of TAAs in the dilute (33 g L^{-1}) system is already relatively high, e.g. 0.2 M.[38] Hence a 9-fold increase of the TAA concentration in line with the enhanced zeolite content is unpractical. In addition, in the case of micelle-forming forming TAAs, e.g. cetyltrimethylammonium (CTA$^+$), a higher concentration may result into lower crystalline structures based on a more pronounced secondary synthesis of (ordered) amorphous silicates.[38,39] Accordingly, in order to increase the zeolite content in the preparation of a USY zeolite with Si/Al = 30 (USY30), diethylamine (DEA) was selected as pore-directing agent.[38] DEA, a common SDA, can be easily applied at higher concentrations. As in the case of Z15, the increased zeolite content and NaOH concentration (USY30-B8) led to enhanced dissolution compared alkaline treatment using 33 g L^{-1} of zeolite (USY30-B7). This enhanced dissolution was adjusted by reducing the NaOH concentration to 0.6 M (USY30-B9). Both USY30-B8 and USY30-B9 displayed impressive external surface areas (**Table 2**). However, as can be judged by the reduced micropore volumes, the USY30 zeolites partially lost their intrinsic zeolitic properties upon increasing the NaOH concentration. Still, these results show that hierarchical zeolites of distinct composition and framework types can be prepared using zeolite contents of up to 300 g L^{-1}. This relates to an order-magnitude increase in reactor productivity compared to the typical desilication.

Recycling of Waste Aluminosilicates

An inherent aspect of the post-synthetic modification of zeolite crystals by acid or base leaching is the transfer of crystalline matter from the solid to the liquid phase. In a sustainable
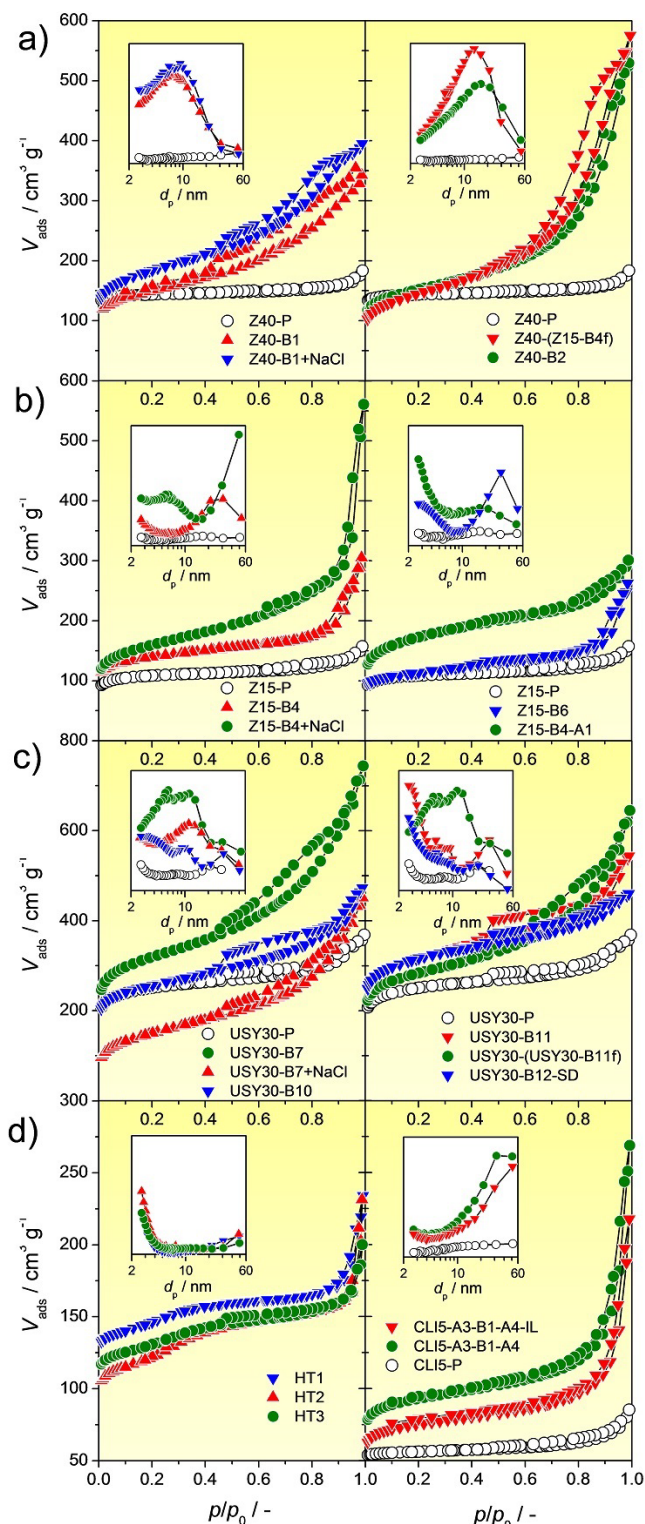

Figure 2. N$_2$ isotherms of conventional and hierarchical zeolites. Insets: BJH mesopore size distributions. Sample CLI5-P is shifted upward by 50 cm^3 g^{-1}.

process, these leached species are recycled. It is well known that filtrates obtained by desilication of zeolites can be used to synthesize pure amorphous ordered mesoporous materials (OMMs) by using micelle-forming compounds like CTA$^+$.[40] In addition, the use of CTA$^+$ as PDA during desilication enables, besides yielding a mesoporous zeolite, to restructure leached species into an amorphous MCM-41-type material yielding hierarchical zeolite/OMM composites.[39,41] The latter type of

Table 2. Properties of faujasite zeolites prepared by base treatment.

Sample[a]	[Zeolite] [g L^{-1}]	[NaOH] [M]	[DEA] [M]	[TPA$^+$] [M]	Yield[b] [%]	V_{micro}[c] [cm^3 g^{-1}]	V_{pore}[d] [cm^3 g^{-1}]	S_{meso}[c] [m^2 g^{-1}]
Y2.5-P	-	-	-	-	-	0.27	0.30	28
Y2.5-A2-B14	33	0.30	0	0	71	0.19	0.39	224
USY30-P	-	-	-	-	-	0.31	0.55	171
USY30-B7	33	0.1	0.2	0	60	0.30	1.10	449
USY30-B7+NaCl	33	0.1	0.2	0	47	0.07	0.67	367
USY30-B8	300	0.9	1.8	0	45	0.15	0.92	369
USY30-B9	300	0.6	1.8	0	56	0.18	0.87	407
USY30-B10	33	0	0.4	0	73	0.26	0.72	315
USY30-B11	150	0	3.6	0	80	0.30	0.83	420
USY30-B12	83	0	0	0.1[e]	73	0.32	0.68	284
USY30-B13	33	0.2	0	0.2[f]	56	0.26	1.08	424
USY30-(USY30-B11f)	33	0	n.d.[g]	0	58	0.28	0.96	356
USY30-(HT2f)	33	n.d.	0	n.d.	86	0.28	0.60	272

[a] Base (suffix '-B*x*') and acid (suffix '-A*x*') treatments were performed on conventional faujasite zeolites with Si/Al = 2.5 (Y2.5-P) and Si/Al = 30 (USY30-P). 'HT*x*' refers to hydrothermal syntheses. The '*x*' represents integers for further specification. In the case 1 M NaCl was included in the alkaline solution, the suffix '+NaCl' was used. Reference to filtrates is made by adding the letter 'f' to the sample code. Treatments performed using the filtrates are labeled using the zeolite code followed by the code of the applied filtrate between brackets. [b] Solid yield after treatment. [c] *t*-plot method. [d] N$_2$ volume adsorbed at p/p_0 = 0.99. [e] Using TPAOH. [f] Using TPABr. [g] Not determined.

material can feature impressive porous properties. However, as was recently demonstrated on a case study on USY, the presence of a secondary OMM phase originates a reduction of the zeolite features, as crystallinity and acidity, which leads to a deterioration of the catalytic performance.[39]

A large disadvantage associated with the synthesis of nanosized zeolites is the incomplete conversion of aluminosilicate precursor to the desired zeolite crystals. These waste streams could be partially recycled by secondary and even tertiary syntheses with the waste precursor gel, hereby yielding additional nanosized zeolites.[42] However, this approach is less attractive as it involves additional hydrothermal and filtration steps. During desilication, the recrystallization of leached zeolites does not to occur due to the mild conditions (65°C and 30 min) and low concentration of Si species (10 g L^{-1}).[39] Nevertheless, the recrystallization of dissolved zeolite crystals was reported to occur after premade zeolites are exposed to alkaline solutions under hydrothermal conditions in the presence of SDAs.[43]. Still, the synthesis of zeolites using purely dissolved zeolite as precursor has not been demonstrated. Advantageously, when a zeolite content of 300 g L^{-1} is used during desilication, a one-third dissolution originates an alkaline stream containing *ca.* 100 g L^{-1} of soluble silica species, *i.e.* making it prone to zeolite crystallization. Using such filtrate (Z40-B3f), we hydrothermally crystallized silicalite-1 (HT1, **Table 3**). As expected,[44] the yields increased

as the pH of the filtrate was lowered prior to hydrothermal synthesis (pH$_B$, see samples HT2 and HT3). After calcination, the samples displayed the XRD pattern (**Figure 3a**) and porosity (**Figure 2d**) typical of high-silica MFI zeolites. Similarly, TEM revealed coffin-shaped crystals typical to silicalite-1 zeolites (**Figure 4**). Hence, the filtrates derived from the preparation of hierarchical zeolites by desilication are can be readily recycled to synthesize additional (conventional) zeolites.

Table 3. Properties of silicalite-1 zeolites prepared by hydrothermal treatment (code 'HT*x*') using the filtrate from treatment Z40-B3.

Sample	pH$_B$[a] [-]	pH$_A$[a] [-]	Yield[b] [%]	V_{micro}[c] [cm^3 g^{-1}]	V_{pore}[d] [cm^3 g^{-1}]	S_{meso}[c] [m^2 g^{-1}]
HT1	11.3	11.8	24	0.18	0.34	108
HT2	10.5	11.6	33	0.13	0.31	129
HT3	9	10.5	58	0.16	0.31	105

[a] pH of the liquid before (pH$_B$) and after (pH$_A$) hydrothermal synthesis. [b] Solid yield after treatment based on an initial silica content of 87 g L^{-1}. [c] *t*-plot method. [d] N$_2$ volume adsorbed at p/p_0 = 0.99.
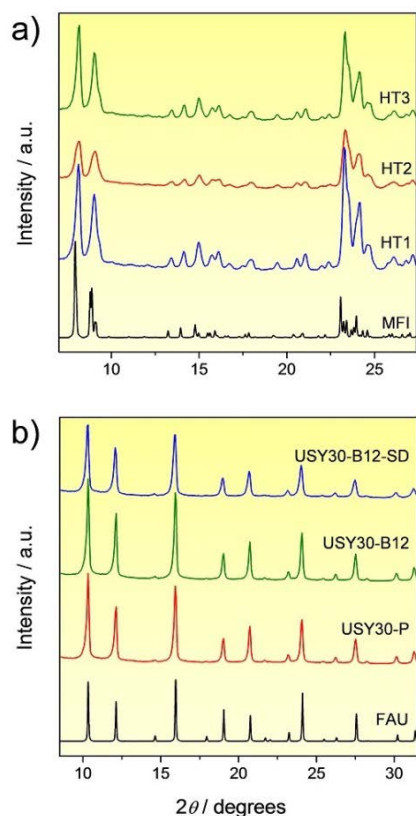
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Figure 3. X-ray diffraction patterns of (a) silicalite-1 and (b) USY30 zeolites. 'MFI' and 'FAU' indicate the theoretical XRD patterns of the MFI and faujasite framework, respectively.[45]

Recycling of Wastewater

A clear opportunity in the synthesis of hierarchical zeolites, independent of the synthetic pathway, is the recycling of waste streams (with *and* without aluminosilicates). As shown in the previous section, a Si-rich filtrate derived from desilication can be used to synthesize zeolites. However, even if zeolite synthesis is not feasible, it remains highly relevant to recycle the waste stream. For example, in the case the silica-content is rather low, one could reuse an alkaline stream to perform (another) base treatment. The principle difference between the latter treatment and a conventional desilication is the enhanced presence of salts, *e.g.* sodium bromide or sodium chloride. This is highly relevant as salts enhance the dissolution of silica in alkaline media.[46] Similarly, the presence of soluble silicates can enhance the base leaching of zeolites.[47] To gain a better insight in the recyclability of the alkaline streams, we have studied the influence of the addition of 1 M NaCl on the desilication of Z40 (sample Z40-B1+NaCl) and Z15 (sample Z15-B4+NaCl, **Table 1**). Indeed, the presence of NaCl enhances the dissolution of the zeolite in alkaline media. For Z40, the addition of salt reduced the solid yield from 63% to 58%, while for Z15 the influence was more pronounced, reducing the yield from 67% to 43%. Additionally, while the porosity of Z40-B1+NaCl was similar to Z40-B1, the treated Z15 sample (Z15-B4+NaCl) displayed a strongly enhanced pore volume and mesoporosity compared to Z15-B4 (**Figure 2).** The latter observations are attributed to a reduced alkaline-induced realumination of the surface, enabling a more
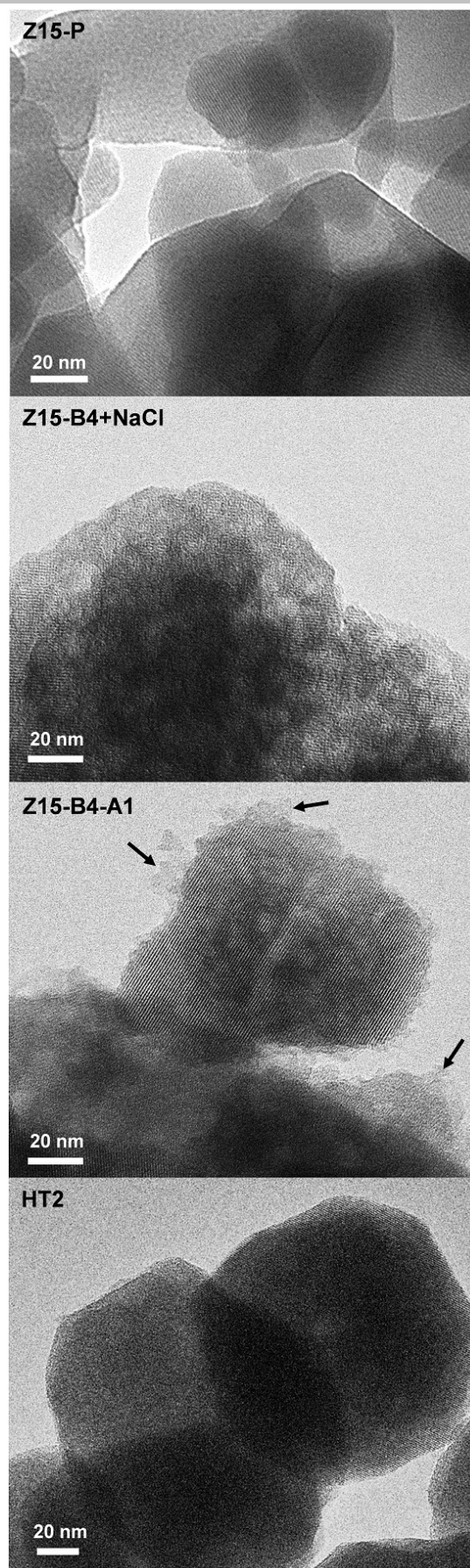

Figure 4. Transmission electron micrographs of selected MFI zeolites. The arrows indicate the amorphous species in sample Z15-B4-A1.

extended dissolution of the zeolite. These results shed new fundamental light on the alkaline dissolution process of Al-containing zeolites. They suggest that the reason why aluminum-rich ZSM-5 zeolites (*e.g.* Z15) require higher NaOH concentrations to dissolve,[37] is not strictly because of the higher pH, but also because of the higher salinity. This concomitantly explains the enhanced dissolution degrees at higher zeolite contents (samples Z15-B6 and Z40-B2).

For the more fragile USY zeolite, amorphizing in aqueous solutions containing only NaOH,[38] the presence of 1 M NaCl has a dramatic influence (**Table 2**). Like for Z40, the yield of sample USY30-B7+NaCl decreased slightly compared to USY30-B7. However, a substantial amorphization occurred, judging by the 70% drop in microporosity (see USY30-B7+NaCl, **Figure 2c**). This result explains why the zeolites treated at higher zeolite contents (USY30-B8 and USY30-B9) displayed lower micropore volumes compared to USY30-B7. Moreover, this implies that highly-crystalline USY zeolites should be preferentially prepared in the absence of mineral salts, *e.g.* using organic bases like TPAOH instead of NaOH. The use of such organic hydroxides as base in desilication was reported,[48] but these can be costly and unpractical. However, amines, like diethylamine, have thus far not been demonstrated effective as base for desilication. To investigate this option, we treated USY30-P in a solution containing only diethylamine (USY30-B10). This Na+-free treatment resulted in substantial dissolution, and a solid comprising substantial meso- and microporosity (**Figure 2c**). The successful implementation of amines as a base facilitates the execution of a base treatment of USY30 at a high zeolite content, without comprising the zeolitic properties of the resulting solid. Subsequently, a high-quality hierarchical zeolite was obtained after increasing the zeolite content to 150 g L^{-1} (USY30-B11). Naturally, as demonstrated below, the applied organic PDAs are ideally recycled.

The close interplay between the salinity, pH, and the zeolite content facilitates the recycling of alkaline waste streams tremendously. For example, one could measure the pH and salinity of a particular stream, and tailor the zeolite content in the subsequent desilication to obtain a hierarchical zeolite of the desired properties. To highlight the versatility of this concept, several treatments were executed, recycling streams derived from treatments of distinct zeolite frameworks, zeolite contents, and type of synthesis (desilication *versus* hydrothermal). For instance, we successfully prepared highly mesoporous Z40 by using the filtrate of Z15-B4, yielding sample Z40-(Z15-B4f). Alternatively, hierarchical USY30 was prepared using the filtrate of USY30-B11, yielding sample USY30-(USY30-B11f). Moreover, a dual recycling was demonstrated feasible by treating USY30 in the filtrate of HT2, yielding sample USY30-(HT2f) (**Figure 5**). This was facilitated by the increase in pH occurring during hydrothermal synthesis (going from 10.5 to 11.6, **Table 3**). By recycling the filtrates, the wastewater derived from preparation of the samples in **Figure 5** was reduced by a factor of three. Together with the 9-fold enhanced zeolite content in preparing sample Z40-B3, this relates to an overall 11-fold reduction in wastewater. Hence, the latter example, including 2 alkaline treatments and 1 hydrothermal synthesis, emphasizes the great recyclability of waste streams originating from alkaline treatments.
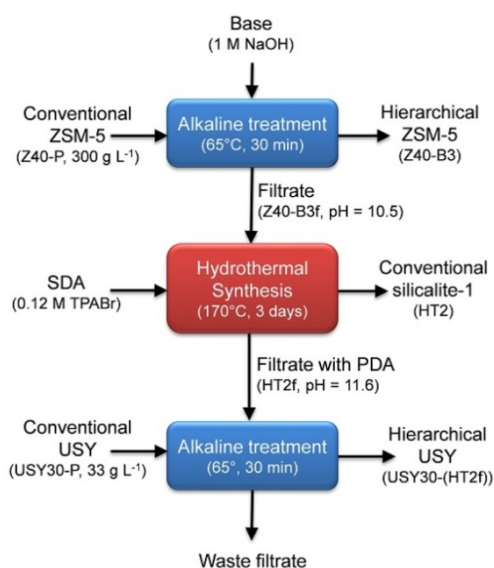

Figure 5. Flow chart and experimental details (in brackets) demonstrating how the strategic combination of 2 conventional zeolites (ZSM-5 and USY) and 2 chemicals (NaOH and TPABr) gives rise to the synthesis of hierarchical ZSM-5, hierarchical USY, and conventional silicalite-1. By recycling the filtrates two times, only one waste stream is generated.

Since filtrates from hydrothermal treatments can be used to desilicate, and filtrates derived desilication are suitable for hydrothermal synthesis, a conceptual low-waste stream flow chart of the manufacture of hierarchical silicalite-1 was devised (**Figure 6**). This process represents a particularly attractive example as the involved TPA+ functions as SDA and PDA. Moreover, the absence of cations omits the need for ion exchange.

Minimizing Separation Efforts

One of the most challenging unit operations in the preparation of zeolite catalysts is their separation from aqueous solutions. The ease of separation relies strongly on the crystal size. Very small crystals should be avoided due to the need for centrifugal filtration and redispersion in ultrasonic baths.[34] Similarly, the number of preparative steps to prepare the (hierarchical) zeolites is of importance. For example, in the preparation of hierarchical clinoptilolite using acid and base treatments, a sequence of up to 6 steps was reported.[49] Some options to reduce the number of steps in the post-synthetic modifications of zeolites were explored. For instance, it is well known that, besides the introduction of a secondary pore network, alkaline treatment of zeolites in aqueous NaOH leads to the ion-exchange of the extra-framework cations to the sodium-form. This implies that an additional subsequent ion-exchange step is required to convert the zeolite to its active protonic form. The latter step could be avoided by using a sodium-free system, involving an organic base instead of NaOH. The latter was demonstrated in the hydrothermal base leaching of zeolite beta.[50]

In many cases, the desilication procedure is combined with an antecedent framework dealumination, and/or a subsequent acid wash.[49] The framework dealumination is performed to enable subsequent alkaline dissolution, while the acid wash is performed to removal Al-debris formed during

desilication of aluminum-rich zeolites like Z15.[37] Since the presence of salt does not necessarily impede the efficiency of desilication (*vide supra*) we performed different sequences without filtration in between. The latter was achieved by adjusting the pH by either adding concentrated aqueous NaOH or HCl directly to the suspension after the first treatment. For example, zeolite Y2.5 (Si/Al = 2.5) requires an acid treatment in H$_4$EDTA, followed by alkaline treatment in NaOH to obtain its hierarchical analogue.[51] After application of the above-mentioned dealumination, an alkaline solution was added to the suspension, yielding sample Y2.5-A2-B14. The solid yield of the two treatments (71%) was similar to the conventional method. Moreover, the almost 10-fold increase in the meso-pore surface renders the desilication treatment very successful (**Table 2**). The acid wash, performed directly after alkaline
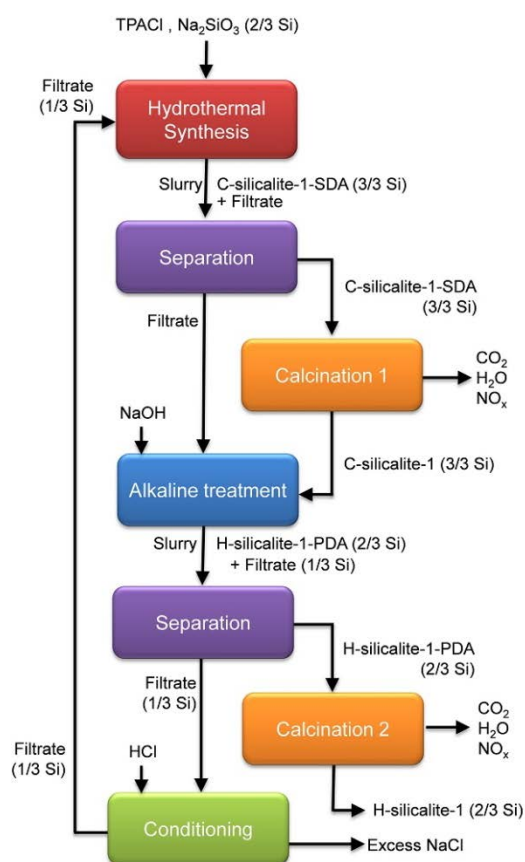

Figure 6. Flow chart of the synthesis of hierarchical silicalite-1, with the fractional silicon economy given in brackets. The hydrothermal synthesis (red) of the conventional (C) silicalite-1 is achieved by recycling the waste stream of a previous alkaline treatment (blue), containing one-third of the required silicon and remaining TPA$^+$. In order to condition this filtrate for the hydrothermal synthesis, the pH may need to be lowered (using HCl) and excess salt removed (NaCl). The filtrate is complemented with two-thirds of fresh silicon source (NaSiO$_3$) and additional structure-directing agent (SDA, in the form of TPACl). After separation, the zeolite is detemplated (Calcination 1), followed by desilication using the filtrate derived from the hydrothermal synthesis (pH adjusted with NaOH) using the remaining TPA$^+$ molecules as pore-directing agents (PDAs). After the alkaline treatment, the PDAs attached to the zeolite are removed (Calcination 2) to yield the hierarchical silicalite-1. The occluded SDA should be considered lost due to their combustion upon removal (Calcination 1). Conversely, the more easily-removed PDA (Calcination 2) may be subject to recycling (*vide infra*).

treatment of Z15 by addition of concentrated HCl, proved more complicated. The sample Z15-B4-A1 was obtained at a yield of 90% and displayed a high mesoporosity. Since the base treatment alone (Z15-B4) resulted a yield of 67%, the 90% yield implies that species must have been reincorporated in the solid due to the lowering of the pH. The latter is confirmed by TEM (see arrows in **Figure 4**), showing amorphous particles around the crystalline mesoporous zeolite crystals. In addition, the high Si/Al ratio (14.5) supports the incorporation of Si into the solid (**Table 1**). Hence, lowering the pH of a Si-containing stream provides another tool to retrieve the siliceous matter. However, for the design of highly-crystalline materials the pathway is less suitable.

Other approaches to reduce separation efforts are based on alternative methods of filtration. For example, in the case of poorly filterable nanocrystals, polymers such as polydiallyldimethylammonium chloride may be used to flocculate the crystals, enhancing the ease and yield of the separation.[26] However, these polymers require additional synthetic effort and need to be removed by calcination. Alternatively, renewable flocculants such as starch or alginates provide a more sustainable alternative, as they do not require chemical synthesis and do not contribute to the CO$_2$ balance of the system.[52] Another way to ease filtration can be achieved by combining simple sedimentation followed by evacuation of the supernatant. This method should be particularly attractive for (non-colloidal) zeolites that require multiple post-synthetic modifications, *e.g.* in the preparation of hierarchical clinoptilolite. The thus-prepared sample (CLI5-A3-B15-A4-IL, **Table 4**) was obtained at a similar yield as the conventional way (including numerous filtration, washing, and drying steps). Like the batch-wise prepared sample, CLI5-A3-B15-A4-IL displayed a strongly enhanced mesoporosity and pore volume, while the separation efforts were largely reduced.

Table 4. Properties of sequentially-treated hierarchical clinoptilolite samples.

Sample[a]	Yield[b] [%]	V_{micro}[c] [cm^3 g^{-1}]	V_{pore}[d] [cm^3 g^{-1}]	S_{meso}[c] [m^2 g^{-1}]
CLI5-P	-	0	0.05	15
CLI5-A3-B1-A4	37	0.11	0.39	77
CLI5-A3-B15-A4-IL	37	0.09	0.30	62

[a] Base (suffix '-Bx') and acid (suffix '-Ax') treatments were performed on a conventional clinoptilolite zeolite with Si/Al = 5 (CLI5-P). The 'x' represents integers for further specification. Sample CLI5-A3-B15-A4-IL was prepared in line (suffix '-IL') using sedimentation-evacuation instead of conventional filtration. [b] Solid yield after treatment. [c] *t*-plot method. [d] N$_2$ volume adsorbed at p/p_0 = 0.99.

Recycling of Hydrocarbons

Like in the case for many conventional zeolites, the most unsustainable aspect in the preparation of hierarchical zeolites is the use and combustion of synthetic hydrocarbons. The latter is based on both economic and safety concerns.[13] In the case of carbon templating, it may not be straightforward to prevent their use or to recycle the applied organic templates, as they comprise either inert solid polymers, *e.g.* carbon

black,[27] or are partially integrated into the zeolite framework, *e.g.* organosilanes.[28,53] In the synthesis of nanosized zeolites, hydrocarbons are also often included to control and stabilize the crystal size.[34] Nevertheless, some types of nanosized crystals can be made in the absence of hydrocarbons, *e.g.* nanosized EMT zeolites.[35] Although post-synthetic modifications are renowned for using bulk chemicals like NaOH and HCl, hydrocarbon supplements are often added to the alkaline solution as a tool to tune the mesopore size, and/or prevent amorphization and realumination.[31,38] While these additives have provided fundamental insights in mesopore formation process,[54] their use should be minimized or completely avoided.

The great variety of effective PDAs provides many opportunities to reduce their economic and ecological impact. For example, many industrially applied SDAs also function as PDA,[38] assuring their large-scale availability. Alternatively, externally-added aluminum and gallium ion complexes efficiently function as PDA, circumventing the use of hydrocarbons altogether.[54] The recovery of pore-directing agents may constitute another attractive path to enhance sustainability in the synthesis of hierarchical zeolites prepared by desilication. The latter is particularly relevant considering that the PDAs should be present predominately on the external surface,[54] where they may be more easily removed compared to template molecules occluded in a pore network. We performed thermo-gravimetric analyses of a template-containing ZSM-5 (Z40-SDA), a USY30 treated with TPA+ as PDA (USY30-B13-PDA) and one treated with diethylamine (USY30-B11-PDA, **Figure 7**). The template-containing ZSM-5

displays a sharp weight loss around 450°C attributed to the decomposition of occluded TPA+. Conversely, the TPA+-containing USY30-B13-PDA zeolite displayed two major peaks: at 250°C and around 365°C. The former peak, constituting around 75% of the weight loss, is attributed to TPA+ on the external surface. The smaller contribution around 365°C on the other hand relates to the TPA+ species occluded in the faujasite micropores.[55] For USY30-B11-PDA, the weight loss was less severe and, like for USY30-B13-PDA, two peaks appeared: one around 180°C, constituting around 85%, attributed to DEA on the external surface of the zeolite, and a second smaller one around 400°C. The latter could be due to diethylamine that diffused into the micropores. Still, the bulk of the DEA is removed at relatively low temperatures.

Although the volatility of diethylamine requires the necessary safety precautions, it enables to recover species adsorbed onto the zeolite. The concentration of DEA was evaluated on USY30-B11-PDA dried in three steps. After overnight drying (step 1), the sample comprised 10.7 wt.% of DEA (**Table 5**), which is substantially less than what was observed in the case of a TPA+-treated USY30 sample (17 wt.%).[38] Moreover, using vacuum drying (step 2) over 50% of the diethylamine could be removed and isolated, showing that a large part of the employed organics in desilication can be recycled. After a final calcination (step 3), the remaining diethylamine was completely removed.
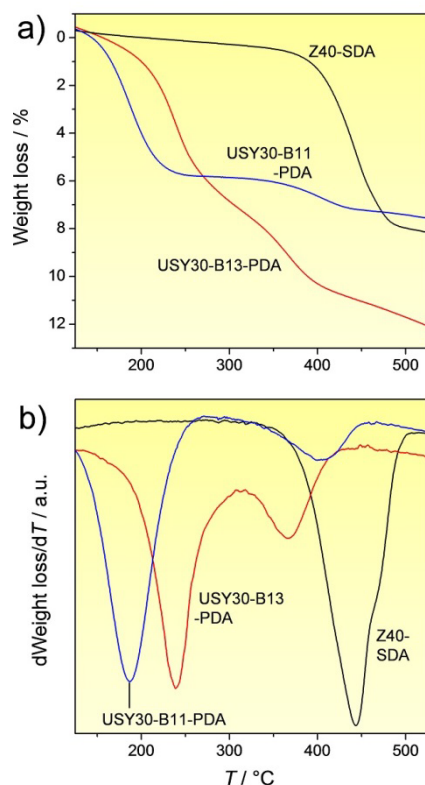

Figure 7. (a) Thermo-gravimetric analysis of selected samples containing structure-direct agent (SDA) or pore-directing agent (PDA). (b) Derivative of the thermo-gravimetric profiles in (a).

Table 5. Properties of sequentially-dried USY30-B11-PDA[a] samples

Step	Yield[b] [%]	DEA + H2O[c] [wt.%]	DEA[c] [wt.%]
1-Drying	93	14	10.7
2-Vacuum drying	86	7	5.2
3-Calcination	80	0	0

[a] USY30-B11-PDA was obtained by base treatment using diethylamine (B11, see **Table 2**) of a faujasite zeolite with Si/Al = 30 (USY30-P). The suffix '-PDA' refers to the presence of organic pore-directing agents. [b] Solid yield after treatment starting with 15 g of USY30-P. [c] Elemental analysis.

Continuous-Mode Synthesis

An important way to increase reactor productivity is to switch from the batch to the continuous mode. The latter may be particularly attractive when combined with continuous-mode separation.[56] The continuous mode synthesis of conventional (microporous) zeolites has been reported several decades ago.[57-59] The continuous-mode manufacture of hierarchical zeolites was more recently been demonstrated for the synthesis of hierarchical USY zeolites by desilication.[38] Using the latter approach, the reactor productivity was increased two orders of magnitude from 1 to 100 g L^{-1} min^{-1}.

The continuous mode synthesis of hierarchical zeolites also enables in-line shaping, *e.g.* spray drying (granulation) or extrusion. Shaping represents an integral part of catalysts scale up, which is starting to attract more academic interest.[60] Particularly spray drying represents a highly interesting method as it widely used in industry,[61] and can be easily configured in

line with the continuous-mode synthesis of hierarchical zeolites. Such configuration has as additional advantage that an intermediate separation step is obsolete. In addition, by spray drying the slurry obtained by desilication, leached silicon species will be *in situ* reincorporated into the solid. The latter can be particularly advantageous in the preparation of (mesoporous) USY zeolites, as their main application is in FCC. There they are employed as (a minor) part of catalyst with other additives as amorphous silica and alumina. Favorably, these USY-containing catalysts are commonly shaped into granules by spray drying.[61]

To verify the above hypothesis, spray-drying experiments were performed using the zeolite slurry originating from the desilication of USY30 using TPAOH (USY30-B12). Accordingly, the absence of Na^+ ions eliminates the need for an additional ion exchange. Sample USY30-B12 displayed, besides the generated mesoporosity and preserved microporosity, a high crystallinity of 107% (**Table 6**). The latter is attributed to the use of TPAOH over NaOH and TPABr. The sample obtained after spray drying (USY30-B12-SD) displayed lower crystallinity and a higher micro- and mesoporosity (**Figure 2c**). The reduced crystallinity is attributed to the presence of amorphous leached species (see sample USY30-B12f-SD). Also, the enhanced microporosity and external surface area of this the spray-dried sample are attributed to the presence of the secondary amorphous phase. It should be noted that the microporosity of the amorphous-silica phase should not be considered zeolitic.[39] SEM evidenced that the presence of the silica in the filtrate resulted into spheres of hierarchical USY zeolites (**Figure 8**). This proves that the leached species are homogeneously incorporated into the solid, where they fulfill an additional role in shaping.

By combining the ability to produce continuously technical USY catalysts with the option to recover the organic pore-directing agents, a conceptual low-impact synthesis of shaped hierarchical USY zeolite can be envisioned (**Figure 9**). In this configuration, the desilication has a minimal impact, as leached species are recycled and the hydrocarbons adsorbed on the zeolite can be largely recycled (*ca.* 80% based on the TGA). Naturally, in addition to the PDA that bound to the zeolite, the PDA remaining in solution is also easily recycled.

Table 6. Properties of base-treated and spray-dried USY30-B12 zeolites.

Sample[a]	Crystallinity[b] [%]	V_{micro}[c] [cm^3 g^{-1}]	V_{pore}[d] [cm^3 g^{-1}]	S_{meso}[c] [m^2 g^{-1}]
USY30-P	100	0.31	0.55	171
USY30-B12	107	0.32	0.68	284
USY30-B12-SD	74	0.34	0.71	334
USY30-B12f-SD	0	0.29	0.38	91

[a] USY30-B12 was obtained by base treatment using TPAOH (B12, see **Table 2**) of USY30-P. The suffix '-SD' indicates that the slurry or filtrate obtained after base treatment was spray-dried. USY30-B12f-SD refers to the sample obtained by spray drying of the filtrate of USY30-B12. [b] XRD. [c] *t*-plot method. [d] N_2 volume adsorbed at p/p_0 = 0.99.
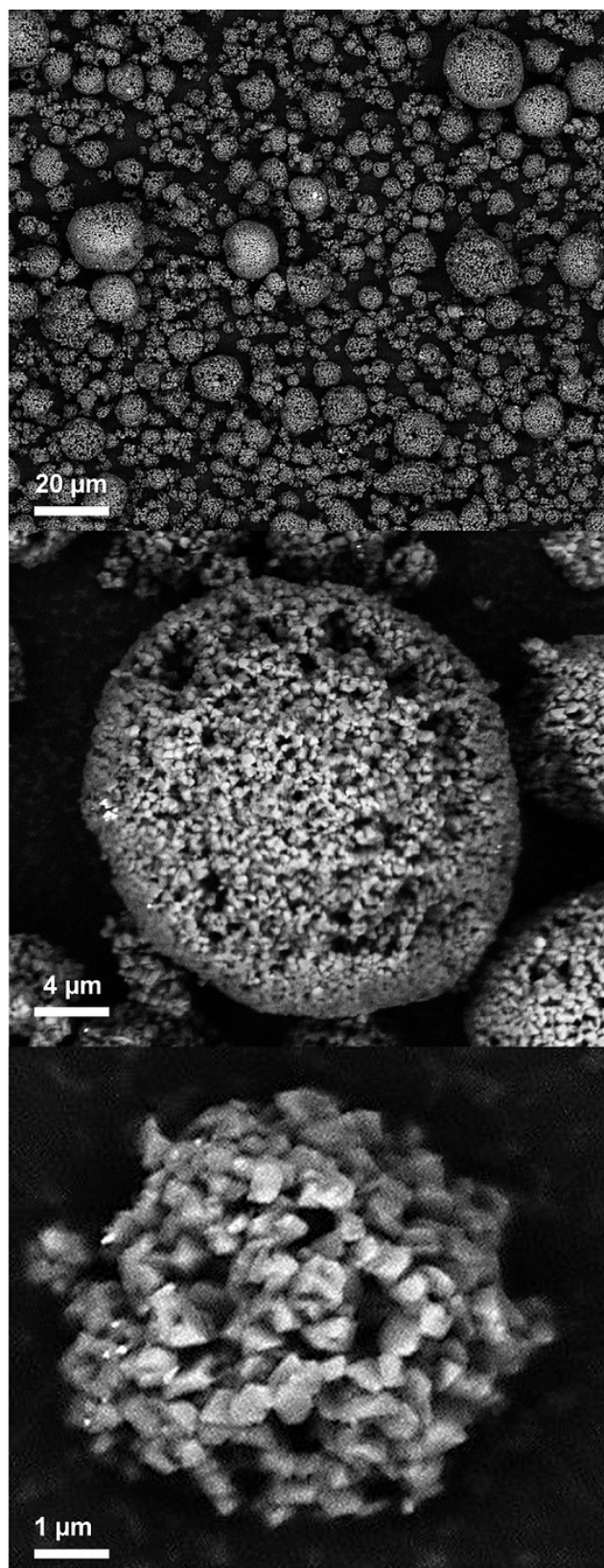

Figure 8. Scanning electron micrographs of the USY30-B12-SD zeolite prepared by sequential desilication and spray drying.
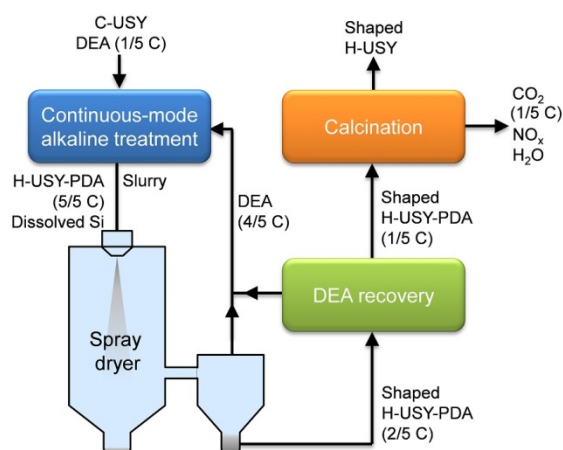
Figure 9. Flow chart for the continuous synthesis of shaped USY catalysts by sequential desilication-spray drying. By application of diethylamine (DEA) as pore-directing agent (PDA) *and* base, a subsequent ion exchange and the combustion of hydrocarbons is (largely) prevented. The values in brackets refer to the fractional carbon economy based on DEA adsorbed onto the zeolite. Leached silicon species are integrated in the technical catalysts where they serve as binder/shaping agent.

Conclusions and Outlook

The sustainability in the manufacture of hierarchical zeolite plays an important role in order to ensure their longevity as superior catalysts. Still, while the variety of novel synthetic methods is ever increasing, the economic and ecological aspects have remained overlooked. Herein, we have underlined the scarcity of the available methods to address these points, and have presented various conceptual and experimentally-verified approaches in a case study using post-synthetic modifications. The attained enhanced reactor productivity, the ability to recycle waste streams and hydrocarbons, and the facile integration into batch- and continuous-mode production, highlight the prospects of hierarchical zeolites prepared by post-synthetic design. By attracting attention to the synthesis of superior *and* sustainable hierarchical zeolites, we aim to direct hierarchical zeolites from lab-scale porous curiosities towards ton-scale technical catalysts.

Experimental Section

Sample Preparation

To distinguish among the numerous treated zeolites, each sample is given a code referring to the type and Si/Al ratio of the starting zeolite (suffix '-P', for parent), from which they were derived (**Table 7**). In general, post-synthetic modifications were followed by filtration, extensive washing with distilled water, and drying at 65°C for 12 h. In addition, unless indicated otherwise, samples contacted with hydrocarbons were calcined at 550 °C for 5 h (ramp rate of 5 °C min^{-1}). Uncalcined samples, containing structure-directing agents (SDAs) or pore-directing agents (PDAs), were labelled with the suffixes '-SDA' or '-PDA', respectively. Treatments comprising volumes up to 100 cm^3

were performed in an Easymax 102 instrument from Mettler Toledo under magnetic stirring. Treatments involving larger volumes were performed using round-bottom flasks heated by oil baths under magnetic stirring. Base treatments (with suffix '-Bx') were performed at 65°C for 30 min under magnetic stirring using the zeolite contents and reactants listed in **Tables 1** and **2**. For the base, acid, and hydrothermal treatments, the 'x' represents integers for further specification. B15 was performed at 65°C for 15 min using 0.4 M NaOH and a zeolite content of *ca.* 40-50 g L^{-1}. In the case 1 M NaCl was included in the alkaline solution, the suffix '+NaCl' was used. Reference to filtrates is made by adding the letter 'f' to the sample code. Treatments performed using the filtrates are labeled using the zeolite code followed by the code of the applied filtrate between brackets. For example, Z40-(Z15-B1f) denotes a Z40-P zeolite treated in the filtrate Z15-B1f. The latter filtrate is derived from the preparation of sample Z15-B1. Alternatively, USY30-(HT2f) denotes USY30-P treated in the filtrate derived from HT2 (see **Figure 5**). Four distinct acid treatments ('-Ax') were performed. Acid treatment A1 was performed by lowering the pH of the suspension after treatment Z15-B4 to 1 by adding an 18 wt.% solution of HCl dropwise during *ca.* 10 min at 65°C under vigorous stirring. Afterwards, the reaction was maintained under these conditions for 6 h. Acid treatment A2 was performed by reacting 6.6 g of Y2.5-P with 3.2 g of H$_4$EDTA in 100 cm^3 distilled water under vigorous stirring for 6 h. The subsequent base treatment (B14, see **Table 2**) was performed by adding to this suspension 100 cm^3 of a 0.6 M NaOH solution. The acid treatment A3 was performed by contacting the zeolite with a 1 M HCl treatment at 100°C for 4 h under vigorous stirring 3 consecutive times. Treatment A4 was performed similarly, but only once. Sample CLI5-A3-B15-A4-IL was performed in line ('-IL'), *i.e.* without filtration steps in between the separate treatments. Instead, after reaction, the solid was allowed to settle to the bottom of the reactor during 10 min. Afterwards, the top 80% of the liquid was carefully evacuated. In the case of CLI5-A3-B15-A4-IL, washing steps were included in between acid and base treatments in order to reduce neutralizations effects. Hydrothermal syntheses ('HTx') were conducted statically under autogenous pressure in Teflon-lined 30 cm^3 Parr reactors. Syntheses were performed on *ca.* 10 cm^3 of Z40-B3f complemented with 0.12 M of TPABr. In some cases, the pH was lowered from 11.3 (HT1) to 10.5 (HT2) or 9 (HT3) by a drop-wise addition of 18 wt.% HCl under magnetic

Table 7. Details of the parent zeolites used in this study.			
Code	Type	Supplier, commercial code	Si/Al[a] [mol mol^{-1}]
Z15-P	ZSM-5	Zeolyst, CBV 3024E	15
Z40-P	ZSM-5	Zeolyst, CBV 8014	40
Z40-SDA[b]	ZSM-5	Zeochem, ZEOcat PZ-2/80	40
Y2.5-P	Y	Zeolyst, CBV 300	2.5
USY30-P	USY	Zeolyst, CBV 760	30
CLI5-P	Clinoptilolite	KMI Zeolite, Mesh no. 100	5

[a] Value provided by suppliers. [b] This sample was used only in **Figure 7**.

stirring and cooling with ice. The samples in **Table 5** were prepared by exposing sample USY30-B11-PDA to (atmospheric) drying at 65°C for 12 h (step 1), followed by drying at a pressure of 4 mbar at 200°C for 2 h (step 2), followed by the above-described calcination (step 3). Species removed during step 2 were isolated using a liquid nitrogen trap. Spray drying was performed using a Mini Spray Dryer B-290 from Büchi equipped with a two-fluid nozzle (diameter 0.7 mm). Accordingly, after base treatment, 50 cm³ of zeolite suspension (USY30-B12) or filtrate (USY30-B12f) was continuously stirred and fed (6 cm³ min⁻¹) to the nozzle together with the spray air flow (0.4 m³ h⁻¹). The inlet temperature was set at 220°C and the aspirator rate at 80%. The hot drying gas (*ca.* 30 m³ h⁻¹) flowed concurrently in the spray nozzle direction. The outlet temperature, which is a function of the aspirator rate, inlet temperature, and liquid feed rate, was *ca.* 103°C. After evacuation, the sample was dried and calcined as mentioned above.

Characterization Methods

Nitrogen sorption at -196°C was carried out in a Micromeritics TriStar II instrument. Prior to the measurement, the samples were degassed in vacuum at 300°C for 3 h. The *t*-plot method was used to discriminate between micro- and mesoporosity. The mesopore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) model applied to the adsorption branch of the isotherm. Powder X-ray diffraction (XRD) patterns were acquired in a PANalytical X'Pert PRO-MPD diffractometer (Bragg-Brentano geometry) using Ni-filtered Cu Kα radiation (λ = 0.1541 nm). Data were recorded in the 2θ range of 3-60° with an angular step size of 0.05° and a counting time of 8 s per step. Transmission electron microscopy (TEM) was performed using a FEI Tecnai F30 microscope. Scanning electron microscopy (SEM) was carried out on a Zeiss Gemini 1530 FEG microscope. Si and Al concentrations in the solids were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Horiba Ultima 2 instrument equipped with photomultiplier tube detection. C, H, and N concentrations in the solids were attained by quantitative infrared spectroscopy performed using a LECO CHN-900 combustion furnace. Thermo-gravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DSC 1 Star system analyzer. The measurements were conducted in air (30 cm³ STP min⁻¹) ramping the temperature from 25°C to 700°C at 10°C min⁻¹.

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FULL PAPER

Superior *and* sustainable. Hierarchically-structured zeolites have been established as a superior type of catalysts compared to conventional zeolites. However, the sustainability of their preparation has remained neglected. In this paper, we address the need for a sustainable manufacture of hierarchical zeolites and substantiate opportunities in a case study using post-synthetic modifications.
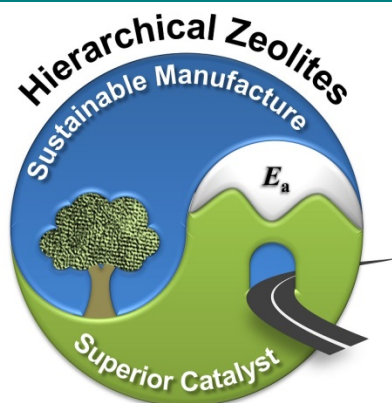
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Towards a Sustainable Manufacture of Hierarchical Zeolites