

# Thermal Stability and Thermal Transformations of Co<sup>2+</sup>- or Ni<sup>2+</sup>-Exchanged Zeolites A, X, and Y

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The stability of Co<sup>2+</sup>- and Ni<sup>2+</sup>-exchanged zeolites strongly depends on the exchanged transition metal and the experimental conditions of the ion-exchange. An overexchange of both Co<sup>2+</sup> and Ni<sup>2+</sup> is observed with the zeolites A and X, enhanced at elevated temperatures. The interaction of the zeolite framework with acidic species formed during the exchange leads to structural damage. After the collapse of the zeolite frameworks during the calcination of the exchanged zeolites, the crystallization of CoAl<sub>2</sub>O<sub>4</sub> and NiAl<sub>2</sub>O<sub>4</sub> starts. During the calcination of Ni<sup>2+</sup>-exchanged zeolite A and X, NiO crystallizes prior to the formation of spinel and dissolves as the spinel crystallization starts. Depending on the zeolite precursor and the thermal conditions, SiO<sub>2</sub> phases such as quartz or cristobalite are formed. The amounts of crystalline and amorphous phases vary with calcination temperature and time. The phase formation processes are dependent on the ion-exchange procedures and thermal treatments. By controlling these parameters, materials with well-defined properties are accessible.

## Introduction

Transition-metal exchanged zeolites are active catalysts in many chemical reactions, e.g., in redox or aromatization processes.<sup>1–6</sup> The exchanged zeolites are interesting not only for catalytic applications but also as precursors for the synthesis of ceramic materials. Previous works describe the decomposition of zeolite precursors as a novel route for the synthesis of aluminosilicate-based ceramics.<sup>7,8</sup> After the heat induced collapse of the framework structure, an amorphous phase is formed from the zeolite precursors, followed by the crystallization of dense aluminosilicate and oxide phases. The formation of spinel-based ceramics from the heat induced transformation of cobalt exchanged zeolite A was reported by Colyer et al.<sup>9,10</sup> Transition metal containing spinels are used as catalysts, e.g., in steam reforming or oxidation processes,<sup>11,12</sup> as well as in sensor and semiconductor technology.<sup>13,14</sup>

The ion-exchange properties of zeolites for specific metal cations and the thermal stability of the exchanged zeolites depend strongly on the identity of the exchanged cation, the structure of the zeolite host, and the ion-exchange conditions chosen for the experiment. This paper describes detailed studies of the ion-exchange behavior of three different zeolites, A, X, and Y, exchanged with Co<sup>2+</sup> and Ni<sup>2+</sup> ions from aqueous salt solutions and their stability against thermal treatment. The comparison of the results reveals the influence of the crystal structure, the chemical composition, and of the degree of exchange on the stability and thermal transformation processes of the zeolite host. The amounts of crystalline and amorphous phases and their behavior during the temperature treatment are quantified by the Rietveld method.

## Experimental Section

The starting zeolites Na-A (Na<sub>12</sub>Al<sub>12</sub>Si<sub>12</sub>O<sub>48</sub>, structure type LTA<sup>15</sup>), Na,K-X (Na<sub>78</sub>K<sub>18</sub>Al<sub>96</sub>Si<sub>96</sub>O<sub>384</sub>, structure type FAU<sup>15</sup>), and Na-Y (Na<sub>59</sub>Al<sub>59</sub>Si<sub>133</sub>O<sub>384</sub>, structure type FAU) were provided by AlSi-Penta. The chemical compositions of the zeolites were obtained by X-ray fluorescence analyses.

The Ni<sup>2+</sup> or Co<sup>2+</sup> containing zeolites were prepared by ion exchanging Na-A, Na,K-X, and Na-Y with 0.1 M Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Fluka) or NiSO<sub>4</sub>·6H<sub>2</sub>O (Fluka) salt solutions. For each exchange 5 g of zeolite were stirred in 250 mL of the respective salt solution. The exchanged zeolites were filtered, washed, and dried at 90 °C. The exchange times were successively increased from 10 to 120 min and the exchanges were repeated

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**Table 1.** Ni<sup>2+</sup> and Co<sup>2+</sup> Contents of the Zeolites 5 Times Exchanged at 70 °C, and Ni<sup>2+</sup> Content of Once Exchanged Zeolite Ni,Na,K-X

	Co,Na-A	Co,Na-X	Co,Na-Y	Ni,Na-A	Ni,Na-X	NiNa-Y	Ni,Na,K-X*
Me <sup>2+</sup> /Al <sup>3+</sup>	1.2	1.1	0.5	0.6	0.65	0.5	0.4

\*Once Ni<sup>2+</sup>-exchanged zeolite X.

5 times. Samples were taken after defined time periods and after each exchange cycle. To study the effect of temperature on the degree of exchange, a second series of samples was exchanged at 70 °C. The cation contents of all samples were determined by EDX analyses on an Oxford EDX unit attached to a Hitachi S-3500N scanning electron microscope (Table 1). The cation to aluminum ratios in Figures 1–6 were also determined from EDX data. The experimental error of these ratios was calculated to be ±0.01, which is sufficient to follow trends.

The thermal stability of the exchanged zeolites and the phase transformation temperatures were studied qualitatively by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The DTA and DSC curves were measured on a Netzsch STA 449C with a heating rate of 10 °C/min from room temperature to 1400 °C. The in situ high-temperature X-ray diffraction patterns were collected in air from room temperature to 1000 °C with a Johanna Otto HDK/S1 high-temperature chamber (HTC) mounted on a Stoe STADI P  $\theta$ - $\theta$  powder diffractometer. Data collection was performed between 5 and 50° 2 $\theta$  with a step width of 0.05° 2 $\theta$  and 2s data collection per step. For the ex situ experiments, 0.3-g portions of the exchanged zeolites were filled into alumina crucibles and heated in a furnace at a rate of 5 °C/min. Between 800 and 1350 °C, every 50 °C samples were removed out of the oven and quenched in air. The samples were milled and then prepared for X-ray data collection. For quantitative phase analyses and the determination of the amorphous phase fractions, the samples were mixed with defined amounts of fluorite (CaF<sub>2</sub>) as internal standard. All refinements were performed with the FullProf98 Rietveld program.<sup>16</sup> The determination of the weight fractions in a multicomponent Rietveld analysis using the scale factors is described for example by Hill and Howard<sup>17</sup> and Hill et al.<sup>18</sup> The weight percentage  $W$  of a phase  $i$  is calculated by

$$W_i = \frac{S_i Z_i M_i V_i}{\sum_k S_k Z_k M_k V_k} \quad (1)$$

where  $S_i$  is the scale factor obtained for phase  $i$ ,  $Z_i$  is the number of formula units,  $M_i$  is the molecular weight, and  $V_i$  is the volume of the unit cell. The sum is calculated over all crystalline phases.

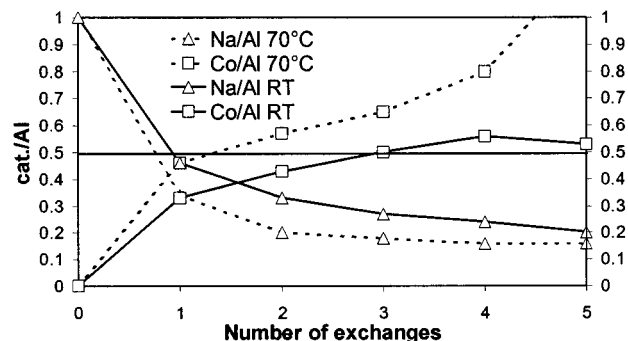
The weight fraction of the amorphous phase is calculated by

$$W_a = \left(1 - \frac{W_{fw}}{W_{fc}}\right) (1 - W_{fw})^{-1} \quad (2)$$

where  $W_a$  is the weight fraction of the amorphous phase,  $W_{fw}$  is the weight fraction of the internal standard as weighted, and  $W_{fc}$  is the weight fraction of the internal standard calculated from the Rietveld refinements. The corrected weight fractions  $W_j$  of the crystalline phases are then calculated by

$$W_j = W_i (1 - W_a) \quad (3)$$

**1. Ion Exchange.** *1.1. Ion Exchange in Zeolite A.* Systematic studies of the exchange behavior of zeolite A for Co<sup>2+</sup> and Ni<sup>2+</sup> show that the degree of exchange is more strongly



**Figure 1.** Influence of the number of exchanges at room temperature (solid lines) and at 70 °C (dotted lines) on the degree of exchange for Co,Na-A.

influenced by the number of exchanges than by the duration of the ion-exchange. The exchange equilibrium at room temperature is obtained after 10–30 min. An extension of the exchange time leads to no significant increase of the transition metal content. Even after 2 h only about 50% of the Na<sup>+</sup> cations are replaced. After five exchanges for 30 min, using fresh salt solutions for each repetition, the amount of replaced Na<sup>+</sup> ions is increased to 80%. This indicates an overexchange of Co<sup>2+</sup> since there is still Na<sup>+</sup> present in the zeolite. In general multiple short exchange cycles are preferable to prolonged exchange times for the exchange of Co<sup>2+</sup> in zeolite A at room temperature. The experiments at 70 °C reveal that after one exchange 70% of the Na<sup>+</sup> ions are exchanged by Co<sup>2+</sup>, compared to 50% at room temperature (Figure 1). The cation-to-aluminum ratio is plotted against the number of exchanges. For bivalent cations the maximum cation-to-aluminum ratio for fully and stoichiometrically exchanged zeolites is 0.5, which is marked by a horizontal line in the figures. In general the amount of exchanged cations is about 15% higher at elevated temperature but, as observed for the exchange at room temperature, Na<sup>+</sup> cannot be fully removed even after five exchanges, despite the drastic overexchange of Co<sup>2+</sup>. The exchange solutions are slightly acidic due to a hydrolysis reaction of the Co<sup>2+</sup> cation ( $pK_a = 9.6$ ).<sup>19</sup> The pH of the initial solution increases slightly from 5.6 to 5.9 during the first exchange. The pH values of the solutions, measured after further exchanges, decrease and reach a plateau at pH 5.4 after four exchanges.

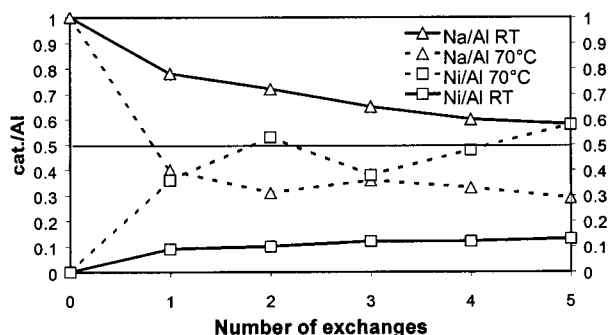
The ion-exchange experiments with Ni<sup>2+</sup> reveal that the capacity of zeolite A for Ni<sup>2+</sup> at room temperature is lower than for Co<sup>2+</sup> (Figure 2). Prolonged exchange times do not influence the amount of exchanged cations significantly and repeating the exchange with fresh salt solution leads successively to a maximum Na<sup>+</sup> exchange of only 40%. Figure 2 shows the cation to aluminum ratios for exchanges performed at 70 °C and room temperature. For the Ni<sup>2+</sup> system after one exchange at elevated temperature already 60% of the Na<sup>+</sup> ions are exchanged, compared to only 20% at room temperature. But as observed at room temperature the content cannot be further increased by additional exchange repetitions. The final nickel to aluminum ratio of about 0.6 indicates an overexchange of Ni<sup>2+</sup>, which is not as high as that observed in the Co<sup>2+</sup> system. The Ni<sup>2+</sup> solutions are also slightly acidic because Ni<sup>2+</sup> cations hydrolyze water molecules likewise ( $pK_a = 9.4$ ).<sup>19</sup> The starting pH of the Ni<sup>2+</sup> solution of 5.3 increases to 6.5 during the subsequent exchange reactions at 70 °C.

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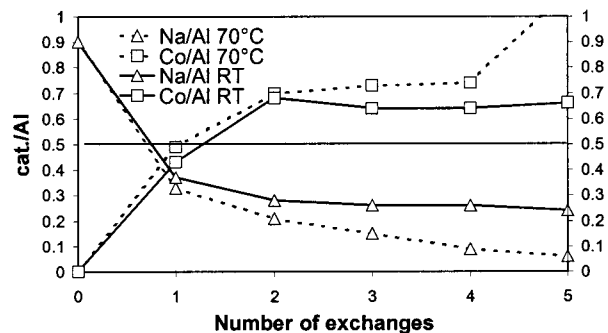
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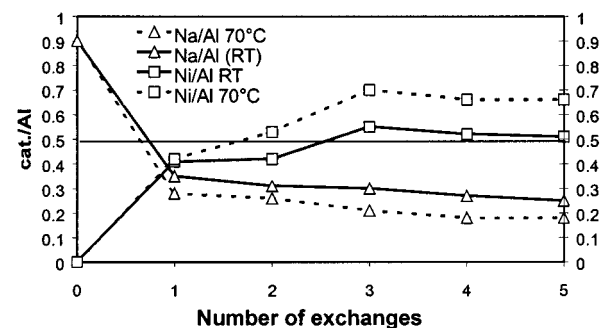
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**Figure 2.** Influence of the number of exchanges at room temperature (solid lines) and at 70 °C (dotted lines) on the degree of exchange for Ni,Na-A.



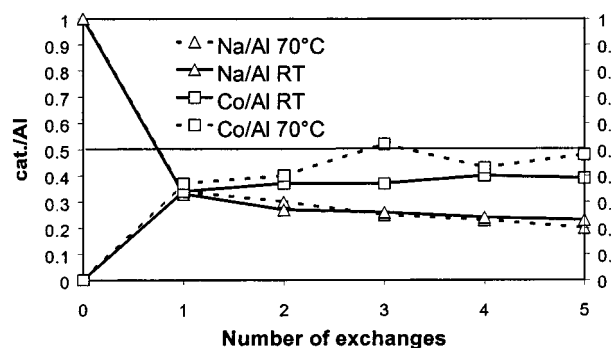
**Figure 3.** Influence of the number of exchanges at room temperature (solid lines) and at 70 °C (dotted lines) on the degree of exchange for Co<sup>2+</sup> in Na,K-X.



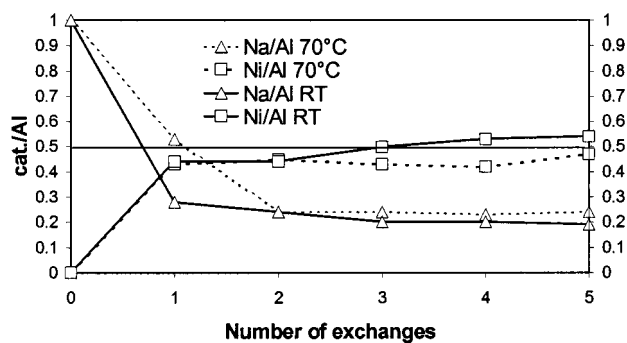
**Figure 4.** Influence of the number of exchanges at room temperature (solid lines) and at 70 °C (dotted lines) on the degree of exchange for Ni<sup>2+</sup> in Na,K-X.

**1.2. Ion Exchange in Zeolite X.** Zeolite X tends to overexchange Co<sup>2+</sup>, while Na<sup>+</sup> is not fully removed as shown in Figure 3. Again, the equilibrium was attained within 30 min at room temperature. Repeating the exchange leads to an overexchange which is more pronounced at 70 °C. Despite the high amount of cobalt in the samples, no extra phases such as cobalt salts or cobalt hydroxide are detected by X-ray diffraction. The pH of the Co<sup>2+</sup> solution does not change much during the ion-exchanges, it decreases slowly from 5.6 to 5.5 during the first two exchanges and remains constant at 5.3 after additional exchanges.

The results of the ion-exchanges with Ni<sup>2+</sup> show that after only 10 min a plateau of the nickel to aluminum ratio is obtained. Prolongation of the exchange leads to no significant increase of the cation content, only about 60% of the Na<sup>+</sup> ions are removed. Repetition of the exchanges removes about 70% of the Na<sup>+</sup> ions and the amount of Ni<sup>2+</sup> cations in the zeolite is increased. A comparison of the results obtained at different temperatures reveals that the degree of exchange is much higher at 70 °C (Figure 4). However, as observed for zeolite A, Ni<sup>2+</sup> is also overexchanged in zeolite X. In general, using the same exchange conditions, zeolite X contains less Ni<sup>2+</sup> ions than Co<sup>2+</sup> ions. This behavior is the same as that observed



**Figure 5.** Influence of the number of exchanges at room temperature (solid lines) and at 70 °C (dotted lines) on the degree of exchange for Co,Na-Y.



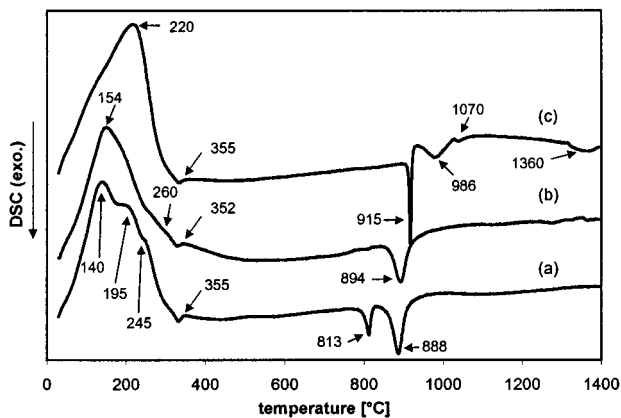
**Figure 6.** Influence of the number of exchanges at room temperature (solid lines) and at 70 °C (dotted lines) on the degree of exchange for Ni,Na-Y.

with zeolite A. Similar pH changes as observed with zeolite A are found with zeolite X. The pH of the exchange solution increases during the exchange from 5.3 to 6.2 and remains constant at a value of 6.2 after the subsequent exchanges. Since practically all K<sup>+</sup> ions are exchanged by Co<sup>2+</sup> or Ni<sup>2+</sup>, the exchanged samples are denoted as Co,Na-X and Ni,Na-X, respectively.

**1.3. Ion Exchange in Zeolite Y.** As observed with the zeolites A and X an exchange equilibrium is achieved after about 30 min. But in contrast to these zeolites, the ion-exchange of Co<sup>2+</sup> and Ni<sup>2+</sup> into zeolite Y is rather insensitive to the number of exchanges. The cation to aluminum ratio plateaus after a few short exchange cycles as indicated by Figures 5 and 6. Subsequently, using longer exchange periods and performing additional exchanges has little effect. After five exchanges for 30 min at room temperature, 80% of Na<sup>+</sup> is removed. At that temperature the exchange of Co<sup>2+</sup> is nearly stoichiometrically, no significant overexchange of Co<sup>2+</sup> is observed. At 70 °C, Co<sup>2+</sup> overexchanges slightly but much less pronounced than in zeolite A or X. The pH of the exchange solution is decreased from 5.6 to 5.7 during the first exchange. After the additional exchanges it is decreased to 5.2.

A similar behavior is observed for the exchange of Ni<sup>2+</sup> in zeolite Y. Overexchange of Ni<sup>2+</sup> is not prominent at room temperature, independent of the exchange time or number of exchange cycles (Figure 6). About 80% of the Na<sup>+</sup> ions are removed after 2–3 exchange repetitions, a behavior which is also observed at 70 °C where the overexchange of Ni<sup>2+</sup> is slightly increased.

Within the experimental errors, the exchange behavior of zeolite Y for Co<sup>2+</sup> and Ni<sup>2+</sup> is almost similar. There is no overexchange at room temperature and a slight overexchange of the transition metal ion at 70 °C. A few exchange cycles with exchange times of 15–30 min are obviously sufficient for a maximum exchange. Similarly to the A and Y zeolites, not all Na<sup>+</sup> ions are exchanged by the transition metal cations. Unlike with zeolite A and X, the pH of the exchange solution does not reach a plateau at a slightly higher pH than that of the parent solution (pH = 5.3). After achieving a value of 6.2



**Figure 7.** DSC curves for 5 times exchanged (a) Co,Na-A, (b) Co,Na-X, and (c) Co,Na-Y heated in air from room temperature to 1400 °C, heating rate 10 K/min. The reaction temperatures in degrees Celsius are given in the figure.

after the first ion-exchange, the pH decreases subsequently to 5.0 during the additional exchanges.

## Results

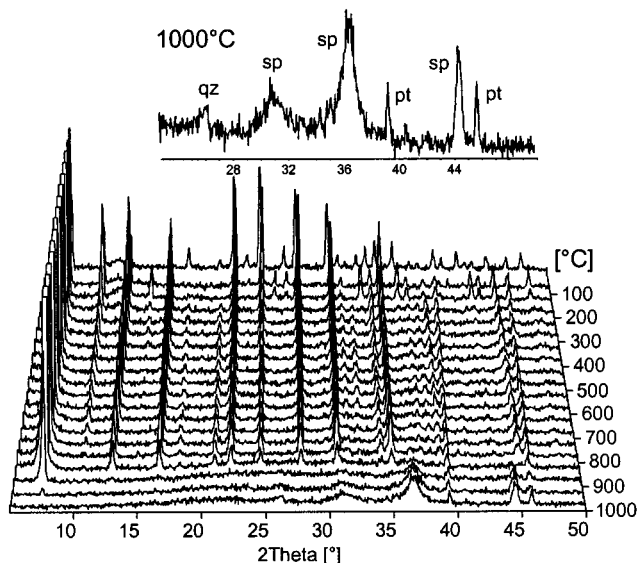
### 1. Thermal Stability of the Exchanged Zeolites.

The aim of this work was to investigate the thermal behavior of exchanged zeolites. Therefore, most of the subsequently described experiments were performed with samples exchanged 5 times at 70 °C. In some cases these samples were compared with those exchanged only once at 70 °C. This was done to determine the influence of the degree of exchange on the stability of the zeolites and on the phase transformation processes at higher temperatures.

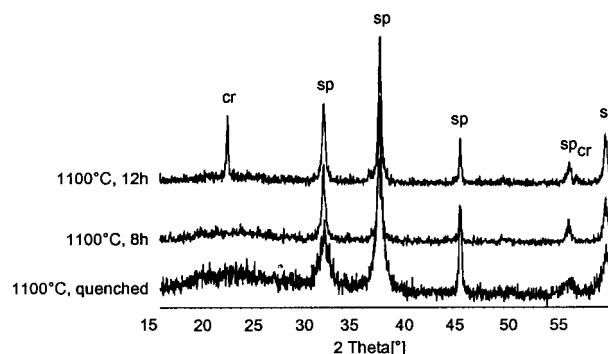
**1.1. Co,Na-A.** The dehydration of zeolite A exchanged 5 times with  $\text{Co}^{2+}$  proceeds in at least three steps as the endothermic DSC signals at 140, 195, and 245 °C in Figure 7a show. The origin of the additional endothermic signal at 355 °C is difficult to interpret. Most likely it has to be assigned to the condensation of hydroxyl groups, since combined TG/DSC-MS measurements show the release of water at that temperature. The hydroxyl groups are either associated with defect sites in the zeolite framework or with free valences of the overexchanged cobalt. An alternative cause of this signal might be the migration of the  $\text{Co}^{2+}$  cations onto sites accessible in the sodalite cages of zeolite A after the dehydration. At higher temperatures two exothermic reactions at 813 and 888 °C are observed. The first reaction is related to the breakdown of the zeolite structure, the latter results from the crystallization of  $\text{CoAl}_2\text{O}_4$  spinel.

*In situ* X-ray experiments (Figure 8) show the zeolite structure to be stable up to 800 °C. Between 820 and 860 °C the zeolite structure collapses and broad  $\text{CoAl}_2\text{O}_4$  peaks (sp) appear. Further increases in the temperature result in the crystallization of quartz between 900 and 950 °C in addition to the spinel phase. The reflection at  $26.2^\circ 2\theta$  observed in the pattern measured at 1000 °C is assigned to high quartz (qz) since the patterns were measured *in situ* and a transformation into  $\alpha$ -quartz is not probable at these conditions.

To get information about the crystallization kinetics of the phase transformation processes, three samples of  $\text{Co}^{2+}$ -exchanged zeolite A were calcined at 1100 °C

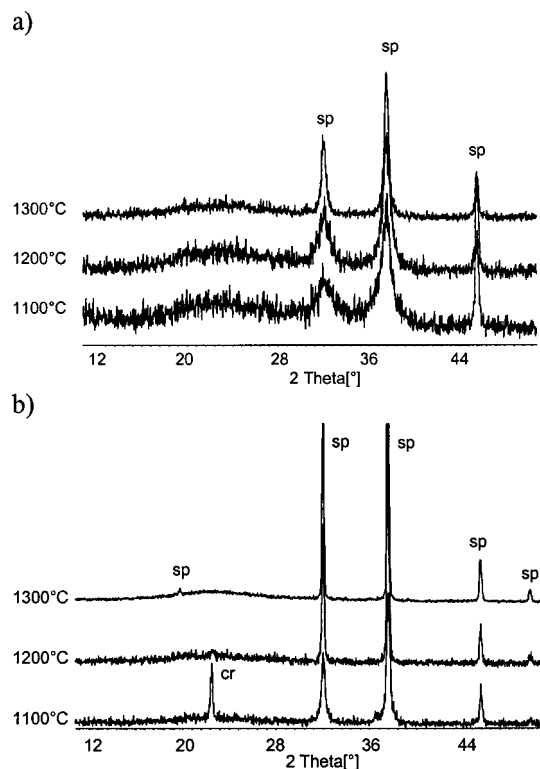


**Figure 8.** *In situ* HTC X-ray patterns of Co,Na-A recorded between 100 and 1000 °C in steps of 50 deg. The insert shows a part of the powder pattern collected at 1000 °C ("qz", quartz; "sp", spinel; "pt", platinum).



**Figure 9.** X-ray patterns of ex situ calcined Co,Na-A samples, treated at 1100 °C for different times. The cristobalite peaks are marked with "cr" and the spinel peaks are marked with "sp".

for different times (Figure 9). The first sample was quenched immediately at 1100 °C; the next two samples were kept for 8 and 12 h at 1100 °C, respectively. The XRD patterns of the quenched sample and of the sample tempered for 8 h exhibit only reflections belonging to  $\text{CoAl}_2\text{O}_4$  spinel (sp). The quartz phase observed between 950 and 1000 °C has dissolved. The sample tempered for 12 h shows a new byproduct identified as cristobalite (cr). Further influence of temperature and heating time is shown in Figure 10. Raising the temperature from 1100 to 1300 °C and quenching the samples when reaching the appropriate temperature does not cause the crystallization of any other phase than  $\text{CoAl}_2\text{O}_4$ . The full width at half-maximum (fwhm) of the spinel reflections decreases with temperature as shown in Figure 10a. The amount of amorphous phase is not reduced significantly by raising the temperature, as the results of the quantitative Rietveld analyses given in Table 2 show. The samples quenched at 1200 and 1300 °C contain 50 wt % amorphous phase and 50 wt %  $\text{CoAl}_2\text{O}_4$ . Figure 10b shows the formation of cristobalite as a function of heating time at different temperatures. Heating the samples at 1100, 1200, and 1300 °C for 12 h leads to the formation of 8, 2, and 0 wt % cristobalite, respectively.



**Figure 10.** Influence of calcination temperatures on Co,Na-X samples (a) quenched in air after achieving 1100, 1200, and 1300 °C. (b) calcined for 12 h at 1100, 1200, and 1300 °C.

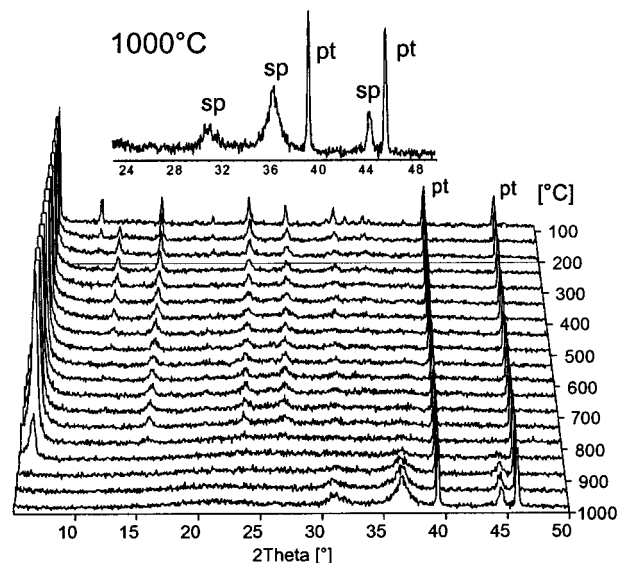
**Table 2. Results of the Quantitative Rietveld Analyses for Zeolite A Exchanged Five Times with Co<sup>2+</sup>**

calc. temp. [°C]	calc. conditions	amorphous phase [wt %]	spinel [wt %]	cristobalite [wt %]
1100	qu	-	-	-
1100	12 h	40	52	8
1200	qu	50	50	-
1200	12 h	46	52	2
1300	qu	48	52	-
1300	12 h	49	51	-

qu: quenched in air

Higher temperatures and/or calcination for several hours does not reduce the amorphous phase fraction but increases the size of the CoAl<sub>2</sub>O<sub>4</sub> crystallites, which is indicated by the reduction of the full width at half-maximum of the X-ray reflections. TEM investigations show that the sizes of the CoAl<sub>2</sub>O<sub>4</sub> crystallites of quenched samples change from about 10 nm at 850 °C to 60–80 nm at 1300 °C, which is in good agreement with the observed peak widths. Longer calcination at 1300 °C lead to CoAl<sub>2</sub>O<sub>4</sub> particles with sizes of some hundred nanometers. Between 1100 and 1300 °C, the weight fraction of CoAl<sub>2</sub>O<sub>4</sub> keeps constant at about 50 wt %, independent of which temperature or calcination time is applied. Cristobalite occurs at about 1100 °C, but it takes some time until the crystallization starts. Cristobalite peaks appear in the X-ray patterns of samples calcined for 12 h at 1100 °C but are not present in pattern of samples taken after 8 h.

**1.2. Co,Na-X.** The DSC curve of a Co,Na-X zeolite exchanged 5 times shows first an endothermic event with at least two distinct signals at 154 and 260 °C (Figure 7b), attributed to dehydration processes. A third endothermic reaction at 352 °C is attributed either to the loss of hydroxyl groups, e.g., from Co–OH species,



**Figure 11.** In situ HTC X-ray patterns of Co,Na-X recorded between 100 and 1000 °C in steps of 50 deg.

or to cation migration. The X-ray patterns of in situ high-temperature measurements, shown in Figure 11, reveal that in contrast to Co,Na-A the collapse of the Co,Na-X crystal structure is a gradual process. Therefore, no distinct peak in the DSC trace is caused by the breakdown of the structure but a very broad exothermic signal between 400 and 800 °C is seen. The exothermic reaction at 894 °C is attributed to the crystallization of CoAl<sub>2</sub>O<sub>4</sub> spinel, which is confirmed by the in situ XRD measurements. Up to a temperature of 1000 °C, no in situ crystallization of quartz is observed. The thermal behavior at higher temperatures was studied on ex situ calcined samples. A sample quenched at 1100 °C shows only CoAl<sub>2</sub>O<sub>4</sub> reflections, but heating the sample for 12 h at 1100 °C causes the crystallization of about 25 wt % cristobalite beside 60 wt % CoAl<sub>2</sub>O<sub>4</sub>. At 1200 °C a small amount of cristobalite is already observed in the quenched sample; calcination for 12 h then leads to a contribution of 31 wt % cristobalite and an increased amount of CoAl<sub>2</sub>O<sub>4</sub> (64 wt %). Cristobalite is also observed in the samples quenched at 1300 °C (18 wt %) and calcined for 12 h at 1300 °C (27 wt %). The amount of amorphous phase is small after 12 h at 1100 °C (15 wt %), at 1200 °C the fraction is further reduced to about 5 wt % accompanied by an increase of cristobalite with 31 wt % in addition to 64 wt % CoAl<sub>2</sub>O<sub>4</sub>. At 1300 °C the weight fraction of the amorphous phase increases again to 13 wt %, while the amount of cristobalite (27 wt %) and CoAl<sub>2</sub>O<sub>4</sub> (60 wt %) decrease. The amounts of the spinel phase fractions are not strongly affected by higher calcination temperatures or longer calcination times, but the CoAl<sub>2</sub>O<sub>4</sub> crystallites grow with temperature and calcination time, which results in sharper X-ray diffraction peaks. The sizes of the CoAl<sub>2</sub>O<sub>4</sub> crystallites at different temperatures and after a distinct time are similar to those formed from Co<sup>2+</sup>-exchanged zeolite A. Prolonged calcination increases the amount of cristobalite which is formed from the amorphous silica after an induction period. The results of the quantitative phase analyses for the samples quenched at different temperatures or calcined for 12 h are given in Table 3.

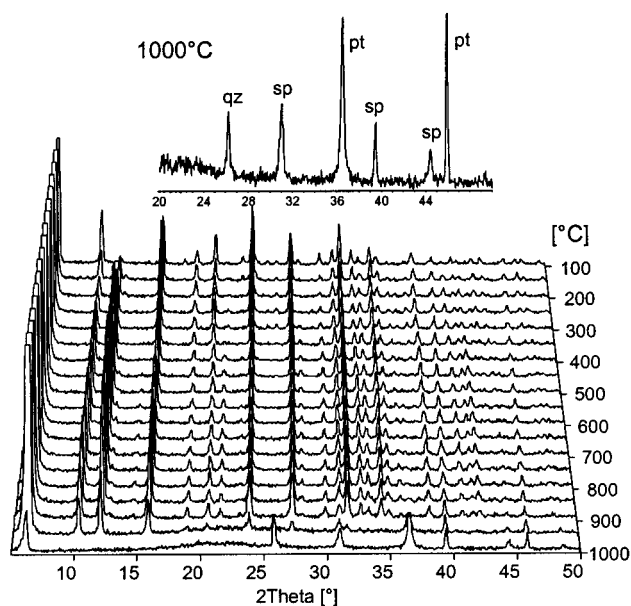
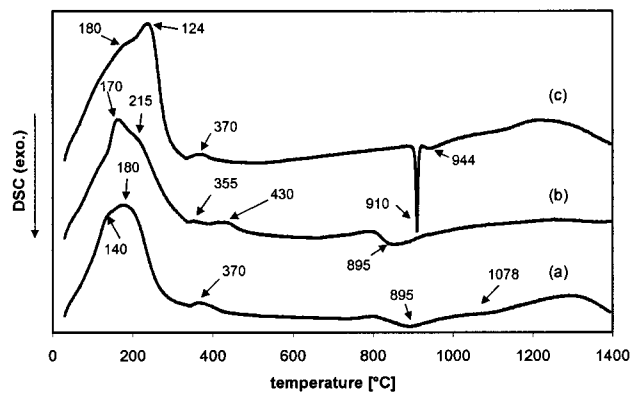
**1.3. Co,Na-Y.** The DSC plot of Co,Na-Y zeolite exchanged 5 times is shown in Figure 7c. The dehydration

**Table 3. Results of the Quantitative Rietveld Analyses for Zeolite X Exchanged Five Times with Co<sup>2+</sup>**

calc. temp. [°C]	calc. conditions	amorphous phase [wt %]	spinel [wt %]	cristobalite [wt %]
1100	qu	-	-	-
1100	12 h	15	60	25
1200	qu	41	58	1
1200	12 h	5	64	31
1300	qu	21	61	18
1300	12 h	13	60	27

of the zeolite corresponds to a broad endothermic signal at about 220 °C. A second endothermic signal at 355 °C is attributed to a dehydroxylation process. The mass spectra measured simultaneously with the TG/DTA traces show the evolution of water at that temperature. The presence of hydroxyl groups within the zeolite is confirmed by IR bands at 3532, 3642, and 3740 cm<sup>-1</sup>. The bands at 3642 and 3740 cm<sup>-1</sup> are typical for acidic OH groups in zeolite Y. Their presence indicates a partial protonation of the zeolite framework caused by the slightly acidic exchange solutions. The band at 3740 cm<sup>-1</sup> is typical for terminal silanol groups at defect sites or on the crystal surface. An additional shoulder at 3667 cm<sup>-1</sup> can be assigned to Co-OH groups. The condensation of all these hydroxyl groups probably leads to the endothermic signal at about 355 °C in the DTA curve. The OH bands are only visible in the IR spectra of zeolite Y due to its low aluminum content. In zeolite A and X only broad absorption bands are observed since hydrogen bridges, caused by the high local concentration of aluminum atoms in these samples, lead only to a broad and ill-resolved IR signal.

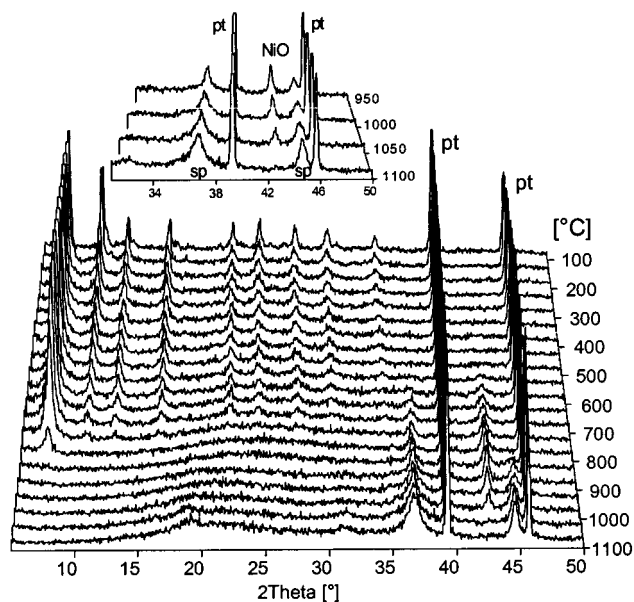
An exothermic DSC signal at 915 °C represents the collapse of the crystal structure and the signal at 986 °C the concurrent crystallization of quartz and CoAl<sub>2</sub>O<sub>4</sub> spinel. The small exothermic signal at 1070 °C is probably caused by the amorphization of quartz, and the one starting at about 1300 °C by the amorphization of cristobalite. The in situ X-ray measurements confirm the stability of the crystal structure and the collapse of the zeolite framework at about 900 °C (Figure 12). At the same temperature the crystallization of  $\beta$ -quartz and CoAl<sub>2</sub>O<sub>4</sub> starts. A second, more detailed study with heating steps of 20 °C reveals that at 880 °C no other reflections than those of the zeolite are present. At 900 °C the observed reflections are attributed to three phases, residual not yet amorphoused zeolite, quartz, and spinel. At 940 °C no more zeolite reflections are observed. Studies on heated and quenched samples corroborate the results of the in situ experiments. The X-ray pattern of a Co,Na-Y sample quenched at 900 °C shows only reflections of the zeolite. A sample quenched at 950 °C shows no more reflections of the zeolite, but those of quartz and CoAl<sub>2</sub>O<sub>4</sub> spinel. In the samples quenched at 1000 and 1100 °C only a very small amount of quartz is observed. Calcination at 1100 °C for 12 h leads to the formation of cristobalite in addition to quartz and spinel. At this stage cristobalite is the main crystalline phase (31 wt %) followed by spinel (30 wt %) and quartz (1 wt %). The amorphous amount of the samples calcined 12 h at 1100 and 1200 °C is nearly constant (38 and 36 wt %), but it increases rapidly to 59 wt % after 12 h at 1300 °C. This process is accompanied by a reduction of the amount of cristobalite to 12 wt %. The amount of spinel remains essentially

**Figure 12.** In situ HTC diffraction patterns of 5 times exchanged Co,Na-Y recorded between 100 and 1000 °C in steps of 50 deg. The upper diagram shows an enlarged section of the pattern collected at 1000 °C.**Figure 13.** DSC curves for 5 times exchanged (a) Ni,Na-A, (b) Ni,Na-X, and (c) Ni,Na-Y heated in air from room temperature to 1400 °C, heating rate 10 K/min.**Table 4. Results of the Quantitative Rietveld Analyses for Zeolite Y Exchanged Five Times with Co<sup>2+</sup>**

calc. temp. [°C]	calc. conditions	amorphous phase wt. [%]	spinel [wt %]	cristobalite [wt %]	quartz [wt %]
1100	qu	75	24		1
1100	12 h	38	30	31	1
1200	qu	58	33	9	
1200	12 h	36	36	28	
1300	qu	66	31	3	
1300	12 h	59	29	12	

constant. The results of the quantitative Rietveld analyses are given in Table 4.

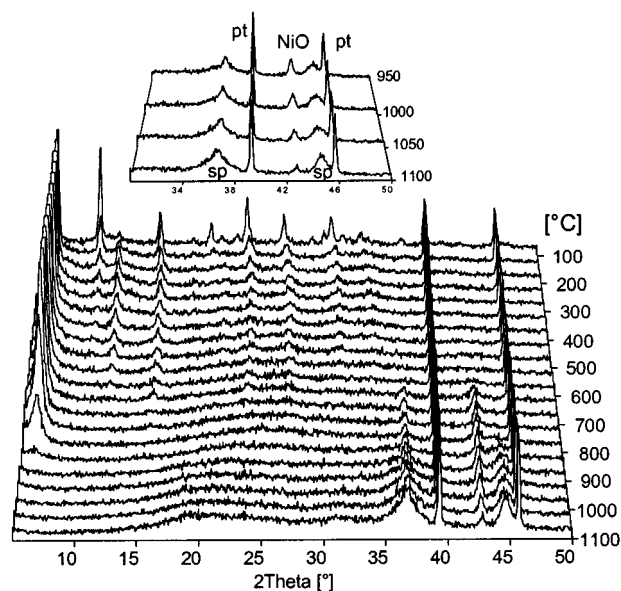
**1.4. Ni,Na-A.** The DSC plot of a Ni,Na-A zeolite exchanged 5 times is shown in Figure 13a. A broad endothermic signal with peaks at 140 and 180 °C is observed, caused by the dehydration of the zeolite. At 370 °C an additional endothermic signal attributed to the dehydroxylation of the exchanged zeolite occurs. After the dehydration, the zeolite structure transforms successively into an amorphous phase while NiO starts to crystallize between 500 and 550 °C, as shown in Figure 14. The amorphization of the zeolite and the crystallization of NiO are gradual processes only leading



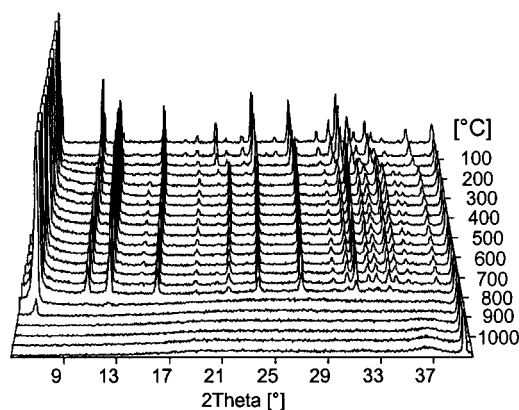
**Figure 14.** In situ HTC diffraction patterns of 5 times exchanged Ni,Na-A recorded between 100 and 1100 °C in steps of 50 deg. The insertion shows the vanishing of NiO at higher temperatures.

to a weak deviation of the DSC signal from the baseline between 450 and 800 °C. The crystallization of NiAl<sub>2</sub>O<sub>4</sub> initiates at approximately 800 °C causing an exothermic DSC signal with a maximum intensity at 895 °C. The XRD pattern in Figure 14 proves the absence of a zeolite phase above 750 °C. Between 1000 and 1050 °C NiO disappears and NiAl<sub>2</sub>O<sub>4</sub> spinel is the only crystalline phase. In the whole temperature range up to 1300 °C, no crystalline SiO<sub>2</sub> phase is observed. At this temperature the samples obtained are glasslike pieces. The amorphous phase forms a melt around the crystalline particles. The melting of the amorphous fraction causes an endothermic signal in the DSC trace starting at about 1080 °C with a maximum intensity at about 1300 °C (Figure 13a). The crystallinity of the quenched samples is too poor to perform quantitative Rietveld refinements. Only data collected from samples calcined 12 h at 1200 or 1300 °C are of a quality sufficient for refinement. At 1200 °C, 59 wt % of the sample is amorphous and 41 wt % is spinel. The content of the amorphous phase at 1300 °C is much lower with 57 wt %, and the amount of crystalline spinel is 43 wt %. As observed for CoAl<sub>2</sub>O<sub>4</sub>, the crystallite sizes of the NiAl<sub>2</sub>O<sub>4</sub> spinel grow with increasing temperature and prolonged calcination time.

**1.5. Ni,Na-X.** The DSC plot of a Ni,Na-X zeolite exchanged 5 times is similar to that of Ni,Na-A (Figure 13b). After the stepwise dehydration of the zeolite and the dehydroxylation near 355 °C, the structure collapses gradually. Above 600 °C the crystallization of NiO starts, but zeolite reflections are still observed as shown in Figure 15. Between 700 and 750 °C the zeolite reflections disappear. Beside the NiO phase, spinel formation occurs at about 850 °C and the NiO content is reduced. The sample quenched at 1100 °C still shows X-ray reflections of NiO, but after 12 h at 1100 °C NiO has disappeared. Consistent with the results of Ni,Na-A before, no SiO<sub>2</sub> phases are formed within the whole temperature range. The results of the quantitative phase analyses show that the high amount of amor-



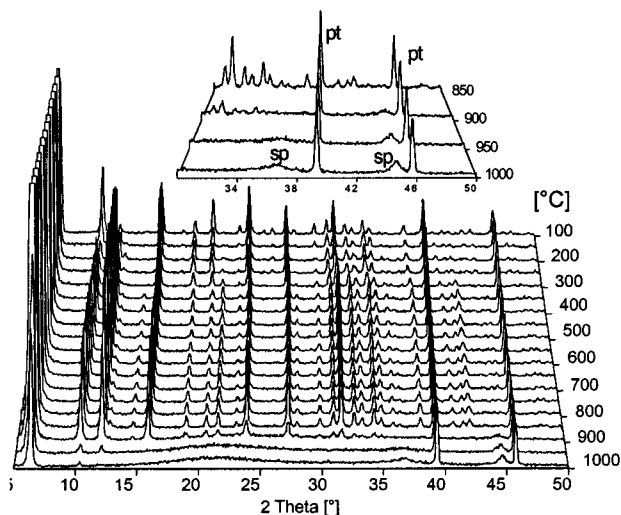
**Figure 15.** In situ HTC diffraction patterns of 5 times exchanged Ni,Na-X recorded between 100 and 1100 °C in steps of 50 deg. The enlarged section shows the coexistence of spinel and NiO.



**Figure 16.** In situ HTC diffraction patterns of 1 time exchanged Ni,Na-X recorded between 100 and 1100 °C in steps of 50 deg.

phous components of a sample calcined 12 h at 1200 °C (59 wt %) cannot be reduced significantly by raising the temperature to 1300 °C (57 wt %).

To check how much the framework structure and the thermal stability of the exchanged zeolites are affected by the exchange treatment, samples exchanged only once were studied. The comparison of the X-ray patterns shows that the framework structure of the zeolite exchanged 5 times is much more damaged than that of a once exchanged zeolite. Therefore, the thermal stability of the zeolites exchanged 5 times is reduced. In situ high-temperature X-ray experiments with the once exchanged zeolite reveal that the collapse of the framework structure happens at 750 °C (Figure 16). A gradual collapse during the heating, as observed for the 5 times exchanged zeolite, is not observed. Above 600 °C, where the formation of NiO starts with the 5 times exchanged zeolite X, no NiO is obtained with the once exchanged zeolite. At 850 °C, NiAl<sub>2</sub>O<sub>4</sub> spinel forms as the only observed crystalline phase. The number of exchanges has a significant influence on the stability of the resulting zeolite. The zeolite framework seems to be-



**Figure 17.** In situ HTC diffraction patterns of 5 times exchanged Ni,Na-Y recorded between 100 and 1000 °C in steps of 50 deg. The insertion presents the formation of only spinel.

come partially destroyed by the slightly acidic salt solution used for the exchanges.

**1.6. Ni,Na-Y.** The thermal behavior of Ni,Na-Y zeolite exchanged 5 times is similar to that of the Ni<sup>2+</sup>-exchanged zeolites A and X in the temperature range up to 400 °C. After the dehydration, a dehydroxylation process at about 370 °C is observed. Similar to Co,Na-Y, the presence of hydroxyl species is verified by IR signals at 3544, 3645, and 3739 cm<sup>-1</sup>.

At higher temperatures, Ni,Na-Y behaves differently than Ni,Na-A or Ni,Na-X. The destruction of the zeolite framework is not a gradual process. A sharp exothermic signal with its maximum intensity at about 910 °C indicates the rapid collapse of the framework structure (Figure 13c). In situ X-ray studies show that the framework structure of the Ni<sup>2+</sup>-exchanged zeolite Y remains stable up to 800 °C (Figure 17). Higher temperatures lead to the collapse of the structure between 850 and 900 °C. Between 900 and 950 °C NiAl<sub>2</sub>O<sub>4</sub> spinel formation occurs and the zeolite disappears completely. The crystallization of the spinel causes an exothermic signal at 944 °C in the DSC curve. Further studies with calcined samples reveal that NiAl<sub>2</sub>O<sub>4</sub> is the only crystalline phase present in samples quenched at 1100 or 1200 °C. Calcination for 12 h results in the crystallization of cristobalite in addition to spinel at both temperatures. The crystallinity of the calcined samples is quite low and the quality of the X-ray data is not sufficient for quantitative Rietveld refinements. Only data of the sample calcined at 1300 °C for 12 h is appropriate for refinement. The calculated amount of spinel is 31 wt % and that of the amorphous fraction is 69 wt %.

## Discussion

In general, the exchange of Co<sup>2+</sup> and Ni<sup>2+</sup> into the zeolites A, X, and Y is more strongly affected by the number of exchanges than by prolongation of the exchange time. The equilibrium of the exchange is obtained after short exchange times of 15–30 min. Elevated exchange temperatures lead to increased overexchanges of the zeolites, particularly with zeolites A and X. Co<sup>2+</sup> or Ni<sup>2+</sup> do not fully displace Na<sup>+</sup> in all three

zeolites. K<sup>+</sup>, which is initially present along with Na<sup>+</sup> in zeolite X, is totally removed by the ion-exchange. Neither Ni<sup>2+</sup> nor Co<sup>2+</sup> exchanges stoichiometrically into the zeolites. Usually a significant overexchange is observed. For zeolite Y, the overexchange is less extensive, and in the case of Co<sup>2+</sup> the exchange at room temperature is nearly stoichiometric. It is easier to exchange Co<sup>2+</sup> than Ni<sup>2+</sup> in zeolite A, whereas the opposite is observed for zeolite Y. The overexchange of Co<sup>2+</sup> and Ni<sup>2+</sup> cations in zeolites A and X raises the question of which type of species these cations exist as in the zeolite. X-ray diffraction gives no indication for crystalline phase impurities as transition metal salts. IR spectroscopy and coupled DSC-MS measurements show the existence of hydroxyl groups. Therefore, we presume the presence of both silanol groups and of Ni–OH and Co–OH species. The formation of Me–OH groups due to the hydrolysis of water molecules within transition-metal-exchanged zeolites has been reported by several groups.<sup>20–24</sup> Silanol groups are usually formed due to structural damage of zeolites, e.g., by treatment with acidic solution. Repetition of the ion-exchange procedure clearly reduces the crystallinity of the zeolite frameworks, particularly in the case of Ni<sup>2+</sup>-exchanged zeolite A and of Co<sup>2+</sup>- and Ni<sup>2+</sup>-exchanged zeolite X. The formation of silanol groups results from the hydrolysis of Si–O–Al bonds during treatment with the acidic transition metal salt solutions. Due to its lower aluminum content, the crystal structure of zeolite Y is less affected by the exchange than the structures of the zeolites A and X. Nevertheless, IR spectroscopy shows both silanol and Me–OH groups are formed in zeolite Y. Further discussion concerns mainly zeolite A and X, where the structure damage and the overexchange are much more pronounced. The structures of the exchanged zeolites are not destroyed completely by the ion-exchange, but the X-ray reflections are broadened and the amorphous fraction is increased, indicating a loss of crystallinity. It has to be considered carefully whether the loss of crystallinity is worth a higher degree of exchange. On the other hand, the phase formation processes at higher temperatures remain the same even though the crystallinity of the 5 times exchanged zeolites is significantly reduced.

During the calcination process the structures of some exchanged zeolites collapse at comparatively low temperatures. During water removal the transition metal cations have to change their coordination and coordinate oxygen atoms of the zeolite framework. A complex process of change in coordination and migration within the zeolite structure during dehydration is described for Co<sup>2+</sup>- and Ni<sup>2+</sup>-exchanged zeolites by various authors.<sup>20–22,24–26</sup> In the hydrated zeolites, Co<sup>2+</sup> and Ni<sup>2+</sup> are octahedrally coordinated by six water molecules. Dehydration leads to the removal of some of the complexing

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water molecules and to tetrahedral coordination with water molecules. Further dehydration leaves one water molecule close to the transition metal cation which is coordinated additionally by three oxygen atoms from the zeolite framework. Complete dehydration of FAU-type zeolites causes the migration of transition metal cations into hexagonal prism sites, where they are coordinated almost octahedrally by framework oxygen atoms. In completely dehydrated LTA-type zeolites, the transition metal cations are coordinated trigonally by framework oxygen atoms of a ring consisting of alternating silicon and aluminum atoms bridged by six oxygen atoms. While crystal field stabilization energies enable Co<sup>2+</sup> to be coordinated tetrahedrally without problems, Ni<sup>2+</sup> prefers octahedral coordination. Thus, the dehydration forces Ni<sup>2+</sup> into a nonpreferred coordination which is energetically unfavorable. This leads to an additional destabilization of the crystal structure. The frameworks of Ni<sup>2+</sup>-exchanged zeolites collapse at lower temperatures than those of Co<sup>2+</sup>-exchanged ones. Further destabilization is most probably caused by hydronium cations and hydroxide ions, which are formed at elevated temperatures. The presence of these ions within Co<sup>2+</sup>- and Ni<sup>2+</sup>-exchanged zeolites has been observed by several groups.<sup>21,23,24</sup> The hydronium ions break additional Si–O–Al bonds, causing further damage to the zeolite framework.

However, even the damaged crystal structures of Co<sup>2+</sup>-doped zeolites A and Y are rather stable up to 850 and 900 °C, respectively. At higher temperatures the structures collapse rapidly and the crystallization of CoAl<sub>2</sub>O<sub>4</sub> is observed. The breakdown of the Co<sup>2+</sup>-exchanged zeolite X proceeds as a continuous process between 400 and 800 °C. Cristobalite, the second main crystalline phase in the quenched samples beside spinel, is detected for all three zeolite precursor systems, but the conditions for the crystallization of cristobalite vary significantly for all three systems.

*In situ* high-temperature XRD analyses of 5 times Ni<sup>2+</sup>-exchanged zeolite A and X show that the amorphization of these multiple exchanged zeolites is a gradual rather than an immediate process. With Ni-Na-A and Ni,Na-X the crystallization of new phases starts with the occurrence of NiO together with residual zeolites, followed by the crystallization of NiAl<sub>2</sub>O<sub>4</sub>. At higher temperature NiO dissolves and spinel remains the only crystalline phase. As observed for the zeolite A precursor, no SiO<sub>2</sub> phase is detected in the whole temperature region up to 1300 °C for zeolite X. *In situ* experiments with once exchanged Ni,Na-X zeolite show the structure collapse and the spinel crystallization at similar temperatures as observed with the 5 times exchanged samples. In contrast to the latter, the collapse of the zeolite structure is not a gradual process, but occurs abruptly at 750 °C. A further difference to the 5 times exchanged sample is the complete absence of a NiO phase. The formation of NiO during the calcination process is also not observed for 5 times exchanged Ni,Na-Y. Both samples, once exchanged Ni,Na-X and 5 times exchanged Ni,Na-Y exhibit no overexchange and thus no excess of Ni<sup>2+</sup>. The Ni<sup>2+</sup> cations are completely consumed during the formation of the spinel phase. The structure of 5 times exchanged Ni,Na-Y, is less affected by the exchange treatment. The

zeolite framework collapses at higher temperatures compared to zeolites A and X. In Ni,Na-Y samples quenched at temperatures between 1100 and 1300 °C, NiAl<sub>2</sub>O<sub>4</sub> is the only crystalline phase. Only prolonged calcination at these temperatures results in the formation of cristobalite in addition to spinel.

During the calcination of overexchanged Ni<sup>2+</sup> zeolites NiO is formed prior to the NiAl<sub>2</sub>O<sub>4</sub> spinel. In the Co<sup>2+</sup> system, crystalline CoO is not observed. Excess cobalt which is not incorporated within the CoAl<sub>2</sub>O<sub>4</sub> spinel remains in the amorphous matrix. These observations could be explained with the coordination of the transition metals within the amorphous zeolite, which should not differ much from that in the zeolite precursor. Crystal field stabilization energy forces Ni<sup>2+</sup> into an octahedral rather than a tetrahedral coordination. In the dehydrated zeolites A, X, and Y the transition metal cations are coordinated tetrahedrally. The octahedral coordination of the nickel cations within the nickel oxide structure is thus energetically favored, and NiO is formed easily. Co<sup>2+</sup> has no such strong preference for one specific coordination. Crystal field stabilization energies are similar for octahedral and tetrahedral coordination of Co<sup>2+</sup>. Therefore, the formation of cobalt oxide is not as energetically driven as that of NiO.

In contrast to the formation of NiO from excess nickel, which is a thermodynamically controlled process, the crystallization of cristobalite at higher temperature from the amorphous SiO<sub>2</sub> matrix is rather a kinetically controlled process. Cristobalite forms after an induction period and the amount of cristobalite increases with time at a given temperature. The amounts of the spinels remain more or less constant, independent of the calcination time or temperature. Their amounts depend only on the type of zeolite used.

## Conclusions

The ability of the different zeolites to exchange alkali cations depends strongly on the transition metal used for the exchange. In none of the zeolites Na<sup>+</sup> is removed completely, but a significant overexchange of both Co<sup>2+</sup> and Ni<sup>2+</sup> is observed with zeolites A and X. The more siliceous zeolite Y exchanges almost stoichiometrically. The exchange of Co<sup>2+</sup> and Ni<sup>2+</sup> into all three zeolites is generally enhanced at elevated temperature, leading to an increased overexchange. Repetition of the exchange leads to structural damage of the zeolites A and X, due to interaction of the zeolite framework with acidic species formed within the micropores and with the acidic exchange solutions. Calcination of the exchanged zeolites leads to a loss of the zeolite structures. The temperature of framework collapse depends mainly on the silicon content of the zeolite and the framework damage caused by the ion-exchange. The collapse of the zeolite framework varies from a gradual progression over a large temperature range, e.g., in the case of Co,Na-X, to a very rapid process, e.g., in the cases of Co,Na-Y or Ni,Na-Y. Independent of the zeolite and transition metal used, spinel phases are formed from the amorphous matrix. The crystallite sizes grow with increasing temperature and calcination time, while the amount of spinel remains constant over large temperature ranges. With use of zeolites which contain excess nickel cations due to overexchange, nickel oxide is

formed beside the spinel phase at lower temperatures. Cobalt oxide is not observed, probably due to the fact that its formation is less energetically favored than that of nickel oxide. Excess cobalt remains in the amorphous solid matrix. At higher temperatures, nickel oxide dissolves and the excess nickel is also found in the amorphous matrix. The silicon oxide from the zeolite precursors transforms into crystalline phases only after an induction period at temperatures above 1000 °C. The amount of crystalline SiO<sub>2</sub> phases varies with calcination temperature and time. In some cases large amounts of the solid material remain amorphous even at high temperatures.

The transition metal exchanged zeolites and the composite materials obtained from these can be used for different applications. Whatever application is planned, the zeolite, the exchange conditions, and the thermal conditions have to be chosen with care. To obtain a thermal stable cobalt- or nickel-containing

zeolite, high aluminum contents of the zeolite should be avoided. On the other hand, low silica zeolites and long calcination times at temperatures above 1000 °C are to be preferred for the production of a composite containing of spinel and cristobalite without too high amounts of amorphous material. The knowledge of the phase composition after distinct exchange procedures and thermal treatments as shown in the present work enable the production of materials with well-defined properties for any application in a distinct field.

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