Interaction and solid-state reaction between manganese chloride tetrahydrate and Y zeolites (NaY or LaNaY)

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Mixtures of Y zeolites (NaY or LaNaNH$_4$Y) and manganese chloride tetrahydrate are treated in air at atmospheric pressure. Depending on the treatment temperature, T_t, three successive processes can occur: maximum halide insertion into the supercages at low temperature (503 K); maximum cation exchange at 683 K and solid–solid reactions with the appearance of new crystalline phases at *ca.* 1073 K.

1 Introduction

Modified zeolites are of interest in industrial heterogeneous catalysis, where zeolites are often mixed with various oxides, either as catalysts or as binders. For this reason, over the last 10 years we have undertaken a solid-state study devoted to the interactions and reactions of zeolites (NaY or LaNaNH$_4$Y) with oxides.[1–4] We have shown that the maximum degree of insertion of these oxides is related to their physical and chemical properties, as well as to the differences in the structural composition of the zeolites. We shall denote LaNaNH$_4$Y by LaNaY in what follows, in order to remain consistent with previous publications. In this article we shall complete this study by extending it to (NaY or LaNaY)–MnCl$_2 \cdot$ 4H$_2$O systems. The reasons for the choice of tetrahydrated manganese chloride are related to both its physical and catalytic properties. Its physical properties predispose it to insert into the cavities of Y zeolite; it has a relatively low melting point and high solubility in hot water (152 g l^{-1}). It is tetrahydrated up to 513 K. Between 513 and 773 K it becomes anhydrous and its solubility in hot water is 72 g l^{-1}.[5] Beyond 773 K, it is transformed into Mn$_2$O$_3$ (bixbyite) and Mn$_3$O$_4$ (hausmannite).

Some work on the solid-state interactions of salts with different zeolites has already been reported,[6,7] in particular, manganese salts [MnCl$_2$, MnSO$_4$ and Mn(CH$_3$CO$_2$)$_2$] with H-ZSM-5, where the Mn^{2+} ions have more or less replaced the OH group protons on the zeolite.[7] Complexes such as Mn$_2$(CO)$_{10}$ have also been deposited in NaY supercages from the vapour phase, without decomposition.[8]

Among the catalytic applications of zeolites containing manganese, we can mention: the production of adipic acid by the oxidation of cyclohexene by H$_2$O$_2$ on catalysts in the form of *cis*-manganese bis-2,2′-bipyridyl occlusions in the supercages of NaX or NaY,[9] and the transformation of methanol in oxygen to hydrocarbon at *ca.* 670 K and the conversion of toluene in nitrogen at 790 K on ZSM-5 modified by Mn^{2+}.[10]

2 Experimental

The starting materials are: MnCl$_2 \cdot$ 4H$_2$O, NaY (LZY-52 from UOP with a Si/Al ratio of 2.44), La(NO$_3$)$_3 \cdot$ 6H$_2$O (Fluka) and NH$_4$Y (LZY-64 from UOP). LaNaNH$_4$Y is obtained from LZY-64.[4,5]

Before mixing each of the Y zeolites (NaY or LaNaY) with MnCl$_2 \cdot$ 4H$_2$O it is necessary to pretreat both compounds separately. NaY and LaNaY must be kept for 36 h in a dessicator containing a supersaturated solution of NH$_4$NO$_3$ in order to saturate them with water. The samples are weighed regularly in order to follow water uptake with time; when the weight is constant, within experimental error, the zeolite is ready to be mixed with the chloride. All the mixtures are defined by R_{Mn} which corresponds to the number of Mn atoms per TO$_4$ tetrahedron (T = Al, Si). To obtain exact, reproducible compositions certain precautions regarding hydrated manganese chloride are required. Since it is hygroscopic its weight increases by *ca.* 1.5% every hour in air at 298 K, but at 358 K no hydration occurs. Therefore, before mixing with the zeolites it is necessary to heat the chloride to 358 K for 12 h, to weigh out a sample immediately and to run an X-ray diffractogram (which should be absolutely identical with that given by the JCPDS n° 22-721 card). For the weight m of manganese chloride it is easy to take the weight m' of hydrated zeolite (which hardly varies in the time required for the measurement) to obtain a mixture with the exact composition R_{Mn}. 2 g of each zeolite–chloride mixture with different R_{Mn} values (0–0.400) were prepared.

Because MnCl$_2 \cdot$ 4H$_2$O is hygroscopic, the weight difference of the mixtures before and after thermal treatment is random. This, however, does not prevent one following the evolution (Δa_0) and the crystallinity of the zeolite by X-ray diffraction of the mixtures, since the cell parameter a_0 depends very little on the degree of hydration.

The treated samples, which have a one-phase system, are thoroughly washed with hot water at slight pressure in order to remove, if this is possible, the added material (reversible occlusion). Finally, the elements contained in the zeolite are determined by elemental analysis before and after thermal treatment and after washing of the one-phase systems.

The evolution of a_0, the crystallinity, the pore volume and the Si/Al ratio of each treated zeolite is obtained from the X-ray diagrams, adsorption isotherms and ^{129}Xe and ^{29}Si NMR; the various methods have been described in previous work.[3,4]

3 Results and discussion

3.1 X-Ray diffraction at ambient temperature

3.1.1 NaY–MnCl$_2 \cdot$ 4H$_2$O system. *Insertion.* The results depend on both T_t and R_{Mn}. Table 1 gives the variations in the cell parameter, the percentage increase (decrease) in a_0 and the crystallinity (%) of the zeolite with those two parameters.

For $T_t < 443$ K, two initial phases coexist, whatever the composition and the treatment time; the cell parameter is unchanged.

For $T_t = 443$–523 K and $R_{Mn} = 0.052$ the system is one-phase (NaY). In this temperature range the zeolite and the manganese chloride tetrahydrate lose their water molecules,

Table 1 Unit cell parameters (a_0/Å), percentage increase in a_0: $\Delta' = 100(\Delta a_0)/a_0$ and crystallinity (%) of NaY and LaNaY at different R_{Mn} values and treatment temperatures T_t

T_t/K	NaY				LaNaY			
	R_{Mn}	a_0	Δ'	cryst.	R_{Mn}	a_0	Δ'	cryst.
503	0	24.659		100	0	24.672		100
	0.025	24.666	0.03	95	0.015	24.676	0.02	96
	0.040	24.676	0.07	92	0.030	24.687	0.08	92
	0.052	*24.681*	*0.08*	*88*	*0.066*	*24.694*	*0.09*	*88*
	0.100	24.672	0.05	86	0.100	24.684	0.06	86
	0.150	24.673	0.05	86	0.150	24.682	0.04	86
	0.400	24.666	0.03	83	0.400	24.677	0.02	87
553	0	24.659		98	0	24.671		99
	0.025	24.668	0.04	96	0.025	24.679	0.03	96
	0.044	*24.675*	*0.06*	*87*	*0.055*	*24.691*	*0.08*	*90*
	0.050	24.670	0.04	88	0.060	24.686	0.07	87
	0.075	24.667	0.03	89	0.070	24.684	0.05	86
	0.100	24.662	0.01	84	0.100	24.685	0.05	87
	0.400	24.664	0.02	85	0.400	24.682	0.04	84
593	0	24.657	−0.01	99	0	24.671		99
	0.039	*24.669*	*0.05*	*88*	*0.043*	*24.679*	*0.03*	*89*
	0.050	24.670	0.05	84	0.050	24.679	0.03	85
	0.100	24.665	0.04	81	0.100	24.675	0.02	80
	0.200	24.663	0.02	82	0.200	24.675	0.02	83
	0.400	24.664	0.02	84	0.400	24.676	0.02	81

Entries in italics correspond to maximum insertion.

dissolving the $MnCl_2$, which, by a wetting phenomenon, lines the zeolite cavities. This maximum insertion leads to a percentage increase in the cell parameter $\Delta' = 0.08$. Elemental analysis on the $R_{Mn} = 0.052$ sample before and after treatment for 16 h at 503 K gives the same values for Cl, Mn, Na, Si and Al, showing that the $MnCl_2$ is clearly inside the pores. After prolonged washing with water at slight pressure, the Na content is the same but the Cl and Mn have completely disappeared. This insertion is reversible and there is no cation exchange at 503 K. When R_{Mn} is greater than 0.052 the system is two-phase: NaY and $MnCl_2 \cdot 4H_2O$.

For $T_t = 523–563$ K, only the NaY phase is detected up to $R_{Mn} = 0.044$, at 553 K. For $R_{Mn} > 0.044$ the zeolite coexists with anhydrous manganese chloride.

For $T_t = 563–613$ K the R_{Mn} range over which the only phase is NaY is much reduced: $R_{Mn} \leqslant 0.039$ at $T_t = 593$ K. Above this R_{Mn} value anhydrous $MnCl_2$ is found with the zeolite.

Cation exchange. For $T_t = 613–813$ K and for $R_{Mn} \leqslant 0.087$ all the NaY–$MnCl_2 \cdot 4H_2O$ mixtures treated for 16 h give a one-phase system. When washed with hot water at slight pressure Mn^{2+} and NH_4^+ are partially eliminated as chlorides (elemental analysis) in contrast to the one-phase systems from the previous temperature ranges, where the manganese chloride was completely eliminated. In this composition range therefore, both insertion and cation exchange occur. At $T_t = 683$ K for initial $R_{Mn} = 0.087$, corresponding to 8.3 Mn^{2+} per cell there are 7.1 Mn^{2+} per cell corresponding to $R_{Mn} = 0.074$ after washing with hot water. The difference, 1.2 Mn^{2+} per cell, corresponds to reversible insertion.

For $R_{Mn} > 0.087$ the system is multi-phase but becomes one-phase after washing with hot water. The partial elimination of Mn^{2+} and NH_4^+ can be used to calculate the different degrees of cation exchange. Table 2 gives the degree of cation exchange for each initial $R_{Mn} \leqslant 0.200$ at 683 K; the maximum (30.5%) is reached for initial $R_{Mn} = 0.100$ and is almost constant up to initial $R_{Mn} = 0.200$.

Solid–solid reaction. Between 813 and 963 K there is a multi-phase system: the Y zeolite coexists with the oxides, Mn_2O_3 and Mn_3O_4, for $R_{Mn} < 0.200$.

For $R_{Mn} > 0.150$ at 1023 K there is a solid–solid reaction with the appearance of new crystalline phases: $Na_{0.2}MnO_2$ [tetragonal; $a_0 = 9.74$ Å, and $c_0 = 2.86$ Å (JCPDS n° 27-747)]; Na_4MnO_4 [triclinic; $a_0 = 5.72$ Å, $b_0 = 8.54$ Å, $c_0 = 6.34$ Å, $\alpha = 97.30°$, $\beta = 123.30°$ and $\gamma = 99.30°$ (JCPDS n° 32-1127)] and $Na_2Mn_5O_{10}$ [monoclinic; $a_0 = 13.81$ Å, $b_0 = 2.86$ Å, $c_0 = 9.74$ Å and $\beta = 95.30°$ (JCPDS n° 27-749)]. All these phases are accompanied by amorphous zeolite.

Table 2 Dependence on R_{Mn} of the degree of exchange of Na^+ and NH_4^+ by Mn^{2+} in unwashed and washed NaY and LaNaY zeolites calcined at $T_t = 683$ K

unwashed zeolite		washed NaY (one-phase)				washed LaNaY (one-phase)			
initial R_{Mn}	initial Mn^{2+} uc^{-1}	R_{Mn} Mn^{2+} uc^{-1}	Na^+, NH_4^+ uc^{-1}	degree of exchange (%)	a_0/Å	R_{Mn} Mn^{2+} uc^{-1}	Na^+, NH_4^+ uc^{-1}	degree of exchange (%)	a_0/Å
0	0	0	56	0	24.659	0	17	0	24.67
	one-phase	0				0			
0.087	8.3	0.074	41.6	25.4	24.653	0.065	4.5	22.2	24.66
	one-phase	7.1				6.2			
0.100	9.6	0.088	38.8	30.5	24.647	0.072	3	24.6	24.66
	multi-phase	8.5				6.9			
0.150	14.4	0.086	39.3	29.7	24.650	0.072	3	24.6	24.66
	multi-phase	8.3				6.9			
0.200	19.2	0.088	38.8	30.5	24.648	0.071	3.2	24.2	24.66
	multi-phase	8.5				6.8			

uc: unit cell.

Above 1073 K the zeolite is seen to disappear and a new crystalline phase appears; for $R_{Mn} = 0.6$ at 1113 K this is $Na_2Mn_6Si_7O_{21}$ [monoclinic; $a_0 = 9.80$ Å, $b_0 = 13.32$ Å, $c_0 = 5.40$ Å and $\beta = 73°$ (JCPDS n° 30-1220)], accompanied by other, unidentified crystalline phases.

3.1.2 LaNaY–MnCl$_2$·4H$_2$O system. *Insertion.* Table 1 gives the variations in a_0 and the crystallinity with R_{Mn} for a given temperature.

When $T_t < 443$ K, the two initial phases coexist, whatever the composition and the treatment time, as in the previous system.

For $T_t = 443$–533 K, X-ray diffraction indicates a one-phase ($R_{Mn} \leqslant 0.066$) or multi-phase system ($R_{Mn} > 0.066$) at $T_t = 503$ K. This temperature range is fundamental, since it was seen for all oxides which insert, for the same reasons as were given above for NaY. Elemental analysis for $R_{Mn} = 0.066$ before and after thermal treatment and after washing shows, as for NaY, that insertion is reversible and that there is no cation exchange.

For $T_t = 533$–573 K, the maximum insertion corresponds to $R_{Mn} = 0.055$. For $R_{Mn} > 0.055$ the system is two-phase.

For $T_t = 573$–623 K, LaNaY alone is limited to $R_{Mn} \leqslant 0.043$ at $T_t = 593$ K. Beyond this R_{Mn} value anhydrous MnCl$_2$ accompanies the zeolite.

Cation exchange. For $T_t = 623$–823 K, as in the previous system, washing the LaNaY-MnCl$_2$·4H$_2$O mixtures with $R_{Mn} \leqslant 0.200$, which have been treated at 683 K for 16 h, leads to partial elimination of the Mn^{2+} and NH$_4^+$ (elemental analysis). Table 2 gives the different degrees of cation exchange at 683 K for each initial $R_{Mn} \leqslant 0.200$. The greatest degree of exchange, obtained as soon as initial $R_{Mn} = 0.100$, is smaller than with NaY. This can be explained by the lesser population of Na$^+$ and NH$_4^+$ in the supercages and the absence of even partial substitution of La^{3+} by Mn^{2+}.

Solid–solid reaction. Between 823 and 963 K there exists slightly amorphous LaNaY zeolite, with Mn$_2$O$_3$ and Mn$_3$O$_4$, for the same R_{Mn} range as with NaY.

For $R_{Mn} > 0.150$ at $T_t > 1013$ K, apart from partially broken down zeolite, there is a solid–solid reaction with formation of the same sodium manganites as with NaY.

Finally, upon treatment at high temperature ($T_t = 1273$ K) for 72 h, LaNaY progressively disappears, and LaMnO$_3$ [orthorhombic; $a_0 = 5.53$ Å, $b_0 = 5.72$ Å and $c_0 = 7.69$ Å (JCPDS n° 33-713)] is formed with other unidentified crystalline phases.

3.2 Xenon adsorption and ^{129}Xe NMR

The xenon adsorption isotherms for Y zeolites and the mixtures treated at 503 K for 16 h (maximum insertion) and those treated at 683 K for 16 h (maximum exchange) are determined at 299.5 K. All these isotherms are reversible and there is no adsorption of Xe by MnCl$_2$·4H$_2$O. The plots of log N vs. log P are almost parallel (Fig. 1) for all the samples; N is the number of xenon atoms adsorbed per g of dehydrated zeolite and P is the equilibrium xenon pressure. For $P < 1000$ torr the isotherm of LaNaY is above that for NaY (supercages less crowded and stronger interaction with the La^{3+} cations). It is the same for the isotherm of the LaNaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.066$) sample treated at 503 K, which is above that of the NaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.052$) sample treated at the same temperature. However, both of these isotherms are below that for pure zeolite. These results show that the pore system has been affected by the introduction of the halide.

On the other hand, the isotherms for the samples treated at 683 K, which show the greatest cation exchange (30.5% for NaY, corresponding, after washing, to $R_{Mn} = 0.088$, and 24.6% for LaNaY, corresponding to $R_{Mn} = 0.072$), differ slightly from those where insertion occurs (Fig. 1). The isotherms are curved at low Xe pressures and then run almost
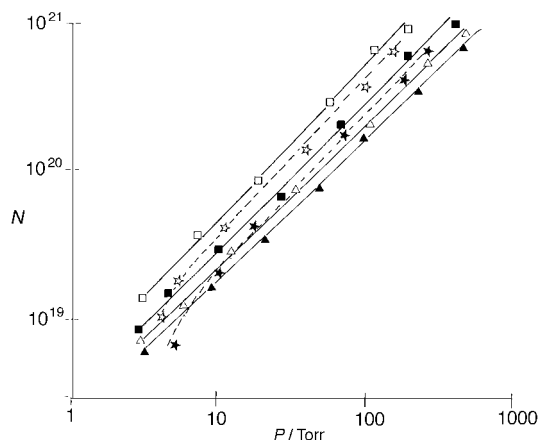

Fig. 1 Log–log plots of the number N of adsorbed xenon atoms per g of anhydrous zeolite at 299.5 K vs. xenon pressure P for samples treated at 503 K for 16 h (insertion): (■, ———) NaY (▲, ———) NaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.052$); (□, ———) LaNaY; (△, ———) LaNaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.066$). Samples treated at 683 K for 16 h then washed with hot water (exchange): (★, – – – –) NaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.088$); (☆, – – – –) LaNaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.072$).

parallel to the isotherms for pure NaY and LaNaY zeolites; both are very close to the corresponding zeolite. For a given Xe pressure, the quantity adsorbed is much greater for the exchanged zeolites than when there is insertion, since exchange modifies the supercage volume less than insertion.

Whatever the sample, the ^{129}Xe NMR spectrum consists of only one line. For the pure zeolites the chemical shift δ_{Xe} increases linearly with N (Fig. 2). For the mixtures treated at 503 K, where insertion is greatest, the $\delta_{Xe} = f(N)$ plots go through a shallow minimum at low xenon concentrations and are then linear slightly above the previous ones, with a slightly greater slope. This variation in the slope is related to the decrease in the free pore volume in which the xenon is adsorbed.

The increase in δ_{Xe} and the presence of a minimum indicate that there are stronger xenon adsorption centres in the supercages than in the pure zeolites and that these can only be inserted species. In this case, when the xenon concentration is
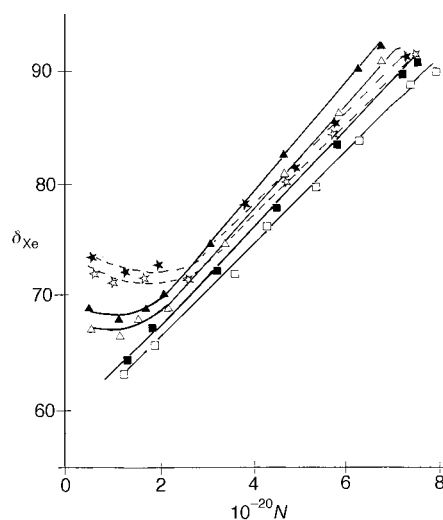

Fig. 2 ^{129}Xe chemical shift δ_{Xe} vs. the number N of adsorbed xenon atoms per g of anhydrous zeolite for samples treated at 433 K for 7 h (insertion): (■, ———) NaY: (▲, ———) NaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.052$); (□, ———) LaNaY; (△, ———) LaNaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.066$). Samples treated at 683 K for 16 h, then washed with hot water (exchange): (★, – – – –) NaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.088$); (☆, – – – –) LaNaY–MnCl$_2$·4H$_2$O ($R_{Mn} = 0.072$).

low, it is mainly adsorbed on these sites; then, when the concentration increases, adsorption on the weaker sites occurs. As a result of fast exchange between sites the chemical shift of the single coalescence signal falls when N increases, goes through a minimum and then increases when Xe–Xe interactions become important.

The $\delta_{Xe} = f(N)$ plots for the systems which exchange the most at $T_t = 683$ K (Fig. 2) are the same shape, but they show a higher shift and a more pronounced minimum, displaced towards high concentrations. This difference can be attributed to an even stronger interaction than before between the xenon and the strong sites. It can easily be explained by the fact that, in cation exchange, the Mn^{2+} cations are free to interact directly with the xenon. In the case of insertion, the Mn^{2+} interaction is more or less masked and hindered by the presence of Cl^-. Finally, the smaller slope clearly corresponds to the elimination of the initially inserted phase.

3.3 ^{29}Si NMR

3.3.1 NaY–MnCl₂·4H₂O system. The experimental ^{29}Si MAS NMR spectrum of NaY with a Si/Al ratio of 2.44 consists of five lines, corresponding to five possible environments of Si [Fig. 3(a)]. The spectra of the samples with R_{Mn} and T_t less than or equal to 0.052 and 503 K, respectively [Fig. 3(b)], are identical with that of NaY with the same Si/Al ratio.

At $T_t = 593$ K and $R_{Mn} = 0.039$ the spectrum is still identical with the previous ones. This is true also for the sample with the greatest degree of exchange (30.5% for $R_{Mn} = 0.088$ at $T_t = 683$ K).

When $T_t = 953$ K, for $R_{Mn} \leqslant 0.400$ the spectra of the treated samples become less well resolved [Fig. 3(c) and (d)]; this result is consistent with the X-ray diffraction data.

3.3.2 LaNaY–MnCl₂·4H₂O system. LaNaY treated at 730 K for 24 h shows the ^{29}Si spectrum given in Fig. 4(a).[3,4] That corresponding to the sample with $R_{Mn} = 0.066$ at $T_t = 503$ K, where insertion is most important, is identical with the previous one, showing that insertion does not affect the lattice. The sample whose greatest degree of exchange is 24.6% for $R_{Mn} = 0.072$ at $T_t = 683$ K has the same spectrum as the two previous ones.
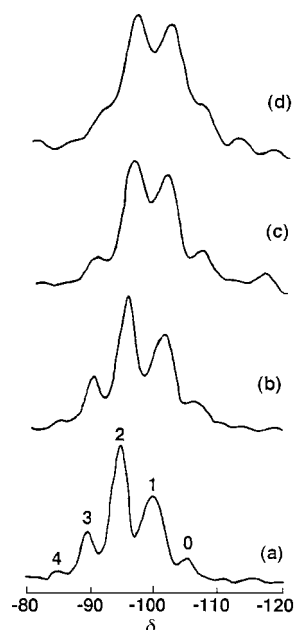

Fig. 3 ^{29}Si MAS NMR spectra of: (a) NaY zeolite at room temperature and treated with MnCl₂·4H₂O at various temperatures and compositions to give (b) $R_{Mn} = 0.052$, $T_t = 503$ K (insertion) or $R_{Mn} = 0.047$, $T_t = 653$ K (exchange); (c) $R_{Mn} = 0.200$, $T_t = 953$ K (solid–solid reaction) and (d) $R_{Mn} = 0.400$, $T_t = 953$ K (solid–solid reaction). In (a) the integer $n = (0$–$4)$ means Si(nAl), the number of aluminium atoms surrounding a silicon atom.
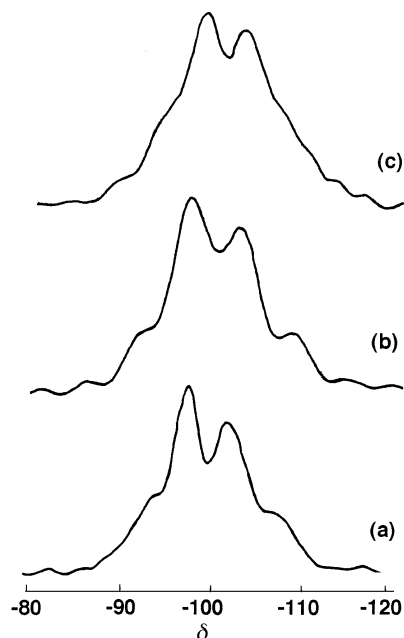

Fig. 4 ^{29}Si MAS NMR spectra of (a) LaNaY zeolite at 730 K treated with MnCl₂·4H₂O at various temperatures and compositions to give: (b) $R_{Mn} = 0.200$, $T_t = 953$ K (solid–solid reaction) and (c) $R_{Mn} = 0.400$, $T_t = 953$ K (solid–solid reaction)

Finally, for $R_{Mn} \leqslant 0.400$ and $T_t = 953$ K [Fig. 4(b) and (c)] the spectra consist of broad signals. These results are in agreement with the X-ray diffraction results which indicate partial amorphization.

4 Conclusions

X-Ray diffraction, xenon adsorption isotherms, ^{29}Si MAS NMR and ^{129}Xe NMR have been used to study the interactions and reactions of manganese chloride with Y zeolites between 443 and 1273 K. The differences in the structural properties of NaY and LaNaY (in the latter case, the lesser crowding of the supercages, higher acidity and stronger interaction with the cations remaining in the cages) explain why, at 443–533 K, the maximum degree of MnCl₂ insertion is greater for the latter and the cation exchange capacity of Mn^{2+} at 613–823 K is lower (24.6% instead of 30.6% for NaY at 683 K). Beyond 1013 K solid–solid reactions are observed between each of the zeolites and the halide.

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