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# Generation of Basic Centers in High-Silica Zeolites and their Application in Gas-Phase Upgrading of Bio-Oil

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High-silica zeolites have been reported recently as efficient catalysts for liquid- and gas-phase condensation reactions because of the presence of a complementary source of basicity compared to Al-rich basic zeolites. Herein, we describe the controlled generation of these active sites on silica-rich FAU, BEA, and MFI zeolites. Through the application of a mild base treatment in aqueous Na<sub>2</sub>CO<sub>3</sub>, alkali-metal-coordinating defects are generated within the zeolite whereas the porous properties are fully preserved. The resulting catalysts were applied in the gas-phase condensation of propanal at 673 K as a model reaction for the catalytic upgrading of pyrolysis oil, for which an up to 20-fold increased activity compared to the unmodified

# Introduction

Bio-oil obtained through the fast pyrolysis of lignocellulosic biomass is one of the most promising approaches to reduce in a sustainable manner the environmental footprint of our society that results from the excessive consumption of fossil fuels.<sup>[1]</sup> However, as crude bio-oil consists of a complex mixture of oxygen-functionalized hydrocarbons, the resulting low heating value, limited chemical stability, and corrosive nature of the condensate prevent its application in blends with traditional fuels.<sup>[2]</sup> As a consequence, catalytic pathways for the deoxygenation of pyrolysis oil constitute a vivid area of research, in which oxygen is transformed either into CO<sub>2</sub> through cracking and decarboxylation reactions<sup>[3]</sup> or into H<sub>2</sub>O through hydrodeoxygenation (HDO) treatments.<sup>[4]</sup> Both approaches have disadvantages intrinsically connected to the nature of the reaction: CO<sub>2</sub>-based pathways suffer from the loss of carbon as gases and, therefore, comprise a substantially reduced yield, and the high hydrogen consumption of the H<sub>2</sub>O-based pathways hampers industrial<sup>[5]</sup> and ecological<sup>[6]</sup> profitability. In contrast, the catalytic upgrading of pyrolysis oil through condensation reactions enables the removal of oxygen as water without the consumption of external resources and enables the conversion of low-boiling fractions of pyrolysis vapor into desired heavier molecules simultaneously. Therefore, a cascade

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[<sup>+</sup>] These authors contributed equally to this work. zeolites was attained. The moderate basicity of these new sites leads to a coke resistance superior to traditional base catalysts such as CsX and MgO, and comparable activity and excellent selectivity is achieved for the condensation pathways. Through strategic acid and base treatments and the use of magic-angle spinning NMR spectroscopy, the nature of the active sites was investigated, which supports the theory of siloxy sites as basic centers. This contribution represents a key step in the understanding and design of high-silica base catalysts for the intermediate deoxygenation of crude bio-oil prior to the hydrotreating step for the production of second-generation biofuels.

process that exploits the heat of a pyrolysis outlet stream for catalytic upgrading appears environmentally and economically highly attractive as the H<sub>2</sub> and energy demand during a subsequent HDO step can be reduced efficiently (Scheme 1). In contrast to acid-catalyzed pathways such as esterification<sup>[7]</sup> and alkylation<sup>[8]</sup> reactions, base-catalyzed refining pathways have received little attention despite their promising potential.<sup>[9]</sup> Apart from solid bases such as alkaline earth metal oxides,<sup>[10]</sup> hydrotalcites,<sup>[11]</sup> and alumina-supported alkali metal salts,<sup>[12]</sup> zeolites have been investigated in depth as catalysts for condensation reactions in a fine-chemistry-related context because of their remarkably selective character.<sup>[13]</sup> In contrast to stronger bases, the tunable basicity of zeolites enables the prevention of overactivation of the substrates, and, therefore, limits the extent of undesired side reactions and catalyst deactivation, which will likely pose a key issue for the targeted application. This aspect, combined with their hydrothermal stability and water tolerance renders zeolite base catalysts as promising candidates for intermediate bio-oil upgrading. Traditionally, they utilize the intrinsic basicity of their framework oxygen atoms, which increases with the amount of adjacent Al atoms and the size of the charge-balancing cations.<sup>[14]</sup> The resulting high loading (up to 35%) of costly alkali metal cations such as Cs, however, renders these zeolites rather unattractive for bio-oil refining, especially if we consider the low price of the obtained products. Recently, we discovered the outstanding activity of high-silica zeolites in a broad range of base-catalyzed reactions, which include Knoevenagel, aldol, and nitroaldol condensations.[15] Although they do not experience the increased electron density on the framework oxygen atoms because of the absence of Al, these catalysts outperformed their Al-rich counterparts,



**Scheme 1.** Potential scheme for the production of second-generation biofuels from lignocellulosic biomass. An intermediate catalytic deoxygenation of biooil by means of condensation, ketonization, and esterification reactions will decrease the oxygen content ( $w_0$ ) prior to hydrotreatment, which reduces the hydrogen consumption in the last step substantially.

which could not be explained by traditional concepts. Accordingly, their activity was attributed to the presence of a new secondary type of basic site, siloxy groups, that correspond to stabilized, deprotonated silanol groups. The sites were linked to defects in the zeolite that originate from the hydrothermal synthesis.<sup>[16]</sup>

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In agreement with observations made for Al-rich zeolites,<sup>[17]</sup> the introduction of mesoporosity by postsynthetic modification increased the activity of the highsilica zeolites in liquid-phase condensations substantially,<sup>[15]</sup> as the severe diffusion limitations were addressed. Surprisingly, the influence of the applied base



Scheme 2. Reaction pathways for the gas-phase conversion of a) propanal and b) propionic acid over basic catalysts.

treatments was even more pronounced in the gas-phase condensation of propanal at 673 K. If we consider the small reactant size, strong diffusion limitations should not be expected. Nevertheless, the alkaline treatment applied to USY zeolites resulted in an activity increase by a factor of 20 with respect to the parent zeolite, which is unlikely to result solely from the approximately 2.5-fold increased external surface area. This indicates that other factors likely influence the catalytic activity, such as the possible generation of basic siloxy sites by the desilication treatment. However, as a result of the lack of adequate characterization techniques, the deconvolution of the effects of the supplementary external surface area and active site generation is not possible based on the reported samples. This aspect deserves further attention to accomplish the rational design of the catalytic material.

In this work, we investigate the nature of this new type of basic sites on silica-rich zeolites and their application in catalytic reactions relevant to bio-oil upgrading. As crude bio-oil obtained through the fast pyrolysis of lignocellulosic biomass contains a high amount of short-chain aldehydes (up to 18 wt%) and carboxylic acids (up to 10 wt%),<sup>[18]</sup> the aldol condensation of propanal and the ketonization of propionic acid were investigated as model reactions at an operating temperature similar to that of a pyrolysis outlet stream (674 K).<sup>[19]</sup> The main reaction pathways that occur in the gas-phase conversion of propanal over base catalysts comprise the aldol condensation, the Tishchenko reaction, and the subsequent ketonization of the ester (Scheme 2a). Further oligomerization leads to the formation of a C<sub>9</sub> fraction through the cross-aldol condensation of  $\alpha$ -methylpent-2-enal with propanal to form the aldol condensation trimer. The desired pathways comprise the elimination of oxygen in the form of water, which prevents carbon loss. If carboxylic acids are used as model compounds, propionic acid is converted to the corresponding acetal, which then reacts into 3-pentanone by a ketonization reaction (Scheme 2 b).

The formation and passivation of basic centers in high-silica materials is illustrated through strategic base and acid treatments, which provides an understanding of their nature and their catalytic impact decoupled from the influences of porosity. The resulting catalysts combine high activity, selectivity, and stability, which put forward high-silica zeolites as promising candidates for the upgrading of bio-oil.

# **Results and Discussion**

In this study, high-silica zeolites with different frameworks, FAU (Si/AI=385, denoted USY), BEA (Si/AI=220), and MFI (Si/AI=1060), were investigated. The parent zeolites (denoted -P) were subjected to a range of acid and base treatments (Table 1). As an example, USY-Na-CT0.05-HCI refers to the USY zeolite submitted to a treatment with 0.5  $\times$  Na<sub>2</sub>CO<sub>3</sub> and 0.05  $\times$  tetrapropylammonium bromide (TPABr) followed by a treatment with 0.1  $\times$  HCI.

Table 1. Coding of the applied treatments.				
Code	Treatment			
-Na-CT <i>x</i> -K-CT <i>x</i> Na- -HCI -NH₄ -NH₄OH	0.5 M Na <sub>2</sub> CO <sub>3</sub> and x M TPABr, RT, 10 min 0.5 M K <sub>2</sub> CO <sub>3</sub> and x M TPABr, RT, 10 min 0.1 M NaCl, RT, 8 h 0.1 M HCl, RT, 10 min 0.1 M NH <sub>4</sub> NO <sub>3</sub> , RT, 8 h 0.5 M NH <sub>4</sub> OH, RT, 10 min			

### Generation of basic sites for bio-oil upgrading

If ion exchanged in a basic environment, high-silica zeolites possess a cation-exchange capacity that exceeds the amount expected based on their Al content. This effect was first discovered by Chester et al.,<sup>[20]</sup> who postulated its origin to be anionic species on the surface that resemble ion-exchanged silanol groups. We took a similar approach aimed at the generation of basic centers and we subjected a USY zeolite to treatments in aqueous solutions of NaOH. To minimize dissolution and damage to the framework, the treatments were performed at room temperature with a contact time of only 1 min. Despite the short time, a pronounced amorphization of the zeolites was observed under conditions that comprised a pH greater than 12 ( $c_{NaOH}$  > 0.01 M). N<sub>2</sub> sorption experiments evidenced an up to three times increased external surface area (S<sub>meso</sub>) accompanied by a strong decrease in the micropore volume ( $V_{micro}$ ) and crystallinity (Figure 1). The successful generation of basic sites was confirmed upon catalytic application in the gasphase condensation of propanal, in which the partially collapsed zeolites displayed an 18-fold increased conversion compared to the parent zeolite (Figure 1 b). In contrast, the samples with preserved structural properties did not attain this improved catalytic performance, which suggests that active sites are only generated under conditions under which a gradual dissolution and thus degradation of the framework occurs. Accordingly, control over the amorphization process is crucial if the decoupling of the effects of porosity and site generation is the aim.

In the preparation of hierarchical high-silica zeolites, tetraalkylammonium cations are used commonly to increase their stability in an alkaline environment.<sup>[21]</sup> The adsorption of quaternary ammonium cations leads to a stabilization effect that is comparable to the situation during template-assisted zeolite synthesis,<sup>[16a]</sup> and thus enables a preservation of the framework. Therefore, a treatment that combined a milder base and a structure-preserving agent was developed that included the activation of the zeolite for 10 min in a 0.5 M solution of Na<sub>2</sub>CO<sub>3</sub> (pH 12) in the presence of 0–0.2 M TPABr. To remove the adsorbed tetraalkylammonium cations, the samples were calcined in air prior to their use as catalysts. For samples treated with  $c_{\text{TPABr}} \ge 0.02 \,\text{m}$ , the porous properties remained unaltered compared to those of the parent zeolite (Figure 2a). Nevertheless, a major improvement in the catalytic activity was achieved, which confirms that the activity of these zeolites does not result from the introduction of mesoporosity but from the creation of new active sites (Figure 2b).



**Figure 1.** a) External surface area, micropore volume, and b) crystallinity of the USY samples treated in varying concentrations of NaOH for 1 min at 298 K. The conversion of propanal over the samples in the gas-phase condensation at 673 K after 2 h on stream is shown in b. Open symbols represent the parent USY-P zeolite.

Although crucial to maintain the crystallinity of the zeolite, the presence of a pore-directing agent was detrimental for the aldol condensation activity, which decreases linearly with the increasing amount of TPABr. If large quantities are applied, activation does not occur and the sample performs identically to the parent zeolite. This behavior could result from two different contributions: first, TPABr adsorbs unselectively on the surface of the zeolite, and, therefore, inhibits the generation of active sites in its close proximity. The second effect is a competitive adsorption of the cations on the generated sites. As siloxy groups are anionic species, a cation is needed to counterbalance the net negative charge, which can be both Na<sup>+</sup> and TPA<sup>+</sup>. If TPA<sup>+</sup> is adsorbed, the corresponding site is protonated again during the calcination step, and its activity is lost. However, if Na<sup>+</sup> is coordinated, the site is unaffected by the calcination and contributes to the catalytic activity. Accordingly, the higher the concentration of quaternary ammonium cations, the higher the fraction of siloxy groups that is reconverted into silanol species. The effect of TPABr could be confirmed by atomic absorption spectroscopy (AAS), which yields a negative correlation between the applied TPABr concentration and the Na content in the final solid (Figure 3a). However, the linear correlation between the alkali metal content and the catalytic performance identifies the generated sites as active centers in the reaction (Figure 3b).

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**Figure 2.** a) External surface area, micropore volume, and b) crystallinity of the USY samples treated in 0.5 M Na<sub>2</sub>CO<sub>3</sub> and varying concentrations of TPABr for 10 min at 298 K. The conversion of propanal over the samples in the gas-phase condensation at 673 K after 2 h on stream is shown in b. Open symbols represent the parent USY-P zeolite.

For further investigations, the USY zeolite submitted to treatment with  $0.5 \text{ M} \text{ Na}_2\text{CO}_3$  and 0.02 M TPABr (denoted USY-Na-CT0.02) was considered as a reference as it corresponds to the highest activity that was obtained with the full retention of the textural properties and crystallinity of the sample.

# Nature of the active sites

The high-silica zeolites were subjected to additional treatments to improve the fundamental understanding of the active sites through indirect evidence of their nature. The questions addressed in this section tackle the role of the type of cation, pH, and reversibility of the activation procedure.

First, the zeolite was ion exchanged to the sodium form at neutral pH (Na-USY) to investigate the role of Al-coordinated sodium cations. Through this treatment, a lower amount of sodium was incorporated (0.27 wt%) compared to the alkaline-activated benchmark sample (0.61 wt%). The chemical environment of the incorporated sodium atoms was then investigated by <sup>23</sup>Na magic-angle spinning (MAS) NMR spectroscopy (Figure 4). The spectrum of the Na<sup>+</sup>-exchanged USY zeolite was measured as a reference sample. This zeolite provided one dominant signal at  $\delta = -5$  ppm, which can be attributed to the SI cationic sites in the zeolite. Contributions in the range of chemical shifts from -10 to -20 ppm result from quadrupole coupling.<sup>[22a]</sup> In the alkaline-activated sample, a broad



**Figure 3.** a) Na content of the USY zeolites treated with 0.5 M Na<sub>2</sub>CO<sub>3</sub> as a function of the TPABr concentration in the alkaline solution. b) Correlation between the Na content in the zeolites and the conversion rate of propanal in the gas-phase condensation at 673 K.



**Figure 4.** <sup>23</sup>Na MAS NMR spectra of Na<sup>+</sup>-exchanged and alkaline-activated USY zeolites. The dashed lines denote the a deconvolution of the measured spectrum into the contributions of different Na species in the samples. The spectra were normalized to the number of scans (ns).

signal at  $\delta = -2.0$  ppm is observed, which can be deconvoluted into the contribution of ion-exchanged Na observed previously and a more pronounced, second signal at  $\delta = 1.9$  ppm. This line originates from the excess sodium cations incorporated during the alkaline activation and indicates that the surplus

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sodium is not present in form of occluded sodium oxide particles but rather in an environment similar to that of sodium silicate samples.<sup>[22b]</sup>

A second group of samples was prepared to confirm the necessity of Na for the catalytic activity. Two approaches were considered: the treatment of the USY zeolite in a 0.5 м ammonium hydroxide solution and the ion exchange of alkaline-activated samples with protic cations at neutral or acidic pH (USY-Na-CT0.02-NH<sub>4</sub> and USY-Na-CT0.02-HCl, respectively). In the sample treated with NH<sub>4</sub>OH, the external surface was increased by a factor of two, whereas the microporosity was mostly preserved (Table 2). This result deserves to be highlighted as it

Table 2. Porous properties and coke content of the catalysts.						
Code	$V_{\text{pore}}^{[a]}$ [cm <sup>3</sup> g <sup>-1</sup> ]	$V_{\text{micro}}^{[b]}$ [cm <sup>3</sup> g <sup>-1</sup> ]	$S_{meso}^{[b]}$ [m <sup>2</sup> g <sup>-1</sup> ]	$S_{BET}^{[c]}$ [m <sup>2</sup> g <sup>-1</sup> ]	Weight loss <sup>[d]</sup> [%]	
USY-P	0.53	0.29	108	668	_	
USY-Na-CT	0.57	0.18	257	594	-	
USY-Na-CT0.01	0.53	0.23	109	551	-	
USY-Na-CT0.02	0.58	0.29	118	674	1.6	
USY-Na-CT0.03	0.58	0.29	119	680	-	
USY-Na-CT0.04	0.57	0.29	116	668	-	
USY-Na-CT0.05	0.57	0.30	113	688	-	
USY-Na-CT0.2	0.58	0.30	112	679	-	
USY-K-CT0.02	0.58	0.27	123	635	-	
USY-NH₄OH	0.63	0.25	216	688	-	
USY-Na-CT0.02-HCI	0.58	0.28	132	659	-	
USY-Na-CT0.02-NH <sub>4</sub>	0.54	0.29	117	679	-	
BEA-P	0.31	0.18	129	481	-	
BEA-Na-CT0.02	0.30	0.16	99	403	3.1	
MFI-P	0.19	0.16	22	328	-	
MFI-Na-CT	0.19	0.16	14	314	-	
MFI-Na-CT0.02	0.18	0.17	21	336	5.0	
MFI-Na-CT0.1	0.20	0.18	21	352	-	
MFI-Na-CT0.2	0.21	0.18	24	358	-	
MFI-AT	0.21	0.13	199	456	6.4	
SiO <sub>2</sub>	0.60	0.23	192	638	-	
SiO <sub>2</sub> -Na-CT0.02	0.52	0.16	165	526	1.9	
Cs-X	0.02	0.18	14	365	14.1	
MgO	0.49	0	127	127	7.0	
MgO nano	0.49	0	770	770	7.0	
[a] Volume adsorbed at $P/P_0=0.99$ . [b] <i>t</i> -plot method. [c] BET method. [d] Thermogravimetric analysis after use in the addel condensation of						

propanal for 2 h.

opens possibilities to prepare hierarchical high-silica zeolites without relying on organic pore-directing agents. However, the ion exchange of the alkaline-activated sample with NH<sub>4</sub>NO<sub>3</sub> or HCl did not result in altered textural properties.

Lastly, alkaline activation was performed using 0.5 MK<sub>2</sub>CO<sub>3</sub> with 0.02 M TPABr (USY-K-CT0.02) to create a sample with K-coordinating defects and thereby investigate the influence of the charge-balancing cation. The crystallinity of this sample was reduced slightly because of the increased basicity of the solution linked to the larger cation size (Table 2).

The catalytic performance of the prepared samples can be seen in Figure 5. The Na-exchange procedure did not result in a material with an enhanced activity compared to the parent



Figure 5. Conversion rate of propanal in the gas-phase condensation at 673 K over USY samples subjected to distinct acid and base treatments after 2 h on stream.

counterpart ( $X_{propanal} = 2.2\%$ ), which indicates that the cationic sites induced by Al do not contribute to the basicity.

The introduction of mesopores through the NH<sub>4</sub>OH treatment also failed to improve the catalytic activity of the sample. As no thermally stable cation was present, no active sites could be generated, and the sample performed at the level of the parent zeolite. Similarly, if an alkaline-activated sample is subjected to the presence of protic cations, the sites generated previously are removed and the catalytic activity is lost.

The K-containing catalyst attained a slightly higher conversion compared to the Na-based counterpart. This result confirms that siloxy sites can be generated with other cations, which increases the opportunities to tune their basic strength and should be further investigated.

To gain additional understanding of the reaction, the temperature-programmed desorption (TPD) of the propanal-saturated USY-Na-CT0.02 zeolite was followed by MS (Figure 6). Three signals were observed characteristic of propanal (m/z =29), the aldol condensation dimer (m/z=98), and the trimer



Figure 6. TPD profiles of parent and activated USY zeolites saturated with propanal vapor.

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(m/z = 138). If the trace of propanal is followed, four distinct contributions can be observed for the alkaline-activated sample. The first contribution at T = 402 K corresponds to weakly adsorbed propanal, whereas the signals at T = 463 and 553 K originate from the desorption of weakly adsorbed dimer and trimer species as evidenced by the contributions of the corresponding traces. The signal at T = 667 K, however, corresponds to propanal that is chemisorbed strongly on the basic sites in the zeolite. Interestingly, this signal is not observed for the USY-P sample, which suggests that the active sites are probed. Unluckily, the partial overlap with the signal of the weakly adsorbed trimer makes an accurate quantification of the number of active sites problematic.

In conclusion, basic sites can be generated easily in highsilica zeolites through an alkaline treatment in the presence of thermally stable cations such as Na or K (Scheme 3). To prevent



**Scheme 3.** Postulated generation and deactivation of siloxy species by postsynthetic treatments in alkaline and acid media.

the amorphization of fragile frameworks, stabilizing agents such as tetraalkylammonium cations are required, which coordinate to a fraction of the generated defects. Upon calcination, these organic-coordinating siloxy groups are transformed back into silanol groups so their amount needs to be minimized. Additionally, the active sites can be reconverted into silanol groups through acid treatment or ion exchange with protic cations.

#### Influence of the zeolite framework

After we had elaborated the fundamental understanding of the generation and deactivation of the active sites, the validity of the concept for other framework types (BEA and MFI) was investigated. Again, the catalytic activities of the Na ion-exchanged zeolites are minor for both frameworks (< 2%).

For comparative purposes, the BEA sample was also subjected to a treatment with  $0.5 \text{ M} \text{ Na}_2\text{CO}_3$  and 0.02 M TPABr. A larger amount of Na could be incorporated into this zeolite compared to the USY sample activated under identical conditions (1.81 vs. 0.61 wt%) and the obtained catalyst surpassed the activity of the best FAU sample despite the decreased micropore volume (Table 2). The BEA sample was found to be more sus-

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In contrast, the MFI zeolite features a high stability in basic media and no excessive dissolution occurred during the activation treatment even in the absence of TPABr, as evidenced by the unaltered pore volume ( $V_{\rm pore}$ ) and crystallinity of the samples (Figure 7 a). In an attempt to protonate the siloxy groups



**Figure 7.** a) Crystallinity and micropore volume of the MFI samples treated in 0.5 mm Na<sub>2</sub>CO<sub>3</sub> and varying concentrations of TPABr for 10 min at 298 K. The initial conversion of propanal over the samples in the gas-phase condensation at 673 K and their Na contents are shown in b. Open symbols represent the parent MFI-P zeolite.

gradually, the amount of pore-directing agent applied during the treatment was varied. However, with the increasing TPABr concentration, the Na content in the samples decreased to approximately 50% of its maximum value, at which it reached a plateau (Figure 7b). Unlike the observations made for USY, the generation of active sites cannot be fully suppressed by the application of large amounts of pore-directing agent. This dissimilarity is likely related to the smaller micropores size of the MFI framework, through which the large TPA<sup>+</sup> cations cannot diffuse efficiently. Therefore, the inner part of the zeolite is activated to the same extent regardless of the amount of TPABr present in the solution, and only the external surface is passivated. Accordingly, for MFI samples prepared in the presence of TPABr, only the active sites located in the micropores are expected to contribute to the catalytic activity. As the amount of Na is related to the number of active sites, the selective inhibition of the mesopore surface enables us to probe diffusion limitations through comparison of the turnover frequencies (TOFs). As the catalysts with Na located solely in the micropores reach the same average TOFs values (MFI-Na-CT*x*, TOF = 18.2 h<sup>-1</sup>) as the samples with Na<sup>+</sup> also on the external surface (MFI-Na-CT, TOF = 18.5 h<sup>-1</sup>), the reaction does not occur under micropore-diffusion control even for the MFI zeolite.

However, the small pores of the MFI framework influence the distribution of products, which induces shape-selective properties. The selectivity to the aldol condensation trimer is mapped against the observed reaction rate in Figure 8. Gener-



Figure 8. Conversion of propanal versus the selectivity to the aldol condensation trimer over the alkaline-activated zeolites.

ally, higher rates favor the formation of the trimer, and the obtained selectivity follows a clear trend for the FAU and BEA samples. As a result of the confined space in the MFI micropores, the dimer is less likely to react to the trimer for this framework, therefore, the fraction of the trimer is reduced. Moreover, the slow diffusivity of this compound induces a significant disadvantage as the long residence time in the pores favors further oligomerization and thus deactivation of the catalyst through pore blockage. This effect is more pronounced for samples in which the active sites are located purely in the micropores, such as MFI-Na-CT0.02 (Figure 9), compared to the MFI sample prepared without TPABr, in which the active sites are also located on the external surface. Accordingly, the presence of an auxiliary mesopore network should result in a slower deactivation of the catalyst as the residence time of dimers in the pore system is reduced and a larger fraction of the reaction takes place on the external surface. Through desilication assisted by pore-directing agents,<sup>[23]</sup> the porosity of the MFI zeolite could be increased and the crystallinity was mostly preserved (MFI-AT, Table 2). As a result of the high pH applied during this treatment, a larger amount of Na (2 wt%) could be introduced into the zeolite to lead to a doubled catalytic activity compared to the sample activated with sodium carbonate. As expected, the hierarchical MFI was deactivated much more slowly than its conventional counterparts and stabilized at around 85% of its initial activity (Figure 9). Although the



Figure 9. Percentage of the initial activity in the gas-phase condensation of propanal at 673 K versus time-on-stream over different MFI zeolites.

shape-selective characteristics of the MFI framework are not of particular interest in the scope of bio-oil upgrading, they could be highly beneficial in fine chemistry, in which the dimer has applications as a fragrance and intermediate.<sup>[24]</sup>

In conclusion, the activation procedure described for the FAU zeolite is easily extendable to diverse zeolite frameworks. The presence of relatively small micropores in the zeolite is, however, a non-negligible drawback as it reduces the lifetime of the catalyst. In this case, the introduction of a secondary mesopore network proved to be crucial to overcome this disadvantage.

### Comparison with other base catalysts

To estimate the potential of the new catalysts, their activity, selectivity, and stability were compared to state-of-the-art base catalysts. A Cs<sup>+</sup>-exchanged zeolite X (denoted Cs-X), a conventional and a nanosized MgO sample, and an alkaline-activated SiO<sub>2</sub> sample (SiO<sub>2</sub>-Na-CT0.02) were investigated as reference materials. With regard to the initial activity, the nanosized MgO sample was identified as the most active catalyst, followed closely by the alkaline-activated beta sample (Figure 10a). The porous properties of the catalysts are provided in Table 2. Upon alkaline activation of the commercial SiO<sub>2</sub>, its surface area was reduced, which suggests that partial dissolution occurred. Apparently, as a result of the amorphous character of silica, Si extraction is difficult to suppress. Nevertheless, the activated silica provided an excellent catalytic performance, which suggests that the generation of active sites is not restricted to zeolites. Accordingly, the application of highly porous silica could be a promising opportunity; however, its preparation is not straightforward as its susceptibility to dissolution is even higher.

The deactivation of the catalysts was assessed by normalizing their rate to the initial rate (Figure 10b). The Cs-X zeolite deactivated quickly because of coking and contained the highest amount of coke after the reaction (Table 2). The nanosized MgO sample suffered from slower deactivation than its lowsurface-area analogue but still fell below 70% of its initial activity after 2 h on stream, which indicates the need for im-

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Figure 10. a) Initial rate and b) percentage of the initial activity in the gasphase condensation of propanal versus time-on-stream for activated silicabased materials and traditional base catalysts.

proved stability if established basic materials are considered. In contrast, the siloxy-based catalysts displayed very slow deactivation after an initial stabilization and preserved up to 85% of their initial value. As observed previously for MFI samples, the accessibility of the active sites is key to avoid deactivation; therefore, the alkaline-activated USY zeolite provided the highest stability. The stability of this catalyst was further investigated in a longer experiment (Figure 11). After the initial equilibra-



Figure 11. Stability of the USY-Na-CT0.02 catalyst in the gas-phase condensation of propanal at 673 K.

tion, the performance was very stable, and 87% of the original activity was retained even after 15 h on stream. These results suggest that the amount of coke deposited on the catalyst is minor, which was confirmed by thermogravimetric analysis (1.3% after 15 h on stream), whereas in acidic upgrading pathways a substantial fraction of the carbon can be lost.<sup>[3a]</sup> In terms of selectivity, the aldol condensation dimer was observed as the major product for all the catalysts tested, accompanied by the formation of the aldol condensation trimer (Figure 12). However, the fraction of trimer was very small for the MgO-based samples, which indicates that the strong adsorption of this species might lead to oligomer formation on the surface that subsequently contributes to the deactivation of the catalyst. Additionally, the formation of 3-pentanone was observed for all of the catalysts that deactivated strongly, which adds to the deactivation caused by the formation of coke.



Figure 12. Product yields in the self-condensation of propanal at 673 K over selected catalysts after 2 h on stream.

#### Extrapolation to ketonization reactions

To demonstrate the efficiency of high-silica zeolites in further reactions relevant in the upgrading of bio-oil, the ketonization of propionic acid to form 3-pentanone was investigated (Scheme 2b). Besides deoxygenation, this coupling reaction is crucial to reduce the corrosive character of carboxylic acids in bio-oil. In agreement with previous reports,<sup>[25]</sup> the parent zeolite attains around 12% conversion in this reaction, and methyl propanoate, propionic anhydride, and 3-pentanone are formed as the major products (Figure 13). The anhydride is formed through the base-catalyzed acetalization of propionic acid and can be further converted into 3-pentanone in the presence of stronger basic sites (Scheme 2b). In contrast, methyl propanoate is likely formed over an acid-catalyzed pathway that uses the weak acidity of certain silanol groups.<sup>[26]</sup> Although the activation of the USY sample only leads to a moderate activity enhancement, the selectivity pattern is altered significantly. As

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**Figure 13.** Product yields in the ketonization of propionic acid at 673 K over USY zeolites and traditional base catalysts after 2 h on stream.

the acid sites are deactivated in the alkaline environment, and basic siloxy sites are formed, only the anhydride and ketonization products are observed, and the selectivity to the latter product is increased significantly. A similar increase in the 3-pentanone selectivity was reported for MFI zeolites modified by treatment with  $3.7 \text{ M} \text{ NH}_3 + 0.7 \text{ M} \text{ NH}_4 \text{NO}_3$ .<sup>[25]</sup> The interplay between the strength of basic sites and the level of the formation of this compound is also reflected if traditional basic materials are considered. The acetal intermediate was converted to 3-pentanone to a high extent over Cs-X zeolite. With the MgO catalyst that possesses an even stronger basicity, propionic anhydride was not detected anymore. These observations suggest that the basic sites generated in the USY zeolite have a moderate strength.

Besides their outstanding performance in the aldol condensation of aldehydes, high-silica zeolites also catalyze acetalization and ketonization reactions of carboxylic acids efficiently. These findings underline the advantage of an intermediate catalytic deoxygenation of bio-oil, in which a pronounced reduction of the oxygen content of pyrolysis vapors can be expected through the combination of multiple catalytic pathways. Besides the improved stability, decreased corrosivity, and increased heating value of the thereby obtained bio-oil condensate, catalytic upgrading through C-C bond formation reactions also has the unique property of increasing the contents of higher hydrocarbons by the assembly of short-chain molecules. Although it poses challenging tasks in terms of catalyst design, we expect intermediate catalytic deoxygenation to play a key role in the production of second-generation biofuels.

# Conclusions

We demonstrate the generation of siloxy sites in silica-rich materials through alkaline activation treatments, which prove to

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be an attractive source of moderate basicity. The resulting catalysts combine high activity, selectivity, and stability in reactions of relevance to the upgrading of bio-oil, in which they outperform traditional basic zeolites and strong bases such as MgO and rely only on abundant and accessible raw materials. The catalysts introduced in this work represent a cost-efficient and environmentally benign solution to reduce hydrogen consumption in the cascade upgrading of bio-oil, and thereby accelerate the industrial realization of sustainable fuels.

# **Experimental Section**

### **Catalyst preparation**

Parent high-silica zeolites were obtained in the protonic form from Tosoh Corporation: HSZ-390HUA with molar Si/Al = 385 (USY-P), HSZ-890HOA with molar Si/Al=1060 (MFI-P), HSZ-980HOA with molar Si/AI = 220 (BEA-P). Zeolite X with molar Si/AI = 1.4 (X) was supplied by Sigma-Aldrich in the Na form. Silicon dioxide nanopowder 10-20 nm (SiO<sub>2</sub>) was purchased from Sigma-Aldrich, and MgO samples (magnesium oxide 99.5% mesh 375, MgO; magnesium oxide nanopowder, MgO nano) were obtained from Strem Chemicals. The properties of the as-received catalysts are summarized in Table 2. Activation treatments of high-silica zeolites were performed in 50 cm<sup>3</sup> glass reactors at RT. In a typical experiment, the reaction solution was prepared by dissolving the desired amount of base (NaOH, Na<sub>2</sub>CO<sub>3</sub>, or NH<sub>4</sub>OH, 10<sup>-4</sup>–1 M) and TPABr (0-0.2 M) in water (30 mL). Then, the zeolite (1 g) was treated under vigorous stirring (1-10 min), collected by filtration and washed thoroughly with deionized water. Acid treatments were conducted in aqueous 0.1 M HCl. Ion-exchange procedures with NH<sub>4</sub>NO<sub>3</sub>, NaCl, and CsCl were performed by subjecting the zeolite to three subsequent treatments in aqueous solutions of the salt  $(0.1 \text{ M}, 8 \text{ h}, 298 \text{ K}, 10 \text{ g}_{\text{zeolite}} \text{L}^{-1})$ . Hierarchical MFI zeolite was obtained by treating the zeolite (33 g L<sup>-1</sup>, 0.5 h, 338 K) in a solution of NaOH (0.2 M) and TPABr (0.2 M). To remove organic species adsorbed during the treatment, all catalysts were calcined in static air (823 K, 5 h, 5 Kmin<sup>-1</sup>). Sample names are summarized in Table 1.

#### Characterization

Porous properties were determined by  $N_2$  sorption at 77 K on dried samples (673 K, 3 h, 10<sup>-5</sup> bar) by using a Micromeritics TriStar II instrument. The total surface area  $(S_{BET})$  was calculated using the BET model, and the t-plot method was used to determine the micropore volume ( $V_{micro}$ ) and mesopore surface area ( $S_{meso}$ ). XRD patterns were measured by using a PANalytical X'Pert PRO-MPD diffractometer using Ni-filtered CuK<sub>a</sub> radiation ( $\lambda = 0.1541$  nm). Data were recorded in the  $2\theta$  range of 5–70° with an angular step size of 0.05° and a counting time of 8 s per step. The sodium content in the solids was determined by AAS by using a Varian SpectrAA 220 FS instrument. <sup>23</sup>Na MAS NMR spectra were recorded at a spinning speed of 10 kHz by using a Bruker Avance 700 spectrometer equipped with a 4 mm probe head and 4 mm ZrO<sub>2</sub> rotors at 185.2 MHz. Spectra were obtained using 4096-8192 accumulations with a pulse length of 1  $\mu s,$  a recycle delay of 0.25 s, and 0.1  $\kappa$ NaCl in D<sub>2</sub>O as a reference. Before the measurement, samples were evacuated at 573 K for 4 h. Thermogravimetric analysis (TGA) of the used catalysts was performed by using a Mettler-Toledo TGA/ DSC 1 instrument by heating the solid (20 mg, 298-1173 K, 10 Kmin<sup>-1</sup>) in flowing air (60 cm<sup>3</sup>min<sup>-1</sup>). The TPD of propanal was performed by using a Micromeritics Autochem II analyzer. The catalyst (100 mg) was pretreated in a He flow ( $20 \text{ cm}^3 \text{min}^{-1}$ , 823 K, 10 K min<sup>-1</sup>, 1 h), cooled to 338 K, and subjected to 50 pulses (1 cm<sup>3</sup>) of He saturated with propanal vapor at 318 K. The sample was purged under a He flow ( $20 \text{ cm}^3 \text{min}^{-1}$ , 338 K, 1 h) and subsequently heated to 873 K at a ramp rate of 10 K min<sup>-1</sup>. The composition of the outgas flow was monitored by using a Cirrus 2 quadrupole mass spectrometer.

## **Catalytic tests**

The aldol condensation of propanal and the ketonization of propionic acid were both performed under atmospheric pressure by using a continuous-flow fixed-bed reactor (12 mm i.d.) loaded with 0.3 g of catalyst (particle size=0.2–0.4 mm). Prior to the reaction, the catalyst was pretreated in He (50 cm<sup>3</sup>min<sup>-1</sup>, 723 K, 10 Kmin<sup>-1</sup>, 1 h). The reactant was fed into the reactor by using a syringe pump (1.2 cm<sup>3</sup>h<sup>-1</sup>) through a vaporization line and diluted with He (50 cm<sup>3</sup>min<sup>-1</sup>). The reactions were typically conducted at 673 K for 2 h and analyzed by an on-line HP Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID) and a capillary HP-5 column. Conversion (*X*) and yields (*Y*) of the different products i were calculated based on the FID area of the compound of interest by normalization to the total FID area. Turnover frequencies were obtained by normalization of the amount of converted reactant per unit of time to the amount of Na in the catalyst.

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# **FULL PAPERS**

**Creating new basic sites:** Through activation treatments in alkaline media, basic sites with high activity, stability, and selectivity are generated in highsilica FAU, BEA, and MFI zeolites, which enable the efficient deoxygenation of pyrolysis oil by condensation reactions. Intermediate bio-oil upgrading is key for the sustainable and profitable production of advanced biofuels.

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Generation of Basic Centers in High-Silica Zeolites and their Application in Gas-Phase Upgrading of Bio-Oil