Layer-Like Zeolite X as Catalyst in a Knoevenagel Condensation: The Effect of Different Preparation Pathways and Cation Exchange

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Abstract: This study is dedicated to the comparative investigation of the catalytic activity of layer-like Faujasite-type (FAU) zeolite X obtained from three different synthesis routes (additive-free route, Li2CO3 route, and TPOAC route) in a liquid-phase Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate to ethyl trans-α-cyanocinnamate. It is shown that the charge-balancing cations (Na+ and K+) and the morphological properties have a strong influence on the apparent reaction rate and degree of conversion. The highest initial reaction rate could be found for the layer-like zeolite X synthesised by the additive-free route in the potassium form. In most cases, the potassium-exchanged zeolites enabled higher maximum conversions and higher reaction rates compared to the zeolite X catalysts in sodium form. However, very thin crystal plates (below 100 nm thickness), similar to those obtained in the presence of TPOAC, did not withstand the multiple aqueous ion exchange procedure, with the remaining coarse crystals facilitating less enhancement of the catalytic activity.

Keywords: zeolite X; morphological modification; layer-like zeolites; ion exchange; Knoevenagel condensation; heterogeneous catalysis

1. Introduction

The Knoevenagel condensation is a special case of aldol condensation and one of the most established carbon coupling reactions for the synthesis of fine chemicals and biologically active substances [1,2]. This carbon–carbon bond-forming reaction is typically catalysed by homogeneous bases and basic microporous materials [1,3]. The Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate in the liquid phase catalysed by conventional Faujasite-type (FAU) zeolites X and Y exchanged with various charge-balancing cations (Li, Na, K, and Cs) was initially described by Corma et al. [4,5]. There, an increase in the catalytic activity of the FAU-type zeolites was linked with an increase of the average negative charge on the framework oxygen atoms, which occurred when the radius of the charge balancing cation was increased, or the molar Si/Al ratio was decreased [4]. Verboekend et al. performed the Knoevenagel condensation with differently sized reactants over hierarchical FAU- and Linde Type A (LTA) zeolites [6,7]. They showed that it was possible to enhance the activity of a zeolite up to 10 times in a base catalysed Knoevenagel condensation of benzaldehyde with malononitrile via the introduction of a secondary porosity [6,7]. In 2002, Zhan et al. described how the external surface area of FAU-type zeolite NaX could be controlled on the basis of the crystal size, which was found to be dependent on the synthesis gel composition and the crystallisation conditions in an organic-free synthesis medium [1,7]. Interestingly, the morphology of the zeolite crystals shown in their SEM images was already quite similar to the now widely investigated layer-like NaX systems [2]. These materials synthesised in the absence of any morphology modifying additive were further referred to as additive-free layer-like zeolite X, according to the nomenclature suggested by Reiprich et al. [8]. Besides the additive-free synthesis route, which yields quite coarse...
layer-like zeolite X, also the addition of morphology modifying agents (MMAs) can be used to achieve layer-like zeolites, which can facilitate even higher specific external surface areas, larger mesopore volumes, thinner layer-like crystals, and different contents of the zeolitic intergrowth structure EMT (Elf Mulhouse Chimie Two) [9–11]. Such MMAs can be, e.g., inorganic salts as reported for the addition of Li₂CO₃ or organic mesoporogens such as 3-(trimethoxysilyl)propyl dimethyloctadecylammonium chloride (TPOAC) or 3-(trimethoxysilyl)propyl dimethylhexadecylammonium chloride (TPHAC) [9,10]. Independent of their synthesis route the thus obtained modified NaX particles consist of intergrown layer-like FAU(X)/EMT crystals. The thickness of their single layers can be controlled via a variation of the synthesis gel composition [8]. Medeiros-Costa et al. conducted an in-depth characterisation of the physical and chemical properties of additive-free and Li₂CO₃-derived layer-like zeolite X in the sodium as well as in the barium exchanged form [12].

Compared to conventional octahedral zeolite X, the layer-like modifications exhibited an increased external surface area and, in addition, as shown for the TPOAC-based material, a significantly increased intracrystalline mesoporosity, which together with the reduced crystal thickness could enable faster transport of reactants to the active sites inside such hierarchical zeolite particles [13,14].

 Also, FAU zeolites with Si/Al⁻¹ molar ratios between 1.4 (zeolite X), 2.6 (zeolite Y), and 385 (ultra-stable zeolite Y/USY containing additional mesopores) were applied for the carbon coupling of benzaldehyde with malononitrile in the liquid phase with H⁺, Na⁺, K⁺, and Cs⁺ as charge-balancing cations. A favoured conversion of benzaldehyde with increasing cation radius and mesopore surface area was monitored. In addition, the ultra-stable zeolite Y with Na⁺ and Cs⁺ as charge-balancing cations was applied as catalyst for a gas-phase reaction of propanal [15,16]. A higher conversion of propanal was found, especially for additionally alkaline treated USY, which again correlated with an increase of the mesopore surface area [15]. Recently, Yutthalekha et al. showed that mesoporous layer-like zeolite X (in the Na, Ca, and Ba form) obtained via the TPOAC route is capable of catalysing the aldol condensation of 5-hydroxymethylfurfural and acetone [17,18]. Again, the mesoporous X catalyst showed higher conversion compared to conventional X.

Here, we present the results of our comparative investigations on the catalytic activity of layer-like zeolite X obtained from the three above-mentioned synthesis routes (additive-free route, Li₂CO₃ route, and TPOAC route) in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. In particular, it will be shown how the thickness of the layer-like crystals, the different textural properties, and the charge-balancing cations (Na⁺ and K⁺) affected the apparent reaction rate and degree of conversion over those zeolite catalysts.

2. Results and Discussion
2.1. Material Characterization before and after Ion Exchange
2.1.1. Parent NaX Samples

The XRD patterns of all synthesis products dried after filtration and in the case of NaX-TPOAC after subsequent calcination are shown in Figure 1a. All reflections in Figure 1 belong to the FAU(X) structure [19]. This identification was based on the assignment of the XRD reflections to the Miller hkl indices of the FAU structure given in Figure S1 in the Supplementary Information. The broadened reflection at a diffraction angle of 6.11° 2-theta was due to the intergrowth with the EMT twin structure, which is characteristic for the layer-like zeolite X materials [11]. Furthermore, the higher portion of the external surface area in the layer-like crystals (Table 1) caused a higher amount of gas/solid interfaces, i.e., crystal defects, which also contributed to the broadening of reflections. This showed that, independent of the chosen synthesis route, zeolite X was formed with a fraction of EMT intergrowth for all three layer-like materials.
According to the SEM images in Figure 2a–d all NaX samples exhibited the expected morphology, i.e., NaX-Conv was characterised by compact octahedral crystals with only a slight twinning as described by Ferdov et al. [20], while NaX-TPOAC (Figure 2d), NaX-Li$_2$CO$_3$ (Figure 2c), and NaX-Addfree (Figure 2b) showed layer-like morphology as described for these synthesis routes by Inayat et al. [10] and Reiprich et al. [8]. Crystalline and amorphous impurities could not be observed in the SEM images (Figure 2a–d). The samples NaX-Conv and NaX-Addfree were synthesised with the same amount of Na$_2$O in the synthesis gel and only differed from each other in temperature and duration of the hydrothermal treatment (Table 4).

Besides the formation of a layer-like morphology with a reduced hydrothermal treatment temperature of 50 °C, the average particle size decreased from 2.56 µm to 1.60 µm (Table 2). As mentioned above, without changing the hydrothermal treatment temperature but with the addition of the morphology modifiers Li$_2$CO$_3$ and TPOAC a layer-like morphology could also be formed. Both of these synthesis routes took place with reduced amounts of Na$_2$O in the synthesis gel. For NaX-Li$_2$CO$_3$, the ratio of Na$_2$O to Al$_2$O$_3$ was reduced from 4.0 to 3.7, and for NaX-TPOAC further on to 3.5. With a decreasing ratio of Na$_2$O to Al$_2$O$_3$, the overall particle size increased from NaX-Conv to NaX-Li$_2$CO$_3$ and NaX-TPOAC in the row from about 2.56 µm to 3.56 µm and 5.9 µm, respectively. Additionally,
the plate thickness was changing depending on the synthesis route. NaX-TPOAC exhibited the thinnest plates with an average thickness of 96 nm. NaX-Li₂CO₃ had the thickest plates with an average thickness of 183 nm, while the crystallisation of NaX-Addfree led to the formation of plates with a thickness of 126 nm.

Table 1. Textural data from N₂ physisorption and elemental molar ratios from ICP-OES of all four zeolites with different morphologies before and after the 1st and 6th ion exchange. (- = not determined).

| N₂ Physisorption Results | ICP-OES Results |
|--------------------------|------------------|
|                          | A$_{\text{spec}}$ m$^2$ g$^{-1}$ | A$_{\text{ext}}$ m$^2$ g$^{-1}$ | V$_{\text{micro}}$ cm$^3$ g$^{-1}$ | V$_{\text{meso}}$ cm$^3$ g$^{-1}$ | Si Al$^{-1}$ | Na Al$^{-1}$ | K Al$^{-1}$ | Li Al$^{-1}$ |
| As-synthesised 923      | 110              | 0.308                          | 0.093                          | 1.45                  | 0.87       | -          | -          | -          |
| 1st ion exchange 789    | 97               | 0.261                          | 0.076                          | 1.50                  | 0.33       | 0.53       | -          | -          |
| 6th ion exchange 781    | 98               | 0.258                          | 0.077                          | 1.33                  | 0.01       | 0.95       | -          | -          |
| (change compared to as-synthesised) | -15%                 | -11%                           | -16%                           | -17%                 | -          | -          | -          | -          |

Table 2. Average plate thickness and particle diameter from SEM images of around 50 plates and particles. The variance of the values is also given.

|                          | NaX-Conv | NaX-Li₂CO₃ | NaX-Addfree | NaX-TPOAC |
|--------------------------|----------|------------|-------------|-----------|
| Plate thickness\(\text{nm}\) | -        | 183 ± 34   | 126 ± 22    | 96 ± 19   |
| Particle diameter\(\text{µm}\) | 2.56 ± 0.42 | 3.56 ± 0.39 | 1.60 ± 0.22 | 5.90 ± 1.32 |

This illustrates that the morphology of the particles could be adjusted systematically on the basis of the chosen synthesis route and conditions. The reasons for these changes might be on the one side the addition of the growth modifiers Li₂CO₃ and TPOAC and on the other side the changes in synthesis gel composition, in particular, their Na₂O content and hydrothermal treatment temperature and duration. Reiprich et al. [8] showed for X-Addfree that the size of the zeolite particles and the layer-like crystal thickness decreased with decreasing water content of the synthesis gel and therefore increasing Na₂O concentration. NaX-TPOAC and NaX-Li₂CO₃ had the largest overall particle size, which might be the result of the lowered Na₂O content in the synthesis gel, while the formation of very thin crystal plates below 100 nm was induced by the presence of TPOAC [10].
Figure 2. SEM images of zeolite samples with different morphology (a–d) before (as-synthesised, NaX-forms) and (e–h) after the first (Na/K-mixed forms) and (i–l) sixth ion exchange (mainly KX-forms) as indicated by the column headings.

The textural properties determined via nitrogen physisorption of all applied catalysts are summarised in Table 1. The respective nitrogen physisorption isotherms are depicted in Figure 3a–d. The nitrogen physisorption isotherm of zeolite X with conventional morphology (X-Conv) shown in Figure 3a was a type I isotherm independent of the potassium content. This means that this material had predominantly micropores with a volume of 0.301 cm$^3$·g$^{-1}$. The mesopore volume of 0.093 cm$^3$·g$^{-1}$ and the mesopore size distribution shown in Figure 4 were a result of nitrogen condensation in interparticle void spaces and within the imperfect regions of the zeolite X crystals. The specific surface area was 923 m$^2$·g$^{-1}$ with an external surface area of 110 m$^2$·g$^{-1}$.
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The textural properties determined via nitrogen physisorption of all applied catalysts are summarised in Table 1. The respective nitrogen physisorption isotherms are depicted in Figure 3. The nitrogen physisorption isotherm of zeolite X with conventional morphology (X-Conv) shown in Figure 3a was a type I isotherm independent of the potassium content. This means that this material had predominantly micropores with a volume of 0.301 cm$^3$·g$^{-1}$. The mesopore volume of 0.093 cm$^3$·g$^{-1}$ and the mesopore size distribution shown in Figure 4 were a result of nitrogen condensation in interparticle void spaces and within the imperfect regions of the zeolite X crystals. The specific surface area was 923 m$^2$·g$^{-1}$ with an external surface area of 110 m$^2$·g$^{-1}$.

Figure 3. Nitrogen physisorption isotherms of the zeolite X materials with conventional morphology (a), layer-like morphology via temperature reduction (b), layer-like morphology due to the addition of Li$_2$CO$_3$ (c), and the addition of the organosilane TPOAC (d). Each zeolite is shown before and after the first ion exchange and after the sixth ion exchange.
Figure 4. Pore size distributions of zeolite X from the different synthesis routes with varying amounts of potassium ions before (NaX, no K content) and after (NaKX with a mixture of Na and K; KX with almost 100% K) ion exchange.

This indicates that the majority of the catalytic centres were located inside the micropores. The nitrogen physisorption isotherms of the layer-like zeolites NaX-Addfree (Figure 3b) and NaX-Li₂CO₃ (Figure 3c) showed the presence of micropores with very similar micropore volumes of 0.258 cm³·g⁻¹ and 0.248 cm³·g⁻¹, respectively. The external surface area increased for both synthesis routes from 110 to 153 m²·g⁻¹ (NaX-Addfree) and 131 m²·g⁻¹ (NaX-Li₂CO₃). An additional effect concerning the shape of the isotherms was possible cavitation due to the layer-like morphology formation. During the formation of the intergrowth regions of the crystal plates, larger void volumes could be enclosed as described by Khaleel et al. [11]. As a result, with increasing relative adsorption pressure, a void space in the size range of meso- or macropores was filled with liquid nitrogen, which was surrounded by a microporous material. During desorption, this nitrogen evaporated and additionally removed the nitrogen also from the micropores. This effect could falsify the description of the mesopore volume. The addition of the organosilane (NaX-TPOAC) enabled the additional formation of mesopores
inside the intergrown NaX plates, whose presence was responsible for the hysteresis in the nitrogen physisorption isotherm [10]. Therefore, the NaX-TPOAC in this study had a micropore volume of 0.17 cm$^3$·g$^{-1}$ and a mesopore volume of 0.24 cm$^3$·g$^{-1}$. Furthermore, the slope of the isotherms in Figure 3b,d, close to saturation pressure, was an additional indication for the presence of the layer-like morphology, i.e., an external surface that was not attributed to mesopores. It could generally be found that the layer-like morphology caused a decrease in the micropore volume and specific surface area and an increase in the external surface area and additional mesopores [21].

The acid-base properties of zeolites were based on the presence of tetrahedral aluminium atoms in the zeolite structure. To investigate if all the different synthesis pathways enabled a proper integration of the aluminium atoms in the zeolite framework or if octahedral extra-framework aluminium species occurred, solid-state $^{27}$Al NMR measurements were conducted. The results are shown in Figure 5a–d.

![Figure 5. Solid-state $^{27}$Al NMR spectra of the zeolite X materials with conventional morphology (a), layer-like morphology via temperature reduction (b), layer-like morphology due to the addition of Li$_2$CO$_3$ (c), and the addition of organosilane (d). Each zeolite is shown before and after the first ion exchange and after the sixth ion exchange.](image-url)
For all four parent zeolite samples (NaX), solely one large signal at 62 ppm was visible, which was indicative for tetrahedrally coordinated aluminium. A signal at around 15 ppm, which would be indicative for (AlO$_5$)- or (AlO$_6$)-species, i.e., external aluminium species \[22\], was not found. This allows the conclusion that all four synthesis routes presented in this study led to a (within the detection limits of solid-state NMR) complete incorporation of aluminium atoms in the zeolite framework.

2.1.2. Na/KX Ion Exchange: Effect on Structure, Texture, and Morphology

To increase the base strength of the oxygen sites in zeolite X, the counter-ion sodium was exchanged for potassium ions. The ion exchange was repeated up to 6 times to achieve a full potassium exchange according to the ICP-OES results shown in Table 1. The X-ray diffraction patterns after each exchange step for each zeolite X morphology are presented in Figure S2 in the Supplementary Information. The normalised XRD patterns obtained after the first and sixth ion-exchange step can be found in Figure 1b,c. The reflections of all samples could still be attributed to the FAU/EMT structure, and no new reflections occurred, which indicated that the zeolite X structure was retained during the multiple exchange steps.

The relative crystallinities in dependence of increasing potassium fraction as charge-balancing cation are shown in Figure 1d and based on the XRD patterns shown in Figure S2 in the Supplementary Information. The crystallinities were calculated as the sum of the areas under the reflections of the (113), (133) and (044) planes at 11.7°, 15.5° and 20.1° 2-theta, respectively. The relative crystallinity was this measured crystallinity value of each sample related to the crystallinity of our standard material NaX-Conv. Accordingly, the relative crystallinity of NaX-Conv was set to 100% since it showed the highest area under the chosen three reflections. All three layer-like zeolite samples showed, in comparison to NaX-Conv, already a reduced crystallinity, which was the result of the layer-like morphology. With progressive ion exchange for potassium, the apparent relative crystallinity for all samples was further reduced, for all morphologies in nearly the same gradual way (see Figure 1d), which could be related to the higher absorption coefficient of the heavier potassium, compared to the lighter sodium for X-rays \[23\]. However, slight structural damage of some samples upon ion exchange cannot be excluded because the textural data obtained from the nitrogen physisorption isotherms indicated stronger changes, e.g., of the micropore volume, for some of the samples, which will be discussed in the following.

The textural properties of all zeolite variants with varying amounts of potassium and sodium cations are summarised in Table 1. With increasing amounts of potassium, a general decrease in micropore volume and specific surface area could be observed. This decrease seemed to be the result of the accumulation of potassium cations (which had a larger ion diameter than sodium) in the micropore framework. Therefore, it reduced the space in which nitrogen could adsorb. Accordingly, with rising amounts of potassium, X-Conv lost micropore volume and specific surface area but also showed a reduced external surface area and mesopore volume (Table 1).

The mesopore size distributions of X-Conv before and after the first ion exchange, as well as after the sixth ion exchange (Figure 4a), showed no significant changes, i.e., the ion exchange procedure did not create or diminish mesoporous voids within the conventional zeolite crystals. Instead, the similar degree of reduction of all textural parameters was rather due to the presence of the heavier potassium cations after ion exchange, which led to a higher framework density.

Further, for X-Li$_2$CO$_3$, X-TPOAC, and X-Addfree, the micropore volume and specific surface area decreased upon potassium exchange (Table 1). Yet, the mesopore volume and external surface area varied with increasing amounts of potassium. For X-TPOAC, the mesopore volume decreased slightly with increasing amounts of potassium, while for X-Li$_2$CO$_3$ and X-Addfree, there was an increase in mesopore volume.

For X-TPOAC, the reduction of mesopore volume and external surface area could be associated with the destruction of the outer very thin parts of the crystal plates of the particles, which could be seen in the SEM images of Figure 2h,l. For X-Li$_2$CO$_3$ and
X-Addfree, the multiple aqueous ion-exchange steps seem to extract surface silica from the samples, which is evident from the widening and right shift of the pore size distributions in Figure 4a and the progressing decrease in the silica to aluminium ratio with subsequent ion-exchange steps.

In contrast to X-TPOAC, the morphology of the intergrown zeolitic plates in X-Li$_2$CO$_3$ and X-Addfree did not change during the ion exchange, which can be seen from the SEM images in Figure 2f,i for X-Addfree and Figure 2g,k for X-Li$_2$CO$_3$, which indicates a much higher mechanical and chemical stability due to the larger plate thickness compared to X-TPOAC.

Furthermore, the zeolite samples were investigated with solid-state $^{27}$Al NMR after the first and sixth potassium exchange in order to find out whether all aluminium would remain within the zeolite framework (AlO$_4$) species upon ion exchange or if some structural damage would lead to disintegration of aluminium, i.e., (AlO$_6$) or (AlO$_5$) species. The resulting spectra can be found in Figure 5. While the parent NaX samples exhibited only AlO$_4$ species, the first ion exchange (NaKX samples) led to the formation of some (AlO$_6$) or (AlO$_5$) species outside the framework [22], which is evident from the additional NMR signal at 15 ppm and which occurs for all morphologies except X-Li$_2$CO$_3$. The portion of extra-framework aluminium species was 4%, 5%, and 3% for NaKX-Conv, NaKX-Addfree, and NaKX-TPOAC, respectively. After the sixth ion exchange (KX samples), the portion of extra-framework Al was generally reduced for all samples. For KX-Addfree and KX-TPOAC 3% and 2% extra-framework Al could be found, respectively. KX-Li$_2$CO$_3$ and KX-Conv both showed only (AlO$_4$) species and no other aluminium species present after the sixth potassium exchange. Accordingly, the extra-framework aluminium species, which were formed during the first ion exchange in X-Conv, disappeared after subsequent ion-exchange steps. Possibly, the extra-framework Al formed after the first ion exchange was washed out during subsequent ion-exchange steps, and the remaining zeolite framework was stable enough to disable any further disintegration of aluminium. This might be related to the already assumed higher mechanical and hydrolytic stability due to thicker crystal size and less external surface area in X-Conv and X-Li$_2$CO$_3$. Additionally, X-Addfree and X-TPOAC seemed to stabilise during subsequent ion-exchange steps, which lead to the occurrence of less extra-framework aluminium.

In general, NMR showed for the conventional as well as the layer-like morphologies that the majority (95–100%) of the aluminium atoms remained tetrahedrally coordinated after the ion exchange for potassium. Thus, since the oxygen atoms next to those tetrahedral aluminium atoms were the base-catalytically active sites, we assume that the catalytic activity of the ion-exchanged zeolite samples would not be significantly affected by the disintegration of a minor fraction (<5%) of aluminium and would rather be influenced by the change of the charge-balancing cation, the different zeolite morphology, and crystal thickness. However, at this point, we do not know if the extra-framework aluminium was predominantly formed at the external surface of the zeolite crystals or also within the micropores. For a definite clarification of this question, surface analytical technique with probe molecules, which can selectively adsorb only at external surface sites, would have to be applied and should be the focus of future studies.

2.2. Catalytic Behaviour in Knoevenagel Condensation

As shown in Table 1 and Figure 1, all parent zeolite X samples have almost identical compositions and structures. Therefore, the differences in catalytic activity, which will be discussed in the following, could be ascribed to the previously discussed morphological and textural specifications as well as the type of charge-balancing alkali cations.

2.2.1. Catalytic Activity of the Parent NaX Samples

Figure 6 shows the average conversion of ethyl cyanoacetate (ECA) in the Knoevenagel condensation with benzaldehyde over the four parent NaX catalysts, each with a different morphology. Each parent zeolite X was tested four times at the same reaction conditions to determine the variance of the catalytic test results. Additional to this, the ECA conversion
in the presence of the liquid base NaOH (156 µL of 1 molar sodium hydroxide solution) was monitored as well as the conversion in absence of any catalyst. Independent of the presence or absence of homogeneous or heterogeneous catalyst, no reaction products besides the Knoevenagel condensation product ethyl trans-α-cyanoacetate were formed. Accordingly, the product selectivity for ethyl trans-α-cyanoacetate was always 100%. The amount of sodium hydroxide solution was calculated according to the approximate average amount of sodium atoms in the NaX-Conv parent zeolite X sample, which equalled in the ideal case the moles of aluminum atoms and thus the amount of active basic sites in the zeolite sample. The calculation for the needed amount is shown in the Supplementary Materials (Table S1). One hour after the addition of the sodium hydroxide solution, a conversion of ECA above 80% was reached. In absence of any catalyst, the conversion of ethyl cyanoacetate was negligible.

The low activity of NaX-Conv was seen as a result of the transport limitation to the catalytically active centres because the large crystal extension in all three directions hindered a fast transport of the reactants through the long micropore channels. For comparison, NaOH solution was tested as a homogeneous basic catalyst where no transport limitation due to confinement in pores could exist. In agreement with the above assumption, the initial reaction rate was the highest using NaOH as a homogenous catalyst.

Table 3 summarises the initial reaction rates for each parent zeolite as well as for the zeolites after the first and sixth ion-exchange step, i.e., the respective zeolite morphologies with different types and ratios of charge balancing Na⁺ and K⁺ cations. The conversion of ECA was monitored for 6 h each. Depending on the investigated zeolite morphology, the overall conversion and the error margin varied. After 6 h of batch reaction, NaX-Conv showed 34% conversion of ECA with an error margin of up to 3.4%, whereas the three layer-like variants NaX-Addfree, NaX-TPOAC, and NaX-Li_2CO_3 enabled 75–80% conversion after 6 h and accordingly a higher reaction rate (Table 3). The initial reaction rate _k_i was almost double for X-Li_2CO_3 and more than tripled for NaX-Addfree compared to NaX-Conv. Right from the start of the reaction, the ECA conversion over both layer-like NaX samples exceeded the conversion of ECA in presence of the conventional NaX crystals (NaX-Conv). The layer-like catalyst NaX-TPOAC caused the highest initial reaction rate among all NaX samples.

Figure 6. Conversion of ethyl cyanoacetate (ECA) in the Knoevenagel condensation with benzaldehyde for all four zeolite X samples and, for comparison, the conversion in presence of NaOH solution as well as without catalyst at 100 °C reaction temperature.
Table 3. Initial reaction rates for all four zeolite X samples at 100 °C reaction temperature after the first and sixth potassium exchange.

|                  | Parent (NaX) /mol L⁻¹.min⁻¹ | 1st Ion Exchange (Na/KX) /mol L⁻¹.min⁻¹ | 6th Ion Exchange (KX) /mol L⁻¹.min⁻¹ |
|------------------|------------------------------|----------------------------------------|-------------------------------------|
| X-Conv           | 0.013                        | 0.031 (60% K)                          | 0.054                               |
| X-Li₂CO₃         | 0.025                        | 0.051 (60% K)                          | 0.087                               |
| X-Addfree        | 0.045                        | 0.047 (55% K)                          | 0.133                               |
| X-TPOAC (calcined) | 0.092                      | 0.050 (50% K)                          | 0.069                               |

Before discussing the Knoevenagel condensation over layer-like zeolite X catalysts in more detail, it is to mention that, in the case of NaX-Li₂CO₃, lithium cations partially substituted the charge balancing sodium cations. Due to the lower electropositivity, lithium ions induced lower basicity in the neighbouring oxygen atoms of the zeolite structure, which were, therefore, base-catalytically less active [24]. However, even under these circumstances, NaX-Li₂CO₃ exceeded the catalytic activity of NaX-Conv (Figure 6), which could be attributed to the enlarged external surface area and thus the better accessibility of the active sites in the micropore system due to shorter diffusion path length through the thinner (plate-shaped) crystals. On average, as shown in Table 2, NaX-Li₂CO₃ had the thickest plates (183 nm) of all three layer-like NaX samples. NaX-Addfree had, besides reduced overall particle sizes, also smaller plates with an average thickness of 126 nm.

In the case of X-TPOAC, the small crystal plate thickness (96 nm) and the presence of a high portion of intracrystalline mesopores inside each crystal plate [10] led to a further enhancement of the catalytic activity compared to the other layer-like X samples.

Concerning the catalytic activity of all four zeolite NaX samples, it can be stated that with increasing external surface area and mesopore volume as well as decreasing plate thickness, the catalytic activity increased, while, for layer-like zeolites, the overall particle size (assembly of the layer-like crystals) seemed to have no significant influence on the catalytic activity.

2.2.2. Catalytic Activity after Ion Exchange (NaKX and KX)

In the second part of the catalytic investigation of zeolite X with different morphologies, the potassium-exchanged samples were applied as catalysts to determine if the presence of increasing amounts of potassium could further increase the conversion of ECA over layer-like zeolite X.

Figure 7 shows the obtained ECA conversion curves over time before (NaX) and after the first (NaKX) as well as the sixth (KX) ion exchange. The low activity of NaX-Conv is seen as a result of transport limitation to the catalytically active centres because the large crystal extension in all three directions hindered a fast transport of reactants through the long micropore channels. For comparison, NaOH solution was tested as a homogeneous basic catalyst where no transport limitation due to confinement in pores could exist. In agreement with the above assumption, the initial reaction rate was the highest using NaOH as a homogenous catalyst.
For zeolite X with conventional morphology (X-Conv), the ECA conversion and initial reaction rate increased with increasing potassium content in the zeolite sample. The final conversion of ECA in the presence of zeolite X with conventional morphology rose from 34% to 72% and 82% with increasing amounts of potassium. Accordingly, after six hours of reaction time, KX-Conv reached a similarly high conversion as the layer-like zeolites. This indicated that film diffusion at the external crystal surface was not the reaction-rate-limiting step in NaX-Conv because otherwise, an increase in catalytic activity would not be possible just by changing the charge balancing cation inside the micropores. Instead, the reason for the increased catalytic activity of NaKX and KX was seen in the increased basicity of the active centres, if potassium instead of sodium was present as the charge-balancing cation. Thus, faster conversion of ECA at such stronger basic sites in zeolite KX might take place already at the outer rim of the conventional zeolite crystal so that the diffusion limitation imposed by the longer micropore channels in X-Conv had less impact on the overall catalytic activity. As summarised in Table 3 and visualised in Figure 8, the initial reaction rate of 0.013 mol·l$^{-1}$·min$^{-1}$ with NaX-Conv was almost quadrupled after the complete ion exchange in KX (after the sixth ion exchange) and exceeded even the initial reaction rate of NaX-Addfree and NaX-Li$_2$CO$_3$.  

Figure 7. Conversion of ethyl cyanoacetate (ECA) in Knoevenagel condensation with benzaldehyde over time for all four zeolite X morphologies: X-Conv (a), X-Addfree (b), X-Li$_2$CO$_3$ (c), and X-TPOAC (d) with varying amounts of Na$^+$ and K$^+$ (as-synthesised NaX with 100% Na content, partially ion-exchanged NaKX after the first ion-exchange step and almost completely exchanged KX after the sixth ion-exchange step).
reaction rate of $0.013\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ with NaX-Conv was almost quadrupled after the complete ion exchange in KX (after the sixth ion exchange) and exceeded even the initial reaction rate of NaX-Addfree and NaX-Li$_2$CO$_3$.

![Figure 8. Effect of the potassium content in zeolite X obtained from different morphology modifying synthesis pathways on the initial reaction rate in the Knoevenagel condensation of ethyl cyanoacetate and benzaldehyde.](image)

Similar to X-Conv, the catalytic activity of X-Li$_2$CO$_3$ increased with a rising amount of potassium cations, leading to an initial reaction rate of NaKX-Li$_2$CO$_3$ (60% K$^+$) of $0.051\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$, which is almost doubled compared to Na-Li$_2$CO$_3$. The calculated initial reaction rate over NaKX-Addfree, which had thinner crystal plates (126 nm) compared to X-Li$_2$CO$_3$ (183 nm), did not significantly change after the first potassium exchange but was probably only due to the uncertainty of the linear regression in the conversion range below 10%. After the complete potassium exchange (after six-fold ion exchange), both layer-like zeolite variants (KX-Li$_2$CO$_3$ and KX-Addfree) show almost a three-fold initial reaction rate compared to their parent counterparts.

In general, for all zeolite morphologies as well as for the homogeneous NaOH catalyst, the final conversion did not exceed 88%, even after the acceleration of the reaction rate through potassium exchange. This might indicate that, with a conversion of around 88%, the thermodynamic equilibrium of this reaction was reached. For a more precise value, thermodynamic calculations would be required, but which was beyond the scope of the here presented study.

Furthermore, in contrast to other zeolite X samples, X-TPOAC showed a decrease in catalytic activity with increasing amounts of potassium in the catalyst. The initial reaction rate decreased from $0.092\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ to $0.05\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ after the first ion-exchange step. Further, five ion exchanges slightly increased the initial reaction rate up to $0.069\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$, which was still low compared to the parent NaX-TPOAC sample. In addition, for both potassium-containing X-TPOAC samples, the ECA conversion after 6 h dropped to 77% in comparison to NaX-TPOAC, which achieved 80% conversion of ECA. The reason for this behaviour might be a progressing partial destruction/dissolution of the thinnest (outer) parts of the crystal plates upon the subsequent aqueous ion-exchange treatments. This was evident from the SEM images in Figure 2, where only X-TPOAC showed a significant morphological change upon the ion exchange. The initially very thin parts of the crystal plates disappeared, and only much coarser parts remained. Accordingly, this increased average thickness of the remaining KX-TPOAC plates (which are still highly crystalline because the specific micropore volume decreased only slightly due to the larger potassium ions) seemed to impose a longer diffusion path length on reactants, which reversed the positive effect an increased potassium content would have on the reaction rate.
However, according to Table 1, KX-TPOAC still exhibited a higher mesopore volume and external surface area than KX-Conv, leading to still higher conversion and reaction rates. This showed that, for the application as catalyst layer-like zeolite, crystals should have a certain minimum thickness, which provides mechanical and chemical stability against the stress induced by ion exchange and catalytic reaction.

3. Materials and Methods

3.1. Zeolite Synthesis

For the synthesis of conventional zeolite NaX (NaX-Conv), NaOH pellets (synthesis grade, Merck, Darmstadt, Germany) were dissolved in deionized water and mixed with a sodium silicate solution (mass%: 27.1 SiO$_2$, 8.2 Na$_2$O, 64.7 H$_2$O, Merck) at room temperature in a polypropylene flask before a sodium aluminate solution (mass%: 19.6 Al$_2$O$_3$, 20.1 Na$_2$O, 60.3 H$_2$O, CWK Chemiewerk Bad Köstritz, Bad Köstritz, Germany) was added under vigorous stirring with an overhead propeller stirrer at 1300 rpm. After this, the synthesis gel was stirred for 40 min at 1300 rpm. Subsequently, the synthesis gel was filled into PP bottles of a size allowing about 80% filling, closed with a cap, aged for 20 h at room temperature, placed in a preheated oven, and then crystallised at the conditions given in Table 4.

Table 4. Molar synthesis gel compositions and crystallisation parameters of all four synthesis routes with NaX-Conv giving conventional FAU morphology and NaX-add-free, NaX-Li$_2$CO$_3$, and NaX-TPOAC giving layer-like crystal morphology [8–10].

| 1.0 Al$_2$O$_3$: 3.0 SiO$_2$: 180 H$_2$O: | Crystallisation Temperature/Duration |
|----------------------------------------|------------------------------------|
| Na$_2$O | Li$_2$CO$_3$ | TPOAC | MeOH |
| NaX-Conv [8] | 4.0 | - | - | 75 °C/4 d |
| NaX-Addfree [8] | 4.0 | - | - | 50 °C/3 d |
| NaX-Li$_2$CO$_3$ [9] | 3.7 | 0.6 | - | 75 °C/4 d |
| NaX-TPOAC [10] | 3.5 | - | 0.06 | 0.62 | 75 °C/5 d |

For the synthesis of the three layer-like zeolite NaX samples, three different synthesis modifications (according to the preparation pathways described in the literature [8–10]) were applied to the above synthesis method for NaX-Conv after the 40 min stirring at 1300 rpm with the final synthesis gel compositions given in Table 1.

(a) for NaX-Addfree (additive-free synthesis), the synthesis gel preparation was done in the same way as for NaX-Conv, just the crystallisation conditions were different (see Table 4).

(b) for NaX-Li$_2$CO$_3$, the inorganic salt lithium carbonate (mass%: 96. Li$_2$CO$_3$, Merck, Darmstadt, Germany) was suspended in 30 mL deionised water and then added into the conventional synthesis gel. The mixture was then stirred at 1300 rpm for another 10 min before ageing in PP bottles.

(c) for NaX-TPOAC, a methanolic solution of the organosilane TPOAC (mass%: 40.0 TPOAC, 60.0 methanol, Sigma-Aldrich, St. Louis, MO, USA) was added into the synthesis mixture. The mixture was then stirred at 800 rpm for another 10 min before ageing.

The amounts of chemicals per synthesis route needed to obtain around 20 g of zeolite powder are summarised in Table 5.

Independent of the intended synthesis product morphology, the synthesis gel was aged for 20 h at room temperature in static condition. Duration and temperature of the crystallisation are given for all zeolite syntheses in Table 4. Afterwards the different synthesis products were separated from the mother liquor via vacuum filtration, washed with distilled water until a pH of 7 was reached, and dried at 75 °C. In the case of NaX-TPOAC, the organic template (TPOAC) was removed via calcination in a muffle furnace.
at 550 °C in 100 mL-min⁻¹ synthetic air flow with a heating ramp of 2 K-min⁻¹ and an isothermal step at 550 °C for 12 h.

Table 5. Amount of reactants (in g) needed for each synthesis route to obtain approximately 20 g of desired product.

| Sample          | Sodium Silicate Solution | Sodium Aluminate Solution | NaOH | Deionized Water | Li₂CO₃ | TPOAC Solution |
|-----------------|--------------------------|---------------------------|------|-----------------|--------|----------------|
| NaX-Conv [8]    | 47.15                    | 37.03                     | 8.20 | 175.50          | -      | -              |
| NaX-Addfree [8] | 47.15                    | 37.03                     | 8.20 | 175.50          | -      | -              |
| NaX-Li₂CO₃ [9]  | 47.15                    | 37.03                     | 6.47 | 175.90          | 12.59  | -              |
| NaX-TPOAC [10]  | 47.15                    | 37.03                     | 5.32 | 176.18          | -      | 5.29           |

3.2. Ion Exchange

Ion exchange was used to exchange the sodium ions in NaX for potassium ions. This was done at room temperature using a 1.0 molar aqueous potassium chloride solution. For a homogeneous suspension of the zeolite in the exchange solution (8.5 mass% of zeolite), the ion exchange was carried out in a polypropylene bottle, which was agitated by a reciprocating shaker at 300 rpm and room temperature. After one hour, the zeolite was separated via vacuum filtration. To ensure that no excess ions remained inside the micropores, the zeolite was washed until no further chloride was detected in the filtrate via 0.1 molar Ag(NO₃) test. After this step, the zeolite was dried at least for 12 h at 75 °C in a convection oven. This exchange procedure was repeated up to six times.

3.3. Catalytic Testing

Prior to the catalytic testing, all zeolite samples were heated for 12 h at 350 °C at ambient pressure and atmosphere. After this, 40 mg of activated zeolite was added to 70 mmol benzaldehyde in a 25 mL round-bottom-two-neck flask, in which the catalytic testing was conducted. To ensure for each morphology the same starting condition, i.e., to destroy loose particle agglomerates and enable complete wetting of the whole particle surface, the sealed flask containing benzaldehyde and zeolite was treated in an ultrasonic bath for 10 min with 100 W at 80 °C. Reproducible catalytic test results were only possible when this ultrasonic pretreatment of the reaction suspension was applied before the catalytic runs.

After this ultrasound pretreatment, the flask was attached to a reflux cooler, the catalyst suspension stirred with a magnetic stirrer bar at 400 rpm and heated to the reaction temperature of 100 °C with the help of an oil bath, which was also stirred with a magnetic stirring bar. In a second oil bath, a round-bottom flask filled with ethyl cyanoacetate was meanwhile heated to a temperature of 100 °C. From this reservoir, 70 mmol of ethyl cyanoacetate was added to the benzaldehyde/zeolite suspension. This addition marked the beginning of the catalytic test reaction. Samples of 0.1 mL each were taken with a syringe after certain time intervals while stirring of the reaction mixture was maintained. The catalyst was then separated from the sample using a syringe filter of 0.2 μm pore size. The conversion was monitored via gas chromatography (GC) using the instrument Varian G3900 with an Agilent Technologies CP8907 column (Santa Clara, CA, USA). For this, 0.1 mL of the sample was mixed with a solvent (1.5 mL absolute ethanol) in GC vials. The chosen injection volume of this solution into the gas chromatograph was 2 μL with an injector temperature of 250 °C. The column was heated with 7 K-min⁻¹ from 40 °C to 100 °C and kept for 1 min at 100 °C. After this, a heating ramp of 20 K-min⁻¹ to 250 °C was applied followed by an isothermal step of 2 min at 250 °C. The helium volume flow through the column was 1.0 mL-min⁻¹. Ethyl cyanoacetate (ECA) conversions were determined from the respective areas under the GC curves. The initial reaction rate was determined as the slope of the linear regression in the time-conversion plot between no conversion and 10% conversion of ECA.
For comparison, a catalytic test with NaOH as a homogeneous catalyst was performed. The amount of NaOH required to provide a similar amount of active sites compared to the zeolites catalysts was calculated according to the description given in the Supplementary Materials (Table S1). Catalytic testing and sampling were done in the same manner as for the zeolite catalysed reactions, with the exception that the NaOH solution was directly added into the reaction mixture without ultrasonication, and that no catalyst separation was done after sampling. Further conversion of the sample was avoided by cooling down the sample after sampling and immediate GC measurement.

3.4. Characterisation Methods

Powder XRD patterns were recorded in a Philips X’pert Pro diffractometer operated at 40 kV and 40 mA using CuKa radiation in steps of 0.017. Nitrogen physisorption was conducted at 77 K in a Quantachrome Autosorb-1 instrument. Prior to the physisorption measurements, the samples were outgassed for 12 h at 250 °C under vacuum. Specific surface areas were obtained from the Multipoint-Brunauer–Emmett–Teller (BET) equation in the linear range between 0.01 and 0.20 p/p₀⁻¹. The external surface area was determined as the difference between the specific surface area and the micropore surface area calculated using the t-plot method in the range of 0.2 to 0.4 p/p₀⁻¹. Pore size distribution curves were obtained using the Quantachrome NLDFT equilibrium model for N₂ desorption from cylindrical pores at 77 K.

SEM images were recorded with an SE2 detector in the electron microscope ULTRA55 (Carl Zeiss MST AG) at 1.0 eV and 6 mm working distance, for which the samples were fixed on a self-sticking carbon pad.

For elemental analysis, inductively coupled plasma optical emission spectroscopy (ICP-OES, instrument Plasma 400, PerkinElmer, Waltham, MA, USA) was used. The samples were digested via microwave treatment in a mixture of 4 mL HCl (37 wt%), 2 mL HNO₃ (65 wt%), and 8 mL HF (40 wt%).

³⁷Al solid state NMR direct excitation experiments were recorded on an Agilent WB 500 MHz (11.7 T) spectrometer at a resonance frequency of 130.2 MHz, in a 1.6 mm zirconia rotor at a magic angle spinning rate of 20 kHz. Short hard pulses (10° pulse of 0.08 us, 300 kHz RF) were applied with a recycle delay of 0.5 s between the scans. 100 kHz spineal-64 decoupling was applied on protons during acquisition. The number of accumulated scans varied between 460 and 38.000 scans, depending on the Al content. Spectra were referenced to a 1 M solution of Al(NO₃)₃ (0 ppm). The percent fractions of tetrahedral and extra-framework aluminium were calculated via integration of the signals at 62 ppm and 15 ppm, respectively, and relating each signal area to the sum of both signal areas, multiplied by 100.

4. Conclusions

Zeolite X is a suitable heterogeneous catalyst for the Knoevenagel condensation between ethyl cyanoacetate (ECA) and benzaldehyde. It was shown that a modification of the crystal size towards layer-like morphology could significantly increase the initial reaction rate and conversion, which can be attributed to shorter diffusion path lengths through the micropore system in layer-like crystals, where the crystal dimension was reduced in one direction.

Ion exchange of sodium for potassium could further enhance the catalytic activity of the zeolite catalyst. Full ion exchange for K⁺ could be reached after five to six consecutive ion-exchange steps for all zeolite X morphologies except the one obtained with the organosilane TPOAC, where only 81% of the sodium was exchangeable for potassium. However, this ion exchange procedure affected the catalytic activity differently depending on the zeolite crystal morphology. In the case of conventional (compact) zeolite X crystals, an increasing exchange for potassium increased the reaction rate and conversion. Further, for most layer-like zeolites, the potassium exchanged variant was found to be the most active catalyst, reaching up to 82% (close to equilibrium) conversion in a shorter time interval. This effect was most pronounced
if the morphology and crystal structure of zeolite X was maintained after the ion exchange \( \text{Na}^+ \rightarrow \text{K}^+ \). It was found that very thin crystal plates, as in the case of X-TPOAC, seemed to exhibit insufficient chemical or mechanical resistance against the ion exchange procedure, which seemed to cause partial dissolution of the very thin parts of the crystal, and only the more compact crystal parts remained, which resulted in a loss of catalytic activity and counteracted the gain of catalytic activity by potassium exchange.

**Research highlights:**

- Reaction rate and conversion in Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate over layer-like zeolite X exceed that over conventional zeolite X.
- Depending on the zeolite crystal morphology, the charge balancing cation (\( \text{Na}^+ \) and/or \( \text{K}^+ \)) affected the catalytic activity differently. In most cases, zeolite KX with layer-like morphology was found to be the most active catalyst, reaching around 80% conversion after 6 h.
- The crystal structure of zeolite X remained widely intact upon ion exchange \( \text{Na}^+ \rightarrow \text{K}^+ \).
- Full ion exchange for potassium can be reached after six consecutive ion-exchange steps.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/catal11040474/s1, Figure S1: XRD patterns of all four parent NaX samples with the hkl assignments associated with FAU(X) structure according to the ICSD database. Figure S2: XRD patterns of X-Conv, X-Addfree, X-Li\(_2\)CO\(_3\) and X-TPOAC before and after each of the 6 consecutive potassium exchange steps. Figure S3: Changes in the molar composition of all zeolite samples with different morphology through the six consecutive potassium exchange steps determined via ICP-OES. Table S1: Values used to estimate the required amount of sodium hydroxide solution for catalysis.

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