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the crystal surface (Fig. 2 c, treatment 3), where they readily re-oxidise into (probably) bulky Ga₂O₃ oxidic species upon the final calcination in air.

Our RRS data suggest that if mobility, redispersion and specific re-location of extra framework Ga species is desired to achieve an efficient catalytic phase, the calcination treatment must involve a combined steaming-reducing step.

REFERENCES

1. V. Kanazirev, V. Mavrodinova, L. Kosova and G.L. Price, *Catal. Letters*, **9**, 35 (1991) 2.
G. Giannetto, G. Leon, J. Papa, R. Monque, R. Galiasso and Z. Gabelica, *Catal. Letters* **22**, 273 (1993)
3. G. Giannetto, R. Monque and R. Galiasso, *Catal. Rev.-Sci. Eng.* **36**, 271 (1994)
4. V.R. Choudhary, P. Devadas, A.K. Kinage and M. Guisnet, *Zeolites*, **18**, 188 (1997)
5. E.G. Derouane, S.B. Abdul Hamid, I.I. Ivanova, N. Blom and P.E. Højlund-Nielsen, *J. Mol. Catal.*, **86**, 371 (1994),
6. Z. Gabelica, G. Giannetto, F. Dos Santos, R. Monque and R. Galiasso, in: Proceedings of the 9th International Zeolite Conference, Edited by R. von Ballmoss, J.B. Higgins and M.M.J. Treacy (Butterworth and Heinemann, Boston, Massachusetts, 1993), pp 231-238
7. G.L. Price, V.I. Kanazirev and K. Dooley, *Zeolites*, **15**, 725 (1995)
8. A.V. Kucherov, A.A. Slinkin, H.K. Beyer and G. Borbely, *J. Chem. Soc. Faraday Trans*, **1**, 85, 2737 (1989)
9. A. Montes, Z. Gabelica, A. Rodriguez and G. Giannetto, *Appl. Catal. A*, **161**, L1 (1997)
10. K.J. Chao, S.P. Sheu, H.L. Lin, M.J. Genet and M.J. Feng, *Zeolites*, **18**, 18 (1997)
11. M. Jacobs and F. Bodart, *Nucl. Instr. and Meth. in Phys. Res. B*, **118**, 714 (1996)
12. Z. Gabelica and S. Valange, *Res. Chem. Intermediates* **24**, 227 (1998)
13. Z. Gabelica, C. Mayenez, R. Monque, R. Galiasso and G. Giannetto, in: Synthesis of Microporous Materials. Vol I: Molecular Sieves, Edited by M. L. Occelli and H. E. Robson (Van Nostrand Reinhold, New-York, 1992), pp 190-221.

CHARACTERIZATION OF K⁺ ION EXCHANGE INTO Na-LSX USING TIME RESO SYNCHROTRON X-RAY POWDER DIFFRACTION AND RIETVELD REFINEMENT

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ABSTRACT

The pathway along which K⁺ replaces Na⁺ in Low-Silica X (LSX) has been determined using a combination of time-resolved synchrotron X-ray powder diffraction data collected translating imaging plate and Rietveld structure refinement. In agreement with the *ex situ* collected on this same system, the exchange proceeds through a two-phase region. The two phases are distinguished by K⁺ occupancy of site I in the second phase to appear during continuous exchange. To obtain kinetic information and to automatically monitor the experiment, the Target Transformation Factor Analysis (ITFA) was used to analyze the data. To investigate exchange mechanism in detail, higher time resolution was provided by using a CCD detector preliminary modeling of the diffraction data collected using the CCD indicates that only the sites, II and III', are replaced at the early stage of the exchange.

INTRODUCTION

Of the faujasite-type zeolites [1], Low-Silica X (LSX) [2-3] has improved performance characteristics in ion exchange and adsorption applications [4]. While most ion exchange studies have been performed on bulk samples using *ex situ* analysis techniques, time-resolved studies have the potential to provide information on transient phenomena masked in *ex situ* studies.

We have previously reported a combined NMR and *ex situ* X-ray powder diffraction [5] on materials in the Na-K LSX solid solution series. Samples were equilibrated at the 42%, and 80% K⁺-exchange levels following the ion exchange isotherm by Sherry [6], as well as the end members of the solid solution series. At low levels of K⁺ exchange, samples had single MAS NMR bands, and potassium ions preferentially replaced sodium ions at sites I' and were determined from Rietveld refinement. For the sample equilibrated at the 80% K⁺-exchange

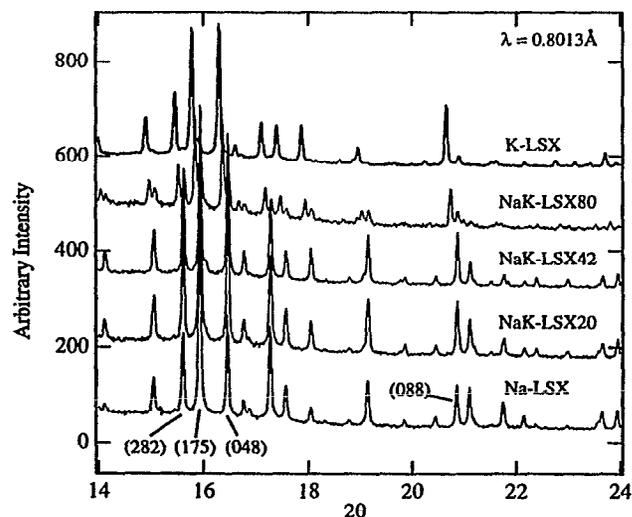


Figure 1. Five synchrotron X-ray powder diffraction patterns (from the *ex situ* study [5]) showing the changes in the relative intensities and peak positions as K^+ -exchange percentage increases in the Na-K LSX solid solution series. Note the two phases in NaK-LSX80 which was equilibrated at the 80% K^+ -exchange level [6].

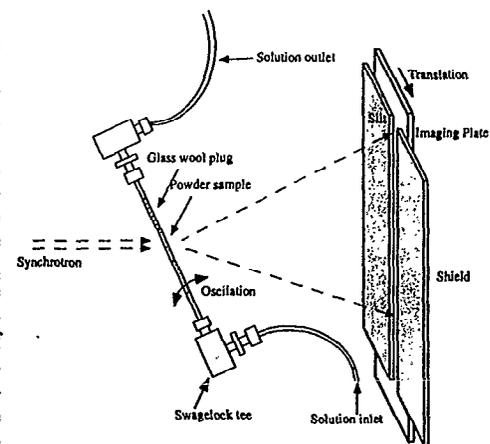
two phases were observed in both the X-ray powder diffraction pattern (Figure 1) and as evidenced by the two ^{29}Si resonances in the NMR [5]. The phase to appear at the higher K^+ -exchange levels has a larger unit cell volume. Rietveld structure refinement confirmed the abrupt increase in volume coincided with the occupancy by K^+ ions of site I, the double 6-ring site (Figure 1). In the present study, *in situ* synchrotron X-ray powder diffraction was utilized to examine the pathway along which K^+ ion exchange occurs in Na-LSX. By using imaging plates and monochromatic synchrotron X-radiation, time-resolved data of sufficient quality to allow full Rietveld refinement [7-8] were obtained. We have also performed a preliminary study using a CCD detector in an effort to monitor this reaction with higher time resolution, especially at the beginning of the exchange process.

EXPERIMENTAL

Na-LSX was prepared by ion exchange of NaK-LSX ($\text{Na}_{1-x}\text{K}_x\text{Al}_2\text{Si}_6\text{O}_{14}\cdot n\text{H}_2\text{O}$) with 1.0 M NaCl solution. The ^{29}Si and ^{27}Al MAS NMR measurements indicated a Si to Al ratio of unity, and ICP elemental analysis confirmed complete exchange after four 24-hour treatments at 80 °C. This material, Na-LSX ($\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}\cdot n\text{H}_2\text{O}$), was used for *in situ* ion exchange.

Time-resolved powder diffraction studies were performed at beamline X7B of the National Synchrotron Light Source (NSLS), using a Small Environmental Cell for Real Time Studies (SECRets) [9] and a Translating Image Plate (TIP) [10] detector system (Figure 2). The Na-LSX powder was loaded into a 0.5 mm glass capillary that was plugged with glass fiber at both ends.

Figure 2. The Translating Imaging Plate system, as used at beamline X7B of the NSLS along with a schematic representation of the SECRets setup for *in situ* ion exchange. The capillary is held in place with a Swagelock tee, which is then mounted on a standard goniometer head (not shown), where centering adjustments and translations can be made. The exchange solution is passed over the sample through the inlet port using N_2 over pressure and then exits through the outlet port. Diffracted X-rays are collected on an imaging plate, a portion of which is covered by shields. Translation of the plate (arrow) behind a slit allows a fresh region of the plate to receive X-rays, while covering the exposed portion.



This capillary was mounted on SECRets (Figure 2) and a 0.01 M KCl exchange solution was passed over the sample using an over pressure of 30 psi of N_2 gas at room temperature. The TIP detector recorded the diffraction pattern over 6 hours ($\lambda = 0.9949\text{\AA}$) behind a slit of width 3 mm with a step counting time of 24 seconds and a step size of 0.2 mm.

A similar setup with a CCD detector was utilized at beamline X7A of the NSLS. The detector was set at $2\theta = 23^\circ$ with a sample to detector distance of 30.9 cm, covering a 2θ range from 17.7° to 28.2° ($\lambda = 0.7000\text{\AA}$). Diffraction patterns were recorded for every 60 second on a small area CCD chip (6.25×6.25 cm) without the slits (Figure 2).

RESULTS AND DISCUSSION

Only one set of peaks were observed during the first 30 minutes of the ion exchange (Figure 3). Two sets of peaks, which could be indexed as two separate face-centered cubic phases, were present after this initial stage. The second set of peaks were shifted to a lower 2θ value relative to the peaks from the original phase, indicating a larger unit cell. This was consistent with the *ex situ* observation where the sample of 80% K^+ -exchanged LSX consisted of two different phases [5]. These two phases were designated as A and B (Figure 3) for the discussion below.

Rietveld refinement of structural models for phases A and B was performed using data integrated at different times during the exchange. The structural parameters refined from the previous *ex situ* study [5] were used to construct and constrain starting models. Since knowledge of the cation distribution in each phase was important to understand the ion exchange process, only occupancies of cations and water molecules were refined in those cases where two phases were present

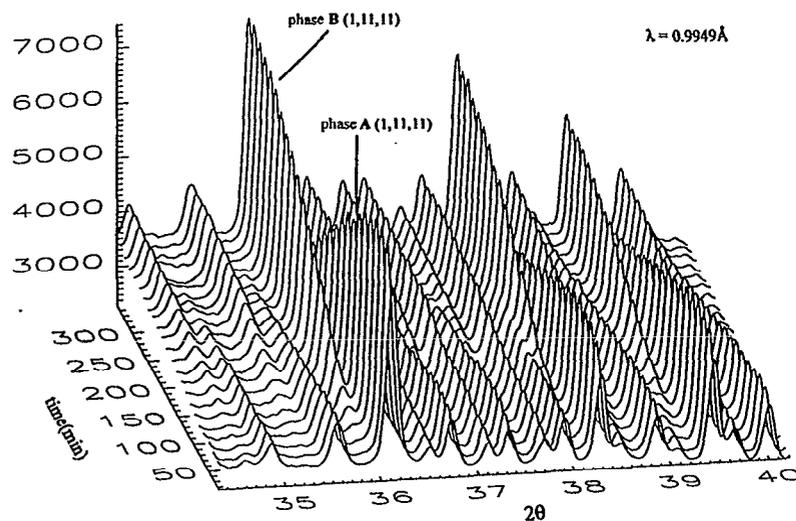


Figure 3. Plot of the X-ray powder diffraction profiles as a function of time during the 6 hours of K^+ exchange into Na-LSX. The patterns are obtained by integrating the imaging plate vertically with an integration width of 3 mm, about the size of the slit (Figure 2).

in the patterns (Figure 3). The positions of all the atoms were held fixed according to the result from the *ex situ* study (Figure 4) [5].

The results of the refinements using data taken at the initial and final portions of the *in situ* scan (Figure 3) were similar to the structural models of the Na-LSX and K-LSX from the previous *ex situ* study [5]. In the two-phase region, phase A was characterized by having K^+ ions at sites I' and II while phase B was distinguished from phase A by having K^+ ions at site I as well as at sites I' and II. It is this occupancy of site I by K^+ ions that is responsible for the lattice parameter expansion in agreement with the *ex situ* observation [5]. In both phases, sites I' and II exhibited mixed occupancies by Na^+ and K^+ ions (Figure 4). Site III' was modeled using an oxygen scattering factor due to the possible disordering at this weakly bound site [11].

The changes in potassium occupancy at sites I, I' and II (Figure 5) indicated a time-dependent and site-specific ion exchange process. In phase A, potassium ions first replaced sodium ions at site II. The occupancy of K^+ at site II increased until sodium ions at site I' were exchanged, at which stage phase B appeared. In phase B, potassium occupancy at sites I and I' as a function of time trended in opposite directions, suggesting the diffusion of K^+ ions from site I' into site I (Figure 5). There was a continuous increase of potassium ions at site II during the *in situ* scan.

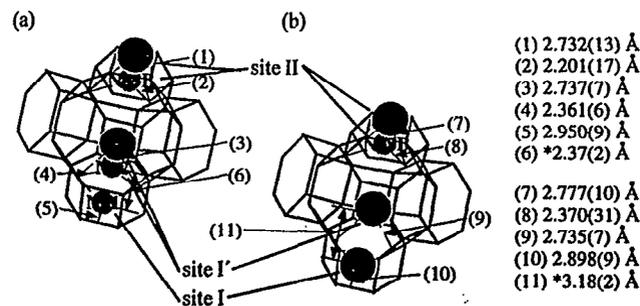
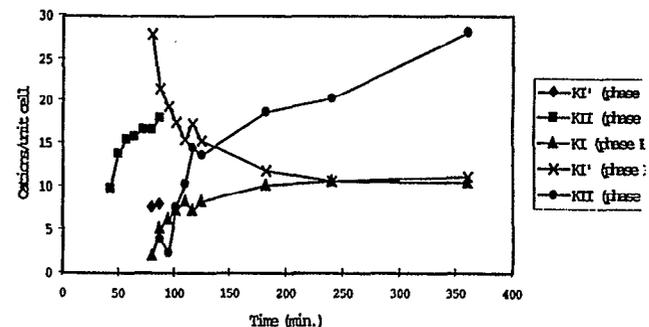


Figure 4. A schematic illustration of cation distribution in phase A and phase B. The coordination distances shown here were determined from the *in situ* study on NaK-LSX80 [5] were used as fit parameters in present work (

multaneous occupancy is not allowed at these closely separated sites).

Figure 5. Changes in potassium occupancy at sites I, I' and II as determined from the Rietveld refinement (data from phase A are shown only up to 87 minutes for clarity).



Kinetic information and which initial patterns to use for Rietveld refinement were obtained using Iterative Target Transform Factor Analysis (ITTTFA) [12]. Component phases identified from the ITTTFA were categorized as four different 'events' (Figure 6a). Event 1 was attributed to errors associated with imaging plate geometry such as tilt and zero point errors, which were corrected [13]. Events 2 and 4 represented the disappearance of phase A and the growth of phase B respectively. The remaining event 3 reflected the two-phase region where phases A and B were present. Events 2, 3, and 4 were combined, and normalized fractions of the combined events were plotted against reaction time (Figure 6b). These data were fit with the Avrami [14] equation [$\alpha \exp(-kt)^n$] where α is a normalized fraction of each component phase. From fits of both curves the rate constant (k) was determined to be 4×10^{-6} and $n = 2.3$.

Some information regarding the exchange mechanism may be obtained from these curves. For example, previous *in situ* X-ray diffraction studies have used the exponential factor (n) to propose reaction mechanisms [13, 15]. A value of 2.3, as determined in the present study, is suggestive of a diffusion controlled process with a decreasing rate of nucleation [16]. A more thorough

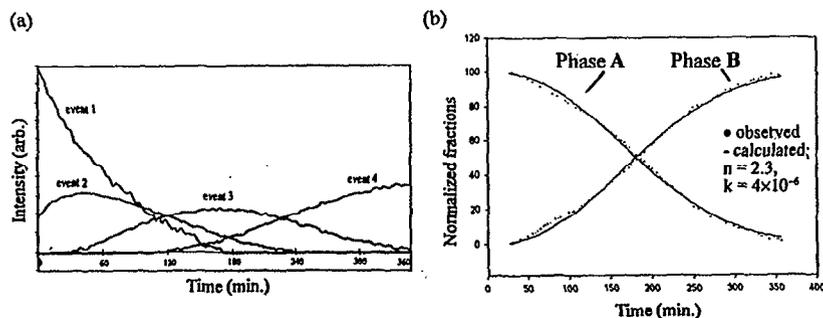
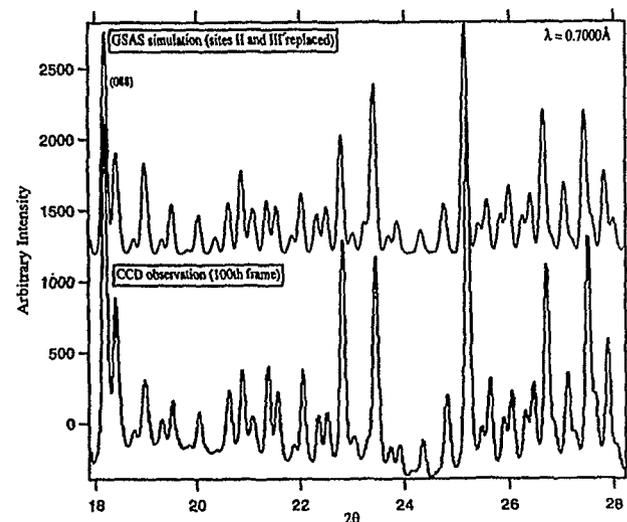


Figure 6. (a) ITTFA results showing the four 'events' of the ion exchange reaction. (b) Normalized fractions of the combined events and fits to the Avrami equation ($\alpha=1-\exp(-kt)^n$, see text for details)

analysis of how ITTFA results can be correlated to reaction mechanism and used to determine critical data for Rietveld analysis is underway.

One disadvantage of the TIP system is the requirement that the plate needs a full exposure before readout. This makes it difficult to observe transient phenomena which can occur in the early stages of reaction. An electronic detector, such as a Charge Coupled Device (CCD) detector, can provide a higher time resolution and real time observation. For this investigation, the CCD detector

Figure 7. Calculated and observed powder diffraction patterns suggesting the initial transient stage where the wall sites (sites II and III') in the supercage are first replaced by K^+ ions (also note the difference in backgrounds).



was set for 1 minute exposures during the ion exchange reaction. Two phases were observed: the quasi-real time scan, and a model for the initial stage of the ion exchange was compared with a calculated powder diffraction pattern with a CCD detector observation.

Considering this simulation and the Rietveld refinement results derived from the full pathway of K^+ ion exchange into Na-LSX can be drawn as follows. Potassium ions replace sodium ions at sites II and III' in the supercage in the early stage of the ion exchange. This is followed by the diffusion of K^+ ions into the sodalite cage where they are exchanged (Figure 5). With those sites loaded with potassium cations, further K^+ ion exchange into Na-LSX causes a phase transition, expanding the unit cell by positioning K^+ ions in the double 6-ring site (Figure 4).

This work, combined with the previous *ex situ* study [5], illustrates how cation influence zeolite structures to a significant degree. The key here is the location of potassium at site I, the center of the double 6-ring. Careful examination of the zeolite X structure suggests that expansion or contraction of the double 6-ring potentially has the most impact on structural parameters.

It is notable to consider, however that the *ex situ* study [5] was performed on equilibrated samples at each desired K^+ -exchange level while the initial transient stage was from the *in situ* work. More detailed kinetic information can be derived by performing experiments at different temperatures. For example, information on the activation energy of the exchange can form a basis to tailor the properties such as the selective adsorption [17] as a function of different cation distribution and the structural phase transitions they induce.

CONCLUSIONS

Time-resolved synchrotron X-ray powder diffraction was utilized to investigate the transition occurring upon K^+ ion exchange into Na-LSX. The results from the previous *ex situ* X-ray powder diffraction study performed on several equilibrated samples in the solution series of LSX formed the basis for this *in situ* work and were consistent with our findings. Rietveld structural refinement on the two phases formed during the *in situ* work focused on different cation distribution in each phase. Potassium siting at site I characterizes the expanded phase which was last exchanged by K^+ ions.

The extraction of kinetic information from ITTFA treatment of the time-resolved data, though preliminary, demonstrated the potential for this combination of techniques in diffraction experiments. Exploratory use of a CCD detector enabled us to observe the initial stage of the exchange of Na^+ by K^+ where the supercage wall sites, II and III', were first replaced by potassium ions.

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REFERENCES

1. D. W. Breck, *Zeolite Molecular Sieves*. (Robert E. Krieger, Malabar, FL, 1984).
2. G. H. Kuhl, *Zeolites*, **7**, 451 (1987).
3. S. W. Carr; F. Hollway and J. D. Hopwood, Unpublished data.
4. C. G. Coe, S. M. Kuznicki, R. Srinivasan and R. J. Jenkins, ACS Symposium Series, **368**, 478 (1988).
5. Y. Lee, S. W. Carr and J. B. Parise, *Chem. Mater.* (In press) (1998).
6. H. S. Sherry, *J. Phys. Chem.* **70**, 1158 (1966).
7. R. A. Young, *The Rietveld Method* (Young, R. A., Ed., Oxford University Press Inc., New York, 1995).
8. A. C. Larson and R. B. VonDreele, "GSAS: General Structure Analysis System", (Report LAUR 86-748, Los Alamos National Laboratory, 1986).
9. P. Norby, C. L. Cahill, C. Koleda and J. B. Parise, *J. Appl. Cryst.* **31**, 481 (1998).
10. P. Norby, *J. Appl. Cryst.* **30**, 21 (1997).
11. D. H. Olson, *J. Phys. Chem.* **74**, 2758 (1970).
12. X. Liang, J. E. Andrews and J. A. Haseh, *Anal. Chem.* **68**, 378 (1996).
13. Norby, P. *J. Am. Chem. Soc.* **119**, 5215 (1997).
14. Avrami, M. L. *J. Chem. Phys.* **9**, 177 (1941).
15. Clark, S. M.; Evans, J. S. O.; O'Hare, D.; Nuttall, C. J.; Wong, H.-V. *J. Chem. Soc., Chem Commun.* 809 (1994).
16. Hulbert, S. F. *J. Br. Ceram. Soc.* **6**, 11 (1969).
17. C. G. Coe, T. R. Gaffney, J. F. Kirner, H. C. Klotz, J. E. MacDougall and B. H. Toby, *21th National Meeting of the American Chemical Society*, New Orleans, LA, 1996, AN 1996:221366.

JOINT X-RAY DIFFRACTION / NMR STRUCTURE OF MICROPOROUS FLUORINATED ALUMINO-PHOSPHATES ULM-3 Al AND ULM-4 Al

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ABSTRACT

Two new aluminophosphate phases, ULM-3 Al and ULM-4 Al, were synthesized hydrothermally. Single crystals as well as powders have been studied by high resolution solid state 1D and 2D NMR. Several 2D NMR experiments, MQMAS, and high resolution 1D experiments, using various pulse sequences have been combined with X-ray diffraction to solve properly the structures of these compounds and to establish firmly that their symmetries are low.

The hexameric unit, which is found in both structures with a different orientation, is believed to be the structural building unit of a larger class of structures which is replaced by aluminum or iron.

INTRODUCTION

Since the first series of microporous aluminophosphates, denoted ULM-1 Al, were synthesized in 1982⁽¹⁾, these materials have been extensively studied. The introduction of fluorine during synthesis⁽²⁾ strongly modifies the pH of the solutions and has led to new topologies. In many cases, the fluorine is incorporated into the structural cages as in cloverite⁽³⁾ or in the coordination polyhedra (M = Al or Ga) as in the ULM-n⁽⁴⁾ or T-GaPO^{(5),(6)} series. Besides the hexameric unit stabilized by the fluoride anion, the hexameric cluster Ga₃(PO₄)₃F₂ is a common building unit encountered in the fluorinated gallophosphates. This unit has now been extended to the aluminum and iron systems in which it has been observed.^{(8),(9)}

Solid state NMR has been used extensively to characterize microporous materials especially silicate containing materials as well as aluminophosphates. NMR characterization is involved can be sorted out into two situations. If a single crystal is obtained, in order to establish the structure by X-ray diffraction, NMR is used to check the NMR methods. The other situation is to use NMR