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Originally published as:

“2.4.3 Solid-State Ion Exchange in Zeolites”

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In: Handbook of Heterogeneous Catalysis, Vol. 1, (2008) 484-510

ISBN-Nummer: 978-3-527-31241-2

Reprint from

## Handbook of Heterogeneous Catalysis

8 Volumes

*Edited by*  
Gerhard Ertl, Helmut Knözinger, Ferdi Schüth,  
and Jens Weitkamp

Second, Completely Revised and Enlarged Edition



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## 2.4.3

**Solid-State Ion Exchange in Zeolites***Hellmut G. Karge\**

## 2.4.3.1 Introduction

The classical method for modification of zeolites with respect to their charge-compensating cations was, for a long time, ion exchange in an aqueous medium. Systematic studies of the potential of solid-state ion exchange commenced only in the mid-1980s, when two research groups began independent investigations into a broad variety of zeolites and compounds of ions to be incorporated into those microporous solids [1–7]. These studies were also independent of a few earlier observations reported during the 1970s by Rabo et al. [8] and Clearfield et al. [9], who used solid-state ion exchange to eliminate Brønsted acid-based catalytic properties from zeolites, and reacted mixtures of ammonium-containing zeolites with halides, respectively. Slinkin's group [1–4] focused on the solid-state introduction of transition metal cations into high-silica zeolites such as ZSM-5 and mordenite, using mainly electron spin resonance (ESR) spectroscopy for monitoring the reaction, whereas the present author's group began with quantitative investigations on solid-state exchange reactions between alkaline and alkaline earth halides and hydrogen or ammonium forms of zeolites such as  $\text{NH}_4\text{-Y}$ ,  $\text{H-ZSM-5}$  and  $\text{H-MOR}$  (for zeolite structures such as A, X, Y, MOR, L, BETA, SAPOs, MCM-41 and acronyms cf. Ref. [10]). In these latter studies, infrared (IR) spectroscopy and chemical analysis were mainly employed. During the subsequent decades, research into solid-state ion exchange was extended to as-synthesized sodium forms of zeolites as starting materials, and the incorporation of cations of possibly catalytic importance such as lanthanum, iron, copper, manganese, and noble metals. Similarly, the number of techniques suitable

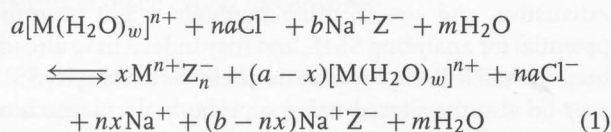
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for monitoring solid-state ion exchange was considerably increased. In this chapter, the potential of the various methods will be demonstrated by appropriate examples. The systems studied with respect to modification via solid-state reaction are summarized in Table 4 (see below). An earlier extended and detailed review of the field has been published previously [11].

#### 2.4.3.2 Comparison of Conventional and Solid-State Ion Exchange

In this section, the general chemistry of ion exchange in aqueous solution (conventional exchange, CE) will be contrasted with exchange in the solid state (solid-state ion exchange, SSIE). In some cases of CE, notably those with highly siliceous, acid-resistant zeolites, the cations of the as-synthesized form (usually  $\text{Na}^+$  or  $\text{K}^+$ ) may be exchanged for protons via a careful treatment with a mineral acid such as diluted  $\text{HCl}$  or  $\text{HNO}_3$ . However, CE is usually carried out by suspending the zeolite powder in aqueous solutions of salts which contain the desired in-going cation. The suspension is stirred for some time, frequently at temperatures higher than ambient. Basically, conventional ion exchange is described by Eq. (1) where, for the sake of simplicity, the chloride anion ( $\text{Cl}^-$ ) is chosen as the counter ion of the in-going cation,  $\text{M}^{n+}$ , and the sodium form of the zeolite (Z) as the solid, is suspended in  $m$  moles of water:

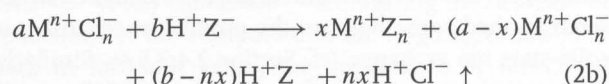
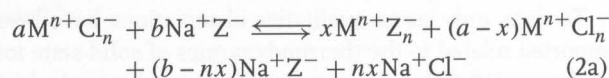


where M is the  $n$ -valent cation;  $\text{Z}^-$  is the monovalent negatively charged zeolite fragment;  $a$ ,  $b$ , and  $x$  are stoichiometric numbers;  $m$  is the number of solvent ( $\text{H}_2\text{O}$ ) moles; and  $w$  is the number of the solvating  $\text{H}_2\text{O}$  in the solvate shell of cation M.

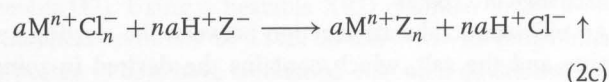
Usually, the equilibrium does not lie heavily on the right hand side of Eq. (1). Thus, the (partially exchanged) solid and the solution must be separated. In order to achieve a high degree of exchange, the procedure must normally be repeated several times, and consequently ion exchange in aqueous solution is a time-consuming process. Moreover, the procedure produces large amounts of waste solutions which must either be regenerated or discarded in an environmentally friendly manner. Likewise, in several instances it is very difficult – or even impossible – to introduce all particular cations into a given zeolite by means of conventional ion exchange – that is, in aqueous solution. Examples are encountered where the cations are strongly solvated or available only in complexes, which are too bulky to enter the narrow pores of the respective zeolites (*vide infra*, e.g., Sections 2.4.3.5.7 and 2.4.3.6.2).

Because of the fundamental importance of ion exchange in zeolite chemistry, there exists a large body of literature on the thermodynamics of CE (see, e.g., Refs. [12–17] and references therein).

Solid-state ion exchange (SSIE) can be described by Eqs. (2a) or (2b), depending on whether the starting material is a cation-containing zeolite such as  $\text{Na}^+\text{Z}^-$  (as in the above case of CE) or a hydrogen (ammonium) form:



With a stoichiometric mixture, as in the case of Eq. (2b), one may reach a complete exchange without any salt remaining in the product [cf. Eq. (2c)]:

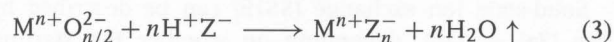


Thus, the solid-state reaction may be conducted in a mixture with the salt being present in a sub-stoichiometric ( $b < na$ ), a stoichiometric ( $b = na$ ), or an excess ( $b > na$ ) amount. This provides us with the possibility of achieving a certain desired degree of exchange.

In the case of Eq. (2a) one arrives at an equilibrium, similar to the case of conventional exchange [cf. Eq. (1) and also Section 2.4.3.5.3]. In order to obtain a higher degree of exchange via solid-state ion exchange into a cation-containing form of a zeolite, one must remove the solid halide (e.g.,  $\text{NaCl}$ ) which has formed during the solid-state reaction (*vide infra*, e.g. Section 2.4.3.5.3). This can be achieved by a brief washing of the reaction product with a small amount of water. However, if the starting zeolite material is the hydrogen or ammonium form [cases of Eqs. (2b) and (2c)], the hydrogen halide ( $\text{HCl}$ ) or a mixture of hydrogen halide and ammonia ( $\text{HCl} + \text{NH}_3$ ) may be continuously removed in a stream of inert gas or into dynamic vacuum. Here, the equilibrium may be therefore completely shifted to the right-hand side of Eqs. (2b) and (2c), and a 100% exchange established (cf., e.g. Sections 2.4.3.5.1 and 2.4.3.5.3). In fact, in many other cases it has been reported that SSIE yielded a degree of exchange which was significantly higher than that reached by CE.

Whilst in the case of SSIE the main feature is that, usually at elevated temperatures, the *pure* solids are brought to reaction, in CE the solvent (water) is involved as a third component. Therefore, the in-going and out-going cations are usually solvated [cf. Eq. (1)]. Solvation of the cations in many cases impedes ion exchange, while

this cannot occur in SSIE. It should be mentioned here that, in several cases, SSIE was also observed when oxides instead of halides or similar compounds of the in-going cation were used [18], according to the following scheme:



In such a case, water is generated instead of a hydrogen halide.

To date, only some qualitative observations have been reported related to the thermodynamics of solid-state ion exchange [19, 20]. A few results have been obtained which seem to shed some light on the possible mechanism of solid-state ion exchange (cf. Section 2.4.3.5.4). Similarly, systematic investigations of the kinetics of SSIE are still rather scarce [21].

#### 2.4.3.3 Experimental Procedure for Solid-State Ion Exchange in Zeolites

An efficient solid-state reaction between the starting zeolite and the salt, which contains the desired in-going cation, requires an intimate mixture of the solids. This can be achieved, for instance, by careful milling or grinding the two components together. In cases where an intense milling or grinding of the mixture may affect the integrity of the zeolite structure [22], it is preferable to prepare a suspension of the powdered salt and the zeolite in an inert solvent such as hexane. When the components have been thoroughly mixed by moving the suspension, the solvent may easily be removed [5]. The mixture obtained in either way is subsequently heated in a stream of inert gas or in high vacuum to remove volatile products such as hydrogen halides, ammonia, water, etc. A reaction temperature of 525–625 K and a reaction time of a few hours are usually sufficient to bring the process of SSIE to its maximum. In some cases, SSIE takes place at lower temperatures (e.g., at 400 K), but in other cases more severe conditions are required. This situation must be determined by appropriate monitoring of the reaction (see Section 2.4.3.4). In any case, it is advisable to check the crystallinity of the zeolite exchanged via SSIE after the reaction although, in the absence of water vapor, the evolution of the hydrogen halides (HCl, HF) does not affect the zeolite structure. The possible effect of water vapor can be reliably avoided if the mixture of the solids is carefully dried at about 400 K in a flow of inert gas, or a vacuum is employed prior to the solid-state reaction. It turns out that, in fact, chlorides of the in-going cations are most suitable for SSIE, while fluorides and bromides seem to be less reactive. In the case of iodides, elemental iodine is easily formed, and more complex cations such as  $CO_3^{2-}$  and  $SO_4^{2-}$  frequently decompose upon SSIE.

In some instances, the reaction between the solids (salts and zeolites) can be facilitated in the presence of an

oxidizing agent (e.g., chlorine, cf. [23]) or reductive gases (see Section 2.4.3.7.4, e.g. Refs. [24, 25]). In the former case, the ion exchange may be mediated through the gas phase as a result of the formation of volatile reactants such as  $PdCl_2$  [23].

#### 2.4.3.4 Methods of Monitoring Solid-State Ion Exchange

In this section, the most important techniques will be described which enable the solid-state reaction between a zeolite and a salt to be monitored. The most prominent methods are:

- chemical analysis, including classical wet analysis (CA) and atomic absorption spectroscopy (AAS)
- temperature-programmed evolution (TPE) of gases
- re-exchange in solution
- catalytic test reactions
- infrared (IR) spectroscopy
- electron spin resonance (ESR) spectroscopy
- Mössbauer spectroscopy
- magic angle spinning nuclear magnetic resonance (MAS NMR)
- X-ray diffraction (XRD)
- extended X-ray absorption fine structure analysis (EXAFS)
- thermogravimetric analysis.

By no means does this overview pretend to be exhaustive, and several other methods might have the potential for analyzing SSIE, and may indeed have already been (or will be) employed in this field. For example, SSIE may be also monitored using a probe molecule such as pyridine (cf., Sections 2.4.3.5.2 and 2.4.3.6.3). However, the techniques discussed below are those most frequently applied, and their application in SSIE is illustrated in the following subsections.

**2.4.3.4.1 Infrared Spectroscopy** Infrared spectroscopy was employed during the aforementioned early observations made by Rabo and coworkers [8, 26] as well as in the first systematic explorations of the new method of post-synthesis modification of zeolites [5, 6]. Essentially, two possible means exist of employing IR spectroscopy in order to disclose the occurrence and to determine the degree of SSIE, whereby wafers (platelets) of the salt/zeolite mixture in an appropriate IR cell are used (cf. Refs. [27, 28]). These two processes are in line with those described by Eqs. (2a) and (2b):

- (i) A probe such as CO or pyridine may be utilized which, after adsorption, produces bands typical of the in-going cation (e.g.,  $Be^{2+}$ ,  $Ca^{2+}$ ,  $La^{3+}$ ,  $Cu^{2+}$ , etc.), or the replaced (i.e., out-going) cation of the starting zeolite (e.g.,  $Na^+$  of Na-Y).

(ii) If the salt containing the in-going cation reacts with OH groups of the hydrogen form of a zeolite, the reaction will result in the decrease in the corresponding OH band intensity, which can be measured via IR spectroscopy. Of course, the same procedure must be carried out with the same zeolite under the same conditions, but in the absence of the salt to ensure that a change in the OH band intensity is not merely a consequence of dehydroxylation [5, 29]. An additional check may be performed by using a suitable probe to verify the incorporation of the respective cation.

**2.4.3.4.2 ESR Spectroscopy** This method was very successfully employed by Slinkin and his group [1–4, 30, 31] when studying the incorporation of transition metals into zeolites, where many of the cations give rise to typical ESR spectra. In most cases, an *ex-situ* heat-treatment of the respective mixtures of powdered salts or oxides and zeolites is carried out prior to running the spectra. However, the use of a particularly designed high-temperature ESR reactor (cf., e.g., Refs. [32, 33]) renders feasible the *in-situ* investigation of the kinetics of transition metal incorporation. Moreover, ESR spectroscopy enables us not only to detect and monitor solid-state reactions involving transition metals but also to obtain an insight into the particular type of coordination, which the incorporated transition metal cation has obtained.

**2.4.3.4.3 Mössbauer Spectroscopy** Mössbauer spectroscopy is a valuable tool for investigating solid-state reactions of iron, which may be interesting in view of the metal's catalytic properties. Other promising candidates among the (unfortunately very limited) number of Mössbauer nuclei are Eu and Sn. Experiments conducted with mixtures of FeCl<sub>2</sub> and NH<sub>4</sub>-Y zeolite have provided a wealth of information about the fraction of Fe<sup>2+</sup> and Fe<sup>3+</sup>, the degree of exchange, the chemical surroundings, and the coordination number of the incorporated species (cf. Section 2.4.3.5.5).

**2.4.3.4.4 Solid-State NMR Spectroscopy** Several ways exist of employing solid-state NMR spectroscopy to investigate SSIE. In analogy to IR spectroscopy, <sup>1</sup>H MAS NMR could be used to determine the extent of reaction between salts and H- or NH<sub>4</sub>-forms via the decrease in the respective signals of OH groups (cf. Chapter 3.2.4.4 of this Handbook, and Ref. [28]). The introduction of several cations such as Li<sup>+</sup>, Na<sup>+</sup>, Al<sup>3+</sup>, which are directly “visible” in MAS NMR, can be studied in the case of microporous structures, even without assistance of probe molecules. The formation of tiny NaCl crystallites on the external surface of zeolite particles (*vide infra*) can be observed

using <sup>23</sup>Na MAS NMR upon the replacement of Na<sup>+</sup> of the parent zeolite, according to Eq. (2a). Furthermore, in favorable cases MAS NMR may provide information concerning the location and chemical surroundings of the cations introduced through SSIE. Moreover, since the development of techniques which allow the heating of samples inside the spinning rotor [34–36], not only *ex-situ* but also *in-situ* MAS NMR experiments have become feasible.

**2.4.3.4.5 X-Ray Diffraction** Monitoring the decrease of reflections of the compound of the in-going cation M<sup>n+</sup> and, in favorable cases, the appearance of reflections originating from the corresponding compound of the out-going cation (e.g., NaCl), demonstrates that SSIE has in fact occurred. The resulting XRD pattern may be compared with that of the same, but conventionally exchanged, zeolite [37]. Using a heatable XRD chamber enables *in-situ* measurements of SSIE. *In-situ* XRD investigations reported to date have confirmed only on a qualitative basis that SSIE had occurred, and provided information of the required reaction temperature. However, future *in-situ* studies should also render possible relatively precise kinetic measurements. In addition, XRD should enable the determination of populations of various cation sites in the zeolite structure as a function of the reaction time.

**2.4.3.4.6 Extended X-Ray Absorption Fine Structure (EXAFS) and X-Ray Absorption Near Edge Structure (XANES)** More recently, Hatje et al. [38, 39] and Förster and Hatje [40] succeeded in studying SSIE of Cu<sup>+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pd<sup>2+</sup> and Pt<sup>2+</sup> into Y or ZSM-5 by EXAFS (cf. also Sections 2.4.3.5.4 and 2.4.3.5.7). This method not only provides evidence as to whether the solid-state reaction has taken place, or not: it also makes available data on the coordination of the introduced metal cations and, after reduction, on the size of produced metal particles.

**2.4.3.4.7 Temperature-Programmed Evolution (TPE) of Volatile Gases** The compound of the cation, M<sup>n+</sup>, may react with the starting zeolite under the formation of volatile gases, in particular when the hydrogen or ammonium form of the zeolite is used. The evolution of gaseous products such as HCl, NH<sub>3</sub>, H<sub>2</sub>O, etc. evolved into vacuum or a flow of a suitable carrier gas can be detected and/or quantitatively determined using mass spectrometry (MS), gas chromatography (GC), or (continuous) titration (in the case of H<sub>2</sub>O via Karl Fischer's method). Different maximum temperatures in the TPE profiles of a homologous series of salt/zeolite systems

provide a measure of the ease of the respective solid-state reactions (cf., e.g., Section 2.4.3.5.1).

**2.4.3.4.8 Thermogravimetric Analysis (TGA)** Frequently, the SSIE between salts and zeolites is accompanied by changes in weight of the reaction mixture. Therefore, the process may be studied using a thermal gravimetric analysis, perhaps utilizing a microbalance. Typically, the loss of weight, which occurs when a chloride reacts with the hydrogen form of a zeolite, provides a measure of the degree of exchange. Such measurement of changes in weight during temperature-programmed heating is combined advantageously with MS, GC or continuous titration to distinguish between the desorption of physisorbed volatiles (e.g., H<sub>2</sub>O) and reaction products such as HCl or NH<sub>3</sub>.

#### 2.4.3.5 Systems Investigated for Solid-State Ion Exchange in Zeolites

Since the mid-1980s, many reports of studies in the field of SSIE have been made (cf. Refs. [11, 41]; see also Table 4). Thus, in the following section only a few examples of SSIE of some selected cations into selected zeolite structures will be discussed in greater detail, namely the incorporation of alkaline, alkaline earth, rare earth, some transition metals (Cu, Fe) and noble metals into ZSM-5, faujasite-type Y, and mordenite (MOR) zeolites.

##### 2.4.3.5.1 Solid-State Ion Exchange with Salts of Alkaline Metals

In the systems M<sup>+</sup>Cl/NH<sub>4</sub>-ZSM-5, M<sup>+</sup>Cl/H-ZSM-5, M<sup>+</sup>Cl/NH<sub>4</sub>-Y (M<sup>+</sup> = Li<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>) and

M<sup>2+</sup>/H-MOR (M<sup>2+</sup> = Ca<sup>2+</sup>, Mg<sup>2+</sup>) IR, TPE combined with MS or TGA were employed to confirm and quantitatively determine the effect of SSIE [5–7]. As an example obtained by application of IR, Fig. 1 shows – for the sake of comparison – the spectra of NH<sub>4</sub>-Y in the absence of CsCl after treatment at 723 K (Fig. 1a), and the almost complete elimination of the acid OH groups resulting from the reaction of NH<sub>4</sub>-Y with CsCl in high vacuum at 723 K. The latter is indicated by the almost complete elimination of absorbances of both the high-frequency (HF, 3640 cm<sup>-1</sup>) and low-frequency (LF, 3550 cm<sup>-1</sup>) band, which proves that the bulky Cs<sup>+</sup> cation enters both the large and small cavities (cf. Ref. [42]). As a result, SSIE yields an almost 100% exchange compared to a degree of only about 60% via CE in aqueous solution.

A high degree of incorporation of cesium is, *inter alia*, interesting in view of the generation of basicity in catalysts (see Refs. [43–46] and Chapter 3.2.4.1). The introduction of Rb<sup>+</sup> from Rb<sub>2</sub>CO<sub>3</sub> via SSIE into H-Y (NH<sub>4</sub>-Y) was studied by <sup>87</sup>Rb MAS NMR and <sup>1</sup>H MAS NMR [47]. Alkaline salt/NH<sub>4</sub>-Y systems are also good examples to demonstrate the potential of TPE. TPE/MS profiles of CsCl/NH<sub>4</sub>-Y are shown in Fig. 2.

One observes dehydration (molecular mass per electron, *m/e*, at 18) between 400 and 500 K. With the M<sup>+</sup>Cl<sup>-</sup>/NH<sub>4</sub><sup>-</sup> or H-zeolite series, one generally observes in TPE experiments a low- (LT) and a high- (HT) temperature peak of HCl (*m/e* = 36) around 500 and 860 K, respectively. In the LT region, there is in the case of NH<sub>4</sub>-zeolites an overlap of NH<sub>3</sub> (evolved upon deammoniation) and HCl due to the reaction of M<sup>+</sup>Cl<sup>-</sup> with OH groups, which have intermittently formed via

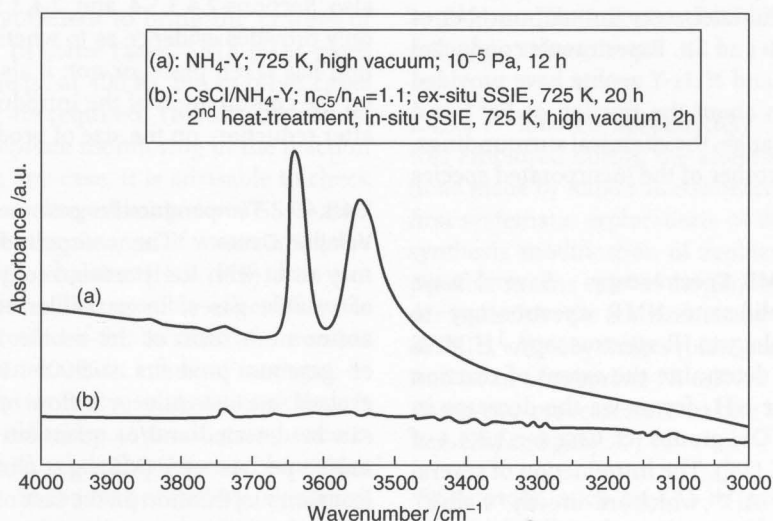


Fig. 1 Infrared spectra of the hydroxyl stretching frequency region after degassing of (a) NH<sub>4</sub>-Y at 725 K for 12 h (final vacuum ca. 10<sup>-5</sup> Pa) and of (b) CsCl/NH<sub>4</sub>-Y (*n*<sub>Cs</sub>/*n*<sub>Al</sub> = 1.1) at 725 K for 20 h (*ex-situ* SSIE) and subsequently for 2 h in high vacuum (*in-situ* SSIE); the degree of exchange in NH<sub>4</sub>-Y was 98%.

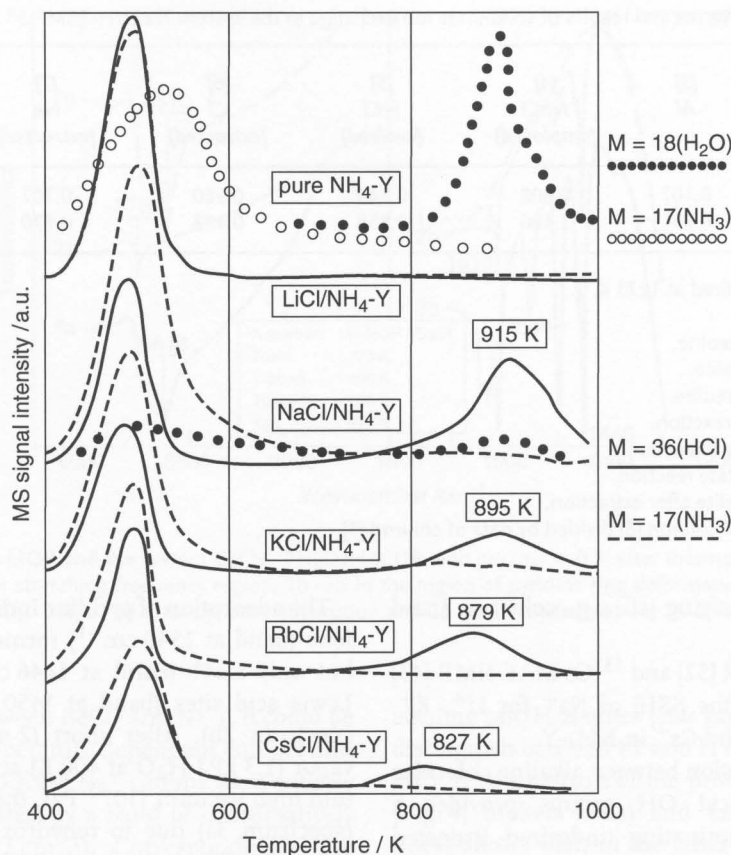


Fig. 2 Temperature-programmed evolution of gases ( $m/e = 36$ , HCl, —;  $m/e = 18$ , H<sub>2</sub>O, ...;  $m/e = 17$ , NH<sub>3</sub>, oooo or ----) from pure NH<sub>4</sub>-Y and MCl/NH<sub>4</sub>-Y mixtures upon solid-state reaction. (After Ref. [48].)

NH<sub>3</sub> evolution. Less-accessible and/or less-reactive OHs react in the HT region. The LT region is particularly pronounced in the case of LiCl; its contribution decreases in the sequence Li > Na > K > Rb > Cs. Simultaneously, the temperature of the HT-HCl peak decreases in the same sequence. It is worth noting that with the exception of LiCl/NH<sub>4</sub>-Y, where the HT peak is almost negligible, the sequence of the HT peak (i.e., Na > K > Rb > Cs) parallels the decrease in the lattice energies of the respective chlorides [5, 48]. This, however, seems not always to be the case with similar homologous series, and especially not with the salts of some transition metals investigated to date [18, 49]. The TPE results with NH<sub>4</sub>-ZSM-5, H-ZSM-5 and H-BETA instead of NH<sub>4</sub>-Y are very similar, and this also holds when, *vice versa*, the starting material NH<sub>4</sub>-Cl was reacted with alkaline zeolite (BETA) [48, 50, 51]. Reaction in mixtures with zeolites exhibiting an  $M^+/Al_F$  ratio of 1 ( $Al_F$  = framework aluminum per unit cell, u.c., of the zeolite) led to an exchange degree of 100%, as derived from the elimination of the OH band intensities originating from acid OH groups. However, the seemingly non-acid so-called "silanol" groups (indicated by an IR

band around 3740 cm<sup>-1</sup>) could also react to some extent (especially if  $M^+/Al_F > 1$ ), but they were easily restored via brief washing of the reaction product with water (hydrolysis), due to the low acid strength of these silanols.

The SSIE of NaCl/H-ZSM-5 eliminated the OH groups of H-ZSM-5, resulting in Na-ZSM-5. When this product was transformed via conventional exchange into NH<sub>4</sub>-ZSM-5 and subsequently deammoniated, the original OH groups reappeared through this "re-exchange" showing that the integrity of the structure was not affected by the SSIE [5]; this was also confirmed by XRD. The re-exchange could be quantitatively determined by TPE of NH<sub>3</sub>.

Solid-state ion exchange between NaCl and H-ZSM-5 was also monitored by a combination of TPE, TGA and continuous titration of the evolved HCl [5]. From the analysis of: (i) the starting zeolite material; (ii) the gases evolved; (iii) the aqueous extracts obtained from the salt/zeolite mixture after reaction; and (iv) the exchanged zeolite, the stoichiometry of the SSIE was determined.



Tab. 1 Starting materials, mixtures and results of solid-state ion exchange in the system NaCl/H-ZSM-5\*

[1] zeolite	[2] $n_{\text{Si}}/n_{\text{Al}}$	[3] Al	[4] NaCl (employed)	[5] HCl (evolved)	[6] Cl (extracted)	[7] Na (extracted)	[8] Na (irrev. held)	[9] $\delta$ (%)
H-ZSM-5 (I)	155	0.107	0.808	0.549	0.260	0.707	0.101	94
H-ZSM-5 (II)	23	0.691	1.306	0.838	0.478	0.670	0.636	92

\*All data in mmol g<sup>-1</sup> zeolite fired at 1273 K.

[1] Parent zeolite.

[2]  $n_{\text{Si}}/n_{\text{Al}}$  ratio of the parent zeolite.

[3] Al content of the parent zeolite.

[4] NaCl admixed to 1 g (dry) zeolite.

[5] HCl evolved on solid-state reaction.

[6] Cl<sup>-</sup> extracted after solid-state reaction.

[7] Na<sup>+</sup> extracted after solid-state reaction.

[8] Na<sup>+</sup> irreversibly held in zeolite after extraction.

[9] Degree of exchange; data of column [8] divided by data of column [3].

The results were very satisfying (cf., e.g., columns 3 and 8 of Table 1).

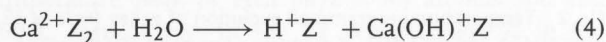
Finally, <sup>23</sup>Na MAS NMR [52] and <sup>133</sup>Cs MAS NMR [43] were used to determine the SSIE of Na<sup>+</sup> for Li<sup>+</sup>, K<sup>+</sup>, Be<sup>2+</sup>, and Ca<sup>2+</sup> in Na-Y and Cs<sup>+</sup> in NH<sub>4</sub>-Y.

The easy solid-state reaction between alkaline chlorides (especially LiCl) and acid OH groups provides a convenient means of eliminating undesired Brønsted acidity, for example, acid OH groups which may form upon reduction of noble metal cations via reduction by H<sub>2</sub> as it occurs in the preparation of selective hydrogenation/dehydrogenation zeolite catalysts. Similar studies of SSIE between alkaline metal chlorides and NH<sub>4</sub>-Y by XRD and IR, as described above, were conducted somewhat later also by Jiang et al. [53]. The same authors [54] also utilized SSIE (with KCl) to decrease the density of acid sites in potassium-containing zeolites loaded with Mo<sub>3</sub>S<sub>4</sub> clusters.

**2.4.3.5.2 Solid-State Ion Exchange with Salts of Alkaline Earth Metals** Some of the examples studied for SSIE in systems of alkaline earth/zeolite included CaCl<sub>2</sub>/H-MOR, CaCl<sub>2</sub>/NH<sub>4</sub>-MOR, MgCl<sub>2</sub>/H-MOR, and CaCl<sub>2</sub>/H-ZSM-5. MgF<sub>2</sub> was also employed as a compound of an in-going cation, but it reacted only to a minor extent (*vide infra* and cf. Refs. [55, 56]). Again, IR spectroscopy (with and without pyridine as a probe, cf. Refs. [57, 58] and Section 2.4.3.4.1), chemical analysis and <sup>23</sup>Na MAS NMR (*vide supra*) were used to monitor the SSIE in such systems.

Figure 3 (spectrum 1a versus 2a) demonstrates the complete elimination of the band of acid OH groups (3610 cm<sup>-1</sup>) and part of the silanol groups (band at 3750 cm<sup>-1</sup>) upon SSIE in CaCl<sub>2</sub>/H-MOR.

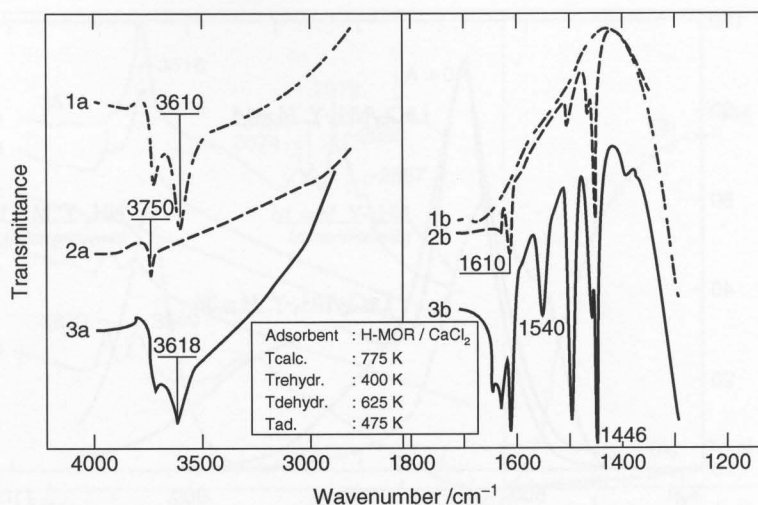
The adsorption of pyridine indicated that no pyridinium ions (band at 1540 cm<sup>-1</sup>) formed because no acid OHs but only Ca<sup>2+</sup> (band at 1446 cm<sup>-1</sup>) and a few "true" Lewis acid sites (band at 1450 cm<sup>-1</sup>) were left (Fig. 3, spectrum 2b). After short (2-min) contact with water vapor (1.3 kPa H<sub>2</sub>O at 400 K) and subsequent degassing into high vacuum (10<sup>-5</sup> Pa), the OH groups reappeared (spectrum 3a) due to rehydroxylation according to the Hirschler-Plank mechanism [Eq. (4)]:



Correspondingly, in spectrum 3b of Fig. 3 the band of pyridinium ions (1540 cm<sup>-1</sup>) emerged. After SSIE, zeolite materials corresponding to spectrum 2 were almost inactive in acid-catalyzed reactions such as the disproportionation of ethylbenzene [58, 59], but became much more active catalysts after treatment with small amounts of water vapor (spectrum 3). This confirms that the bare Ca<sup>2+</sup> ions were unable to act as carboniogenic centers in hydrocarbon reactions. Rather, the presence of acid OH groups (Brønsted acid sites) is an indispensable prerequisite for such reactions to occur (cf. the analogous observations in the case of SSIE with lanthanum salts; Section 2.4.3.5.3).

The mass balance for SSIE in the systems CaCl<sub>2</sub>/H-MOR and CaCl<sub>2</sub>/NH<sub>4</sub>-MOR produced excellent results: 2.18 and 2.50 mmol Al g<sup>-1</sup> water-free zeolite corresponded exactly to 1.09 and 1.26 mmol Ca<sup>2+</sup> introduced via SSIE g<sup>-1</sup> water-free zeolite MOR [6].

Especially in view of selective catalytic reduction (SCR), Ca-Y, Ca-X and Ba-Y (and, similarly, Na-Y, Na-X) were prepared via SSIE by Ebeling et al. [60] (cf. also Section 2.4.3.5.4) and investigated with respect to acidity, adsorption of NO<sub>2</sub>, and stability as catalysts (coke formation).



**Fig. 3** Infrared spectra of H-MOR and the system  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}/\text{H-MOR}$  with  $n_{\text{Ca}}/n_{\text{Al}} = 0.5$ , after thermal treatment at 625 K and  $10^{-5}$  Pa. Spectra 1a–3a in the OH stretching frequency region, 1b–3b in the region of pyridine ring deformation frequencies. 1a, 1b without and 2a, 2b with admixed  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ; 2b after pyridine adsorption and 3a after rehydroxylation, 3b after rehydroxylation and pyridine adsorption. (After Ref. [6].)

In the case of SSIE between  $\text{BeCl}_2$  and Na-Y, it could be shown that indeed a temperature-dependent equilibrium was reached: at about 400 K the  $\text{Na}^+$  cations were entirely replaced by  $\text{Be}^{2+}$  (indicated by a band of coordinatively bound pyridine at  $1453\text{ cm}^{-1}$ ). Correspondingly, the band of pyridine coordinated to  $\text{Na}^+$  (at  $1446\text{ cm}^{-1}$ ) had completely disappeared. At higher temperatures the band at  $1453\text{ cm}^{-1}$  decreased while the band at  $1446\text{ cm}^{-1}$  re-appeared.

#### 2.4.3.5.3 Solid-State Ion Exchange with Salts of Lanthanum

Rare earth cation-containing faujasite-type zeolites are important as components of acidic catalysts for a variety of hydrocarbon reactions. Therefore,  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}/\text{NH}_4\text{-Y}$  was also investigated with respect to SSIE [7, 61, 62]. An exchange degree of almost 100% was reached by only one exchange step, whereas in the case of CE this may be achieved only by repeatedly suspending the solid in an aqueous solution of an La salt, intermittent separations of the suspension and calcinations of the (partially) exchanged material. SSIE in La-salt/zeolite systems was studied by TPD (cf. Fig. 4, Ref. [7]), IR [7, 37], stoichiometric analysis [61, 63], TPE/continuous titration [7], and XRD [61].

For the sake of comparison, Fig. 4 displays the TPE/MS profile [7] obtained during temperature-programmed heating of a finely dispersed sample of the parent zeolite,  $\text{NH}_4\text{-Y}$ . SSIE was carried out with a mixture of  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{NH}_4\text{-Y}$  (deammoniation:  $M = 16$ ; dehydration or dehydroxylation:  $M = 18$ ; evolution of HCl:  $M = 36$ ). Similar to the TPE/MS profiles of

alkaline salt/H-zeolites (*vide supra*), in Fig. 4 one can also distinguish between LT and HT peaks for the evolution of HCl. A comparison of the profiles obtained with  $\text{NH}_4\text{-Y}$  (Fig. 4, broken lines) and  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}/\text{NH}_4\text{-Y}$  (solid lines) shows that, in the latter case, no dehydroxylation (peak around 950 K) occurs, because the OH groups, which may have formed during heating in the LT region, were consumed by the solid-state reaction at higher temperatures.

The stoichiometry of SSIE in the  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}/\text{NH}_4\text{-Y}$  mixture based on chemical analysis is summarized in Table 2 for a ratio  $n_{\text{La}}/n_{\text{Al}} = 0.33$ , and in Table 3 for  $n_{\text{La}}/n_{\text{Al}} = 0.67$ . In both cases, the irreversibly held lanthanum ( $4.80\text{ mequiv. g}^{-1}$ ) corresponded to the amount of framework aluminum ( $4.83\text{ mequiv. g}^{-1}$ ) – that is, the maximum of bridging acid OH groups. Per gram, about  $0.7\text{ mequiv. Na}^+$  and  $0.8\text{ mequiv. Cl}^-$  – that is, approximately one NaCl molecule per  $\beta$ -cage – remained occluded in the SSIE product which, according to Rabo's studies [8, 26], may have enhanced the thermal stability of the structure of the exchanged zeolite.

It could be shown that a La-Y zeolite, prepared via SSIE, was catalytically active in disproportionation of ethylbenzene [7] and *n*-decane cracking [62] only after subsequent brief contact with water vapor (cf. Fig. 5, where the results of reactions in a flow-reactor IR cell are displayed [7]). Again, this demonstrates that bare polyvalent cations (such as  $\text{La}^{3+}$ ) themselves are not catalytic centers but do provide catalytic activity for acid-catalyzed reactions only with the co-catalyst  $\text{H}_2\text{O}$

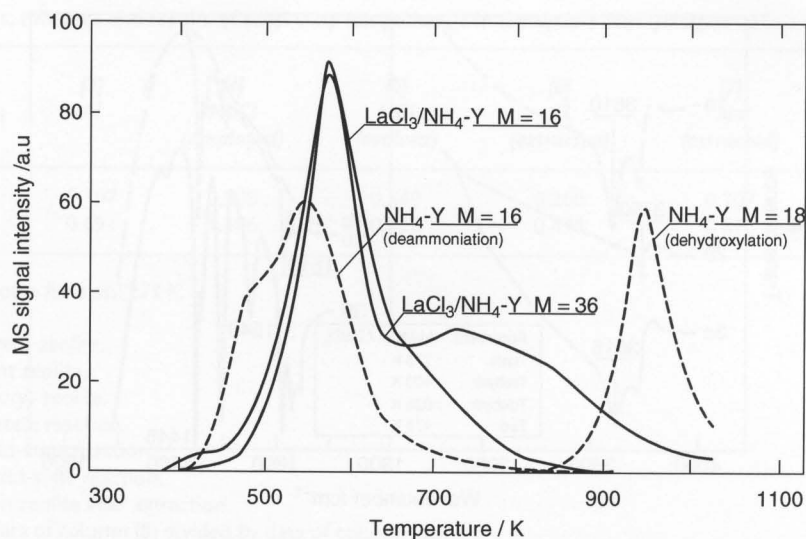


Fig. 4 Temperature-programmed evolution of  $\text{H}_2\text{O}$  ( $m/e = 18$ ) from  $\text{NH}_4\text{-Y}$  and  $\text{NH}_4^+$  ( $m/e = 16$ ),  $\text{HCl}$  ( $m/e = 36$ ) and  $\text{H}_2\text{O}$  ( $m/e = 18$ ) from a  $\text{LaCl}_3/\text{NH}_4\text{-Y}$  mixture. (After Ref. [7].)

Tab. 2 Stoichiometry of solid-state ion exchange in the system  $\text{LaCl}_3/\text{NH}_4\text{-Y}^*$ ;  $n_{\text{La}}/n_{\text{Al}} = 0.33$ ; heat-treatment at 850 K

	$\text{La}^{3+}$	$\text{Cl}^-$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{Al}$
Parent zeolite	÷	÷	1.61	3.29	4.83
Admixed	1.61	4.83	—	—	—
Evolved as $\text{NH}_4\text{Cl}/\text{HCl}$	—	3.29	—	3.29	—
Extracted with water	0.06	0.72	0.94	—	—
Irreversibly held mmol $\text{g}^{-1}$	1.60	0.82	0.67	—	4.83
mequiv. $\text{g}^{-1}$	4.80	0.82	0.67	—	4.83

\*All data given as  $\text{mmol g}^{-1}$ , except for last line (mequiv.  $\text{g}^{-1}$ ).

Tab. 3 Stoichiometry of solid-state ion exchange in the system  $\text{LaCl}_3/\text{NH}_4\text{-Y}^*$ ;  $n_{\text{La}}/n_{\text{Al}} = 0.67$ ; heat treatment at 850 K

	$\text{La}^{3+}$	$\text{Cl}^-$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{Al}$
Parent zeolite	—	—	1.61	3.29	4.83
Admixed	3.22	9.65	—	—	—
Evolved as $\text{NH}_4\text{Cl}/\text{HCl}$	—	3.29	—	3.29	—
Extracted with water	1.57	5.51	0.94	—	—
Irreversibly held mmol $\text{g}^{-1}$	1.65	0.85	0.67	—	4.83
mequiv. $\text{g}^{-1}$	4.95	0.85	0.67	—	4.83

\*All data given as  $\text{mmol g}^{-1}$ , except for last line (mequiv.  $\text{g}^{-1}$ ).

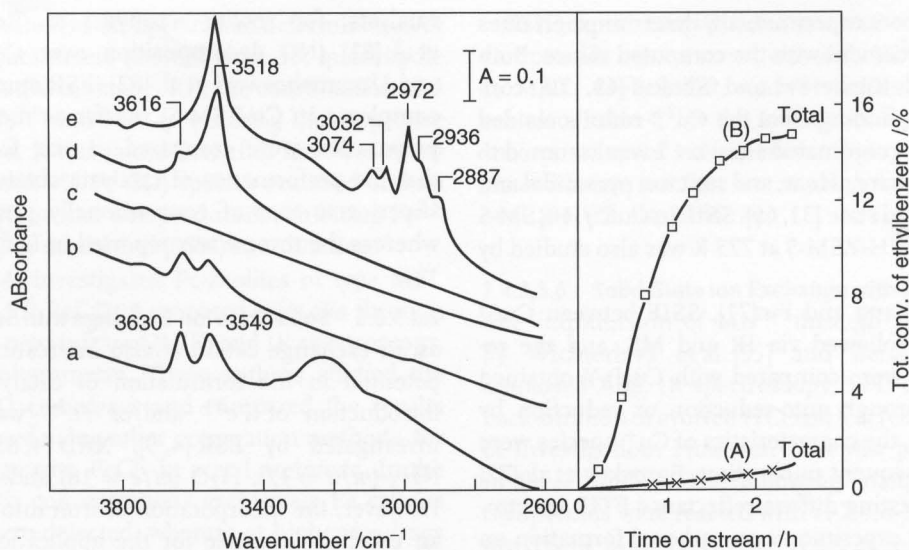
according to the Hirschler–Plank scheme [see Eq. (4)]. Furthermore, when a conventionally exchanged La-Y catalyst with a high degree of exchange was compared with a catalyst of the same exchange degree (98%), but prepared via SSIE, then the latter was even superior with

respect to activity and stability in the disproportionation of ethylbenzene [7].

In a comparative study, Jia et al. [63] prepared La-BETA zeolites through CE and SSIE, and characterized these using XRD, adsorption measurements (BET), Fourier transform IR (FTIR), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and chemical analysis. The La-content achieved by SSIE was as high as 100%, but was low even after several-fold repeated CE. Moreover, the samples obtained via SSIE were highly homogeneous and showed no loss of crystallinity, in contrast to CE materials.

Rare earth Y-type zeolites ( $\text{RE} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Yb}$ ) were obtained by Pires et al. [64] via SSIE from H-Y ( $n_{\text{Si}}/n_{\text{xsAl}} = 2.6, 12.5, 28$ ) and the respective chlorides,  $\text{RECl}_3$ . The authors used the thus-obtained materials as catalysts for the liquid-phase oxidation of cyclohexane with *tert*-butyl hydroperoxide. The catalytic activity followed the sequences ( $n_{\text{Si}}/n_{\text{Al}} = 12.5 > 2.6 > 28$ ) and  $\text{Ce} \approx \text{Yb} > \text{Sm} > \text{Eu} > \text{Nd}$ . The main products were cyclohexene, *n*-hexanal, cyclohexanone and cyclohexanol.

Karge and Beyer [61] also succeeded in preparing catalytically active La-Y catalysts through solid-state reaction between  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  and as-synthesized Na-Y (cf. also “contact-induced” solid-state ion exchange, cf. Section 2.4.3.7.1). The activity for acid-catalyzed reactions was checked by the disproportionation of ethylbenzene as a test reaction [58, 59]. Here, the solid-state cation exchange ( $\text{La}^{3+}$  for  $\text{Na}^+$ ) was not only monitored via IR and  $^{23}\text{Na}$  MAS NMR, but also with the help of XRD patterns: the reflections changed systematically when the SSIE proceeded and, furthermore, the reflections

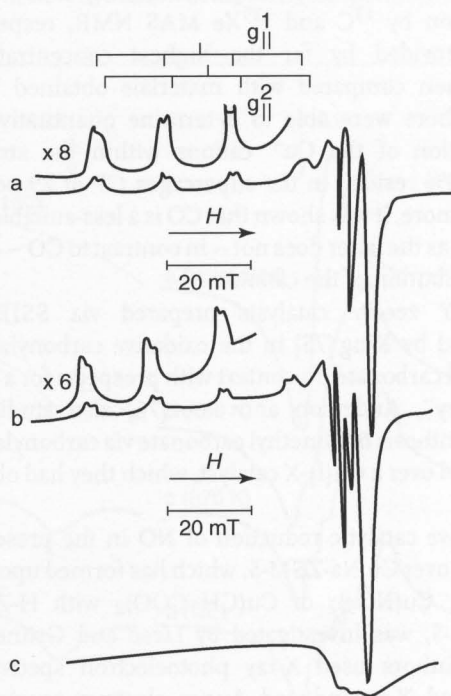


**Fig. 5** In-situ infrared (IR) spectra of and ethylbenzene conversion over La,Na-Y obtained by heat treatment of a  $\text{LaCl}_3/\text{NH}_4\text{-Y}$  mixture in a flow reactor IR cell (A) prior to and (B) after brief contact with 10 Pa water vapor; (a), (b) and (c) pretreatment at 455, 575, and 675 K, respectively; (d) after short contact with 10 Pa water vapor; (e) after admission of the ethylbenzene/helium feed stream. (For details, see text; after Ref. [7].)

of the product NaCl appeared [60]. As reported by Difallah and Ginoux [65], in their study on the introduction of monovalent and polyvalent cations into zeolite Y and mordenite through SSIE (including  $\text{La}^{3+}$  and  $\text{Cu}^{2+}$ ; see below), the incorporation of  $\text{La}^{3+}$  cations resulted in an increased adsorption capacity for CO.

**2.4.3.5.4 Solid-State Ion Exchange with Salts of Copper**  
Copper-containing zeolites were, for some time, intensely studied because of their catalytic activity in DeNOx reactions ([66], cf. also Chapters 11.2 and 11.3 of this Handbook). The introduction of copper (e.g., from  $\text{CuCl}_2$  or  $\text{CuO}$ ) into  $\text{NH}_4$ -forms of various zeolites (A, X, Y) via SSIE was first reported and monitored via titration and ESR by Clearfield et al. [9] in 1973, and more than one decade later was investigated systematically through ESR experiments by Kucherow and Slinkin (besides cations of other transition metals [30, 67–69]) and Karge et al. [20]. As an example, Fig. 6 shows spectra obtained by SSIE in a mixture of  $\text{CuO}$  and H-ZSM-5 [69, 70].

This reaction required a relatively high temperature; typically, the degree of exchange was considerably enhanced when the temperature was increased from 793 to 1073 K. Spectrum b of Fig. 6 is in complete agreement with that obtained after the same treatment of a conventionally exchanged Cu-ZSM-5 (cf. spectrum a). The  $g$ -values and the hyperfine splitting (HFS) constants coincided. Two sets of  $g$ -values and HFS constants were observed:  $g_{\parallel}^1 = 2.29$ ,  $g_{\perp}^1 = 2.05$ ,  $A_{\parallel}^1 = 15.6$  mT,  $A_{\perp}^1 = 2.3$  mT, and  $g_{\parallel}^2 = 2.31$ ,  $g_{\perp}^2 = 2.06$ ,  $A_{\parallel}^2 = 15.3$  mT,



**Fig. 6** Comparison of electron spin resonance (ESR) spectra of  $\text{Cu}^{2+}$ -containing ZSM-5 samples. Sample a prepared by solid-state ion exchange in a  $\text{CuO}/\text{H-ZSM-5}$  mixture in vacuum at 1073 K; sample b obtained by conventional exchange, calcined in air at 1073 K and evacuated at 300 K; spectrum c obtained after contacting sample a with air. (After Refs. [1, 70].)

References see page 504

$A_{\perp}^2 = 2.25$  mT, these experimentally determined  $g$ -values being in good agreement with the computed values. Both Clearfield [9] and Kucherow and Slinkin [69, 70] concluded from their findings that the  $\text{Cu}^{2+}$  cations resided on two differently coordinated sites: set 1 was assumed to correspond to a square planar, and set 2 to a pyramidal and fivefold-coordinated state [31, 69]. SSIE in  $\text{CuCl}/\text{H-ZSM-5}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{H-ZSM-5}$  at 775 K was also studied by XRD [20].

In a study by Jiang and Fu [71], SSIE between  $\text{CuCl}$  and  $\text{NH}_4\text{-Y}$  was followed via IR and MS, and the resulting materials were compared with  $\text{Cu(I)-Y}$  obtained from  $\text{Cu(II)-Y}$  through auto-reduction or reduction by CO: in both cases, the characteristics of  $\text{Cu}^+$  species were similar. In a subsequent publication, Borovkov et al. [72] reported on interesting diffuse reflectance FTIR spectroscopic (DR-FTIR) experiments on carbonyl formation on  $\text{Cu(I)-zeolites}$  produced through SSIE between  $\text{CuCl}$  and zeolites Y, ZSM-5, MOR, and L (for the acronyms, cf. Ref. [10]).

Hartmann and Boddenberg [73, 74] used SSIE of  $\text{CuCl}$  and  $\text{NH}_4\text{-Na-Y}$  with an exchange degree of 70%  $\text{NH}_4^+$  to prepare a  $\text{Cu,Na-Y(70)}$  sample for a study of CO and Xe adsorption by  $^{13}\text{C}$  and  $^{129}\text{Xe}$  MAS NMR, respectively. SSIE provided by far the highest concentration of  $\text{Cu}^+$  when compared with materials obtained by CE. The authors were able to determine quantitatively the distribution of the  $\text{Cu}^+$  cations within the structure: about 70% resided in the supercages (27 of 29 per u.c.). Furthermore, it was shown that CO is a less-suitable probe than Xe, as the latter does not – in contrast to CO – change the distribution of the cations.

$\text{Cu(I)-Y}$  zeolite catalysts prepared via SSIE were employed by King [75] in the oxidative carbonylation to dimethyl carbonate. In context with prospects for a “green chemistry”, Anderson and Root [76] also studied the direct synthesis of dimethyl carbonate via carbonylation of methanol over a  $\text{Cu(I)-X}$  catalyst, which they had obtained by SSIE.

Selective catalytic reduction of NO in the presence of propene over  $\text{Cu,Na-ZSM-5}$ , which has formed upon SSIE of  $\text{CuCl}$ ,  $\text{Cu(NO}_3)_2$  or  $\text{Cu(CH}_3\text{COO)}_2$  with  $\text{H-ZSM-5}/\text{Na-ZSM-5}$ , was investigated by Liese and Grünert [77]. These authors used X-ray photoelectron spectroscopy (XPS) and X-ray-induced Auger electron spectroscopy (AES) to monitor the transport of copper into the near-surface regions of the zeolite crystallites. Further contributions related to DeNO<sub>x</sub> catalysis, which employed zeolite catalysts prepared via SSIE, were provided by Varga et al. [78] (NO reaction over  $\text{Cu-ZSM-5}$ ), Soria et al. [79] (adsorption of NO and/or  $\text{O}_2$  on  $\text{Cu-ZSM-5}$  studied by ESR), Schay et al. [80] (decomposition of NO,  $\text{N}_2\text{O}$ , and SCR of NO by  $\text{C}_3\text{H}_8$  or  $\text{CH}_4$  over  $\text{Cu-[Al]TS-1}$

catalysts; for zeolite acronyms cf. Ref. [10]), Teraoka et al. [81] (NO decomposition over  $\text{Cu-MFI}$  catalysts), and Umamaheswari et al. [82] (ESR studies on  $\text{Cu(I)-NO}$  complexes in  $\text{Cu-ZSM-5}$ ). As far as methods of catalyst preparation were compared, it was found in Ref. [81] that the performance of catalysts obtained by SSIE was superior to that of conventionally prepared materials, whereas the reverse was reported in Ref. [78].

**2.4.3.5.5 Solid-State Ion Exchange with Salts of Iron** Iron as an exchange cation is also interesting because of its potential in the formulation of catalysts. In fact, the introduction of  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$  was systematically investigated by ESR [4, 9], XRD [4, 83] and TPE of  $\text{NH}_3$  ( $m/e = 17$ ),  $\text{H}_2\text{O}$  ( $m/e = 18$ ) and  $\text{HCl}$  ( $m/e = 36$ ). However, the incorporation of iron into  $\text{NH}_4\text{-Y}$  provides an excellent example for the application of Mössbauer spectroscopy. Thus, Fig. 7 displays a set of Mössbauer spectra obtained upon solid-state reaction of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{-Y}$  at various temperatures.

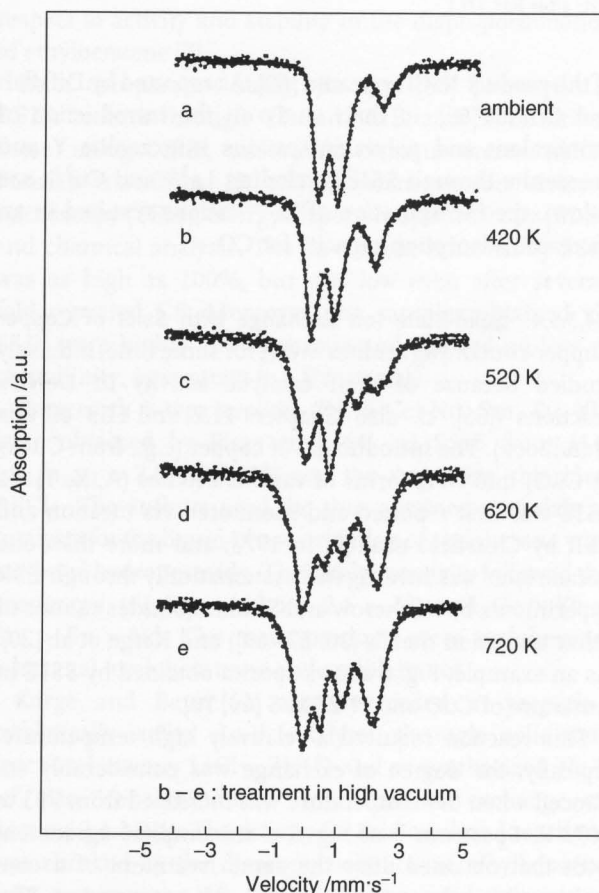


Fig. 7 Mössbauer spectra of a  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{NH}_4\text{-Y}$  mixture (a) ground in air at ambient temperature; material (a) after heat treatment in vacuum at (b) 420 K, (c) 520 K, (d) 620 K and (e) 720 K. (After Ref. [83].)

After decomposition of the spectra and determination of the Mössbauer parameters (isomer shift, IS; quadrupole splitting, QS; relative intensity, RI), the coordination and the fraction of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  populating the respective sites were derived. It was found that after heat treatment at 720 K only about 4% Fe (III) species occurred and an almost pure Fe(II)-zeolite was produced, exhibiting  $\text{Fe}^{2+}$  in trigonal (30%) or octahedral (65%) coordination.

Čapek et al. [84] investigated Fe-zeolites of type MFI, FER, and BETA (cf. Ref. [10]) prepared *inter alia* through SSIE by UV-Vis, near infrared (NIR) and IR spectroscopy, as well as by voltammetry. These authors studied the formation of NO complexes and compared the results with those obtained using other preparation methods, for example exchange with  $\text{FeCl}_3$  in acetyl acetone. In the latter case, at low concentrations exclusively Fe cations at cation sites were detected, whereas at higher loadings dinuclear Fe-oxo complexes were preferably formed in MFI, but were absent in BETA structures. Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  salts (viz.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeCl}_3$ ) were employed by Mohamed et al. [85] in SSIE with  $\text{NH}_4$ -MOR, H-MOR or Na-MOR; the Fe species were characterized by  $\text{N}_2$  adsorption, XRD and Mössbauer spectroscopy. In the experiments with  $\text{NH}_4$ -MOR and H-MOR, 100% of Fe-loading was achieved, but simultaneously formation of a hematite phase was observed.

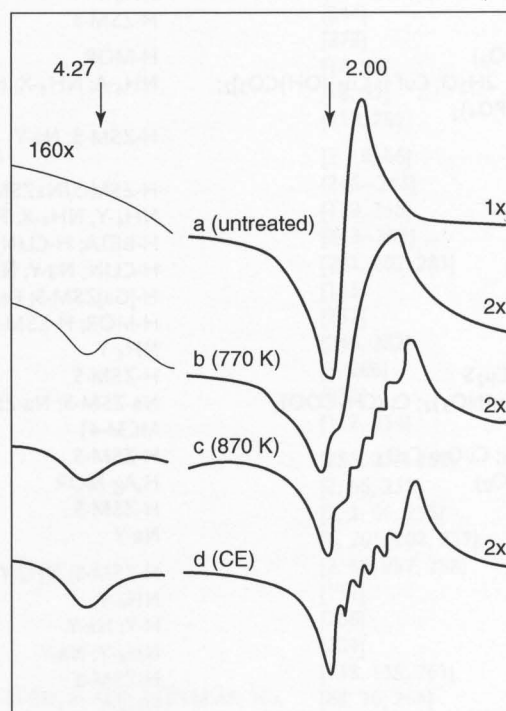
Similar to studies on SSIE with copper (*vide supra*), investigations of the introduction of iron (or other transition metal ions, *vide infra*) into zeolite structures were stimulated by the interest in decomposition of  $\text{NO}_x$  or SCR of nitrogen oxides. Thus, Szalay et al. [86] reported on the decomposition of  $\text{NO}_x$  and reduction of NO by CO over Fe-ZSM-5 catalysts obtained by SSIE. In most reactions, these materials were more active but less stable than conventionally prepared ones. Highly active Fe-ZSM-5 catalysts for  $\text{N}_2\text{O}$  decomposition were prepared by Rauscher et al. [87]; a hematite phase appeared when the ratio  $\text{Fe}^{2+}/\text{Al}$  was above 0.5. An attempt was made by Varga et al. [88] to evaluate the redox mechanism of NO decomposition over Fe- (or Cu)-containing ZSM-5. In contrast to Szalay et al. [86], these authors found catalysts produced through SSIE to be less active than those prepared by CE. However, this may be due to differences in the preparation and pretreatment procedures. Simultaneous reductive removal of NO and  $\text{N}_2\text{O}$  over Fe-MFI catalysts (cf. Ref. [10]) was described by Kögel et al. [89], who also found that the optimum of SSIE occurred at  $\text{Fe}^{2+}/\text{Al} = 0.5$  (cf. Ref. [87]). Fe-ZSM-5 catalysts with systematically varied Fe/Al and Si/Al ratios were prepared via SSIE by Batista et al. [90, 91], and tested for the reduction of NO with *iso*-butane. The catalytic activity was found to depend strongly on the content and coordination of the cationic Fe-species compensating the negative charge of the framework.

SSIE experiments similar to those conducted with Fe-compounds were carried out with  $\text{Ni}^{2+}$  salts and BEA, L, MAZ, MFI, MOR, and Y zeolites (cf. e.g. [92, 93], see also Table 4; for the zeolite acronyms, cf. Ref. [10]). Incorporation of cobalt (and copper) into clinoptilolite via solid-state reaction was studied, *inter alia*, by Astrelin et al. [94] (cf. also Table 4).

#### 2.4.3.5.6 Solid-State Ion Exchange with Salts of Manganese

The introduction of  $\text{Mn}^{2+}$  through SSIE was reported by Wichterlová et al. [95] and Beran et al. [18], who employed XPS, IR spectroscopy, TPD of ammonia, TPE, back-titration of evolved HCl and test reactions as methods of investigation. However, ESR was preferentially used in these studies. The following manganese-containing compounds were reacted with H-ZSM-5:  $\text{MnCl}_2$ ,  $\text{MnSO}_4$ ,  $\text{Mn}_3\text{O}_4$  or  $\text{Mn}(\text{CH}_3\text{COO})_2$ . A set of X-band ESR spectra of  $\text{Mn}^{2+}$  is shown in Fig. 8 [95].

The starting mixture of solid  $\text{MnSO}_4$  and H-ZSM-5 did not exhibit any HFS of the signal at  $g = 2.0$  originating from  $\text{Mn}^{2+}$  in crystalline  $\text{MnSO}_4$ . Only progressive heating up to 770 K and 870 K (Fig. 8, spectra b and c) and subsequent rehydration at ambient temperature made the



**Fig. 8** X band ESR spectra of  $\text{Mn}^{2+}$ : (a) a physical mixture of  $\text{MnSO}_4$  and H-ZSM-5; (b) sample (a) heat-treated at 770 K; (c) sample (a) heat-treated at 870 K; (d) Mn,H-ZSM-5 prepared by conventional ion exchange and calcined at 770 K. (After Ref. [95].)

Tab. 4 An overview over systems investigated for solid-state ion exchange

Compound of the introduced cation	Zeolite	References
LiCl; NaCl; KCl; RbCl; CsCl	H-ZSM-5; NH <sub>4</sub> -ZSM-5; NH <sub>4</sub> -Y, H-MOR; H-BETA; NH <sub>4</sub> -BETA; 3A; 4A; Na-Y	[5, 8, 26, 44, 50, 52, 53, 60, 112, 120, 170, 171, 271–273]
	H-EMT; NH <sub>4</sub> - EMT; Na-Y	[52, 172–174, 272]
	Na-X; Na-[Ge]X	[44, 45, 60, 175, 176]
	NH <sub>4</sub> -X; NH <sub>4</sub> -Y; K-Y; K-L	[47, 53, 54]
RbCl; Rb <sub>2</sub> CO <sub>3</sub> ; CsOH	NH <sub>4</sub> -Y	[43, 47]
NaCl; KCl	H-MOR, MAPO-36; (H,Mo <sub>3</sub> S <sub>4</sub> )-Y; (H,Mo <sub>3</sub> S <sub>4</sub> )-L	[46, 54, 105, 177]
CsCl	H-Y; NH <sub>4</sub> -BETA; Na-[Ge]X	[44, 46, 50]
Cs <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ]	H-ZSM-5	[273]
NH <sub>4</sub> Cl	H-BETA; H,Na-BETA; H,Cs-BETA	[51]
NR <sub>4</sub> Cl (R: organoammonium)	Na-MM <sup>a</sup>	[178, 225]
Na-MM <sup>a</sup> , clay binders	H-ZSM-5; H-MOR; H-Y	[274, 280]
Li-A/Na-A	Na-A/Li-A	[118, 119]
Li-A/Na-Y; Li-A/Na-X; Li-A/Ca-X	Na-A/Li-Y; Na-A/Li-X; Ca-A/Li-X	[120]
CaCl <sub>2</sub> · 2H <sub>2</sub> O; MgCl <sub>2</sub> · 2H <sub>2</sub> O	H-MOR; NH <sub>4</sub> -MOR	[6, 56]
CaCl <sub>2</sub> ; BaCl <sub>2</sub>	NH <sub>4</sub> -X; NH <sub>4</sub> -Y	[60, 120, 210]
BeCl <sub>2</sub>	Na-Y	[52]
LaCl <sub>3</sub> · 7H <sub>2</sub> O	NH <sub>4</sub> -Y; H-ZSM-5; H-BETA; Na-Y	[7, 63, 64, 112]
LaCl <sub>3</sub> (water-free)	NH <sub>4</sub> -Y; H-MOR; H-L; H-FER	[107]
LaCl <sub>3</sub> · 7H <sub>2</sub> O	Na-Y	[61, 179]
CeCl <sub>3</sub> ; NdCl <sub>3</sub> ; SmCl <sub>3</sub> ; EuCl <sub>3</sub> ; YbCl <sub>3</sub>	NH <sub>4</sub> -Y	[64]
EuCl <sub>3</sub>	NH <sub>4</sub> -Y	[181]
CeCl <sub>3</sub>	H-ZSM-5	[180]
Cu <sup>0</sup> (+O <sub>2</sub> )	H-MOR	[1, 142, 143, 276, 277]
CuCl <sub>2</sub> · 2H <sub>2</sub> O; CuF <sub>2</sub> ; Cu <sub>3</sub> [(OH)CO <sub>3</sub> ] <sub>2</sub> ; Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	NH <sub>4</sub> -A; NH <sub>4</sub> -X; NH <sub>4</sub> -Y; H-MOR	[1, 9, 20, 40, 77, 183, 184]
CuCl <sub>2</sub>	H-ZSM-5; Na-Y	[77, 78, 80, 88, 112, 165, 166, 185, 186]
CuCl	H-ZSM-5/NaZSM-5; NH <sub>4</sub> -ZSM-5; 13X	[82, 112, 188–196]
CuCl	NH <sub>4</sub> -Y, NH <sub>4</sub> -X; H-BETA; H-L; H-[Al]TS-1	[20, 77, 80]
CuCl	H-BETA; H-CLIN	[40, 71–76, 197, 198]
CuCl	H-CLIN; Na-Y; Na-MOR; Na-Y	[94, 112, 199, 200]
CuO	H-[Ga]ZSM-5; Fe,H-ZSM-5	[21, 110]
	H-MOR; H-ZSM-5	[1, 3, 4, 20, 201, 202]
Cu <sub>2</sub> O	NH <sub>4</sub> -Y	[187, 203, 204]
Cu <sub>2</sub> O; Cu <sub>2</sub> S	H-ZSM-5	[20, 75, 205]
CuCl; Cu(NO <sub>3</sub> ) <sub>2</sub> ; Cu(CH <sub>3</sub> COO) <sub>2</sub>	Na-ZSM-5; Na-ZSM-5/H-ZSM-5	[1, 20, 81, 94]
CuCl <sub>2</sub>	MCM-41	[1, 20, 77–79, 88]
CuCrO <sub>4</sub> ; CuO+ CrO <sub>3</sub>	H-ZSM-5	[3, 78, 79, 196, 206]
Ag <sup>0</sup> (+O <sub>2</sub> )	H,Ag-MOR	[142, 143, 276]
AgCl	H-ZSM-5	[105]
AuCl <sub>3</sub>	Na-Y	[207]
Zn <sup>0</sup>	H-ZSM-5; NH <sub>4</sub> -Y; NH <sub>4</sub> -USY; H-MOR	[115, 134–137, 208]
ZnCl <sub>2</sub>	NH <sub>4</sub> -Y	[40, 134, 184, 209]
ZnCl <sub>2</sub>	H-Y; Na-Y	[113, 210, 212]
ZnCl <sub>2</sub>	NH <sub>4</sub> -Y; Na-Y	[210–213]
ZnCl <sub>2</sub>	H-ZSM-5	[130]
ZnO	NH <sub>4</sub> -Y	[214]
ZnO	H-ZSM-5	[215–218]
Cd <sup>0</sup>	NH <sub>4</sub> -Y	[135–137, 208]

(continued overleaf)

Tab. 4 (continued)

Compound of the introduced cation	Zeolite	References
Cd(NO <sub>3</sub> ) <sub>2</sub> ; CdCl <sub>2</sub> ; CdO; CdS; CdSO <sub>4</sub>	NH <sub>4</sub> -X; NH <sub>4</sub> -Y; NH <sub>4</sub> -MOR	[210]
Hg <sub>2</sub> Cl <sub>2</sub>	H-ZSM-5	[105]
FeCl <sub>2</sub> · 4H <sub>2</sub> O	NH <sub>4</sub> -A; NH <sub>4</sub> -X; NH <sub>4</sub> -Y	[4, 9, 83, 84, 186, 220, 221]
FeCl <sub>2</sub> ; FeSO <sub>4</sub>	H-BETA; NH <sub>4</sub> -MOR; H-MOR; Na-MOR	[84, 85]
FeCl <sub>2</sub> · 4H <sub>2</sub> O; FeSO <sub>4</sub> · 7H <sub>2</sub> O	H-ZSM-5; H-MFI; H-FER	[84, 86–91, 193, 211, 222, 223]
FeCl <sub>3</sub>	H-ZSM-5	[88, 90, 224, 283]
FeCl <sub>3</sub> ·	H-ZSM-5; Na-ZSM-5; H-[Ga]ZSM-5	[4, 202]
FeO; Fe <sub>3</sub> O <sub>4</sub>	H-ZSM-5	[4]
Fe <sub>2</sub> O <sub>3</sub>	H-ZSM-5; Na-ZSM-5	[95]
Fe(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	Na-MM <sup>a</sup>	[225]
CoCl <sub>2</sub>	NH <sub>4</sub> -Y; H-ZSM-5	[185, 186, 192, 210, 226–234, 236, 283]
CoCl <sub>2</sub> ; Co(NO <sub>3</sub> ) <sub>2</sub> ; CoCl <sub>2</sub> · 6H <sub>2</sub> O	NH <sub>4</sub> -CLIN; H-CLIN; Na-Y	[94, 235, 282]
	H-BETA	[236]
	H-FER	[234]
	H-Y	[140]
Co <sub>2</sub> (CO) <sub>8</sub>	H-Y	[140]
NiCl <sub>2</sub>	NH <sub>4</sub> -Y	[40, 92, 237]
NiCl <sub>2</sub> ; NiSO <sub>4</sub> ; Ni(CH <sub>3</sub> COO) <sub>2</sub> ; NiO	H-ZSM-5	[186, 192, 238]
NiCl <sub>2</sub>	H-ZSM-5	[93, 165, 226, 227]
NiCl <sub>2</sub> ; NiCl <sub>2</sub> · 6H <sub>2</sub> O; NiO	SAPO-42	[96]
NiCl <sub>2</sub>	SAPO- <i>n</i> ( <i>n</i> = 5, 8, 11, 34)	[219, 239–242]
NiCl <sub>2</sub>	H-MOR; H-L; H-MAZ; H-BETA	[92, 93, 231]
NiCl <sub>2</sub>	MCM-41	[244]
Raney nickel	Cu-ZSM-5	[278]
MnCl <sub>2</sub> ; MnSO <sub>4</sub> ; Mn(NO <sub>3</sub> ) <sub>2</sub> ; Mn <sub>3</sub> O <sub>4</sub>	H-ZSM-5	[18, 95]
Mn(CH <sub>3</sub> COO) <sub>2</sub>	H-ZSM-5	[18, 95]
MnCl <sub>2</sub> ; MnCl <sub>2</sub> · 4H <sub>2</sub> O	NH <sub>4</sub> -Y; Na-Y	[210, 282]
V <sub>2</sub> O <sub>5</sub>	H-MOR; H,Na-MOR; H-ZSM-5	[2, 19, 66]
	H,Na-ZSM-5	[246–248]
V <sub>2</sub> O <sub>5</sub>	H,Na-X; H-Y; H-ZSM-5; H-MOR	[179, 248]
V <sub>2</sub> O <sub>5</sub>	Na-Y	[249–251]
V <sub>2</sub> O <sub>5</sub>	H-[Ga]ZSM-5, [Al]BETA; [B]BETA	[201, 202, 281]
VO(NO <sub>3</sub> ) <sub>2</sub>	AlPO <sub>4</sub> -5	[133]
V <sub>2</sub> O <sub>5</sub>	NH <sub>4</sub> -ZSM-5	[252]
VOCl <sub>3</sub> ; VCl <sub>3</sub>	H-ZSM-5; Na-Y	[246, 282]
V <sub>2</sub> O <sub>5</sub> +CuO	H-ZSM-5	[3, 206]
Nb <sub>2</sub> O <sub>5</sub>	NH <sub>4</sub> -Y; NH <sub>4</sub> ,Na-Y	[253]
Sb <sub>2</sub> O <sub>3</sub>	Na-Y; ZSM-5; La,Na-Y	[112, 254]
CrCl <sub>3</sub> ; CrCl <sub>3</sub> · 6H <sub>2</sub> O	H-Y; Na-Y	[255, 279, 282]
CrO <sub>3</sub>	H-MOR; H-ZSM-5	[2, 66, 255]
CuCrO <sub>4</sub>	H-MOR; H-ZSM-5	[2, 3, 66, 255]
CrO <sub>3</sub>	H-[Ga]ZSM-5; H-[Fe]ZSM-5	[4, 201, 202, 257]
Cr <sub>2</sub> O <sub>3</sub>	H-MOR; H-ZSM-5	[2, 66, 257, 258]
CrO <sub>2</sub> Cl <sub>2</sub>	MFI	[132]
CrO <sub>3</sub> +CuO	H-ZSM-5	[206]
CrO <sub>3</sub>	SAPO-11	[259]
MoCl <sub>5</sub> ; (MoOCl <sub>4</sub> ) <sub>2</sub>	NH <sub>4</sub> -Y; NH <sub>4</sub> -DAY; Co,H-Y	[138, 139, 261]
MoCl <sub>3</sub>	H-ZSM-5; H-MOR; H-ZSM-35; H-EU; H-FER; H-ZSM-48; H-L	[68, 96, 264]
MoO <sub>3</sub>	H-ZSM-5; H-USY; H-FER; H-BETA	[2, 66, 138, 139, 261–264]
MoO <sub>3</sub>	Na-Y; Na-ZSM-5	[251, 261]
WO <sub>3</sub>	Na-Y	[251]
WO <sub>3</sub> (+CCl <sub>4</sub> )	H-USY; H-ZSM-5; H-FER	[141]

(continued overleaf)



Tab. 4 (continued)

Compound of the introduced cation	Zeolite	References
Pt <sup>0</sup>	K-L	[101]
Pd <sup>0</sup> (+Cl <sub>2</sub> )	H-Y	[23]
PdCl <sub>2</sub> ; Pd(NO <sub>3</sub> ) <sub>2</sub> ; PdO; PtCl <sub>2</sub> ; PtCl <sub>4</sub> ; PtO <sub>2</sub>	NH <sub>4</sub> -Y; H-ZSM-5	[99, 100, 265]
PdCl <sub>2</sub>	H-ALPHA; H-RHO; H-ZK-5; ZSM-48	[49, 96, 98]
PdO	H-SAPO-42	[45, 96, 231]
PtCl <sub>2</sub>	H-RHO; H-ZK-5; H-ALPHA; H-ZSM-58; H-SAPO-42	[49, 96, 98]
PtCl <sub>2</sub> ; PtBr <sub>2</sub> ; PtO <sub>2</sub>	NH <sub>4</sub> -Y	[38, 39]
RhCl <sub>3</sub>	ALPHA; H-SAPO-42; H-ZK-5	[49, 96, 98]
RhCl <sub>3</sub>	H-ALPO <sub>4</sub> ; H-APO-11; H-APSO-11	[103]
RhCl <sub>3</sub>	DAY	[102]
PdCl <sub>2</sub> +CaCl <sub>2</sub> ; PdCl <sub>2</sub> +LaCl <sub>3</sub>	H-ZSM-5	[99, 100, 260, 265]
Ga <sup>0</sup>	H-ZSM-5	[114, 116, 208]
Ga <sub>2</sub> O <sub>3</sub>	H-ZSM-5; MFI, BETA	[24, 25, 148–150, 156, 164–166]
GaCl <sub>3</sub>	MFI; BETA	[156]
Ga <sub>2</sub> O <sub>3</sub>	NH <sub>4</sub> , Na-Y; H-MOR; H-ZSM-5; H-BETA; H-Y	[155, 157, 266, 267]
Ga <sub>2</sub> O <sub>3</sub>	H-[Ga]ZSM-5	[25]
Ga <sub>2</sub> O <sub>3</sub>	H-SAPO- <i>n</i> ( <i>n</i> = 5, 34, 37) (+template)	[167]
In <sup>0</sup>	H-ZSM-5	[208]
In <sub>2</sub> O <sub>3</sub>	H-ZSM-5; NH <sub>4</sub> -Y; H-MOR; H-OFF; H-BETA	[148, 157, 158, 165, 166, 187]
In <sub>2</sub> O <sub>3</sub>	H-ZSM-5; H, Na-Y; NH <sub>4</sub> -MOR; NH <sub>4</sub> -Y	[266, 267]
In <sub>2</sub> O <sub>3</sub>	H-BETA (TEA-BETA)	[160–163, 268, 269]
In <sub>2</sub> O <sub>3</sub>	H-SAPO- <i>n</i> ( <i>n</i> = 5, 34, 37), (+template)	[151, 154, 163]
In <sub>2</sub> O <sub>3</sub>	MCM-41	[152, 167–169]
InCl <sub>3</sub>	NH <sub>4</sub> -ZSM-5	[159]

<sup>a</sup> MM, montmorillonite.

hyperfine splitting appear. This pointed to a disintegration of the salt crystallites and migration of Mn<sup>2+</sup> cations into the structure. The HFS constant of  $A = 9.8$  mT was interpreted as being indicative of isolated Mn<sup>2+</sup> cations in O<sub>h</sub> coordination. In the parent H-ZSM-5, absorbance of the IR band at 3610 cm<sup>-1</sup>, typical of the acid OH groups of the H-ZSM-5 sample used, corresponded to 0.91 mmol OHs g<sup>-1</sup> dry zeolite. IR spectroscopic measurements evidenced a decrease in the absorbance of the band at 3610 cm<sup>-1</sup> upon SSIE. Monitoring the solid-state reaction showed that in no case was a 100% degree of exchange reached. An increase in the amount of MnCl<sub>2</sub> applied from a substoichiometric ratio (0.33 mmol Mn<sup>2+</sup> versus 0.91 mmol OHs g<sup>-1</sup>) to a stoichiometric ratio (0.45 mmol Mn<sup>2+</sup> versus 0.91 mmol OHs) did not lead to a significantly higher degree of exchange. An increase of the reaction temperature, from 570 to 770 K, enhanced the exchange degree from 21% to 57%. Measurements as a function of the reaction time revealed that most of the Mn<sup>2+</sup> cations were introduced during the initial stage of the process, that is, within the first hour. With respect to the Mn-compounds employed in stoichiometric or

slightly over-stoichiometric mixtures with H-ZSM-5, the degree of SSIE at 770 K increased in the order MnSO<sub>4</sub> (16%) < Mn<sub>3</sub>O<sub>4</sub> (46%) < MnCl<sub>2</sub> (57%).

#### 2.4.3.5.7 Solid-State Ion Exchange with Salts of Noble Metals

Zeolites modified via ion exchange with salts of noble metals are, after reduction, interesting materials because of their potential as catalysts in hydrogenation/dehydrogenation reactions. It could be shown that SSIE is also a suitable route to noble metal-containing zeolites. In fact, SSIE in several cases offers the only route to post-synthesis modification of zeolites by incorporation of noble metal cations: with small-pore zeolites – and especially those with eight-membered oxygen rings (8-MR) as pore mouths – conventional ion exchange either fails or provides only a low degree of exchange. The reason is seen in geometric constraints: the solvated cations or complexes such as Pt(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> are not able to penetrate the narrow-pore openings. Systematic studies of the introduction of noble metals (Pt, Pd, Rh) into 8-MR zeolites (ZSM-8, zeolite Rho, zeolite ZK-5, SAPO-42; cf. Ref. [10]) have been conducted by Bock [96] and

Weitkamp et al. [97, 98]. These authors demonstrated that the resulting materials were, after reduction, highly shape-selective catalysts in the competitive hydrogenation of slim *n*-hexene-(1) and bulky 2,4,4-trimethylpentene-(1); the latter could react only on the external surfaces. Residual Brønsted acidity, which formed upon reduction of the noble metal cations introduced through SSIE, may be eliminated by subsequent SSIE with alkaline metal compounds (*vide supra*, Section 2.4.3.5.1).

However, for some types of reactions, such as hydroisomerization or hydrocracking of hydrocarbons, both hydrogenation/dehydrogenation and acidic functions of a catalyst are required. Such bifunctional catalysts were prepared via SSIE by Karge et al. [99, 100]. These authors used PdCl<sub>2</sub>, PdO and PtCl<sub>2</sub> to incorporate the metal cations into H-ZSM-5. The resulting materials were, after reduction by H<sub>2</sub>, successfully tested for hydrogenation of ethylbenzene. It was further shown that SSIE with Ca- or La-salts prior to (or simultaneously with) SSIE with noble metal compounds improved the performance of the final catalyst. The presence of Ca<sup>2+</sup> or La<sup>3+</sup> decreased the strength of Brønsted acidity. Moreover, the alkaline or rare earth cations play the role of anchors for the metal particles which form upon reduction and, thus, stabilize the particle size distribution.

Other interesting studies of SSIE with noble metal cations were carried out by Hatje et al. using temperature-programmed reduction (TPR), XRD, dispersive extended X-ray absorption fine structure (DEXAFS) and time-resolved X-ray absorption spectroscopy (XAS) [38, 39], by Mkombe et al. [101], who prepared Pt<sup>0</sup> clusters on K-L, by Schlegel et al. [102] (incorporation of Rh into DAY, studied by FTIR and CO adsorption under formation of Rh(CO)<sub>2</sub><sup>+</sup> complexes), and by Wasowicz and Kevan [103], who showed that a significantly higher loading of SAPO-11 with rhodium was achievable via SSIE than through CE and investigated the resulting Rh(II) and Rh(I) species by ESR.

**2.4.3.5.8 Miscellaneous** A great number of further salt or oxide/zeolite systems have been studied with respect to SSIE, and it is beyond the limited size of this book to list and discuss all such systems described hitherto in the literature. Most such systems are listed in Table 4, together with pertinent references.

Only one type of solid-state reaction with zeolites should be briefly mentioned here, namely the SSIE with cations of high oxidation states, for example V<sup>5+</sup> or V<sup>4+</sup>, Cr<sup>6+</sup> or Cr<sup>5+</sup>, and Mo<sup>6+</sup> or Mo<sup>5+</sup> (cf. also Section 2.4.3.7.3). Important examples were described and discussed by Kucherov and Slinkin [68], and by Bock [96]. In this context, the interesting point is that not the bare cations

of such high oxidation states but, frequently after partial reduction, complex cations such as VO(OH)<sup>+</sup>, CrO<sub>2</sub><sup>+</sup>, or MoOCl<sub>2</sub><sup>+</sup> were incorporated. This was elegantly confirmed by Bock [96] for the system MoCl<sub>3</sub>/H-zeolites by carefully measuring the numbers of in-going and out-going Cl<sup>-</sup> anions. (For further details concerning the introduction of cations with a high oxidation state via SSIE, see Refs. [11, 68, 96].)

#### 2.4.3.6 Some Considerations on Thermodynamic and Kinetic Aspects of SSIE

**2.4.3.6.1 Effect of Temperature and Salt Concentration in Salt/Zeolite Mixtures** Although reports on these effects are hitherto rather scarce, it has been observed on several occasions that an increase in reaction temperature (up to an optimum) shifted the SSIE towards a higher degree of exchange (cf. Section 2.4.3.5.4; e.g., SSIE in CuCl/H-ZSM-5, Ref. [104]; SSIE in BeCl<sub>2</sub>/Na-Y, Ref. [52]; SSIE in MnCl<sub>2</sub>/H-ZSM-5, Ref. [18]; and Section 2.4.3.6.3). In several cases the increase in the molar ratio of salt and zeolite in the mixtures also increased the degree of incorporation of the in-going cation. For instance, enhancing the Cu/OH molar ratio in mixtures of CuCl and H-ZSM-5 from 0.32 over 1.00, and 1.60 to 2.25, increased in corresponding steps the degree of exchange (OH consumption) by up to 86% [104]. However, this effect depends on the system under study: in the case of MnCl<sub>2</sub>/H-ZSM-5, no such enhancement in the exchange degree was observed when, at the same reaction temperature, the amount of admixed MnCl<sub>2</sub> was increased (cf., e.g., Section 2.4.3.5.6; see Ref. [18]).

#### 2.4.3.6.2 The Role of Water in Solid-State Ion Exchange

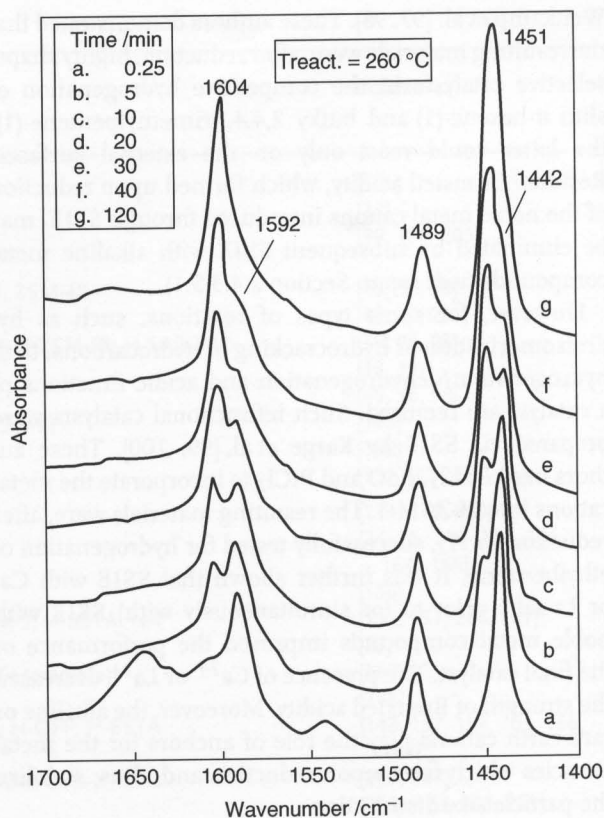
In general, the materials involved in reported SSIE experiments have been "dry", but this does not necessarily mean that H<sub>2</sub>O was absolutely excluded. As the experiments were usually conducted under ambient conditions, strongly adsorbed water molecules or strongly held crystal water may have been present. Although the presence of water may not be detrimental to SSIE, arguments have been made that even traces of H<sub>2</sub>O are not a prerequisite for this type of ion exchange to occur, as shown by the following three types of experiment:

- (i) SSIE was successfully carried out with a great number of systems comprising compounds of the in-going cation which are insoluble in water: AgCl/H-ZSM-5 [105, 106], Hg<sub>2</sub>Cl<sub>2</sub>/H-ZSM-5 [105, 106], CuO/H-ZSM-5 [104], Cu<sub>2</sub>O/NH<sub>4</sub>-Y [104], Mn<sub>3</sub>O<sub>4</sub>/H-ZSM-5 [18], and several others. This is

at least a strong hint that H<sub>2</sub>O molecules are not required for SSIE.

- (ii) A series of SSIE experiments was carefully designed by Sulikowski et al. [107] to secure that any traces of water were excluded. Each step of the procedure was carried out under exclusion of moisture, from the very initial steps and then throughout the whole subsequent process. The reactants were separately treated in high vacuum ( $10^{-6}$  Pa) at about 670 K in ampoules until water vapor was no longer detectable by MS and/or IR. The ampoules were then sealed and transferred into an efficiently working special glove box ( $p_{\text{H}_2\text{O}} \leq 10^{-7}$  Pa). All subsequent steps of the sample preparation were carried out in this glove box: breaking the ampoules; mixing the powders of salts and zeolites; filling the powders into capillaries for XRD runs and sealing them; pressing wafers for the IR measurements, transferring these into sample holders and the sample holders then into an ultra-high vacuum-tight IR cell (cf. Ref. [108]). One experiment was conducted with NaCl/H-MOR [105]. After heating the IR cell, which was connected to an ultra-high vacuum system, IR spectroscopy revealed that the OH groups of the H-MOR had completely disappeared (cf. Section 2.4.3.5.1). This indicated a 100% exchange of the protons of the H-MOR for Na<sup>+</sup> from NaCl.
- (iii) Another set of analogous experiments was carried out with water-free lanthanum chloride, which had been prepared from LaCl<sub>3</sub> · 7H<sub>2</sub>O through a particular procedure in a flow of HCl. As zeolites H-L, H-MOR, ultra-stabilized (dealuminated) H-Y (i.e., H-USY), and H-FER (ferrierite) were employed. The IR measurements indicated that the acid OH groups of the zeolites had reacted, as the corresponding OH bands had disappeared (e.g., in the case of H-L) or were markedly decreased (H-MOR, H-USY). The fact that in the latter cases not all of the OH groups had reacted is easily understood in view of the fact that in these zeolites the distances between the acid OHs are frequently rather large and, therefore, it is more difficult to compensate the negative charge of three of those sites by one La<sup>3+</sup> cation. In the case of H-FER no reaction at all occurred, most likely due to geometric constraints (*vide supra*).

**2.4.3.6.3 Kinetics of Solid-State Ion Exchange** It should be possible to investigate the kinetics of SSIE, for example via time-resolved XRD patterns, through the intensity changes of the reflections of the salt (or oxide)/zeolite mixtures and/or of typical IR bands (framework vibrations, bands in the OH or NH region or bands due to interaction between the cations and



**Fig. 9** Infrared spectra of pyridine adsorbed on a CuCl/Na-Y mixture at 533 K as a function of time. (For details, see text; after Ref. [21].)

probe molecules). In fact, in the latter case one tacitly assumes that the presence of the probe molecules does not affect the kinetics of SSIE. Here, results will be described which were obtained when the solid-state reaction between CuCl and Na-Y or Na-MOR was monitored by IR using pyridine (Py) as a probe [109, 110]. (For the experimental details, see Refs. [27, 108].) In order to illustrate such an experiment, Fig. 9 displays a set of IR spectra obtained during SSIE between CuCl and Na-Y at 533 K in the presence of pyridine (Py → Na<sup>+</sup>). Initially, only those bands (at 1592 and 1442 cm<sup>-1</sup>) were observed which indicate the interaction between pyridine and Na<sup>+</sup>. However, after a few minutes additional bands at 1604 and 1451 cm<sup>-1</sup> began to appear, originating from Py → Cu<sup>+</sup> complexes. While these bands increased with reaction time, concomitantly the bands of Py → Na<sup>+</sup> decreased.

From these changes of intensities with time, kinetic curves can be derived for various reaction temperatures (integrated absorbances versus reaction time; cf., e.g., Fig. 10). Clearly, the data must be corrected in order to account for the temperature-dependence of the adsorption equilibrium of pyridine. Figure 10 shows

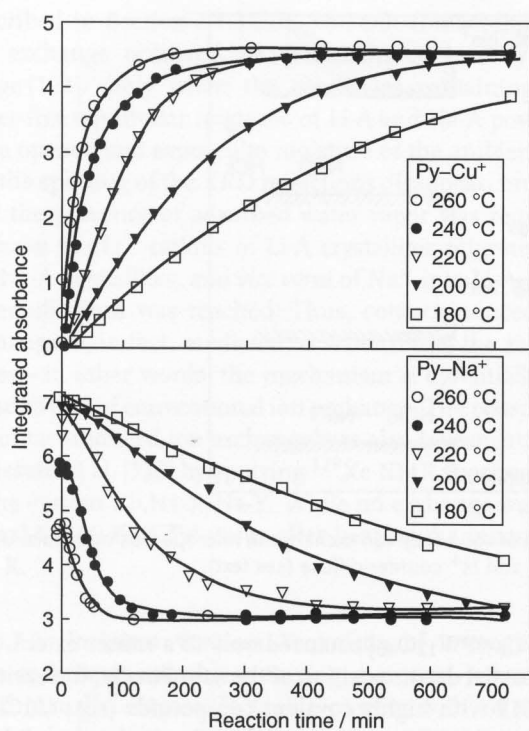


Fig. 10 Normalized and corrected integrated absorbances from pyridine adsorption on CuCl/Na-Y during solid-state ion exchange as a function of reaction time. (For details, see text; after Ref. [21].)

results for the kinetics of SSIE in the system CuCl/Na-Y; analogous graphs may be obtained with the bands of other  $\text{Py} \rightarrow$  cation complexes. It is reasonable to

assume that the absorbance,  $A$ , of the  $\text{Py} \rightarrow \text{Cu}^+$  complex at a given time,  $t$ , and at steady state (i.e.,  $A_t$  and  $A_{t \rightarrow \infty}$ ) are proportional to the amounts,  $M$ , of incorporated  $\text{Cu}^+$  (i.e., to  $M_t$  and  $M_{t \rightarrow \infty}$ ). With this assumption, plots of  $M_t/M_{t \rightarrow \infty}$  versus  $t^{1/2}$  (cf., e.g. Fig. 11) can be developed from figures such as Fig. 10. The data as shown in Fig. 11 can be described by solutions of Fick's second law for diffusion (see broken lines in Fig. 11), and suggest that SSIE in zeolites is possibly diffusion-controlled. Provided that this is correct, one would obtain diffusion coefficients of about  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$  at 500 K, and activation energies of 68–70  $\text{kJ mol}^{-1}$  for the above systems CuCl/Na-Y and CuCl/Na-MOR.

#### 2.4.3.6.4 A Possible Mechanism of Solid-State Ion Exchange

In principle, the transport of the in-going cations may occur through the vapor phase or surface diffusion (cf. Refs. [111–113] and Chapter 2.4.7 of this Handbook). For example, in the case of several metals [114], such as metallic zinc and gallium, transport through the (intercrystalline) gas phase is most probably part of the exchange process. Schneider et al. [115] investigated the reaction between powders of elemental  $\text{Zn}^0$  and H-ZSM-5 with various  $n_{\text{Si}}/n_{\text{Al}}$  ratios by TPE of hydrogen, which occurred above 620 K, XANES, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Similarly, Altwasser et al. [116] reacted elemental  $\text{Ga}^0$  with H-ZSM-5 and monitored the reaction by the TPE of  $\text{H}_2$

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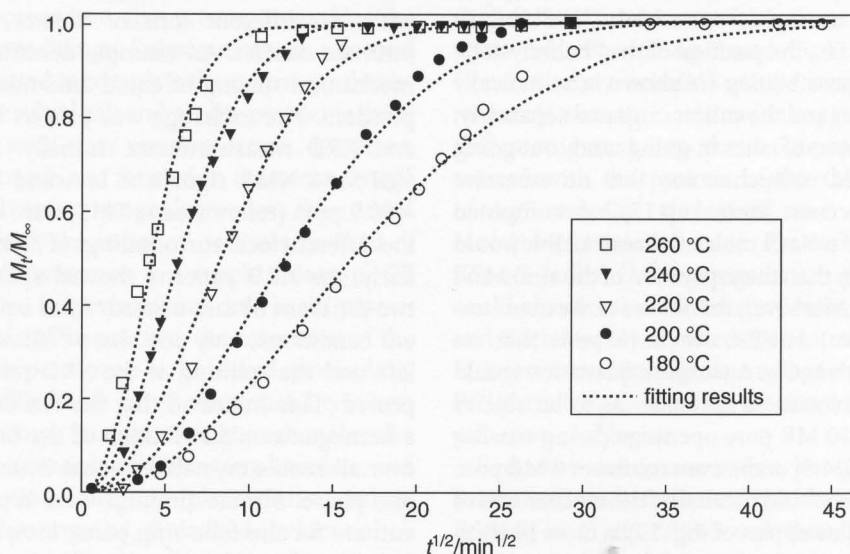


Fig. 11 Description of the kinetics of solid-state ion exchange in the system CuCl/Na-Y through a diffusion model; the symbols represent experimental data derived from the measured integrated absorbances of the probe (pyridine); the broken lines represent results of the fitting to the diffusion model. (For details, see text; after Ref. [21].)

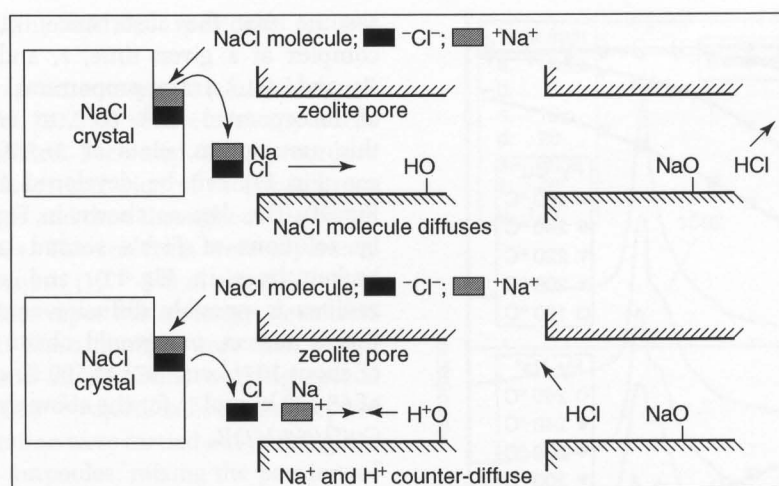


Fig. 12 Schematic representation of two possible models of the mechanism of solid-state ion exchange in microporous materials. Upper part, mechanism A: NaCl molecule diffuses. Lower part, mechanism B: Na<sup>+</sup> and H<sup>+</sup> counter-diffuse (see text).

peaks at about 400 K and 700 K, indicating that univalent Ga<sup>+</sup> was formed at the lower, trivalent Ga<sup>3+</sup> at the higher temperature. This method enabled the introduction of gallium into zeolite structures with pore openings too small as to allow exchange in an aqueous solution of Ga-salts or SSIE with Ga<sub>2</sub>O<sub>3</sub>. However, many of the salts and oxides involved in SSIE have, even at the usual temperatures of solid-state reaction of about 530–730 K, a rather low vapor pressure. Thus, the second possibility of surface diffusion from the intimately contacted salt (or oxide) and to the zeolite particles seems to be more likely in SSIE. In any event, the question then remains as to whether ions or molecules of the respective compound diffuse into the zeolite pores after separation, for example from a kink (“Halbkristallage”, after Stranski, i.e., the position of the “half-crystal”, cf. Ref. [117]). Both possibilities are shown schematically in Fig. 12. If the anion and the cation migrated separately, then counter-diffusion of the in-going and out-going cations must proceed in such a way that no excessive electrical gradient occurs. Stranski [117] has computed that the separation of a NaCl molecule from a kink would require a lower energy than the separation of the anion and cation in a sequence. Moreover, in the case of the medium-pore zeolite ferrierite, H-FER, we have seen that no reaction occurred with LaCl<sub>3</sub>. A simple explanation would be that the LaCl<sub>3</sub> molecule is too bulky as to be able to penetrate either the 10 MR pore openings (being smaller than in the case of ZSM-5) or the even narrower 8 MR pore openings of FER. This would mean that the mechanism of molecular diffusion (lower part of Fig. 12) is more likely to hold. This assumption was supported by experiments of SSIE of H-ZSM-5 with molecules containing bulky anions (e.g., salts of heteropoly acids such as Cs<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] [48]). Compared to the exchange with CsCl (cf. Fig. 1), SSIE

with Cs<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] occurred only to a minor extent, due to a partial decomposition of the salt. Finally, the easiness of SSIE with highly covalent compounds (e.g., CuCl, cf. Section 2.4.3.5.4) suggested that the molecules did not dissociate but rather migrated as an intact species.

#### 2.4.3.7 Modified Solid-State Ion Exchange and Related Processes

**2.4.3.7.1 Contact-Induced Ion Exchange** In an interesting experiment, Kokotailo et al. [118] and Fyfe et al. [119] showed that, even at room temperature, cation exchange occurred when, for example, zeolite crystallites loaded with two different sorts of cations were brought into intimate contact. An example described was the simple mechanical mixing of equal amounts of Li-A and Na-A powders. The exchange was proven by <sup>29</sup>Si MAS NMR and XRD measurements. Initially, two well-separated <sup>29</sup>Si MAS NMR signals of Li-A and Na-A at –85.1 and –88.9 ppm (referenced to TMS) were observed, reflecting the different local surroundings of Si in both zeolites. Similarly, the XRD patterns showed split reflections. Thus, two different phases existed. After equilibrating at ambient conditions, only one sharp <sup>29</sup>Si MAS NMR line was left, and the splitting of the XRD reflections had disappeared. This indicated that the ion exchange had led to a homogeneous distribution of the Li<sup>+</sup> and Na<sup>+</sup> cations over all zeolite crystallites – that is, the existence of only one phase. Similar findings were reported by the same authors for the following pairs: Li-A/NH<sub>4</sub>-A, Li-X/Na-X, Li-X/NH<sub>4</sub>-X, and Li-A/Na-MOR. Huang et al. [120] described analogous results for Li-A/Na-Y, Li-A/NH<sub>4</sub>-X, and Li-A/Ca-X. However, under the absolute exclusion of even of traces of H<sub>2</sub>O (i.e., experimental conditions as

described in Section 2.4.3.6.2), no such contact-induced ion exchange occurred, as demonstrated by Koy and Karge [121]. Only when the capillaries containing the water-free equimolar mixtures of Li-A and Na-A powders were opened and exposed to moisture of the ambient air, did the splitting of the XRD reflections disappear, proving that the presence of adsorbed water vapor was required to make the  $\text{Li}^+$  cations of Li-A crystallites migrate into the Na-A crystallites, and *vice versa* of  $\text{Na}^+$  into Li-A, until an equilibrium was reached. Thus, contact-induced ion exchange is, in fact, mediated by water filling the zeolitic pores – in other words, the mechanism is essentially the same as that of conventional ion exchange. The possibility of contact-induced ion exchange was also investigated by Fraissard et al. [122] by applying  $^{129}\text{Xe}$  NMR spectroscopy to the system  $\text{Rb,Na-X/Na-Y}$ . While no exchange was observed at 300 K, it did occur after heating the mixture to 673 K.

#### 2.4.3.7.2 Incipient Wetness Technique of Impregnation

This technique comprises mixing a certain volume of dried (usually outgassed) zeolite powder with an equivalent volume of the aqueous solution containing a salt of the exchange cation (chloride, nitrate, carboxylates, etc.), thus producing a paste with a distribution of the cations as homogeneous as possible and subsequent heating [123–127]. For the first stage – which is conducted at lower temperatures when the zeolite powder is impregnated and the paste is produced – a fraction of the ions are exchanged in a similar manner as in CE, except that the intermittent washing steps are omitted, so that the out-going cations and the anions of the impregnated salt remain in the product of this procedure; this process resembles the contact-induced ion exchange. Subsequently, in a second stage the paste is heated to complete the exchange; that is, the mixture of the residual salt and zeolite powder is dried and, in fact, a real solid-state reaction occurs. However, if no volatile compounds are formed in the second stage an equilibrium with an exchange degree less than 100% will result. In essence, the incipient wetness method of impregnation lies between, or is a combination of, CE and SSIE. There are, however, some drawbacks associated with the procedure: in practice, the migration of the salt solution into the pores may be hindered, particularly when the pores are filled with gases, the wettability is low, and the pores are narrow. Furthermore, the salt molecules are usually not well-anchored on the internal surface, and therefore redistribution may take place during subsequent treatments (heating and, if desired, reduction; cf. Ref. [128]). Thus, the resulting products are often not homogeneously exchanged, and the concentration of the in-going cations is highest close to the external surface – that is, they exhibit a significant concentration gradient.

#### 2.4.3.7.3 Gas-Phase-Mediated Processes Related to Solid-State Ion Exchange

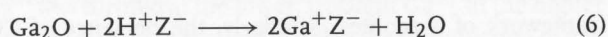
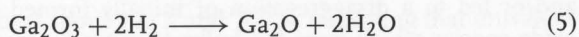
The adsorption of elemental species or compounds of the in-going cation onto, and subsequent incorporation of the cation into, zeolite crystallites may occur in the case of volatile metals (*vide supra*), oxides or halides. Pertinent examples are the introduction of  $\text{Zn}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$  into hydrogen forms of zeolites via the interaction of them with vapors of the respective chlorides [129–131], the incorporation of V-, Ti-, and Cr-containing species from gaseous  $\text{VOCl}_3$ ,  $\text{TiCl}_4$ , and  $\text{CrOCl}_2$ , respectively [132, 133], and the reaction of vapors of metallic zinc or cadmium with, for example, H-Y or H-ZSM-5 [134–137]. In some cases, the presence of additional molecules in the vapor phase may mediate SSIE at elevated temperatures. For instance, the presence of water vapor caused the ion exchange of  $\text{MoO}_3$  with H,Na-Y to occur [138, 139], whereas attempts of SSIE with dry  $\text{MoO}_3$  were unsuccessful [2]. It is possible that the interaction with  $\text{H}_2\text{O}$  prevented  $\text{MoO}_3$  from polymerization and/or led to a disaggregation of initially formed Mo-oxide species which were too bulky to enter the porous framework of Y-zeolites. Similarly, the presence of CO in the gas phase enabled the incorporation of  $\text{Co}^{2+}$  and  $\text{Rh}^+$  via the formation of carbonyl-complexes [102, 140]. Finally, Kucherov et al. [141] determined that the incorporation of  $\text{Mo}^{5+}$ -containing species such as  $(\text{MoOCl}_2)^+$  or  $\text{MoCl}_4^+$  into H-ZSM-5, H-BETA, H-FER, and H-USY was mediated by a flow of  $\text{CCl}_4$ -containing air stream.

#### 2.4.3.7.4 Oxidative and Reductive Solid-State Ion Exchange

Previously, Beyer and colleagues [142, 143] observed during the 1970s that tiny silver and copper particles ( $\text{Ag}_n^0$ ,  $\text{Cu}_n^0$ ) formed on the external surfaces of zeolite crystallites upon reduction of Ag-Y and Cu-Y by  $\text{H}_2$ , respectively. Concomitantly, acid OH groups were restored. When the materials were then calcined in oxygen, however,  $\text{Ag}^0$  and  $\text{Cu}^0$  re-migrated into the zeolite structure, where they reacted with the protons of the OHs under formation of  $\text{Ag}^+$  and  $\text{Cu}^+$  on cation sites. Similarly, Kucherov et al. [144] claimed that, in the case of reduced Cu, H-ZSM-5 bulky  $\text{Cu}^0$  aggregates on the external surface could also be re-oxidized (“oxidative SSIE”), and Feeley and Sachtler [23] reported that introduction of  $\text{Pd}^+$  into H-Y proceeded through an analogous oxidative SSIE from  $\text{Pd}^0$  particles produced on the outer zeolite surface in the presence of chlorine.

Reductive solid-state ion exchange (RSSIE) has been extensively studied, especially with the systems  $\text{Ga}_2\text{O}_3/\text{H-ZSM-5}$ ,  $\text{In}_2\text{O}_3/\text{H-ZSM-5}$  and  $\text{CuO}/\text{H-ZSM-5}$ , as well as in mixtures of oxides with H-MOR, H-BETA and H-Y (for details, see Ref. [145]). In fact, in systems such as

CuO/H-ZSM-5, so-called "auto-reduction" occurs in that a certain amount of the framework oxygen anions is oxidized to molecular oxygen under reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  [146, 147]. In contrast to RSSIE with  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$ , an additional reductive agent is, therefore, not necessary. Price and Kanazirev [24], Price et al. [25] and Kanazirev et al. [148–150] were the first to report on systematic studies of RSSIE. Temperature-programmed reduction monitored by a thermobalance (TPR/TG), XRD, transmission electron microscopy/energy dispersive analysis of X-rays (TEM/EDAX), XPS, and IR were each used to study RSSIE (cf. also Refs. [151–155]). The interest in such investigations was stimulated by the fact that Ga- and In-containing zeolites were assumed to be efficient catalysts for the aromatization of alkanes and redox reactions. Moreover, they appeared to be promising candidates for DeNOx reactions and SCR [156–159]. The stoichiometry of reductive ion exchange with  $\text{Ga}_2\text{O}_3$  is, according to TPR experiments, most likely described by Eqs. (5) and (6):



An analogous stoichiometry was proposed for the RSSIE with  $\text{In}_2\text{O}_3$ , even though no evidence for the intermediate formation of  $\text{In}_2\text{O}$  could be obtained; this suboxide is probably unstable and non-existent in the crystalline state. It was shown that reduction by CO or  $\text{NH}_3$  is also possible. Studies on the incorporation of indium into zeolites (Na,H-Y, H-ZSM-5, H-MOR and H-BETA) were significantly amended and deepened by the investigations of Beyer and colleagues [154, 160–163], who employed IR (with and without probe molecules), TPR, temperature-programmed oxidation (TPO), and differential thermogravimetry (DTG) and a test reaction for acid sites (isomerization of *m*-xylene) to confirm and elucidate RSSIE of  $\text{In}_2\text{O}_3$  in the above systems. For example, these authors clarified the formation and redox behavior of cationic  $\text{InO}^+$  species and provided a consistent picture of the stoichiometric chemistry and mechanism of RSSIE in  $\text{In}_2\text{O}_3$ /zeolites. They also demonstrated that a closed (reversible) redox cycle is operative in the case of these systems, which makes indium-containing zeolite catalysts prepared by RSSIE promising candidates for redox reactions (*vide supra*; for details, see Ref. [145]). Besides the aromatization of alkanes (cf., e.g., Refs. [24, 150, 164, 165]), reactions of amines (cf., e.g., Ref. [166]) were investigated. Related studies concerned mixtures of  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  with SAPO-materials (SAPO-5, SAPO-34, SAPO-37 and the mesoporous material MCM-41 [152, 167–169] (for acronyms, cf. Ref. [10]), including the so-called template-induced introduction. In the latter case, decomposition products of templates used in the synthesis of the porous materials, act as reducing agents.

#### 2.4.3.8 A Tabulated Survey of the Systems Studied in SSIE and Related Processes

As announced previously (see Sections 2.4.3.1, 2.4.3.5, 2.4.3.5.5, and 2.4.3.5.8), the systems studied with respect to modification via SSIE and related processes are summarized in Table 4. This should enable the interested reader to determine, conveniently, where research in this field has been already carried out and where knowledge is still lacking.

#### 2.4.3.9 Concluding Remarks

In recent years, solid-state ion exchange has become a well-established and now routinely used method for the post-synthesis modification of zeolites, and is also applicable to other porous solids such as mesoporous materials, clays, and porous oxides. Hence, a large number of systems has been investigated and appropriate techniques of preparation and investigation developed that, without doubt, will continue to be extended and improved in the future. However, perhaps more important than studying additional systems might be an undertaking of efforts to obtain a deeper understanding of solid-state reactions of zeolites and related materials. As indicated in this chapter, a number of interesting problems remain to be solved systematically, notably the thermodynamics, kinetics, and mechanisms of solid-state ion exchange reactions.

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