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Phase transformation of zeolites Cs,Na–Y and Cs,Na–X impregnated with cesium hydroxide

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Abstract

The thermal stability and porosity of basic zeolites Y and X (zeolite structure-type **FAU**, 12-ring windows), prepared by cesium exchange, impregnation with cesium hydroxide, and subsequent calcination, were investigated by X-ray powder diffraction, ^{27}Al and ^{29}Si NMR spectroscopy, and nitrogen adsorption. It was found that the basic zeolite X (Cs,Na–X/CsOH) exhibits a higher stability than the basic zeolite Y (Cs,Na–Y/CsOH). The micropore system of the latter collapses upon thermal treatment at 923 K. A partial transformation of basic zeolite Y into an amorphous phase and a pollucite-type phase (zeolite structure-type **ANA**, distorted 8-ring pores) was found by X-ray powder diffraction. The formation of a pollucite-type phase occurs with a chemical composition very close to those of cesium-exchanged and cesium-impregnated zeolites Y. ^{27}Al and ^{29}Si MAS NMR spectra of a mineral belonging to the pollucite–analcime series used in the present study as a reference material, agree very well with those of basic zeolite Y, making it difficult to distinguish between these two crystalline phases by NMR spectroscopy. Upon calcination of the cesium-exchanged and impregnated zeolite X at 923 K, ≈50% of the BET surface area and of the micropore volume of the parent material survive. Repeating the impregnation and calcination procedure several times leads to a complete amorphization of the so treated zeolite Y.
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Keywords: Basic zeolites Y and X; Cesian analcime; Phase transformation; NMR spectroscopy; X-ray powder diffraction

1. Introduction

Up till now, relatively scarce attention has been paid to the application of basic zeolites in heterogeneous catalysis. On the other hand, there is a high potential of such materials for a number of industrially important reactions, such as the dehydrogenation of alcohols, the double-bond isomerization of olefins, the side-chain alkylation of toluene, the synthesis of 4-methylthiazol or the aldol condensation of, e.g., *n*-butanal [1]. The chemical properties of basic zeolites are strongly influenced by the nature of their alkali metal cations, which determine the basic character of the oxygen atoms. Exchanging the sodium cations in as-synthesized zeolites by rubidium or cesium cations leads to a decrease in the mean electronegativity of the zeolite framework, whereby the base strength of the oxygen atoms is enhanced [2,3]. Strongly basic sites can be created by incorporating alkali metal guest compounds into the zeolite pores [4–8]. A frequently employed method is the impregnation of the zeolite host by an aqueous solution of cesium hydroxide and subsequent calcination, which has been claimed to lead to well dispersed cesium oxide guest compounds [5]. Due to the strongly basic conditions during the impregnation procedure, the formation of cesium aluminosilicates may also lead to a partial damage of the zeolite host.

In a number of studies, ^{133}Cs, ^{29}Si, ^{27}Al, and ^{1}H MAS NMR spectroscopy was applied for the characterization of the host framework and the guest compounds of basic zeolites prepared by impregnation with alkali metal compounds [9–14]. These investigations showed that impregnation of zeolites Cs,Na–Y and Cs,Na–X with cesium hydroxide followed by calcination at 723–773 K leads to well dispersed oxidic alkali metal guest compounds partly bound at Q^3 silicon atoms (Si(T,OH) with

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T = Si, Al) [10,11,13]. No ^{133}Cs MAS NMR signals of isolated bulk Cs_2O (225 ppm [9]) and Cs_2CO_3 (100 and 180 ppm [9]) were observed. A weak influence of the guest compounds on the NMR signals of silicon and aluminum atoms in the framework of the zeolite host was found [10–12]. The X-ray powder patterns of cesium-exchanged zeolites are strongly affected by an impregnation of the host material with cesium hydroxide and subsequent calcination which increases the background intensity. This effect can be partially attributed to the strong X-ray absorption of cesium atoms, but the diffuse scattering indicates a partial transformation of the zeolite framework under the strongly basic conditions during the impregnation procedure into amorphous products.

In the present work, basic zeolites Cs,Na–Y and Cs,Na–X were investigated before and after impregnation with cesium hydroxide and subsequent calcination. To prove the partial amorphization of the zeolites, we investigated the influence of a repeated impregnation and calcination as well as the effect of a one-step increase of the amount of CsOH in comparison. X-ray powder diffraction, ^{27}Al and ^{29}Si NMR spectroscopy, and nitrogen adsorption were applied to study the influence of the alkali metal guest compounds on the zeolite framework.

2. Experimental section

Zeolite Na–Y ($n_{Si}/n_{Al} = 2.7$), purchased from Degussa AG, Hanau, Germany, and zeolite Na–X ($n_{Si}/n_{Al} = 1.3$), purchased from Union Carbide Corp., Tarrytown, NY, USA, were fivefold ion-exchanged in a 0.4 M aqueous solution of CsCl (CsCl: Aldrich, 19,831-5) at 353 K for 12 h leading to sodium exchange degrees of 70% and 55% for zeolites Cs,Na–Y and Cs,Na–X, respectively, corresponding to the chemical compositions given in Table 1. Subsequently, the materials were suspended in a 0.2 M solution of CsOH (CsOH: Aldrich, 19,833-1) with an absolute amount of CsOH dissolved corresponding to the composition of the final product. The suspension was stirred overnight to dryness at 353 K in air. For the impregnated materials, notations such as Cs,Na–Y/CsOH and Cs,Na–X/CsOH will be used indicating that the zeolites were loaded with 14 CsOH per unit cell (u.c.). Finally, the samples were calcined in a flow of nitrogen at 723 K (zeolites Cs,Na–Y/CsOH723 and Cs,Na–X/CsOH723) or 923 K (zeolites Cs,Na–Y/CsOH923 and Cs,Na–X/CsOH923) for 12 h. Approximately 3 g of zeolites Cs,Na–Y/CsOH723 and Cs,Na–X/CsOH723 were washed with demineralized water (1.5 dm^3) for 2 h at 353 K. The designations of the corresponding samples carry an additional W in Tables 1 and 2. Some samples were prepared as described above, but using 7 CsOH/u.c. for the impregnation of the cesium-exchanged zeolite Y. In this case, the impregnation and calcination were repeated up to four times. The mineral belonging to the pollucite–analcime series (cesian analcime, zeolite structure-type **ANA**), used as a reference material, was obtained from the Helikon II mine, Namibia.

The chemical compositions of the samples were analyzed by atomic emission spectroscopy with an inductively coupled plasma (AES-ICP) using a Perkin Elmer Plasma 400 instrument. The amounts of cesium atoms in the samples dissolved in a 5.0 M aqueous solution of HF were determined by precipitation with sodium tetraphenylborate. X-ray powder diffraction (XRD) data were collected on a STOE STADI-P powder diffractometer equipped with a mini-PSD detector, with a rotating sample in the symmetric transmission mode (germanium monochromator, CuKα_1 and MoKα_1 radiation). The XRD investigations were performed with samples dehydrated in vacuum at 723 K and fused into glass tubes. Samples exposed to air get contaminated by Cs_2CO_3, as can easily be proved by treatment with aqueous HCl which liberates CO_2. Nitrogen adsorption/desorption isotherms were recorded on a

Table 1
Chemical compositions of zeolites Y and X prepared by cesium exchange and elemental analyses of the products obtained after impregnation with cesium hydroxide, calcination at 723 K, and washing in demineralized water

Materials	Chemical compositions and atomic ratios n_{Cs}:n_{Na}:n_{Al}:n_{Si}
Cs,Na–Y	$64\times\lvert Cs_{0.57}Na_{0.25}\rvert[Al_{0.82}Si_{2.18}O_6]$
	0.57:0.25:0.82:2.18
Cs,Na–Y/CsOH723	0.79:0.25:0.82:2.18
Cs,Na–Y/CsOH723W	0.73:0.26:0.84:2.16
Cs,Na–X	$64\times\lvert Cs_{0.72}Na_{0.59}\rvert[Al_{1.31}Si_{1.69}O_6]$
	0.72:0.59:1.31:1.69
Cs,Na–X/CsOH723	0.94:0.59:1.31:1.69
Cs,Na–X/CsOH723W	0.90:0.60:1.33:1.67

Table 2
BET surface areas and micropore volumes of materials under study as determined by nitrogen adsorption

Materials	BET surface area in m^2/g	Micropore volume in cm^3/g
Cs,Na–Y	479	0.260
Cs,Na–Y/CsOH723	177	0.104
Cs,Na–Y/CsOH723W	304	0.155
Cs,Na–Y/CsOH923	53	0.034
Cs,Na–X	354	0.172
Cs,Na–X/CsOH723	264	0.127
Cs,Na–X/CsOH723W	296	0.146
Cs,Na–X/CsOH923	158	0.087

Micromeritics ASAP 2000 instrument after dehydration in vacuum at 623 K for 12 h.

NMR investigations were performed on a Bruker MSL-400 instrument at resonance frequencies of 104.2 MHz for ^{27}Al and 79.5 MHz for ^{29}Si nuclei. ^{27}Al MAS NMR spectra were recorded with a sample spinning rate of 10 kHz, while a spinning rate of 4 kHz was used for ^{29}Si MAS NMR spectroscopy. The repetition times were 0.5 s for ^{27}Al and 10 s for ^{29}Si MAS NMR spectroscopy. The free induction decays were recorded after single-pulse $\pi/2$ (^{29}Si) or $\pi/6$ (^{27}Al) excitation. ^{29}Si MAS NMR spectra were referenced to TMS (tetramethylsilane), while for the ^{27}Al MAS NMR spectroscopy a 0.5 M aqueous solution of aluminum nitrate was used as chemical shift reference.

3. Results and discussion

3.1. Composition of the zeolites under study

Zeolite Y with an n_{Si}/n_{Al} ratio of 2.7 possesses 51.9 Al and 140.1 Si atoms per unit cell (u.c.). A cation exchange degree of 70% corresponds to 36.4 Cs/u.c. present in zeolite Cs,Na–Y. Zeolite X with an n_{Si}/n_{Al} ratio of 1.3 possesses 83.5 Al and 108.5 Si atoms per unit cell. A cation exchange degree of 55% corresponds to 45.9 Cs/u.c. present in zeolite Cs,Na–X. Anticipating that the framework stays intact, the impregnation with cesium hydroxide and calcination at 723 K results in the introduction of additional 14 Cs/u.c. (Cs,Na–Y/CsOH723, Cs,Na–X/CsOH723). In Table 1, the chemical

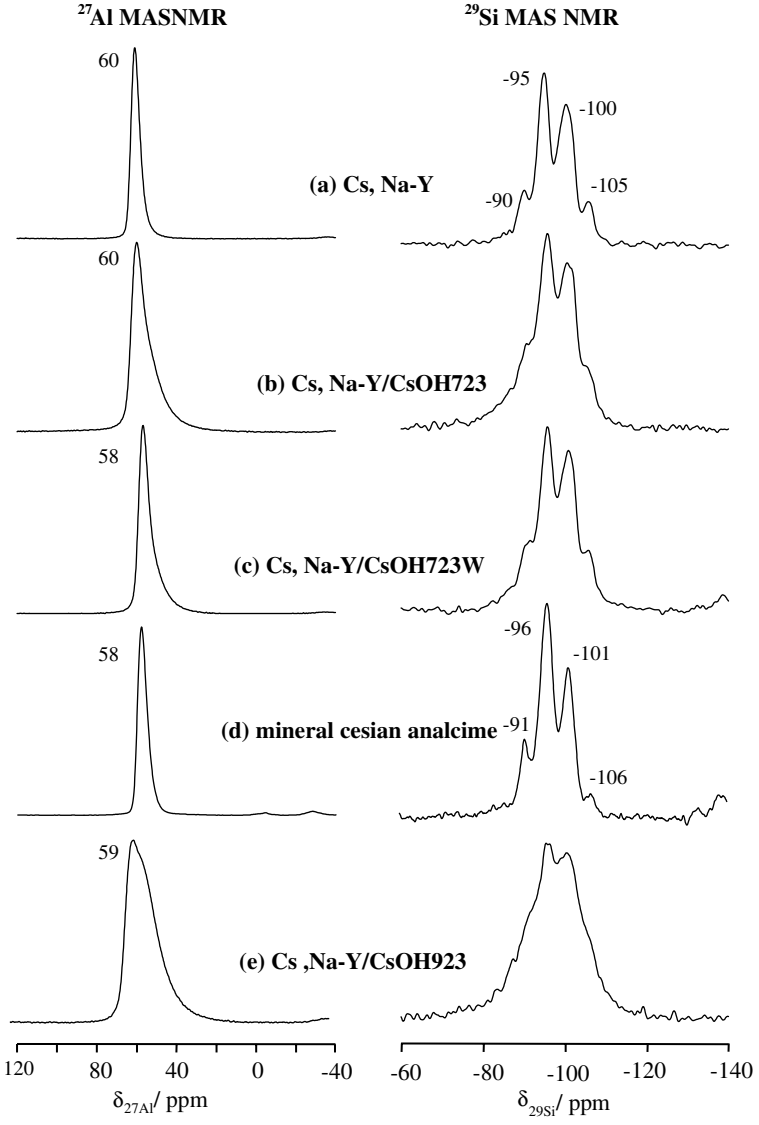


Fig. 1. ^{27}Al and ^{29}Si MAS NMR spectra of hydrated zeolite Y recorded after cesium exchange (a), impregnation with cesium hydroxide (14 CsOH/u.c.) and calcination at 723 K (b), washing of the latter sample (c), and after impregnation with cesium hydroxide and calcination at 923 K (e). In (d), the NMR spectra of the mineral cesian analcime, used a reference material, are shown.

compositions and atomic ratios of the cesium-exchanged, impregnated, calcined, and washed zeolites Y and X are summarized. The samples Cs,Na–Y/CsOH923 and Cs,Na–X/CsOH923, calcined at 923 K after an impregnation with cesium hydroxide, have the same atomic ratios as the samples Cs,Na–Y/CsOH723 and Cs,Na–X/CsOH723 and are, therefore, not listed in Table 1.

Basic zeolites Y and X impregnated with cesium hydroxide and calcined at 723 K (Cs,Na–Y/723, Cs,Na–X/723) are typical for the materials, which are commonly employed as strongly basic solids in heterogeneous catalysis. Washing of these materials in demineralized water at 353 K removes ≈30% of the cesium ions introduced by impregnation with cesium hydroxide. This indicates that most of the guest compounds are strongly coordinated to the solid. A small amount of silicate was found in the aqueous solution after the washing procedure corresponding to ≈1–2% of the total amount of silicon atoms in the zeolite framework. No extracted sodium or aluminum could be detected. The extracted silicate gives evidence for a partial damage of the zeolite host by the alkali metal guest compounds, the degree of damage being possibly obscured by the insolubility of the decomposition products.

3.2. Characterization of the surface area and micropore volume by nitrogen adsorption

In the present work, nitrogen adsorption was used to study the effect of impregnation of the zeolites with cesium hydroxide and subsequent calcination at 723 and 923 K on the BET surface area and micropore volume. The results, which are summarized in Table 2, show that already the zeolites Cs,Na–Y and Cs,Na–X have significantly different adsorption behaviors towards nitrogen. Due to the higher amount of cesium cations in zeolite Cs,Na–X in comparison with zeolite Cs,Na–Y (column 2 in Table 1), the BET surface area and the micropore volume of the former material are by ≈25% and 35%, respectively, smaller than those of the latter material. Impregnation of the cesium-exchanged zeolites Y and X with cesium hydroxide and subsequent calci-

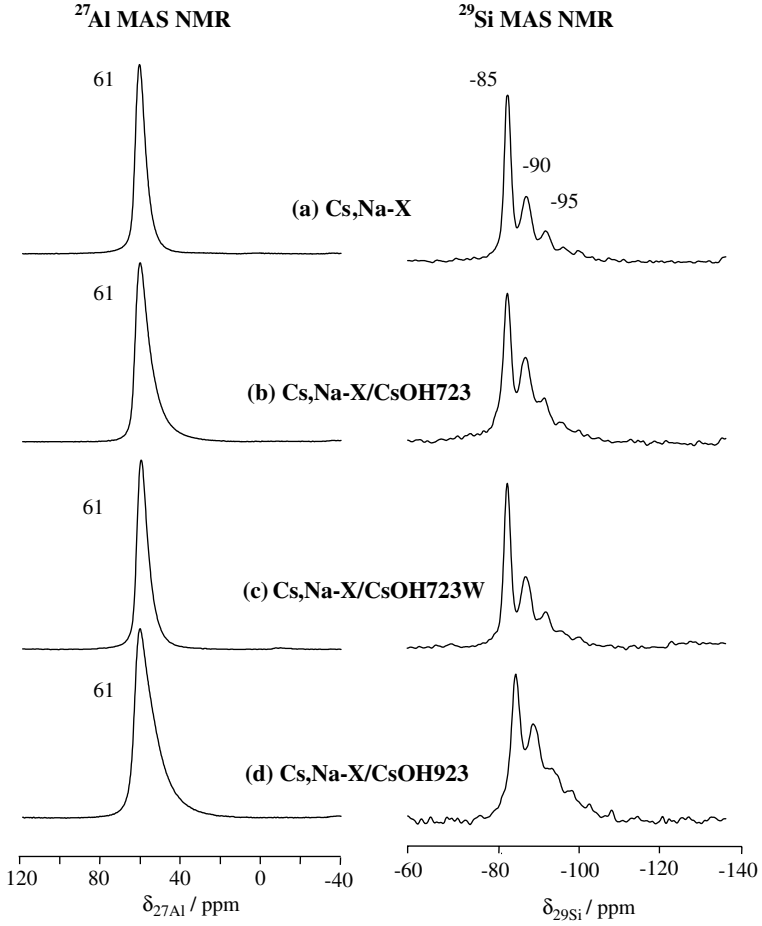


Fig. 2. ^{27}Al and ^{29}Si MAS NMR spectra of hydrated zeolite X recorded after cesium exchange (a), impregnation with cesium hydroxide (14 CsOH/u.c.) and calcination at 723 K (b), washing of the latter sample (c), and after impregnation with cesium hydroxide and calcination at 923 K (d).

nation at 723 K results in a further decrease of both adsorption parameters, however, this effect is significantly more pronounced for zeolite Y than for zeolite X. The small BET surface area of zeolite Cs,Na–Y/CsOH923 determined upon calcination at 923 K indicates a collapse of the micropore system. This decrease in the porosity is not so pronounced in the case of zeolite X calcined at 923 K, which retains ≈50% of the BET surface area and of the micropore volume of zeolite Cs,Na–X.

Washing of the materials calcined at 723 K results in a significant increase of the BET surface areas and the micropore volumes. Considering the small amount of cesium atoms removed by the washing process (column 2 in Table 1), a preferential extraction of extra-framework species blocking the pore openings of the zeolite Y and X particles must be invoked.

Generally, it can be stated, that the micropore system of basic zeolite Y is more affected by impregnation with cesium hydroxide and subsequent calcination than that of basic zeolite X. This finding is relevant to the application of zeolites Cs,Na–Y/CsOH and Cs,Na–X/CsOH in the heterogeneously catalyzed conversion of bulky reactants.

3.3. ^{27}Al and ^{29}Si NMR spectroscopic investigations

The ^{27}Al and ^{29}Si MAS NMR spectra of zeolites Cs,Na–Y and Cs,Na–X shown in Figs. 1a and 2a, respectively, correspond to those of highly crystalline

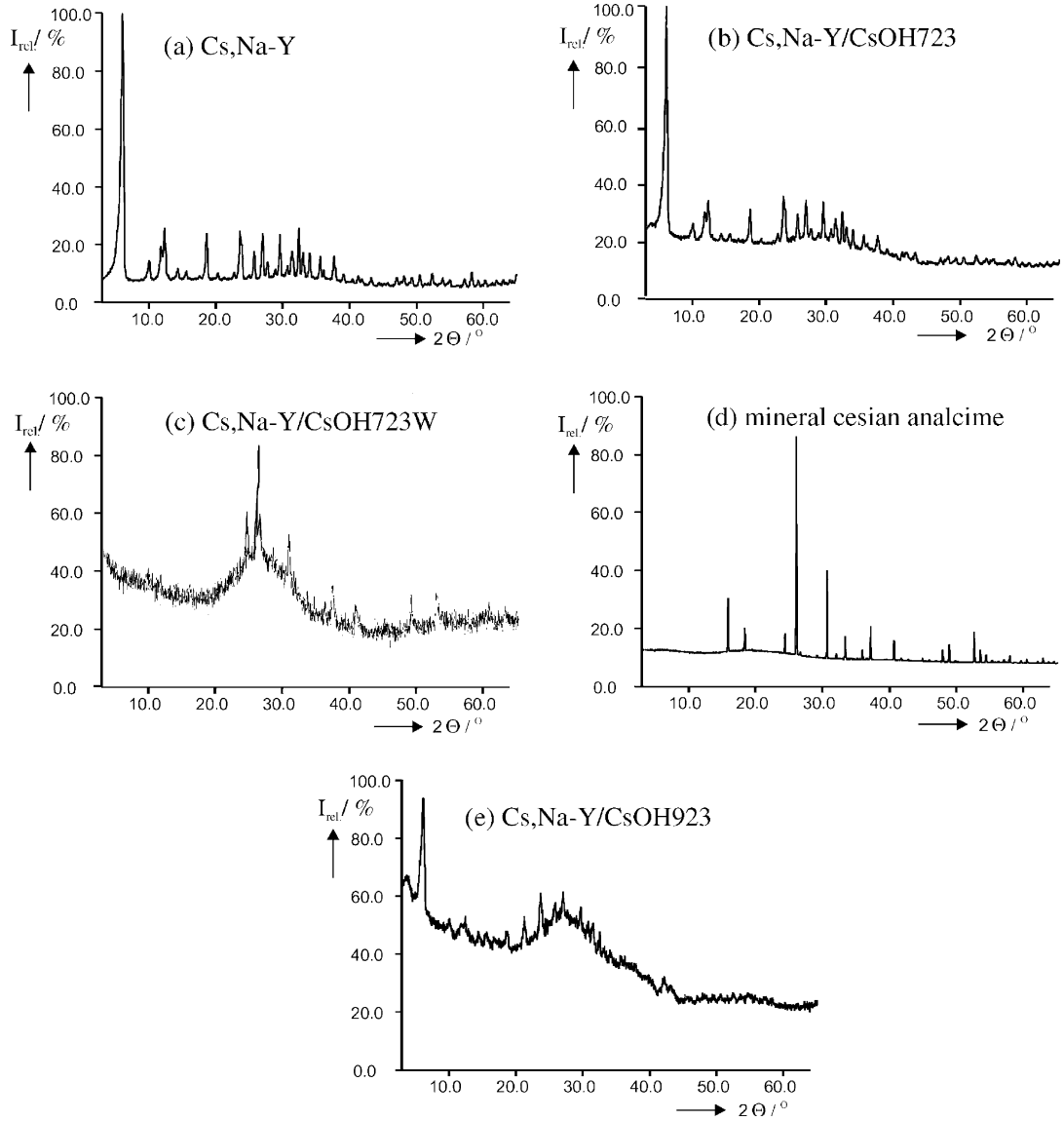


Fig. 3. CuKα_1 X-ray powder patterns of zeolites Y obtained after cesium exchange (a), impregnation with cesium hydroxide (14 CsOH/u.c.) and calcination at 723 K (b), washing of the latter sample (c), and after impregnation with cesium hydroxide and calcination at 923 K (e). In (d), the CuKα_1 X-ray pattern of the mineral cesian analcime, used a reference material, is shown.

materials. The simulation (not shown) and quantitative evaluation of the ^{29}Si MAS NMR spectra yield framework n_{Si}/n_{Al} ratios agreeing with those of the bulk analysis by AES-ICP. Impregnation and calcination of the cesium-exchanged zeolite Y at 723 K cause a broadening of the ^{27}Al and ^{29}Si MAS NMR signals indicating a local framework strain as observed after an exchange with bulky lanthanum cations [15] (Fig. 1b). Upon calcination at 923 K, the line broadening in the ^{29}Si MAS NMR spectra is strongly increased hinting to a partial damage of the zeolite framework (Fig. 1e). In addition, a high-field shoulder caused by a distorted tetrahedral coordination of aluminum occurs in the ^{27}Al MAS NMR spectrum. Washing of zeolite Cs,Na–Y/CsOH723 leads to the sample denoted as Cs,Na–Y/CsOH723W in Tables 1 and 2, and it is accompanied by a decrease of the line widths in the ^{27}Al and ^{29}Si MAS NMR spectra and a high-field shift of the ^{27}Al MAS NMR signal of tetrahedrally coordinated aluminum atoms.

In comparison with the ^{27}Al and ^{29}Si MAS NMR spectra of zeolite Y, the spectra of zeolites Cs,Na–X/CsOH723 and Cs,Na–X/CsOH923 show small differences only (Fig. 2). No resonance shift of the ^{27}Al MAS NMR signals of the tetrahedrally coordinated aluminum or strong line broadenings of the ^{29}Si MAS NMR signals occurred, even upon calcination at 923 K. Washing of zeolite Cs,Na–X/CsOH723 led to ^{27}Al and ^{29}Si MAS NMR spectra identical with those of zeolite Cs,Na–X. Therefore, as already found by the nitrogen adsorption experiments, the results of NMR spectroscopy, too, indicate a significantly reduced stability against the impregnation and the calcination for basic zeolite Y in comparison with basic zeolite X.

3.4. Characterization by X-ray powder diffraction

The CuKα_1 X-ray powder pattern of zeolite Cs,Na–Y, shown in Fig. 3a, corresponds to that published previously [11]. Upon impregnation of zeolite Cs,Na–Y with cesium hydroxide and subsequent calcination at 723 K, the characteristic reflections of the zeolite occurring at $5° < 2\Theta < 35°$ decrease in intensity, and a broad background can be observed at around $2\Theta = 27°$ (Fig. 3b). This background is strongly increased upon calcination at 923 K (Fig. 3e).

The occurrence of the broad background gives evidence for a partial transformation of the framework of zeolite Y into another phase, and this is supported by the simultaneous decrease in intensity of the characteristic reflections of the zeolite. Indeed, repeating the impregnation and calcination procedure a couple of times leads to a drastic increase of the background intensity. As the reaction products contain a large amount of highly absorbing cesium ions, the changes in the X-ray pattern taken with CuKα_1 radiation might reflect the coverage of essentially unchanged zeolite grains by amorphous surface layers. In a further experiment, therefore, the more deeply penetrating MoKα_1 radiation was used. The sequence of the MoKα_1-diagrams taken (Fig. 4) gives clear evidence for a near to complete decomposition of the zeolite in samples Cs,Na–Y/CsOH after a few steps of impregnation and calcination. The diffuse background is shaped in a characteristic way, more specifically indicating a Fourier transform which is due to the formation of a new crystalline phase with a grain size that is subcoherent to X-rays, however, gets larger upon washing.

After washing of zeolite Cs,Na–Y/CsOH723, the product being denoted as Cs,Na–Y/CsOH723W, a pattern of characteristic lines is recorded in addition to the diffuse background (Figs. 3c and 4e). Indexing results in a cubic structure with a cell constant $a = 13.647(4)$ Å, which can be assigned to that of a pollucite-type phase. For a comparison, the X-ray pattern of a sample of the mineral cesian analcime, characterized by a cell parameter $a = 13.668(3)$ Å, is shown in Fig. 3d.

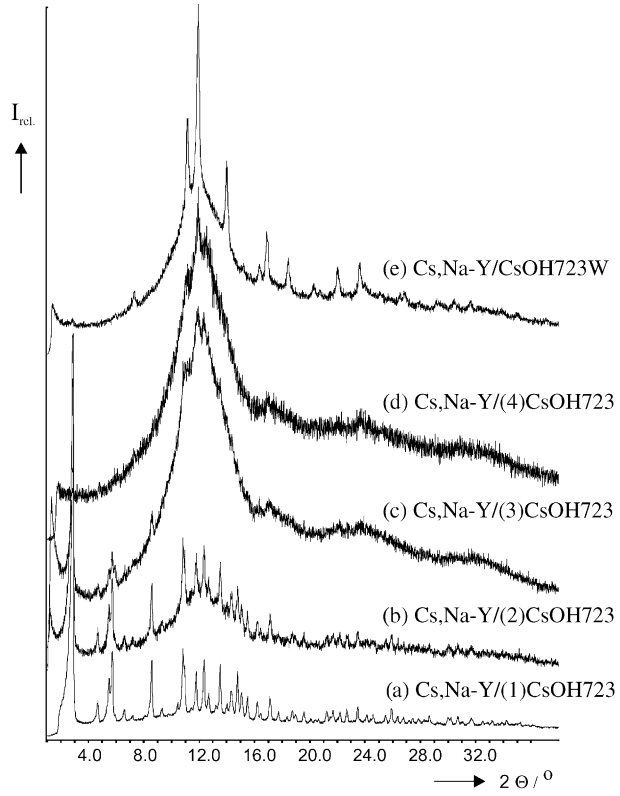


Fig. 4. MoKα_1 X-ray powder patterns of zeolites Y obtained after cesium exchange, impregnation with cesium hydroxide and calcination at 723 K in one step leading to a loading of 7 CsOH/u.c. (a), two steps leading to a loading of 14 CsOH/u.c. (b), three steps leading to a loading of 21 CsOH/u.c. (c), and four steps leading to a loading of 28 CsOH/u.c. (d). In (e), the MoKα_1 X-ray powder pattern of zeolite Y obtained after cesium exchange, impregnation with cesium hydroxide (14 CsOH/u.c), calcination at 723 K, and washing is shown.

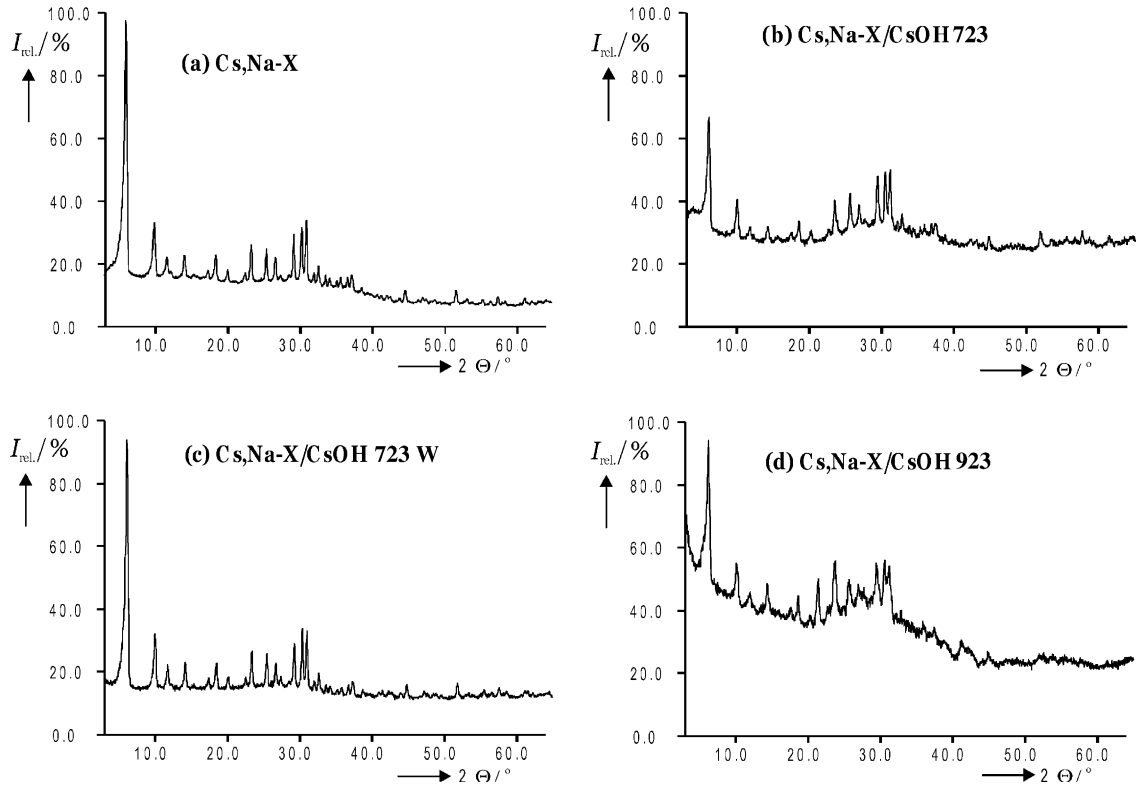


Fig. 5. CuKα_1 X-ray powder patterns of zeolites X obtained after cesium exchange (a), impregnation with cesium hydroxide (14 CsOH/u.c.) and calcination at 723 K (b), washing of the latter sample (c), and after impregnation with cesium hydroxide and calcination at 923 K (d).

In the X-ray patterns of the basic zeolites X, shown in Fig. 5a–c, only minor changes in line shapes and intensities of the characteristic reflections of the zeolite were found as a result of impregnation and calcination at 723 K. On the other hand, a significant background again occurs in the X-ray powder pattern around $2\Theta = 27°$ upon calcination at 923 K (Fig. 5d). After washing of zeolite Cs,Na–X/CsOH723 which leads to the sample denoted as Cs,Na–X/CsOH723W, no reflections of a new crystalline phase were observed (Fig. 5c).

3.5. NMR and XRD investigations of the mineral cesian analcime

The reflections occurring in the X-ray powder pattern of zeolite Cs,Na–Y/CsOH723W (Figs. 3c and 4e) give clear evidence for the formation of a pollucite-type phase. Pollucite is isostructural with the zeolite analcime (framework type **ANA**) which possesses strongly distorted 8-ring pores with diameters of 1.6×4.2 Å [16]. The ideal pollucite structure corresponds to $|CsNa(H_2O)_n|[AlSi_2O_6]$ [17], while the mineral used in the present work as a reference material has the chemical composition $|Cs_{0.25}Na_{0.58}(H_2O)_n|[Al_{0.83}Si_{2.17}O_6]$. It is noteworthy that the alkali metal content and the n_{Si}/n_{Al} ratio are very similar to that of sample Cs,Na–Y/CsOH723W (see line 4 in Table 1). The ^{27}Al and ^{29}Si MAS NMR spectra of the mineral cesian analcime are shown in Fig. 1d. A comparison with the spectra in Fig. 1a–c reveals that not only the resonance positions of the ^{27}Al and ^{29}Si MAS NMR signals of pollucite are equal to those of zeolites Cs,Na–Y and Cs,Na–Y/CsOH, but that the same is true for the line widths and relative signal intensities in the ^{29}Si MAS NMR spectra. Hence, ^{27}Al and ^{29}Si MAS NMR spectroscopy turns out to be not suitable for the detection of the decomposition reaction which occurs upon treating zeolite Cs,Na–Y with CsOH. Only the formation of amorphous phases resulting in a strong broadening of the NMR signals and a high-field shift of the ^{27}Al MAS NMR signals can be evidenced by solid-state NMR spectroscopy. In the case of zeolites X, however, the ^{29}Si MAS NMR spectra of which have significantly different relative intensities, a formation of a pollucite-type phase can be excluded by the spectra shown in Fig. 2, right-hand part.

4. Conclusions

Series of basic zeolites Y and X, prepared by cesium exchange, impregnation with cesium hydroxide, and calcination at 723 or 923 K were investigated by X-ray powder diffraction, solid-state NMR spectroscopy, and nitrogen adsorption. The latter technique was applied to clarify the influence of impregnation and calcination on

the BET surface area and the micropore volume. While calcination at 923 K led to a collapse of the micropore system of zeolite Cs,Na–Y/CsOH, zeolite Cs,Na–X/CsOH retained ≈50% of the BET surface area and micropore volume. Washing of zeolites Y and X impregnated with cesium hydroxide and calcined at 723 K was found to extract ≈30% of the cesium ions introduced by impregnation and ≈1–2% of the silicon atoms, and to result in a significant increase of the BET surface area and micropore volume. This may be due to a preferential extraction of extra-framework species blocking the pore openings of the remaining phases of zeolites Y and X by the washing procedure.

The ^{27}Al and ^{29}Si MAS NMR spectra of the basic zeolites Y under study showed an increasing line broadening upon impregnation with cesium hydroxide and calcination at 723 and 923 K. This line broadening is due to a partial transformation of the zeolite framework into an amorphous phase. Upon washing of zeolite Y impregnated with cesium hydroxide and calcined at 723 K, a line narrowing was found. Simultaneously, reflections of a new crystalline phase occurred in the X-ray powder pattern of the resulting material, which was assigned to the formation of crystals belonging to the pollucite–analcime series as decomposition product of zeolite Cs,Na–Y/CsOH besides other still amorphous phases.

The present investigation has shown that the conditions of the preparation of basic zeolites Y and X by cesium exchange, impregnation with cesium hydroxide, and subsequent calcination are very crucial for obtaining suitable catalyst materials. Both a too high loading with cesium hydroxide acting as guest compound and a too high calcination temperature cause damage and partial transformation of zeolite crystals. Further studies are planned with the aim to find parameters leading to a method for the preparation of cesium-containing zeolite catalysts with a locally damaged framework, i.e., with a mesopore system.

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