

Hierarchical NaY Zeolites for Lactic Acid Dehydration to Acrylic Acid

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The industrial viability of heterogeneous catalysts for the gasphase conversion of lactic acid to acrylic acid will strongly depend on their selectivity and durability. Here, we initially screened various aluminum-rich zeolites confirming that NaY is the most efficient catalyst for this reaction. This material was modified by sequential dealumination and alkaline treatment attaining a solid featuring a hierarchical distribution of microand mesopores, reduced Lewis acidity, and increased basicity

Introduction

The replacement of petroleum with biomass-derived feedstocks has a growing impact in today's energy mix and drives the development of environmentally friendly processes for the production of commodity chemicals. Among bio-based platforms, lactic acid (LA) has gained an increasing importance in recent years. LA is produced through sugar fermentation, but a more scalable, greener, and less expensive two-step route starting from waste glycerol has been recently proposed as an alternative method to sustain the fast growth of its market (+15% per year between 2013 and 2020).^[1] LA can be transformed into various derivatives, of which poly(lactic acid), a biodegradable and biocompatible plastic, and acrylic acid (AA), an important bulk chemical ($\approx 4 \times 10^6 \text{ ta}^{-1}$, 2500 \$ton⁻¹) used in the manufacture of paint additives, adhesives, absorbents, and textiles,^[2] are the most relevant. The production of the latter from LA only consists of an acid- or base-catalyzed dehydration.^[3] Thus, an LA-based process could be economically and environmentally more attractive than the current industrial preparation, which relies on the partial oxidation of the costly propylene. Still, the design of efficient heterogeneous catalysts for the emerging process is a highly challenging task.^[4] Firstly, selectivity is an issue due to the competitive transformations that can take place at the temperature required for the dehydration of LA (573-673 K) (Scheme 1).^[4,5] In this respect, the

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owing to the presence of well-dispersed sodium ions interacting with external siloxy groups, as evidenced by in-depth characterization. These properties were crucial for determining higher selectivity (75%) and minimizing the activity loss in a 6 h run. Remarkably, the catalyst gained in selectivity and stability upon reuse in consecutive cycles. This was ascribed to the depletion of the stronger basic sites and the clustering of sodium into oxidic particles upon the intermediate calcination.



Scheme 1. Different transformations observed in the gas-phase conversion of LA over acidic and basic catalysts.

best solids among those investigated, that is, alkaline-earth phosphates,^[6] supported phosphate salts,^[4] calcium hydroxyapatites, $^{\scriptscriptstyle [7]}$ inorganic salts, $^{\scriptscriptstyle [8]}$ and zeolites (mainly NaY) $^{\scriptscriptstyle [9]}$ modified with alkali or alkaline-earth metals or alkali phosphates, have been found to contain both mild acid and basic sites.^[6,8] In the case of alkali phosphates-modified NaY, the formation of an alkali lactate by the interaction of LA with the metal cations appeared critical to enable the formation of AA.^[5a, 10] In spite of these findings, the speciation and the chemical environment of the active sites remain unclear. Secondly, rapid catalyst deactivation has been observed even in short-term runs and, especially, for the more selective materials. This has driven some researchers to assess the catalytic performance upon reactionregeneration cycles.^[4,11] Interestingly, for alkali phosphatesmodified NaY zeolites, regenerated catalysts have displayed a higher activity owing to an improved dispersion of the phosphate species and a stronger interaction between sodium lactate and the zeolite.^[4] However, the exact mechanism govern-

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ing the different behavior of the material after regeneration is still unknown. As the high deactivation rates have primarily been attributed to the formation of carbonaceous deposits and/or the strong adsorption of products arising from the polymerization of LA,^[5b] the introduction of a secondary mesoporous network by the base-assisted removal of silicon framework atoms appears attractive to generate materials with longer lifetime. Indeed, post-synthetically modified zeolites exhibiting improved accessibility have demonstrated superior in traditional reactions afflicted by coking.^[12] Additionally, previous works on high-silica faujasites have demonstrated the effectiveness of the alkaline treatment in simultaneously generating basic sites.^[13]

Herein, we perform a screening of zeolites with different framework topologies and Si/Al ratios in the dehydration of LA to AA. Having identified Al-rich NaY as the best performer, we investigate the development of hierarchical zeolites with tuned acidic and basic properties from this material by the sequential application of dealumination and base treatments. Thereafter, we explore the effect of consecutive reaction-regeneration cycles on the catalytic properties of the solid attaining the highest AA yield. In-depth characterization of selected fresh and used samples by Ar sorption, temperature-programmed desorption of CO₂ (CO₂-TPD), ²³Na and ²⁷Al magic-angle-spinning nuclear magnetic resonance (MAS NMR) and diffuse-reflectance infrared Fourier transform (DRIFT) spectroscopies, and electron microscopy provide a detailed understanding of the nature and location of the active sites, the role of mesoporosity, and the changes in structure and basicity occurring upon the repeated use and regeneration phases.

Results and Discussion

LA dehydration performance of zeolites with different framework topologies

To date, the study of LA dehydration to AA on zeolites has been mostly limited to FAU materials. Furthermore, little data exist comparing different catalysts under the same reaction conditions. Accordingly, we firstly assessed the performance of commercial zeolites in sodium form with distinct framework topology and Si/Al ratio in the gas-phase conversion of LA at 623 K (Figure 1a). After 1 h on stream, FAU zeolites yielded AA with variable selectivity: the highest value (62%) was measured for the sample featuring a Si/Al ratio of 3 (FAU-3) and the lowest for that with a ratio of 385 (FAU-385). The selectivity to the acetaldehyde (AD) byproduct followed a reverse trend, being the highest (80%) for the Al-poor sample. MFI zeolites were unselective irrespective of their Si/Al ratio, which was varied between 15 and 1000. The AA selectivity was progressively higher over BEA-12.5 (Si/Al = 12.5), MOR-10 (Si/Al = 10), and LTL-2.9 (Si/Al=2.9), in that order, likely owing to the increasing Al content in the materials. Indeed, a higher amount of Lewis acid sites, which are believed to catalyze the dehydration of LA^[6,8] is typically present in zeolites with a low Si/Al ratio. While the selectivity did not change substantially in the subsequent hour on stream over all solids, the LA conversion

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Figure 1. (a) Product selectivity at 30 min of reaction, and (b) evolution of the LA conversion during 2 h on stream over sodium-form zeolites with different framework topologies and Si/AI ratios.

level dramatically decreased over most of the zeolites (Figure 1 b). In view of the better retained activity compared to the other selective material (LTL-2.9), FAU-3 (hereon referred to as NaY) was selected for further investigation.

Post-synthetic modification of NaY by sequential acid and base treatments

The parent NaY zeolite was dealuminated by treatment in an acidic medium (aqueous H₄EDTA, EDTA = ethylenediamine tetraacetate) attaining, after ion exchange to its sodium form, a hierarchical analog coded NaY-DA. This material was further modified by exposure to NaOH solutions of different alkaline strength. These samples are labeled as NaY-DA-y, where y refers to the molar NaOH concentration applied. The compositional, textural, and acidic/basic properties of all these catalysts are summarized in Table 1. As expected, the dealumination led to the development of additional mesoporous surface area, which was accompanied by a drop in crystallinity and microporous volume. In addition, the Si/Al ratio increased with the consequent reduction of the amount of charge-compensating Na⁺ cations. These parameters were not further significantly modified by the alkaline treatment except for the mesoporosity, which developed to a greater extent, as highlighted by TEM (Figure 2). The straight edges and clear crystalline fringes of NaY corroborate its highly crystalline nature, whereas intracrystalline mesopores and indented edges are visualized for NaY-DA-0.15.

Negligible amounts of Brønsted-acid sites were detected by FTIR spectroscopy of adsorbed pyridine for the parent and the hierarchical zeolites, whereas NaY contained a remarkable concentration of Lewis acid sites, which reduced to less than half upon the post-synthetic treatments. This is in line with the decrease of the number of Na⁺ cations, which have been identi-



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Table 1. Characterization data of the NaY zeolite catalysts.												
Catalyst	Si/Al ^[a] (—)	Na ^[a] [wt %]	$V_{pore}^{[b]}$ [cm ³ g ⁻¹]	$V_{\rm micro}^{\rm [c]}$ [cm ³ g ⁻¹]	$S_{meso}^{[c]}$ [m ² g ⁻¹]	$S_{BET}^{[d]}$ [m ² g ⁻¹]	$c_{\text{Lewis}}^{[e]}$ [µmol g ⁻¹]	c _{base} ^[f] [a.u.]	Cryst. ^[g] [%]	Coke ^[h] [wt %]		
NaY	3.6	8.5	0.29	0.25	43	680	161	2.3	100	20.4		
NaY-DA	7.3	5.1	0.21	0.10	128	321	n.d. ^[i]	2.4	51	12.3		
NaY-DA-0.05	6.8	5.7	0.28	0.09	190	443	81	8.3	46	10.3		
NaY-DA-0.10	6.6	5.8	0.35	0.09	203	460	65	18.2	46	4.4		
NaY-DA-0.15	5.7	7.2	0.27	0.12	89	406	78	45.9	44	10.3		
NaY-DA-0.15 used 1x	5.7	6.8	0.07	0.00	45	45	60	21.7	n.d.	n.d.		
NaY-DA-0.15 used 1 x calc.	5.5	7.0	0.13	0.04	57	171	n.d.	18.9	n.d.	n.d.		
NaY-DA-0.15 used 2 x	5.6	6.9	0.07	0.00	37	58	n.d.	16.8	n.d.	n.d.		
NaY-DA-0.20	4.9	6.3	0.27	0.10	122	386	45	15.7	38	9.5		

[a] Si, Al, and Na contents determined by X-ray fluorescence (XRF) spectroscopy. [b] Volume adsorbed at $p/p_0=0.99$. [c] *t*-plot method. [d] BET method. [e] Fourier transform infrared (FTIR) spectroscopy of adsorbed pyridine. [f] Integrated area of the CO₂-TPD curves, normalized by the sample weight. [g] Crystallinity determined by X-ray diffraction (XRD) analysis, ASTM standard D3906. [h] Carbon content determined by thermogravimetric analysis (TGA) in the temperature range from 523 to 1023 K. [i] Not determined.



Figure 2. HAADF-STEM images, EDS mapping of Na (red) and Si (green), and TEM images (from left to right) of (a) NaY and NaY-DA-0.15 in (b) fresh and (c) used forms.

fied as the Lewis acid sites in NaY zeolites.^{[14] 27}Al MAS NMR spectroscopy of the parent sample evidenced an intense and very symmetric peak centered at 61.9 ppm, specific to tetra-coordinated aluminum species in the zeolite framework, and a weak signal at 7.3 ppm, attributed to octahedral aluminum species (Figure 3 a). Upon the acid treatment, the intensity of

the first peak decreased, reflecting the reduction in the aluminum content, and a broad contribution appeared at higher fields (55.0 ppm), which is assigned to aluminum sites with distorted tetrahedral geometry.^[15] The spectrum of the sample retrieved after desilication did not show any further substantial alteration. Based on this analysis, it can be concluded that oc-



Figure 3. (a) $^{\rm 27}AI$ and (b) $^{\rm 23}Na$ MAS NMR spectra of the fresh parent and hierarchical NaY zeolites.

tahedral Al atoms only marginally contribute to the Lewis acidity of these materials.

The basicity of the catalysts was assessed by CO2-TPD (Figure 4 and Table 1). The parent and the dealuminated zeolites produced no significant desorption, confirming their negligible basicity. In contrast, two major peaks between approximately 363 and 553 K became evident in the curves of the alkaline-treated zeolites, indicating the presence of basic sites with a moderate character. The total amount of basic centers in these samples followed a volcano-like trend with a maximum for NaY-DA-0.15. Additionally, this solid also contained a higher fraction of slightly stronger basic sites. As these evidences do not correlate with the sodium loading, Na⁺ cations likely compensate negative charges of different nature. A fraction is present at ion exchange positions, to balance the framework charge caused by the isomorphous substitution of silicon with aluminum atoms. These sites have the same nature as the one found in the parent NaY and possess very mild basicity. Another part is believed to substitute the protons in the silanol



Figure 4. CO₂ desorption profiles of the fresh parent and hierarchical NaY zeolites.

groups present in defect-rich regions (i.e., the external surface of the crystal or the mesopore walls), leading to stronger basic sites similar to those observed for high-silica faujasites.^[13b,c] The presence of the latter species was corroborated by DRIFT spectroscopy, which evidenced the appearance of the silanol band at 3735 cm⁻¹ upon dealumination of the parent sample due to the formation of defects in a protic environment and its partial depletion upon the subsequent deprotonation of these groups during the alkaline treatment (Figure 5).



Figure 5. DRIFT spectra of the fresh parent and hierarchical NaY zeolites.

The chemical environment of the alkali metal atoms was further analyzed by ²³Na MAS NMR spectroscopy (Figure 3 b). In NaY zeolites, three distinct crystallographic sites occupied by Na⁺ cations have been identified, that is, SII in the supercage, SI' in the sodalite cages, and SI in the center of the hexagonal prisms, which exhibit characteristic resonances at -2.0, -5.0, and -7.0 ppm, respectively.^[16] Our NaY sample mainly exhibited sodium in the first two types of locations. Upon dealumination, the alkali metal atoms migrated from the supercages to the sodalite cages. After the base treatment, a feature centered at -3.4 ppm was observed, which could be related to Na⁺ cations at siloxy groups, as previously observed. $^{[13b,c]}$ Still, a further reorganization of sodium between supercages and sodalite cages cannot be excluded. In line with these spectroscopic evidences, sodium mapping by energy-dispersive X-ray spectroscopy (EDS) revealed a homogeneous dispersion of the metal in both the NaY and NaY-DA-0.15 zeolites (Figure 2). Note that the lower concentration of sodium in the modified sample reflects its lower amount in the material (Table 1).

Catalytic performance of hierarchical NaY zeolites

The mesoporous NaY zeolites prepared through the post-synthetic treatments were tested as catalysts in the gas-phase dehydration of LA under the same conditions as applied to the screening of commercial zeolites presented above and their performance was compared after 15 min on stream. In all cases, AA and AD were the only products detected. The dealuminated sample attained an AA yield of only 10% (not shown). This is explained by the presence of Brønsted acid sites formed upon ion exchange of part of the sodium atoms with the protons released by the formation of the metal-EDTA chelate, which catalyze the decarbonylation of LA to AD (Scheme 1). When the dealuminated sample was ion exchanged to its sodium form (NaY-DA), higher activity and selectivity were obtained, which largely exceeded those of the parent NaY zeolite



Figure 6. (a) LA conversion and product selectivity after 15 min and (b) evolution of the AA yield during 6 h on stream over the parent and hierarchical NaY zeolites.

(Figure 6 a). As the amount of basic sites for NaY-DA is similar to that of NaY (Figure 4 and Table 1), the improved catalytic performance is likely the result of the augmented external surface area, which enhances the access of the reactant to the active sites, suppressing its conversion through side reactions.

Catalytic testing of the sequentially dealuminated and alkaline-treated samples evidenced a greater AA selectivity for catalysts prepared using NaOH solutions with progressively higher concentration reaching a maximum for the NaY-DA-0.15 zeolite. Harsher alkaline treatments led to an inferior performance (NaY-DA-0.2). This volcano-like trend is in line with the variation in amount of basic sites determined by CO_2 -TPD and points to a major catalytic role of the basic sites formed upon exchange of the protons of silanol groups by sodium in LA dehydration with respect to the Lewis acid centers. This is corroborated by the fact that the latter are more abundant in the less performing parent material and present in rather similar amount in all dealuminated and alkaline-treated solids.

The stability of the parent and modified zeolites was evaluated in a 6 h test. The data are expressed in terms of AA yield (Figure 6 b) after normalization by the values measured after 15 min of reaction for each catalyst and effectively indicate an alteration in their activity since the selectivity remained almost constant in all of the cases (Figure 6 a). NaY continuously deactivated and retained only 20% of the initial AA yield at the end of the run. The same result was found for NaY-DA but this material exhibited an even faster deactivation rate than the previous. NaY-DA-0.05, NaY-DA-0.10, and NaY-DA-0.20 deactivated more rapidly than NaY within the first 2 h on stream but their AA yield stabilized at different levels in the remainder of the test. The most active and selective catalyst, NaY-DA-0.15, better preserved its activity in terms of both deactivation rate and overall loss in AA yield. The final fraction of AA yield retained by all sequentially dealuminated and alkaline-treated samples follows the same trend observed for their amount of basic sites. This hints that basic sites also lead to a more durable LA conversion than Lewis acid sites.

Notably, the modified zeolites appear less stable than other materials previously reported,^[3,5,8b,17] but their catalytic performance has been evaluated at much higher weight hourly space velocities (WHSV=0.1-1 h⁻¹ versus 6 h⁻¹ in the literature and in this study, respectively) to simulate more industrially relevant conditions and observe deactivation in a much shorter time scale.

Catalyst deactivation, regeneration, and reuse

Coke formation and the strong adsorption of polymeric derivatives have been claimed to encompass the main routes for catalyst deactivation in the gas-phase dehydration of LA. Characterization of the used catalysts by TGA confirmed the deposition of a conspicuous amount of coke, which was about double in the starting NaY with respect to all modified samples (Table 1). Based on these data, the faster deactivation of NaY-DA compared to NaY is surprising. Hierarchically structured porous materials have evidenced higher stability compared to their microporous counterparts in catalytic processes in which deactivation is caused by fouling owing to the possibility to accommodate coke onto the mesopores.^[12b] Our result can only be explained assuming that the Lewis acid sites responsible for the desired reaction and coke formation are predominantly located in the micropores, which are present in a lower quantity in the dealuminated sample. NaY-DA-0.15 was further characterized to gain more understanding of the benefits of the alkaline treatment. The porosity and acidity-basicity analyses uncovered the full depletion of the micropores, the halving of the mesopores and a reduction in the concentration of basic as well as Lewis acid sites (Figure 7 a and Table 1). ²⁷Al NMR MAS spectroscopy evidenced a broadening of the peak originally centered at approximately 61.9 ppm, indicating a rearrangement of the tetrahedral aluminum centers (Figure 7b). Based on these data, as only a minor fraction of the original catalytic activity was lost upon use, it is likely that the advantage of the hierarchical material lies in the additional presence of basic centers and their distinct preferential placement compared to the Lewis acid sites, i.e., the active basic centers present at the external surface of the zeolite crystals are only partly affected by the formation of carbonaceous deposits promoted by the Lewis acid sites mainly in the micropores.

The nature of the fouled species was explored by DRIFT spectroscopy (Figure 8). A band centered at approximately 1600 cm⁻¹ was detected along with three additional absorptions at 2974, 2938, and 2874 cm⁻¹. The first spectral feature corresponds to the stretching of the C=O group in sodium lactate, whereas the second set of signals arises from the stretching of C–H bonds, supporting the generation of adsorbed polymeric species.^[3] Inspection of the O–H stretching region in the spectra of the fresh and used material revealed a significant depletion of the sharp silanol band at 3735 cm⁻¹, suggesting that at least part of the adsorbed species interacted with these



Figure 7. (a) CO_2 desorption profiles and (b) ²⁷Al and (c) ²³Na MAS NMR spectra of NaY-DA-0.15 in fresh, used, and regenerated forms.



Figure 8. DRIFT spectra of NaY-DA-0.15 in fresh, used, and regenerated forms.

surface groups.^[18] Furthermore, the broad band centered at approximately 3400 cm⁻¹ became more intense, indicating a higher content of hydrogen-bonded hydroxyl groups, including the contribution from both the surface groups–adsorbate and adsorbate–adsorbate interactions.

These evidences were corroborated by ²³Na MAS NMR spectroscopy (Figure 7 c). Indeed, the depletion of the resonance at -3.4 ppm and the appearance of a wide signal ranging from -30 to 6 ppm agree with the interaction of sodium with carboxylate groups of lactate and polylactate species.^[19] Additionally, they indicate the clustering of the metal cations into sodium oxide particles.^[19] The sodium atoms that underwent redistribution mostly comprised those having a lower interaction with the framework basic oxygen atoms, i.e., those origi-

nally present in the large sodalite or supercages (-3.4 and -1.1 ppm respectively), while the hexagonal prism seemed to comprise a site offering more stability to the alkali metal cations.

The implementation of reaction-regeneration cycles has been proposed as a strategy to extend the long-term use of the catalysts. Herein, the activity of the best performing zeolite (NaY-DA-0.15) was monitored over three consecutive runs between which the catalyst was thermally treated in air to simulate a typical regeneration procedure. Interestingly, the previously described slight activity loss in the first cycle became less pronounced in the second and third tests and the AA selectivity was fully retained, or even moderately improved (Figure 9).



Figure 9. (a) LA conversion and (b) AA selectivity over NaY-DA-0.15 upon three subsequent catalytic cycles.

CO2-TPD analysis indicated that calcination of the sample retrieved after the first cycle provoked a further reduction of the basic sites, especially of the stronger type (Figure 7a). The absence of the very intense and broad CO₂ desorption signal observed from 573 K, attributed to the decomposition of the organics present on the surface of the catalyst prior to the coke burn-off, confirms the effectiveness of the regeneration with respect to the fouling issue. In line with this, the signals attributed to adsorbed (poly)lactate species in the DRIFT spectrum disappeared, and the band at 3735 cm⁻¹ specific to terminal silanols was restored (Figure 8). The ²³Na MAS NMR spectrum of the calcined sample evidenced a decrease in intensity for the low-field portion of the signal and a strengthening of the high-field contributions (Figure 7 c). This indicates that the depletion of sodium atoms interacting with carboxylic group owing to the removal of the carbonaceous deposits led to the formation of more sodium oxide particles. The latter is supported by the EDS map acquired for the material after the third cycle, which shows well-defined sodium-rich regions (Figure 2 c). The generation of these oxidic aggregates likely is the origin of the beneficial changes in basicity determining the im-



proved catalyst performance upon cycling. Since the characterization data obtained for the catalyst after the first and the second cycle are comparable (Figure 7 and 8), it seems likely that the catalyst reaches equilibration already after the first reaction-regeneration cycle.

Conclusions

In this study, we addressed the identification of zeolite-based catalysts displaying enhanced stability in the gas-phase dehydration of lactic acid to acrylic acid. Initially, we confirmed that NaY zeolite is the best catalyst for a selective conversion of the substrate among commercial aluminosilicates with different framework topologies and Si/Al ratios. Thereafter, we demonstrated that sequential dealumination and alkaline treatment with a specific concentration of sodium hydroxide enable us to produce a hierarchical NaY zeolite showing higher selectivity and durability than the parent material. Based on in-depth characterization, we could unravel the interplay between porosity and site speciation at the basis of the superiority of the modified catalyst. The starting NaY, only featuring Lewis acid sites mostly in the micropores, suffers from rapid deactivation through pore blockage with coke. In contrast, the dealuminated and base-treated sample, additionally containing a secondary mesoporous network and basic sites therein located, remains active and selective for longer time because fouling takes place further away from the sites mostly responsible for the desired catalytic process. The latter are found to likely comprise siloxy groups counterbalanced by sodium cations. Evaluation of this material in consecutive reaction-regeneration tests revealed improved selectivity and stability upon cycling, which was associated with a partial redistribution of sodium from ion exchange positions into clustered oxide species and with a decrease of the basicity. Our findings indicate the superiority of basic over Lewis acid sites, providing new insights into the parameters that govern the selectivity to acrylic acid in the reaction under study. Additionally, they highlight the benefits of an improved understanding of the phenomena related to deactivation and regeneration for the design of efficient catalysts for lactic acid dehydration. For instance, to minimize the formation and irreversible adsorption of polymeric species on the zeolite surface, the utilization of methyl lactate as an alternative substrate could be envisaged.

Experimental Section

Catalyst preparation

FAU (CBV 720, Zeolyst International, bulk Si/AI = 15; HSZ-390HUA, Tosoh Corporation, bulk Si/AI = 385), MFI (CBV 3024E, Zeolyst International, bulk Si/AI = 15; CBV 8014, Zeolyst International, Zeolyst International, bulk Si/AI = 40), BEA (CP814E, Zeolyst International, bulk Si/AI = 12.5), LTL (ZEOcat L, Zeochem, bulk Si/AI = 2.9), and MOR (CBV 21 A, Zeolyst International, bulk Si/AI = 10) zeolites were converted into their sodium form by ion exchange in aqueous NaNO₃ (0.1 m (1 m for MOR), 6 h, 298 K, 100 cm³ g_{zeolite}⁻¹, 3 consecutive treatments) followed by calcination in static air for 5 h at 823 K (5 Kmin⁻¹). FAU zeolite (NaY, Zeochem, bulk Si/AI = 3) was obtained in the sodium form and used as received. Post-synthetic dealumination of NaY was performed at 373 K in a 0.15 m solution of H₄EDTA (Fluka, >99%, 24 h, 15 cm³ per gram of zeolite). The resulting slurry was filtered, washed with deionized water (3×, \approx 30 cm³g_{zeolite}⁻¹), and dried at 338 K for 16 h. A portion of this sample was converted into the sodium form by ion exchange in aqueous NaNO₃ as detailed above, yielding the NaY-DA catalyst. Another portion was treated in aqueous NaOH (Sigma-Aldrich, 97%, 0.05–0.2 m, 338 K, 30 min, 30 cm³g_{zeolite}⁻¹) using an Easymax 102 setup (Mettler Toledo). After quenching in an ice bath and filtering, the zeolites were washed with deionized water (3×, \approx 30 cm³g_{zeolite}⁻¹) and dried at 338 K for 16 h. The resulting catalysts were labeled with the suffix *y*, which stands for the molar concentration of the NaOH solution. All catalysts were calcined in static air as mentioned before.

Catalyst characterization

The Na, Al, and Si contents in the samples were determined by XRF spectroscopy using an EDAX Orbis Micro-XRF analyzer equipped with a Rh source operated at a voltage of 35 kV and a current of 500 µA. Powder XRD was performed using a PANalytical X'Pert PRO-MPD diffractometer with Ni-filtered CuK_a radiation ($\lambda =$ 0.1541 nm), acquiring data in the 5–70° 2θ range with a step size of 0.05° and a counting time of 8 s per step. Ar sorption at 77 K was conducted using a Micromeritics 3Flex analyzer. Prior to the measurements, the samples were evacuated at 573 K for 3 h. CO₂-TPD was carried out using a Micromeritics Autochem II chemisorption analyzer coupled with a MKS Cirrus 2 guadrupole mass spectrometer. The catalyst (0.05 g) was pretreated in He flow $(20 \text{ cm}^3 \text{min}^{-1})$ at 823 K for 2 h, exposed to CO₂ (50 pulses of 1 cm³ in a He flow of 10 cm³min⁻¹) at 323 K, and purged in He at the same temperature for 1 h. Thereafter, the catalyst was heated up to 973 K (10 Kmin⁻¹) to monitor the desorption of CO₂. ²³Na and ²⁷AI MAS NMR spectroscopy was conducted using a Bruker Avance 700 spectrometer operated at 185.2 and 182.4 MHz, respectively, using 4 mm ZrO₂ rotors spun at 10 kHz. For Na, spectra were acquired using 2048 accumulations with a pulse length of 1 µs, a recycle delay of 1 s, and solid NaCl (Sigma, 99.9%) as a reference (δ = 7.21 ppm). In the case of Al, 512 scans were accumulated and $(NH_4)AI(SO_4)_2$ was used as a reference ($\delta = 0.00$ ppm). Prior to the analysis, the samples were dried in vacuum. FTIR spectroscopic studies of adsorbed pyridine were performed using a Bruker IFS66 spectrometer equipped with a liquid-N₂ cooled mercury cadmium telluride (MCT) detector. Spectra were recorded in the range of 650–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and co-addition of 32 scans. Zeolite wafers ($\approx 1 \text{ cm}^2$, 20 mg) were evacuated (10⁻³ mbar) for 4 h at 693 K, prior to adsorbing pyridine (Sigma Aldrich, >99%) at room temperature. Gaseous and weakly adsorbed molecules were subsequently removed by evacuation at 473 K for 30 min. The concentrations of Lewis acid sites were calculated from the area of the bands at 1454 cm⁻¹, using the extinction coefficient $\,\epsilon_{Lewis}\!=\!2.94~cm\,\mu mol^{-1}$. DRIFT spectroscopy was performed using a Vertex 70 spectrometer equipped with a liquid-N₂ cooled MCT detector and a high-temperature cell. Prior to the measurements, the samples were dried at 573 K in N₂ flow (60 cm³min⁻¹) for 2 h. Spectra were recorded in the range of 600–4000 cm⁻¹ with a resolution of 2 cm⁻¹. TGA of the used catalysts was conducted using a Mettler Toledo TGA/DSC1 instrument. A catalyst sample of 15 mg was heated in the range of 323–1023 K (10 Kmin⁻¹) under air flow (40 cm³ min⁻¹). The weight loss between 523–1023 K was ascribed to the removal of deposited coke. TEM and high-angle annular dark field (HAADF) STEM images and EDS elemental maps



were acquired using an FEI Talos instrument operated at 200 kV. Powdered samples were deposited onto Mo grids. HAADF images were collected before and after the EDS measurements to corroborate the absence of morphological changes.

Catalytic testing

The gas-phase dehydration of LA to AA was studied at ambient pressure in a continuous-flow fixed-bed reactor comprising: (i) a mass flow controller for feeding N₂ (PanGas, 99.999%), (ii) a syringe pump for the injection of liquids, (iii) a tubular quartz micro-reactor (i.d. = 6 mm) heated in an oven, and (iv) a liquid-gas separator immersed in an ice bath (Scheme 2). The catalyst (0.2 g, particle size = 0.2-0.4 mm) was loaded into the reactor, which was then filled with 2 mm glass spheres to facilitate the evaporation of the liquid feed. The system was heated at the reaction temperature (623 K) in N_2 flow (100 cm³min⁻¹) and allowed to equilibrate for 10 min. Thereafter, a 10 wt% aqueous LA solution (Fisher, 88%) was fed at a rate of 0.2 cm³min⁻¹. Three consecutive catalytic tests were performed with NaY-DA-0.15. The amount of catalyst and the LA flow were constant in all the experiments to ensure a similar contact time in all cases. After each catalytic test, part of the catalyst was regenerated under an air flow (823 K, 5 h, 5 Kmin⁻¹) prior to the following test. For selected catalytic runs, a fraction of the catalyst before and after the regeneration step was kept for characterization. Liquid samples were periodically collected from the condenser and analyzed by high-performance liquid chromatography using an HPLC system (Merck LaChrome) equipped with an HPX-87H column kept at 308 K and a refractive index detector. A $0.005 \text{ M} \text{ H}_2\text{SO}_4$ aqueous solution flowing at $0.6 \text{ cm}^3 \text{min}^{-1}$ was used as the eluent. Calibration curves were obtained using LA (ABCR, 98%), AA (ABCR, 99%), and acetaldehyde (Sigma-Aldrich, > 99.5%). The conversion was calculated as the ratio between the moles of LA reacted per mole of LA fed, the selectivity to i as the mole of product *i* formed per mole of LA reacted, and the yield of i as the product between LA conversion and selectivity to i. The carbon balance was calculated as the ratio between the moles of carbon in the liquid and the moles of carbon fed. The experimental error, determined on the basis of three repetitions of selected tests, was within 7%.



Scheme 2. Continuous-flow fixed-bed reactor used in this study.

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