Solid-state Incorporation of Mn²⁺ Ions in H-ZSM-5 Zeolite

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The high-temperature interaction between H-ZSM-5 zeolite and solid $MnCl_2$, $MnSO_4$, $Mn(CH_3CO_2)_2$ and Mn_3O_4 has been studied by temperature-programmed desorption of ammonia, IR, EPR and mass spectrometry. It has been shown that the degree of solid-state ion exchange for $MnCl_2$ is strongly affected by the temperature of the heat treatment. Depending on the amount of manganese cations present in the zeolite–salt mixture, at 770 K an exchange degree of 60–85% can be obtained. The solid-state reaction of $MnSO_4$ at the same temperature leads only to 20% exchange of Mn^{2+} ions, while that of Mn_3O_4 results in ca. 50% exchange of Mn^{2+}. Owing to its decomposition above 520 K to Mn oxides, $Mn(CH_3CO_2)_2$ behaves similarly to these oxides; only part of the bridging OH groups are replaced by Mn ions. For all the Mn compounds studied, the solid-state reaction, resulting in replacement of protons of acidic skeletal OH groups by Mn^{2+} ions, appears to take the same course: most of the Mn^{2+} ions are exchanged in the initial stage of the reaction and then the reaction rate considerably decreases, levelling off to zero.

Although the solid-state reaction between zeolitic and other crystalline phases appears to be a promising process for modification of zeolitic catalysts, there are very few data on this phenomenon. Solid-state reactions were first described by Rabo et al.[1,2] in their work on salt occlusion. Clearfield et al.[3] observed by EPR solid-state reaction between halides of various metals and hydrogen forms of A, X, and Y zeolites at temperatures above 570 K. Recently, several studies[4–9] have been devoted to investigation of solid-state reactions between salts of various metals and hydrogen forms of Y- and ZSM-5-type zeolites and mordenites. The results of these studies (based on the IR spectra of OH groups, measurements of the evolved gases and EPR spectra of the metal cations) indicated high-temperature, solid-state ion exchange between the zeolite structural OH groups and metal halides,[4–8] as well as deaggregation of some transition-metal oxides mixed with zeolites.[9] Nevertheless, very little is known about the mechanism and factors controlling these processes.

This paper deals with the high-temperature solid-state interactions between solid Mn^{2+} salts [$MnCl_2 \cdot 4H_2O$, $MnSO_4 \cdot H_2O$, $Mn(CH_3CO_2)_2 \cdot 4H_2O$ and Mn_3O_4] and H-ZSM-5 zeolite. Attention is paid especially to investigation of the effect of the reaction temperature and time.

Experimental

Materials

The H-ZSM-5 zeolite used was synthesized using tetra-propylammonium base according to a common procedure,[10] then heated to 820 K in an oxygen stream and subsequently treated with 0.5 mol dm⁻³ HNO₃ at 298 K. The chemical composition of the ZSM-5 zeolite on a water-free basis (in wt %) was: $Na_2O = 0.12$, $CaO = 0.30$, $Al_2O_3 = 5.90$, $SiO_2 = 93.68$, corresponding to 1.00 mmol OH (g zeolite)⁻¹. The number of the acidic bridging OH groups, determined by temperature-programmed desorption of ammonia (TPDA), was 0.91 mmol g⁻¹. The Mn,H-ZSM-5 ion-exchanged zeolite was prepared by standard ion exchange of the H-ZSM-5 zeolite in solution. A portion of 5 g of H-ZSM-5 zeolite was treated with 300 cm³ of 0.1 mol dm⁻³ Mn (NO₃)₂ solution at 330 K for 3 h. The exchange was performed twice with a fresh

solution, then the zeolite was washed with water and dried at 370 K. The composition of Mn,H-ZSM-5 was, on a water-free basis, (in wt %): $Na_2O = 0.11$, $CaO = 0.28$, $MnO = 2.30$, $Al_2O_3 = 5.80$, $SiO_2 = 91.51$, corresponding to 0.35 mmol OH per gram zeolite. The number of acidic bridging OH groups of the Mn, H-ZSM-5 zeolite determined by TPDA was 0.30 mmol g⁻¹.

Methods

The mixtures of Mn salts and H-ZSM-5 zeolite (the amount of Mn^{2+} ions is given in table 1) were ground in an agate mortar to obtain well powdered and homogenized mechanical mixtures. The prepared mixtures were heated either in a nitrogen stream or in vacuum (temperature increase 5–20 K min⁻¹) to a selected temperature and then maintained at this temperature for 1–60 h. In some cases of re-exchange experiments, the heat-treated mixtures were further treated with 1 mol dm⁻³ NH₄NO₃ solution at 330 K for 10 h.

Changes in the number of acidic bridging OH groups in the zeolites resulting from the heat treatment were monitored by recording the IR spectra (Perkin-Elmer 325 spectrometer)

Table 1. Changes in the number of acidic bridging OH groups[a,b] in the mechanical mixtures of manganese salts with H-ZSM-5 zeolite[c] after heat treatment at given temperatures in vacuum or in a nitrogen stream for 6 h

salt	Mn²⁺ ions[d] /mmol g⁻¹	temperature /K	OH groups consumed /mmol g⁻¹	
			vacuum[a]	flow[b]
$MnCl_2$	0.33	570	0.21	
		670	0.38	0.41[b]
		770	0.56	0.57[b]
	0.45	770	0.57	
$MnSO_4$	0.47	770	0.16	0.18
Mn_3O_4	0.60	770	0.46	
$Mn(CH_3CO_2)_2$	0.31	770		0.36[b]

[a] Determined from IR data (band at 3610 cm⁻¹ after 6 h heat treatment in high vacuum). [b] Determined from TPDA; high-temperature peak, at ca. 700 K. [c] The H-ZSM-5 sample contained 0.91 mmol bridging OH groups per gram zeolite after excitation at 770 K (see Experimental section). [d] The Mn^{2+} content in the MnCl₂/H-ZSM-5 mixtures is related to 1 g dry zeolite.

of the sample in the form of a (binder-free) pellet (thickness *ca.* 5 mg cm^{-2}). In some flow experiments the number of bridging OH groups was estimated from the high-temperature peak of the TPDA spectrum.[11] The formation of electron-acceptor sites in heat-treated solid mixtures was checked by pyridine adsorption (at 470 K followed by desorption of weakly held pyridine at 470 K for 2 h).

Gaseous products evolved during programmed heating in vacuum (5 × 10^{-5} Pa) were detected mass-spectrometrically. The mixture of a salt and H-ZSM-5 zeolite was compressed into wafers (10 mg) and placed in an ultrahigh-vacuum system connected with a mass spectrometer (Balzers QMG 311), degassed at 370 K for 2 h and heated to 870 K at a rate of 20 K min^{-1} [see ref. (12)]. The amount of acid evolved during heating of solid mixtures in the flow arrangement was detected by absorption of eluent gases in an alkaline solution (0.1 mol dm^{-3} NaOH) and back-titration with 0.1 mol dm^{-3} HCl.

X-Band EPR spectra (Varian Model V-4502-15) of heat-treated solid mixtures, subsequently hydrated at room temperature, were recorded at 298 K.

Results and Discussion

MnCl$_2$–H-ZSM-5

Analogous to the behaviour of mechanical mixtures of other metal chlorides[3–6,8] with hydrogen forms of zeolites, heating MnCl$_2$–H-ZSM-5 leads to a solid-state reaction between MnCl$_2$ and the skeletal OH groups of the H-ZSM-5 zeolite. As a consequence of this reaction, the Mn^{2+} ions are exchanged with protons of the bridging OH groups and gaseous HCl is evolved. This has been demonstrated by the following: (i) the decrease in the number of acidic OH groups monitored by the IR spectra and TPDA of the heat-treated mixtures (*cf.* fig. 1 and 2 and table 1); (ii) the amount of HCl evolved, which for individual experiments corresponds to the number of OH groups consumed (*e.g.* heating MnCl$_2$–H-ZSM-5, Mn^{2+}/OH = 0.33 at 770 K for 6 h leads to the release of 0.56 mmol HCl g^{-1}; *cf.* the number of OH groups consumed, table 1); (iii) the bridging OH groups exchanged by Mn^{2+} can be fully regenerated by re-exchange of the calcined mixture with NH$_4^+$ ions [*e.g.* the re-exchange of the mixture, which was heat-treated according to (ii), yields a sample containing 0.89 mmol OH g^{-1} compared to 0.91
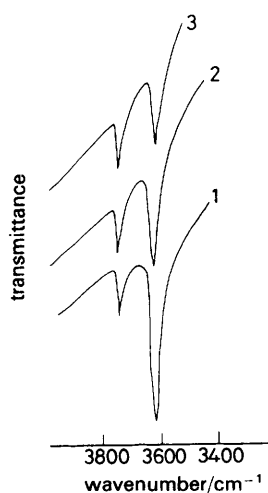

Fig. 2. IR spectra of the system MnCl$_2 \cdot 4H_2O$ + H-ZSM-5 (Mn^{2+}/OH = 0.33) after (1) heating in vacuum at 770 K for 2 h; (2) pyridine adsorption.

mmol g^{-1} found for the original H-ZSM-5]; (iv) deaggregation of MnCl$_2$ was demonstrated by recording the EPR spectra (*cf.* fig. 3); upon heating MnCl$_2$–H-ZSM-5 (followed by its hydration at room temperature) the original isotropic single signal of Mn^{2+} in the MnCl$_2$ salt passes to a split signal with six hyperfine lines (A = 9.8 mT) typical of isolated, octahedrally coordinated Mn^{2+} exchanged in the zeolite cationic sites.[7] After the re-exchange of the calcined mixture with NH$_4$NO$_3$ solution only traces of Mn^{2+} ions were indicated in the EPR spectrum.

To obtain more detailed information on the solid-state reaction, the effect of both the reaction temperature and time on the number of OH groups was examined by IR spectroscopy. It is seen from these experiments (see fig. 4 and table 1) that the degree of solid-state ion exchange strongly depends on the reaction temperature. In any event, the data of table 1 show that not all of the available Mn^{2+} cations were exchanged in cationic sites. A fraction of the manganese compound admixed to the zeolite always remained unreacted. For instance, application of 0.33 mmol MnCl$_2$ per gram H-ZSM-5 should result in a consumption of 0.66 mmol acidic OH groups per gram H-ZSM-5. However, even at 770 K only 0.56 mml OH g^{-1} were, in fact, consumed. The degree of exchange can be calculated as follows. With 0.33 mmol Mn^{2+} g^{-1} zeolite at 570 and 770 K, 0.21 and 0.56 mmol OH g^{-1} zeolite, respectively, were consumed; this corresponds to a degree of exchange of 23 and 62% of OH groups, respec-

Fig. 1. IR spectra of the original pure H-ZSM-5 (1) and of the system MnCl$_2 \cdot 4H_2O$–H-ZSM-5 (Mn^{2+}/OH = 0.33) after heating in vacuum at 770 K for 1 h (2); and after heating in vacuum at 770 K for 15 h (3).

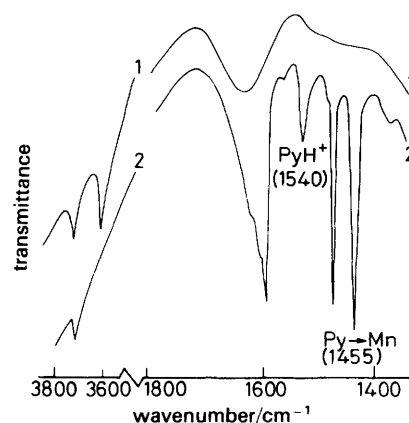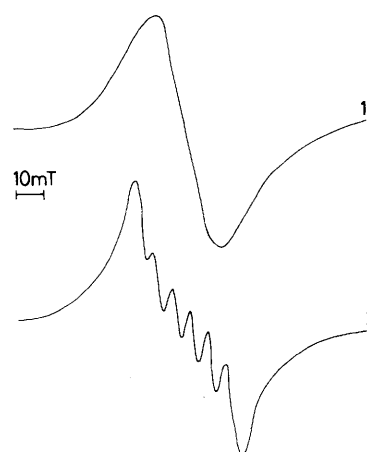**Fig. 3.** X-Band EPR spectra (recorded at 298 K) of Mn^{2+} in the system MnCl$_2 \cdot 4H_2O$–H-ZSM-5; (1) original mixture; (2) heated in vacuum at 770 K for 6 h and hydrated at ambient temperature.

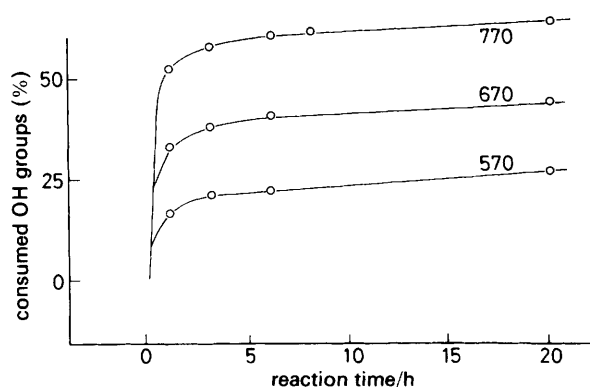**Fig. 4.** Number of bridging OH groups consumed as a function of the reaction time for the system $MnCl_2$–H-ZSM-5 $(Mn^{2+}/OH = 0.33)$ heated in vacuum at 570, 670 and 770 K.

tively. The corresponding degrees of exchange, related to the incorporation of available milliequivalents of manganese cations are $(0.21/2 \times 0.33) \times 100 = 32\%$ and $(0.56/2 \times 0.33) \times 100 = 85\%$, respectively.

An increase of the manganese content to 0.45 mmol g^{-1} in the manganese chloride–zeolite mixture, treated at 770 K, i.e. a ratio of $Mn^{2+}/OH = 1$, did not bring about a higher degree of exchange (see table 1). Most of the Mn^{2+} ions are exchanged in the first stage of the reaction (within 1 h), and then the reaction proceeds very slowly (see fig. 4). However, the effect of temperature and time on the OH group consumption may, to some extent, depend on the cations already incorporated into the zeolite.

The curve obtained from the temperature-programmed evolution of HCl from $MnCl_2$–H-ZSM-5 is shown in fig. 5. It exhibits a slight maximum at 470 K and then increases from 550 to 870 K. The low-temperature maximum could be related to the dehydration of $MnCl_2 \cdot 4H_2O$ which takes place at ca. 470 K and, therefore, the ion exchange could be supported by the presence of water in the system. When the temperature increase is stopped at a particular temperature and the sample is maintained at this temperature, the amount of HCl first quickly decreases (within several minutes) and then slowly decreases to zero (cf. fig. 5). Therefore, it appears that, after reaching a particular temperature, the solid-state reaction quickly proceeds to a certain degree and then continues very slowly. This finding is consistent with the conclusion based on the values of consumed bridging OH groups detected by IR spectroscopy (cf. fig. 4).
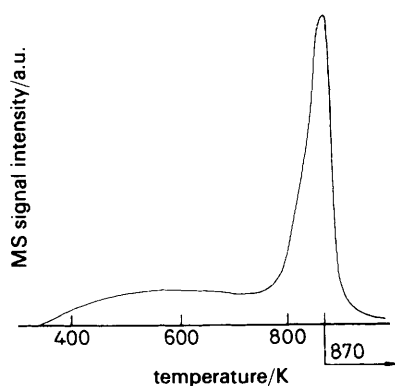
$MnSO_4$–H-ZSM-5

Solid-state interaction between $MnSO_4$ and H-ZSM-5 at 770 K results in evolution of only traces of SO_2 and SO_3 as indicated by mass spectrometry. Simultaneously, a decrease in the number of bridging OH groups is revealed by TPDA and IR, attaining only a fraction of the stoichiometrically feasible value (cf. fig. 6 and table 1). Moreover, comparison of the EPR spectra of Mn^{2+} ions in the original and the heated mixtures indicates that only a fraction of isolated Mn^{2+} ions are formed as a consequence of the heat treatment, while most Mn^{2+} ions remain in the form of the $MnSO_4$ salt (fig. 7). However, the reaction course seems to be similar to that observed for the mixture with $MnCl_2$. As indicated by the number of the zeolite OH groups recorded during the reaction, most of the OH groups are again consumed in the initial stage (cf. fig. 8).

Mn_3O_4–H-ZSM-5

TPDA and IR measurements carried out on Mn_3O_4–H-ZSM-5 heated in vacuum or calcined in a nitrogen stream at 770 K for 6 h (cf. table 1) demonstrate a ca. 50% decrease in the number of bridging OH groups. Therefore, it appears

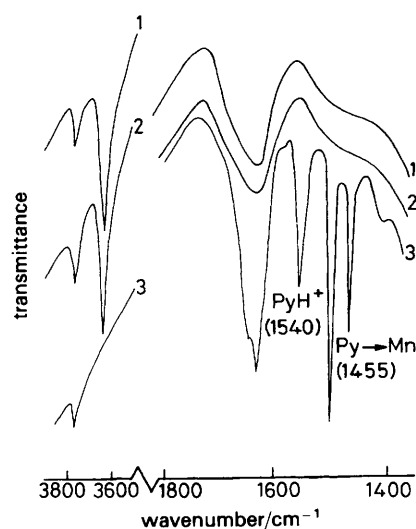**Fig. 6.** IR spectra of the original H-ZSM-5 zeolite (1), and of the system $MnSO_4 \cdot H_2O$–H-ZSM-5 after heating in vacuum at 770 K for 60 h (2); and after pyridine adsorption (3).
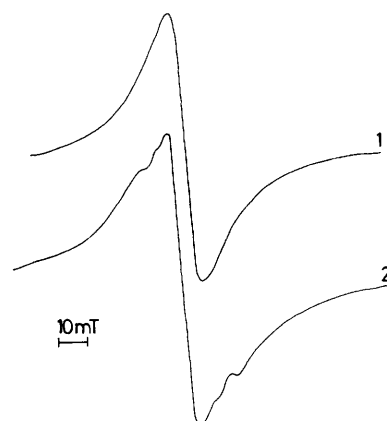
Fig. 5. Temperature-programmed evolution of HCl from the mixture of $MnCl_2$–H-ZSM-5. The sample, degassed in vacuum at 370 K for 2 h, was heated (20 K min^{-1}) to 870 K and then held at this temperature.

Fig. 7. X-Band EPR spectra (recorded at 298 K) of Mn^{2+} in the system $MnSO_4 \cdot H_2O$–H-ZSM-5: (1) original mixture; (2) heated in vacuum at 770 K for 6 h and hydrated at ambient temperature.
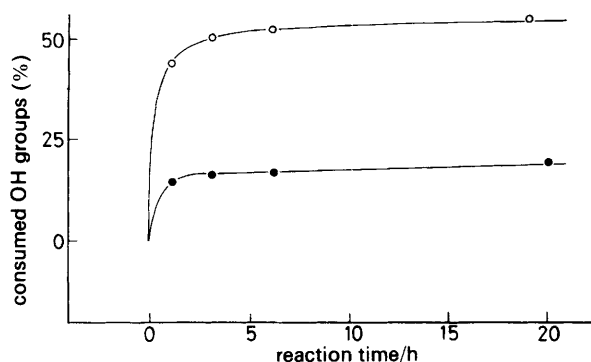
Fig. 8. Number of bridging OH groups consumed as a function of the reaction time for the systems Mn_3O_4–H-ZSM-5 (○) and $MnSO_4 \cdot H_2O$–H-ZSM-5 (●) heated in vacuum at 770 K.
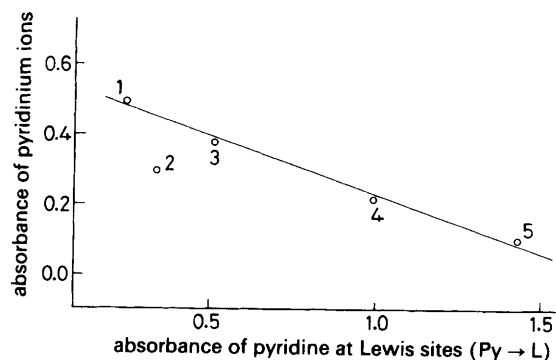

Fig. 9. Plot of log T_0/T (maximum absorbance) of the PyH^+ band (1540 cm^{-1}) against log T_0/T of the PyL band (1450 cm^{-1}) measured for 1, H-ZSM-5; 2, H-ZSM-5–Mn_3O_4; 3, H-ZSM-5–$MnSO_4$; 4, H-ZSM-5–$MnCl_4$; 5, Mn, H-ZSM-5; heated in vacuum at 770 K for 6, 6, 60, 2 and 6 h, respectively.

that, in contrast to NiO [compare ref. (8)], a solid-state reaction between the zeolite OH groups and Mn oxide takes place. The relationship between the degree of exchange and the reaction time is similar to that encountered with $MnCl_2$ and $MnSO_4$ (cf. fig. 4 and 8).

$Mn(CH_3CO_2)_2$–H-ZSM-5

On heating a mixture of $Mn(CH_3CO_2)_2$–H-ZSM-5 in vacuum, decomposition of the acetate anion occurs above 500 K, yielding CO, CO_2, acetone and acetic acid. Simultaneous formation of Mn oxides can be expected. Considering the behaviour of oxides it is, therefore, not surprising that a decrease in the number of OH groups is observed upon heating a mixture of $Mn(CH_3CO_2)_2$–H-ZSM-5, indicating incorporation of Mn^{2+} ions into the zeolite cationic sites.

Pyridine Adsorption

Formation of electron-acceptor sites after the high-temperature solid-state reaction between the H-ZSM-5 zeolite and Mn salts or oxides is evidenced by pyridine adsorption. Pyridine adsorption on the heat-treated mixture of $MnCl_2$–H-ZSM-5 and $MnSO_4$–H-ZSM-5 reveals (compared with the original H-ZSM-5) a decrease in the number of pyridinium ions (band at 1540 cm^{-1}) corresponding to acidic OH groups which is practically identical with the values obtained from the changes in intensities of the IR band of bridging OH groups (3610 cm^{-1}) or the high-temperature peak of TPDA. Simultaneously, a considerable increase in the intensity of the IR band at 1450–1454 cm^{-1}, corresponding to pyridine interacting with electron-acceptor sites, was detected (cf. fig. 2 and 6). Since re-exchange of the heat-treated mixture by NH_4NO_3 was shown to lead to practically full regeneration of the bridging OH groups, only small amounts, if any, of the lattice Al can be responsibe for the formation of new Lewis centres, i.e. electron-acceptor sites. Hence the newly formed Lewis sites should particularly correspond to isolated Mn^{2+} cations located in the cationic positions. Therefore, disregarding the differences in the extinction coefficients, the intensities of the PyH^+ (1540 cm^{-1}) and PyL (1450 cm^{-1}) bands would be correlated, as a decrease in the number of OH groups (or pyridinium ions) should result in an increase in the number of isolated Mn^{2+} cations. Such a correlation for the individual heat-treated mixtures as well as for the conventionally ion-exchanged Mn,H-ZSM-5 zeolite was actually found and is depicted in fig. 9. However, for the heat-treated H-ZSM-5 –Mn_3O_4 mixture, where also the intensity of the PyH^+ band (0.30) corresponds to the number of strongly acidic bridging

OH groups present in the zeolite (determined from the TPDA and IR band at 3610 cm^{-1}), the number of electron-acceptor sites (PyL intensity, 0.31) was considerably lower, as expected. This finding could be due to blockage of the exchanged Mn^{2+} ions by remaining Mn oxide species and/or to the change of some Mn^{2+} ions to higher valency. In both cases a lower number of pyridine molecules coordinatively bonded to Mn^{2+} would result.

Conclusions

The above results demonstrate that the high-temperature solid-state interaction (above 570 K) between the bridging OH groups of H-ZSM-5 and $MnCl_2$ salt takes place analogous to other metal chlorides, leading to metal-exchanged zeolites and evolution of gaseous hydrochloric acid. In contrast to $MnCl_2$, with $MnSO_4$ only a very small number of bridging OH groups are exchanged. The high-temperature reaction of H-ZSM-5 with manganese oxides as well as with Mn salts, decomposing to these oxides at temperatures below 570 K, leads to the incorporation of Mn ions into the zeolite cationic sites. However, the degree of this exchange appears to be considerably lower compared to manganese chloride.

On the basis of the above results no general conclusion can be drawn about the mechanism and the course of solid-state reactions. At the present stage one cannot, for instance, decide which of two possible mechanisms is operative: (i) $MnCl_2$, e.g., may first dissociate and the ions, Mn^{2+} and Cl^-, migrate and act separately, similarly to the case of conventional exchange in solution, or (ii) $MnCl_2$ molecules may be separated at the kinks ['Halbkristall-Lagen', see ref. (13)] of the tiny $MnCl_2$ crystallites, adjacent to the H-ZSM-5 particles, and migrate as such into the zeolite channels where they react with acidic OH groups; this would also result in evolution of HCl and occupancy of cationic sites of the zeolite structure by Mn^{2+} cations.

It appears that the degree of the solid-state exchange is strongly affected by the temperature of the heat treatment and the type of anion, but it is not apparent which step of the solid-state reaction is controlled by temperature. The observed dependences of the degree of exchange on the temperature cannot be interpreted in terms of thermodynamic equilibrium between the salt and OH groups since, at least in the case of $MnCl_2$, one reaction product (HCl) is removed. Taking into account the reaction course, which exhibits a similar shape for the individual temperatures, the kinetics of the reaction do not seem to to be affected by the temperature. Similarly, the observed differences in the degree of exchange for individual anions cannot be explained by differences in

the lattice energies of the studied salts, as their melting points decrease in the order: Mn_3O_4 (1987 K) > $MnSO_4$ (973 K) > $MnCl_2$ (923 K), which does not agree with the above results.

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