Merlinoite synthesis studies with and without organocations

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A novel synthesis of zeolite W (MER phase) was carried out combining the use of an organocation 'template' molecule and zeolite K-Y as the aluminium source. The reaction was carried out at lower than usual OH^-/SiO_2 reactant ratios and that translated into an exceptionally high SiO_2/Al_2O_3 ratio (SAR) of 7.7. This novel synthesis was contrasted with a recently described, wholly inorganic route to zeolite W, and with some previous organocation mediated zeolite syntheses. There is less template found inside the pores of W than in other syntheses to products like chabazite. For the wholly inorganic route, a novel synthesis strategy of removing the initial crystallization products, and then letting the crystallization proceed, was found as a successful route to W. The role of OH^-/SiO_2 ratios was studied in an effort to bridge the inorganic chemistry for W *vs.* LTL crystallization and the role the template can play. A surprising outcome of the study was that the unit cell volumes are quite close for the W zeolites produced by the different syntheses routes we describe, even though their SAR values differ.

The earliest laboratory syntheses of zeolites concentrated on inorganic reactions, with aluminium atoms comprising a sizable number of lattice tetrahedral positions (the limit from Lowenstein's rule is 50%).[1] To compensate for the charge on aluminate centers, the products also contained many alkali- or alkaline-earth-metal cations. In this sense, the reactions mimicked geological compositions for the formation of natural zeolites.[2] Zeolites such as W, which fit the above criteria, were amongst the early zeolite discoveries. Zeolite W has the merlinoite (MER) structure.

Our research program in the study of the synthesis of high silica zeolites has closely followed the influence of organocations on the crystallizing phase selectivities. In the process of scanning the range of influence of a given organocation, one learns that not all inorganic conditions will support the selection of a single unique phase. We recently discussed this issue in terms of finding the 'topological barriers' in a crystallization field of two dimensions, characterized by reactant OH^-/Si and Si/Al ratios.[3–5]

Nonetheless, an empirical observation for high silica zeolite syntheses is that the majority of systems producing new phases occur with OH^-/Si usually <0.5, and the resulting products have SiO_2/Al_2O_3 (SAR, an abbreviation used to describe this oxide ratio) of $\geqslant 15$. In contrast, the earliest inorganic systems required OH^-/SiO_2 reactant values above 0.80 and the SAR of the products was usually below 10. A value of OH^-/SiO_2, $0.5<x<0.8$ gives a transition region with a limited number of products, albeit novel, and possessing SAR in the range 6–15 if an organocation is employed. For this reaction region, the synthesis must compete with the formation of one product which does not even necessitate the presence of the template, and that is mordenite. At $OH^-/Si>0.8$, the reactant silicates will have a very high solubility. The extent of crystallization will depend largely on the Al content. Products will tend to be Al-rich with SAR <6. With the increase in the Al contribution to the T-atom population, no zeolite structures with 5-ring subunits are seen. The majority of high silica zeolites have this subunit as their major contributing substructure. At one time, these zeolites were collectively referred to as pentasils.[6] Fig. 1 is an attempt to summarize some of the relationships.

We had found some unique zeolite materials by operating in the $OH^-/SiO_2=0.5$–0.8 window and using organocations.[7] Consistent with our previous notions about building subunits, all of these materials contain 4- and 6-rings, no 5-rings, and are cavity structures accessed by small pores (8-rings). We have recently shown how the organocation size contributes to this cavity/small pore structure selectivity.[4] Scheme 1 shows the organic structures, the zeolites made, and their structures if they are known at present [ref. 8–12 for SSZ-13, 16, 17, 19 and 39, respectively].

Eventually, our research approach turned to operating within this OH^-/SiO_2 regime but using Y zeolite as the Al source.[13] Na-Y provided for a high surface area, potentially rapidly reacting reagent and the Al centers were already isolated and might be delivered to the reaction at a steady rate, possibly changing the kinetics and, therefore, the phase selectivity. Because of the potential importance of modifying the kinetics, our next extension was to modify the Y zeolite reagent by ion-exchanging other cations into the structure.[14] Some of the transition metals we had exchanged into Y zeolite would have limited solubility (back out of the Y zeolite) in highly alkaline conditions. Changing the rate for Al delivery towards nucleation and the introduction of cations with limited solubility, provided the potential to change both crystallization rate, and more importantly for us, product selectivity.

In the course of studying a potassium-exchanged Y zeolite in reactions with a variety of templates and using sodium silicate as SiO_2 source, a merlinoite phase (MER) crystallized in the presence of template B34 (this template makes SSZ-39 in the all-Na system, as shown in Scheme 1). In order to more carefully understand the unexpected crystallization of a MER phase, we also set to work to make the non-templated, Al-rich MER phase. A key question to resolve was why the new system was successful at a much lower OH^-/SiO_2 ratio.

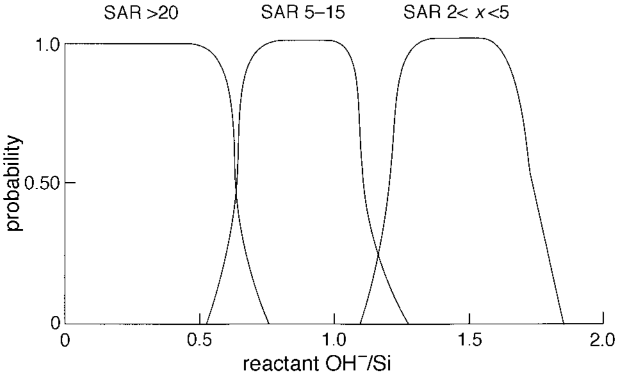
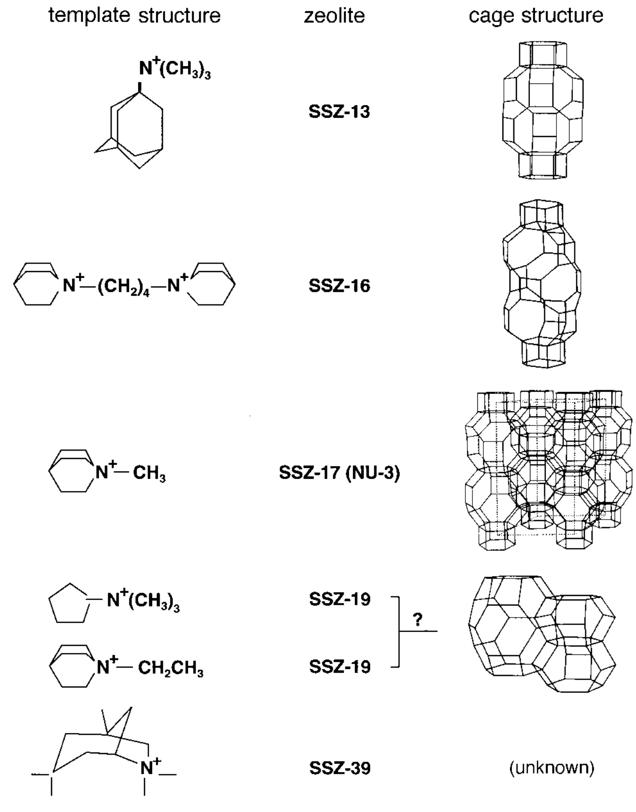


Fig. 1 A graphical representation of the probability of the SiO_2/Al_2O_3 ratio (SAR) of a zeolite product based upon the initial OH^-/Si ratio; this assumes the Si/Al reactant ratio is $\geqslant 5$



Scheme 1

Experimental

Zeolite syntheses

Table 1 contrasts the starting reaction conditions for synthesizing MER with/without template molecules present. The synthesis runs were carried out in the Teflon liners for the respective size Parr stainless steel reactors. The enclosed reactors were heated inside Blue M convection ovens. The pressure within the reactors is autogeneous and, in the range of 140–150 °C, is probably in the range of 40–100 psi (1 psi ≈ 6.89476 × 10^3 Pa) for these reactors.

The detailed syntheses of the two MER products are as follows. For the route using an organocation, 2 mmol of template B34 (its synthesis is described in the next section) was dissolved in 5 ml of water in the Teflon cup for a Parr 23 ml digestion bomb; 3 g of Banco 'N' silicate (41% solids) was added next. Then 3 mM of KOH were added. Finally 0.28 g of K-exchanged Y zeolite was added to the reactor. The closed reactor system was heated at 140 °C, without agitation. The reaction was analyzed after 5 days.

For the wholly inorganic system, the reaction was run static, in the Teflon liner of a 125 ml Parr digestion bomb. A first solution was prepared consisting of 2.42 g of sodium aluminate (Mallinkrodt, 76% solids), 8.63 g of 50% NaOH and 10.42 g of water. A second solution contained 28.36 g of solid KOH dissolved in 66 ml of a 10^{-4} M solution of Methylene Blue, with 19.36 g of Cabosil M5 (97% SiO_2, 3% water) blended in. The aluminate solution was mixed into the silicate solution and the resulting blend was heated at 150 °C for 24 h.

Table 1 Initial start point conditions for MER synthesis

parameter	with template	without template
SiO_2/Al_2O_3	35	29
$NAOH^-/SiO_2$	0.59	0.34
KOH^-/SiO_2	0.28	1.31
template/SiO_2	0.10	0.00
H_2O/SiO_2	30	13.8
net OH^-/SiO_2	0.87	1.65
Si source	'N' silicate	Cabosil
Al source	K-Y	sodium aluminate
temperature/°C	140	150
time/d	5	1–2
rpm	0	0
reactor volume/ml	23	125

At the termination of the zeolite synthesis run, the solids were collected on glass frits and washed several times with the funnels filled with water. The air-dried solids were then characterized.

Template synthesis

Template B34 was used to generate merlinoite product from a combination of K-exchanged Y zeolite as Al source and Banco 'N' silicate. The precursor amine, 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane (Aldrich Chemical Company) was methylated with methyl iodide in the presence of a base to scavenge the HI side-product. A solution of 77 g of the amine and 200 g of potassium hydrogencarbonate was generated in 1 l of methanol. Not all the hydrogencarbonate has to be dissolved at the start of reaction. The solution was chilled in an ice-bath, and 221 g of methyl iodide were added in a steady dropwise manner. An internal thermometer was monitored to slow the drop rate if the exothermic reaction rose above 10 °C. After allowing the reaction to come to room temperature as the ice melts, the reaction was stirred for several days at room temperature. The methanol solvent [and unreacted methyl iodide (**CAUTION**: use a well vented hood)] was removed under reduced pressure in a roto-evaporator. The sizeable quantity of solids was then stirred with chloroform (500 cm^3), and the remaining solids were filtered off. The chloroform filtrate was stripped off under reduced pressure, and the remaining organocation solids were then dissolved in hot acetone. Recrystallization takes place as the solution is allowed to slowly cool to room temperature. The microanalytical data showed that the C and N contents of the crystals were within 0.5% of the expected values.

Characterization of solid products

X-Ray diffraction was carried out on a Siemens D 500 instrument. The scanning electron micrographs were obtained on a Hitachi 570A instrument after coating samples with Pd–Au sputtered over the surface. Micropore volumes and surface areas were determined from experiments with nitrogen using a Micromeritics ASAP 2400 system. The elemental compositions of the materials were obtained by inductively coupled plasma (ICP) analyses, carried out at Galbraith Labs (Knoxville, TN).

Results and Discussion

Reactions using template B34

A detailed synthesis was described in the Experimental section. The zeolite crystalline product from this route was more than 95% MER. The K-Y zeolite was completely consumed in this reaction by the time the product was worked up at 5 days of heating. This reaction can be reasonably well monitored by the rise in pH over the course of the reaction. We have previously discussed some of the issues for pH *vs.* crystallization during the transformation of Na-Y to SSZ-13.[15]

The structural projection of MER is given in Fig. 2. The SAR for the product made in the presence of B34 is 7.76. This value is substantially elevated over some of the values described in the original W patent, working without any organic component.[16] Even with an organocation contained within the cavity, the majority of the charge compensation will still have to be taken up by alkali-metal cations.

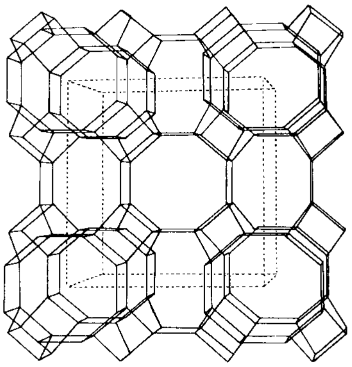


Fig. 2 Model projection of the merlinoite structure. The oxygens, which would appear between the tetrahedral vertices, have been left out to better show the symmetry features of the structure.

The organocation trapped in the zeolite cavities can be removed by thermal decomposition, leaving the porous structure intact for most zeolites. Here, B34 was removed by heating in air, using a slow ramp up to 540 °C. However, prior to calcination, an analysis of the MER product showed that there was only a few mass% carbon in the product. When the organocations fill most of the cavities in these cage-type zeolites, the carbon content is usually 8–12% depending upon the actual zeolite structure. This perspective is certainly well exemplified by the zeolite systems described as specific to certain templates in Scheme 1. What is the evidence that there is B34 in the system? Fig. 3 compares the TG profiles for MER products made with and without B34. In the former case, one sees a high-temperature peak near 450 °C. The desorbed material analyzed as organic fragments (propane and butene). The peak is not large, consistent with the relatively small mass% carbon by analysis. Both samples show similar dominant water loss at much lower temperatures.

While the role of the organocation differs from the previous small-pore zeolites we described above (Scheme 1), where a sizable portion of the interior cavities are filled by organic molecules, we did find that a variety of other organocations had no selectivity to forming MER from K-Y. Some cations could successfully transform the Al source to chabazite-type products (SSZ-13), and some did not produce a transformation of Y zeolite. However, the B34 organocation appears to have a role in at least being able to nucleate the MER crystallization from K-Y and sodium silicate. It may be possible with some tailoring of reaction conditions to grow MER from K-Y in the presence of zeolite seed crystals and removing the need for an organocation like B34 altogether.

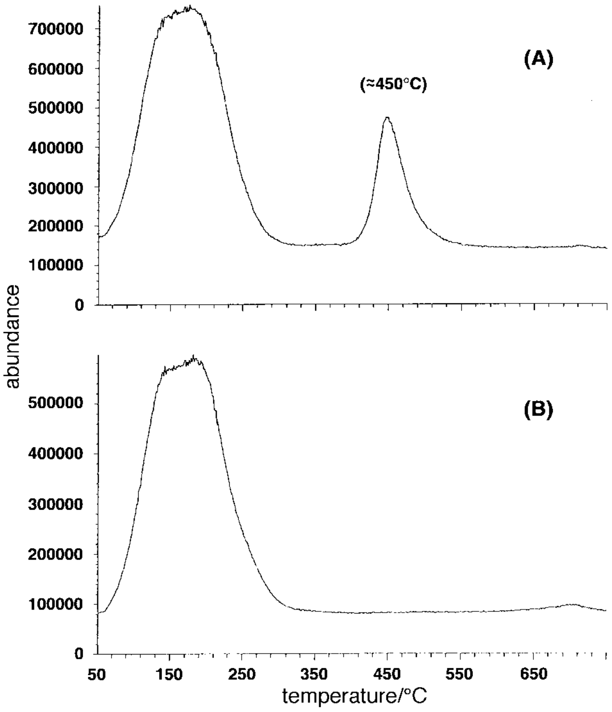


Fig. 3 TG traces for MER products made with and without the B34 organocation. In (A) a high-temperature peak is observed at *ca.* 450 °C. Mass spectrometry shows that it is organic material. The ramp begins at 25 °C and is 10 °C min^{-1}.

Even though there appears to be an insufficient amount of B34 template to fill the cavities of the MER zeolite product, the synthesis reaction is capable of producing a higher SAR product and at considerably lower OH^-/SiO_2 synthesis values. In fact, in this synthesis, the yield based upon use of Al will certainly be higher than conventional MER or zeolite W syntheses; in the 'templated' reaction all the Al is transferred to the product crystal. This is most likely an outcome of the reduced hydroxide contents and subsequent lowered pH values. In the conversion of K-Y zeolite the final pH after several days at 145 °C was 12.4. The pH would need to be still higher for there to be any soluble Al in this solution. This can be compared with the conditions reported by Bieniok *et al.*,[17] which we will explore more thoroughly below, where the pH is always above 13.5 and there is some dissolved aluminate species.

MER synthesis without organocations

In the work of Bieniok *et al.*,[17] the authors define a term $m = (\mathrm{Na+K-Al})/\mathrm{Si}$ for reactant values. Note that if the starting SAR is high, and it is 35 in the 'templated' reaction, then the value of m is not much different from the ratio of the OH^-/Si reactant value. They show that MER crystallization occurs with m above 1.4. In the range of $m = 0.7$–1.2, LTL zeolite is the crystallization product. However, for the synthesis of MER, using the organocation B34 and K-exchanged Y zeolite, we are already crystallizing the product at the low end of the LTL region, at 0.8!

We began to explore the inorganic synthesis, largely adapting conditions from Bieniok *et al.*[17] The synthesis takes place with much higher KOH contents. Our initial runs produced a relatively low yield of product at 24 h of reaction (see Experimental section for details of the synthesis). After 48 h of run there was considerably more product. In both instances, the product was a mixture of MER and CHA (chabazite) phases. Next we tried to make small perturbations in the reaction system towards eliminating the CHA phase. From some of our previous work concerning SSZ-23, we had seen that the CHA nucleation could be inhibited by using small quantities of Methylene Blue dye in the synthesis.[18] The concept here, as described earlier by Whittam and Spencer,[19] was that certain planar, aromatic dye molecules could adhere preferentially to certain crystallographic faces of aluminium-rich zeolites as they were first forming as stable nuclei. This adhesion prevents further crystal growth. In this MER synthesis, the amount of CHA was reduced by this method but certainly not eliminated.

The CHA problem was solved by a rather unusual methodology in zeolite synthesis. The reaction was run at temperature for 24 h, and the reaction was cooled to room temperature (although it was not rapidly quenched as has been described for some zeolite syntheses). At this point, the solids in the bottom of the reactor were separated from the supernatant. The solution was then poured into a clean Teflon liner and heated for an additional 24 h. Further product developed. Upon analysis, it was pure MER. Fig. 4 nicely contrasts the crystallization products with and without CHA formation as a result of employing this tactic. The X-ray diffraction pattern

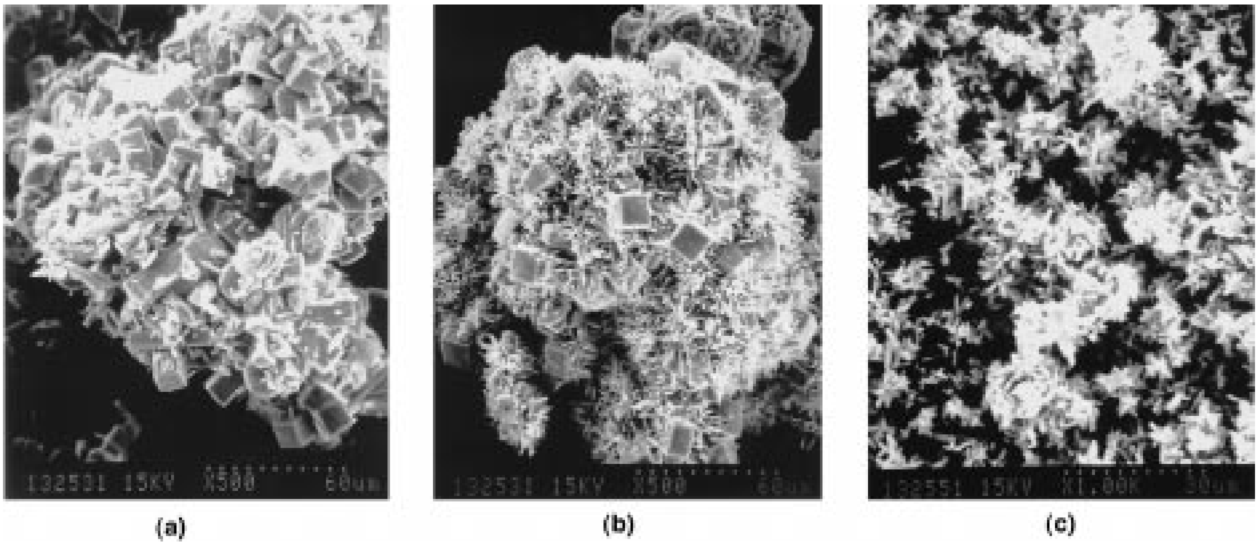


Fig. 4 Scanning electron micrograph pictures for stages of crystallization: (a) 24 h of reaction, (b) 48 h, and (c) 48 h after the 24 hour product was removed. The product is now solely rods of MER.

for the pure MER product is shown in Fig. 5. Also shown is the pattern for the product from the templated route.

MER *vs.* LTL crystallization selectivity

Breck had previously discussed the relationship for LTL and W or MER crystallization in Na,K aluminosilicate gels.[20] We have recast some of Breck's data in Fig. 6, including the location of our experiment *via* the use of this new reagent K-Y. By working with a zeolitic source of aluminium (Y zeolite) and using an organocation we were able to produce an MER structure at lower than usual OH^-/SiO_2 values. Lowering this ratio also allows a higher SAR product to form. This is exactly the same trend we had observed in the synthesis of CHA from Y zeolite and an organocation in contrast to the wholly inorganic route to CHA.[15]

Another interesting trend can be seen in Fig. 6. Both zeolite LTL and Y (FAU) structures can be prepared in the same OH^-/SiO_2 range. It is just the introduction of potassium cations which shifts the product from Y to LTL. Both zeolites are termed 'large pore' because there are portals >7 Å bounded by rings containing 12 tetrahedral atoms. If the OH^-/SiO_2 ratio is increased in the synthesis of LTL, eventually MER becomes the product. MER is a 'small pore' zeolite with the portals defined by an 8-ring of tetrahedral atoms. This exemplifies the trend of more open-pore zeolites to shift to more condensed structures as OH^-/SiO_2 becomes large. If we carried out the same increase in OH^- for Y zeolite, an analogous set of more condensed zeolite structures should result. The principal products would be Na-A and sodalite. Thus, an unusual consequence of the use of some organocations in zeolite synthesis is that while the SAR for a small-pore product is elevated, the OH/SiO_2 barrier for small-pore formation is also being lowered.

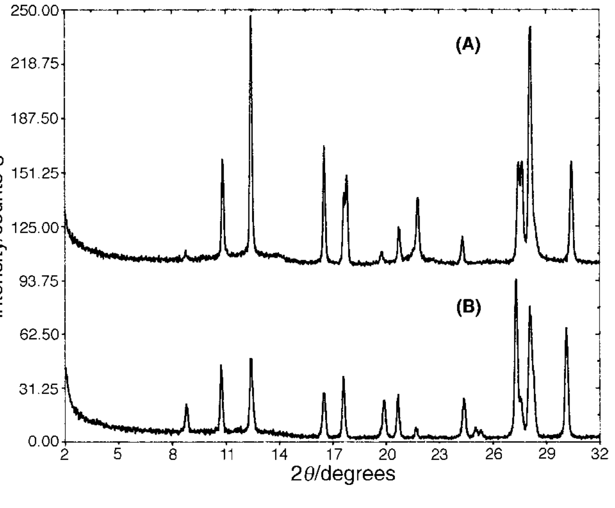


Fig. 5 X-Ray diffraction patterns of the MER phases. (A) is the product from the combined organocation/FAU route and (B) is from the inorganic system (Table 1).

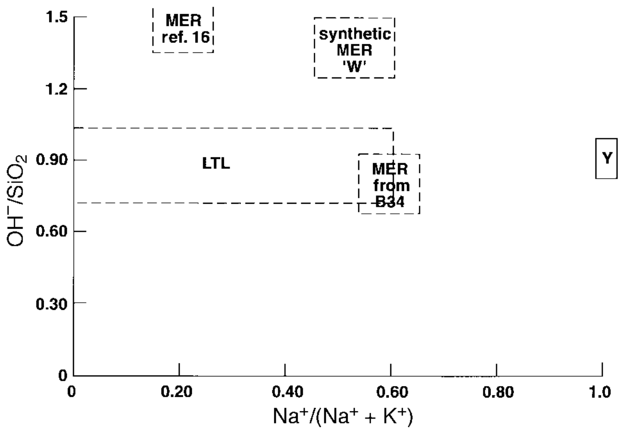


Fig. 6 Product regions for zeolites MER (including 'W'), LTL and Y based upon the OH^-/Si ratio and the relative contribution of Na and K cations. Different synthesis routes can alter the mapping of MER. Adapted in part from Breck.[20]

Changes in reactant OH^-/SiO_2 ratios

One of the more interesting problems is the issue of attempting to bridge the gap in *m* values between the reported Bieniok *et al.* synthesis and the organocation K-Y system we report here. The principal approach in studying this question was to begin to sequentially lower the OH^-/SiO_2 term which dominates the value of *m*. Fig. 7 gives a series of X-ray diffraction patterns for the crystallization experiments run as in Table 1 but with decreasing KOH/SiO_2 reactant values. In this sequence of runs, the Al source used was Reheis F-2000 instead of the original sodium aluminate. The experiments show that, in using this aluminium hydroxide hydrate source, one can produce MER below the $m=1.4$ boundary.

In this sequence, even as *m* is decreasing, LTL does not appear as an impurity although it might be expected as the

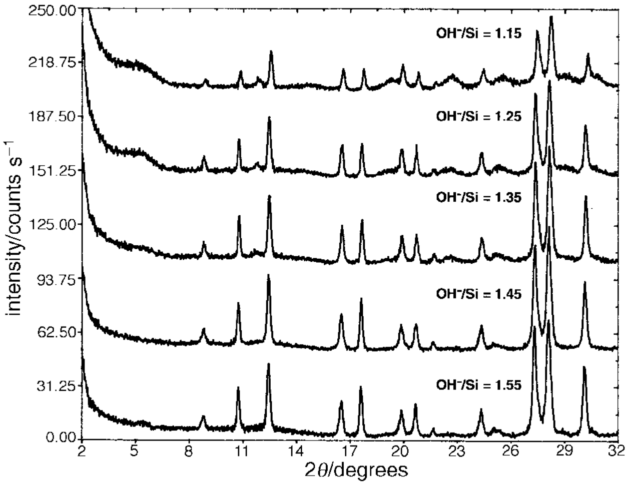


Fig. 7 Changes in XRD patterns as the initial KOH^-/Si ratios are varied

next crystalline phase if OH^-/SiO_2 were to become low enough. Below $OH^-/SiO_2 = 1.35$ there are indications of a broad-lined, layered aluminosilicate forming in minor quantity as well as the MER product. A little amorphous silica is also seen in the lowest OH^-/SiO_2 runs. If we were to lower the OH/SiO_2 ratio to 0.80, LTL would form. At this ratio, in the K-Y template system, MER is already the product; higher OH^-/SiO_2 values would still produce it. Thus the use of the template has already eliminated the chance of LTL zeolite being formed!

Plotting the mass of product recovered as a function of OH^-/SiO_2, the expected inverse relationship is seen (Fig. 8). Generally, decreasing the OH^-/SiO_2 in the reactants results in a lowered solubility for the silicates. In turn, higher yields and higher SAR products are usually expected. However, these experiments are still being carried out at quite high OH^-/SiO_2 levels (see Fig. 1). One of the outcomes is that these syntheses are not at the point of full utilization of the less soluble aluminate species. So, for the mass increase seen in the experiments shown in Fig. 8, the analytical data in Table 2 actually do not give much of an indication of a proportionate SAR increase. Instead, there appears to be an increased utilization of the aluminate molecules, yielding more product at relatively constant SAR. Additionally, the potassium cations make up better than 90% of the charge-balancing cations in these analyzed samples. This shows that potassium is the preferred cation in the developing structure, initially being necessary for this phase to form at all, and then being disproportionately highly represented over sodium in the crystallizing product.

On the other hand, the effective concentration of $[OH^-]$ and its impact on the relative soluble silicates could also be influenced by reducing the overall aqueous solvent volume. Our experimental conditions (Table 1), adapted from Bieniok *et al.*,[17] are already rather concentrated for zeolite reactions with $H_2O/Si = 13.8$. Our observation was that this concentrated system did not produce a criticality in MER synthesis as dilution of the system carried out to $H_2O/Si = 30$ produced no real changes in product. This latter value is close to the value used in the organocation transformation of K-Y to MER.

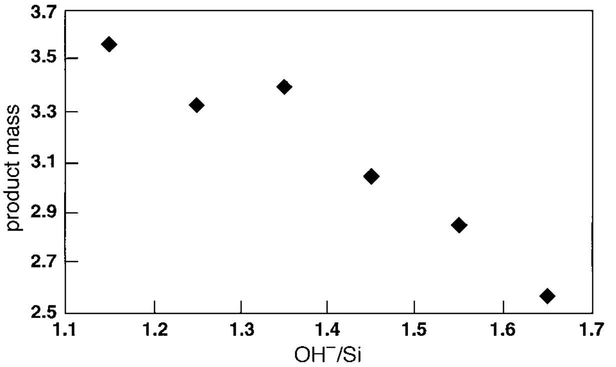


Fig. 8 The change in product mass as the OH^-/Si ratio decreases; same experiments as in Fig. 7

Table 2 Analytical data for MER zeolites made at variable OH^-/Si

run no.	OH^-/Si	relative mass	SAR
1	1.65	1.0	3.85
2	1.55	1.1	4.00
3	1.45	1.2	4.10
4	1.35	1.33	4.80
5	1.25	1.30	4.54
6	1.15	1.40	4.98

Table 3 Comparison of lattice constants for two MER samples[a]

sample SAR	7.76	4.21
synthesis (table 2)	with B34	without B34
space group	*Immm*	*Immm*
cell constants		
a/Å	14.184(6)	14.0948(6)
b/Å	14.189(5)	14.1016(6)
c/Å	9.934(2)	10.0421(5)
cell volume/Å^3	1999.3(3)	2010.3(2)
ref.	this work	17

[a] Cu-Kα radiation ($\lambda = 1.5406$ Å).

Lattice constants for MER prepared by the two methods

A comparison of the lattice constants are given in Table 3 for the products obtained by the two routes. One of the surprising results is that for an almost doubling of SAR, there is very little change in the cell volume. Usually an increase in Si tetrahedral population shrinks a given unit cell. It can be seen that the change in cell parameters is not isotropic. With a net, slight cell contraction for SAR = 7.76, some cell dimensions have actually increased. However, one structural feature in this comparison, which has not been controlled for, is the role of water in hydrating the charged centers. We do not know if water molecules are partially responsible for the unit cell lengths observed in comparing these two materials.

Conclusion

This work has explored two routes to the crystallization of merlinoite zeolites. With the novel approach of removing the initial crystallization products, a subsequently pure phase could be isolated in the purely inorganic system. A higher SAR product is described for the first time in a synthesis combining a 'guest' organocation and a zeolitic source of reactant aluminium. Evidence was shown for the 'trapping' of the guest organocation, although the void volume of the MER structure was not extensively filled by the organocation. In many zeolite crystallizations, a higher extent of void volume-filling is usually observed.

The wholly inorganic system showed considerable flexibility towards reagents. Some variation in ratios was also tolerated. Changes in OH^-/SiO_2 ratio had a larger impact on product mass than on SAR. In some previous systems, we had seen this relationship to be much more linear. Finally, the MER synthesis does show a high dependence upon potassium ions. It could not be crystallized without this cation.

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