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Microwave synthesis of LTN framework zeolite with no organic structure directing agents†

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We present a new microwave synthesis method of Linde Type N zeolite without organic structure directing agents (OSDAs). Linde Type N zeolite (framework type LTN) is one of the most complex zeolite structures with a very large unit cell. It has been synthesised previously using hydrothermal methods. We also report syntheses of zeolite A with LTA framework without OSDAs, by hydrothermal methods at low temperatures (40-60°C). The as-synthesised zeolites were characterised using X-ray powder diffraction, solid state nuclear magnetic resonance, and scanning electron microscopy. LTA and LTN frameworks are obtained at lower synthesis temperatures, while sodalite (SOD framework) is produced at higher temperatures, confirming the crystallisation of denser zeolites at higher temperatures.

1 Introduction

Zeolites are aluminosilicate materials with meso- or micropores inside their framework structure1–3. They have highly crystalline three dimensional frameworks made of SiO₄ or AlO₄ tetrahedral units connected to each other through the oxygen atoms2,4–7. The difference in valence between Si and Al atoms is charge balanced by mainly alkali metal cations such as Na⁺, Li⁺ or K⁺.

Zeolites find many industrial uses due to their diverse and highly selective catalytic and ion-exchange properties8–10. They are used in petrochemical and fine chemistry as solid-state catalysts, in agriculture for nitrogen fixation in soil, in industry for cleaning radioactive spillages, and for production of washing powders as detergent builders. Most recently they are being investigated for drug delivery in medicine11.

In this work, we studied three aluminosilicate zeolite frameworks: SOD, LTA and LTN. All of the mentioned frameworks are cubic in symmetry and have similar secondary building units in the framework structure. SOD framework is made of β-cages linked directly via the 4 ring, as can be seen from figure 1a. To make LTA framework, β-cages are connected through D4R, double 4 ring. When eight β-cages are connected by D4R units, a larger α-cage (LTA unit) is formed in the center. LTN framework is more complex and consists of β-cages connected via both D6R units and cancrinite cages.

† Electronic Supplementary Information (ESI) available: [X-ray powder patterns, solid state NMR spectra and SEM micrographs of as-synthesised zeolite samples]. See DOI: 10.1039/b000000x

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Fig. 1 Three frameworks with β-cage as secondary building unit, viewed along a-axis in ball and stick view – (a) SOD (b) LTA and (c) LTN. T atoms are blue, oxygen atoms are red. T-O bonds are displayed. Grey lines show the unit cell in each framework.
which leads to the formation of slightly distorted \( \alpha \)-cages (figure 1c). This framework has one of the largest unit cells among all known zeolites (\( a = 35.6 \AA \)).

Zeolite with LTA framework has been extensively used for production of washing powders. As the result, both synthesis and properties of zeolite A have been a subject of considerable interest by academics and industry. Sodalite, having relatively small \( \beta \)-cages in its structure, is not a widely used material. It is mainly used as a model for calibration or comparison during measurements on other more complex structures.

Linde Type N zeolite (also known as Z-21) was first synthesized in 1968 by Acara, using tetramethylammonium hydroxide as OSDA\(^{14}\). Acara mentioned in this patent that this zeolite absorbs water preferentially over nitrogen or oxygen, thus suggesting its usefulness as a desiccant for oxygen or nitrogen streams. In 1971, Duecker et al. synthesised this zeolite hydrothermally without using OSDAs\(^{13}\). In 1982, Fahib and Andersson solved the crystal structure of Linde Type N zeolite\(^{13}\), and in 1983 Shepelev et al. reported a crystal structure for Na Z-21 zeolite which has a LTN framework topology. While zeolite A and sodalite have been studied extensively in the last 50 years, there are fewer studies on Linde Type N zeolite. Here for the first time, we report a synthesis of Linde Type N zeolite with no OSDAs using a microwave method.

2 Experimental

Here we describe recipes for synthesis of all zeolites in this study. The synthesis method for zeolite A without OSDAs and sodalite were modified from Smaihi et al.\(^{12}\). The microwave synthesis of Linde Type N zeolite described here is new. We also repeated the hydrothermal synthesis of Linde Type N zeolite following the method described by Duecker et al.\(^{13}\) The summary of the recipes is presented in table 1.

2.1 Hydrothermal synthesis of zeolite A without OSDA

Zeolite A with gel composition \( \text{Al}_2\text{O}_3 : 2\text{SiO}_2 : 15\text{Na}_2\text{O} : 400\text{H}_2\text{O} \) was prepared as follow. 6.78g of sodium hydroxide (Fisher) was dissolved in 40 cm\(^3\) of deionized water and divided into two 20 cm\(^3\) portions. 0.988g of sodium aluminate was added to one portion while 2.42g of colloidal silica (Ludox HS-30, 30wt% SiO\(_2\), Aldrich) was added to the other. Both \( \text{Al}_2\text{O}_3/\text{Na}_2\text{O}/\text{H}_2\text{O} \) solution and silica solution was stirred for 90 minutes at room temperature. The silica solution was then added to the \( \text{Al}_2\text{O}_3/\text{Na}_2\text{O}/\text{H}_2\text{O} \) solution and silica solution was stirred for 24 hours at room temperature to ensure the solution has been thoroughly mixed. The silica solution was then added to the \( \text{Al}_2\text{O}_3/\text{Na}_2\text{O}/\text{H}_2\text{O} \) solution, and stirred for 1 hour at room temperature. 40 ml of the resulting gel was loaded into an ‘easy prep plus’ vessel of Mars 6 microwave. The following conditions were used during synthesis: 40\(^\circ\)C, 60\(^\circ\)C, 80\(^\circ\)C, 90\(^\circ\)C, 100\(^\circ\)C, 120\(^\circ\)C for 1 hour. Two more experiments were repeated using fumed silica (Aldrich) at 60\(^\circ\)C and 90\(^\circ\)C for 1 hour. All of the above reactions once completed were filtered using a Buckner funnel and washed with deionized water. Once filtered, the samples were dried in an oven for 48 hours at 60\(^\circ\)C.

2.2 Microwave synthesis of Linde Type N zeolite without OSDA

Linde Type N zeolite was synthesised using 12.9g colloidal silica (Ludox HS-30, 30wt% SiO\(_2\), Aldrich), 10.1g sodium aluminate (Al\(_2\)O\(_3\) 50-56%, Na\(_2\)O 40-45%, Sigma-Aldrich), 106.6g of sodium hydroxide (analytical reagent grade, 98.86%, Sigma-Aldrich) and 200ml of deionized water. Sodium hydroxide was dissolved in deionized water until a clear solution was formed. The alkaline solution was divided into two equal volumes, e.g. 100ml. Colloidal silica and sodium aluminate was then added seperately to each portion. The Al\(_2\)O\(_3\)/Na\(_2\)O/H\(_2\)O solution and silica solution were stirred for 24 hours at room temperature to ensure the solution has been thoroughly mixed. The silica solution was then added to the Al\(_2\)O\(_3\)/Na\(_2\)O/H\(_2\)O solution, and stirred for 1 hour at room temperature. 40 ml of the resulting gel was loaded into an ‘easy prep plus’ vessel of Mars 6 microwave. The following conditions were used during synthesis: 40\(^\circ\)C, 60\(^\circ\)C, 80\(^\circ\)C, 90\(^\circ\)C, 100\(^\circ\)C, 120\(^\circ\)C for 1 hour. Two more experiments were repeated using fumed silica (Aldrich) at 60\(^\circ\)C and 90\(^\circ\)C for 1 hour. All of the above reactions once completed were filtered using a Buckner funnel and washed with deionized water. Once filtered, the samples were dried in an oven for 48 hours at 60\(^\circ\)C.

2.3 Hydrothermal synthesis of Linde Type N zeolite without OSDA

The method is based on the patent described by Duecker et al.\(^{13}\) 10g of sodium hydroxide was dissolved in 25ml of deionized water followed by 0.95g of aluminium hydroxide and stirred at 95\(^\circ\)C for 1 hour until a clear solution is formed. 2.18ml of sodium silicate solution was then added and shaken vigorously for 1 minute. The resulting gel was transferred into a 60ml polypropylene bottles and heated at 100\(^\circ\)C for 1 hour, then washed with distilled water until pH 7 was attained, and dried in an oven at 100\(^\circ\)C overnight.

3 Characterization

3.1 X-ray powder diffraction (XRPD)

The powder patterns of zeolite A were obtained using a Philips X’pert X-ray diffractometer or a Philips PW1792 X-ray diffractometer both operating with Cu K\(\alpha\) radiation. The powder patterns of LTN zeolites were measured using a D8 powder diffractometer using Cu K\(\alpha\) radiation.
3.2 Solid state magic angle spinning nuclear magnetic resonance (SS MAS NMR)

$^{29}$Si, $^{27}$Al and $^{23}$Na NMR spectra were measured using a VARIAN VNMR 400 spectrometer using direct excitation (DE) method, with neat tetramethylsilane, 1M aqueous aluminium nitrate, and 1M aqueous sodium chloride solution as reference respectively. The spinning rate of $^{29}$Si NMR was 6.8 kHz, $^{27}$Al and $^{23}$Na NMR were 14kHz. Solid-state NMR spectra were obtained at the EPSRC UK National Solid-state NMR Service at Durham.

3.3 Scanning electron microscopy (SEM)

SEM images were obtained from a Hitachi S-4300 scanning electron microscope. The powder samples for SEM were coated with platinum metal of 5nm thickness.

4 Result and Discussion

4.1 X-ray powder diffraction

The powder patterns of as-synthesised zeolite A with no OSDA at various temperatures are shown in figure 2. Pure phase of zeolite A was formed when treated hydrothermally for 24 hours at 40°C, 50°C and 60°C. When the temperature was increased to 70°C, a mix of zeolite A and sodalite was observed. The sodalite 110 peak can clearly be seen around 14°2θ. The amount of sodalite in the as-synthesised sample increases from 70°C to 95°C. The sample synthesised at 95°C for 24 hours consisted mostly of sodalite. When we increased the reaction time from 24 hours to 48 hours at 95°C, single phase sodalite was synthesised. Our data show that zeolite A can be synthesised at temperature as low as 40°C without OSDA.

The transformation from LTA framework to SOD framework with increased temperature has been observed previously. Sodalite is a denser zeolite (framework density 14.7T/nm$^3$), so it is reasonable to expect that it will preferentially form with increased temperature. Increasing the duration of hydrothermal treatment also favors the formation of sodalite at high temperature.

We then decided to reproduce these results using a microwave method instead of standard hydrothermal treatments. We attempted to synthesise zeolite A with no OSDA using a microwave with the same batch composition, and Linde Type N zeolite was formed. The powder pattern of as-synthesised zeolite A samples using microwave synthesis was shown in figure 3. No crystalline phase was observed at 40°C. Linde Type N zeolite was synthesised between 60°C and 90°C. Sodalite was formed at temperature above 100°C (figure 3b). Change of silica source did not affect the formation of Linde Type N between 60°C and 90°C. LTN framework with density 17T/nm$^3$ is comparable with SOD framework with framework density 16.7T/nm$^3$.

We also repeated the hydrothermal synthesis of Linde Type N zeolite in the patent published by Duecker et al. Figure 4 shows the powder pattern of the as-synthesized Linde Type N zeolite at 100°C and the corresponding simulated pattern.
Table 2 SS MAS MNR of as-synthesised zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Temp / °C</th>
<th>Time / hour(s)</th>
<th>Si ppm</th>
<th>Al ppm</th>
<th>Na ppm</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zeolite A</td>
<td>40</td>
<td>24</td>
<td>-84.9, -89.5</td>
<td>58.6</td>
<td>-2.4</td>
<td>Hydrothermal, no OSDA</td>
</tr>
<tr>
<td>2</td>
<td>Zeolite A</td>
<td>50</td>
<td>24</td>
<td>-84.5, -85.4, -86.5, -89.3</td>
<td>58.8</td>
<td>-1.9</td>
<td>Hydrothermal, no OSDA</td>
</tr>
<tr>
<td>3</td>
<td>Zeolite A</td>
<td>60</td>
<td>24</td>
<td>-86.5, -89.4, -91.1</td>
<td>58.6</td>
<td>-3.4</td>
<td>Hydrothermal, no SDA</td>
</tr>
<tr>
<td>4</td>
<td>Zeolite A, Sodalite</td>
<td>70</td>
<td>24</td>
<td>-83.5, -86.6, -89.4, -94.6</td>
<td>58.5</td>
<td>-3.1</td>
<td>Hydrothermal, no OSDA</td>
</tr>
<tr>
<td>5</td>
<td>Zeolite A, Sodalite</td>
<td>80</td>
<td>24</td>
<td>-83.5, -86.5, -89.3</td>
<td>58.5</td>
<td>-3.1</td>
<td>Hydrothermal, no OSDA</td>
</tr>
<tr>
<td>6</td>
<td>Sodalite</td>
<td>95</td>
<td>48</td>
<td>-80.9, -83.8, -85.2</td>
<td>63.7, 65.3</td>
<td>4.0, -4.1</td>
<td>Hydrothermal, no OSDA</td>
</tr>
<tr>
<td>7</td>
<td>Linde Type N</td>
<td>90</td>
<td>1</td>
<td>-83.7, -85.3, -86.3</td>
<td>60.6, 63.5</td>
<td>2.0, -4.8</td>
<td>Microwave, no OSDA</td>
</tr>
</tbody>
</table>

The synthesis was also repeated at 60 °C for 1 hour with no formation of any amorphous or crystallized phase. Compare to this hydrothermal method, using the microwave method we can synthesise Linde Type N zeolite at lower temperature.

4.2 Solid State Magic Angle Spinning Nuclear Magnetic Resonance (SS MAS NMR)

We employed Solid State MAS NMR to study the zeolite A/sodalite synthesised hydrothermally and Linde Type N synthesised using the microwave method. Table 2 summarises the NMR data collected from zeolite samples synthesised using various methods with different reaction temperatures and times.

Variation in spectra were observed when we synthesised zeolite A without OSDA (Table 2, sample 1-6). Since some of the zeolites were synthesised at temperatures as low as 40 °C, we expected to see silanol signals on NMR spectra. The presence of silanol species in zeolite samples was confirmed by using 29Si cross-polarization (CP) MAS NMR.

It is interesting to see that there is one signal around -89.4 ppm which presents in all samples with zeolite A (Table 2, sample 1-5). This might indicate that it is an intrinsic signal for the LTA framework. This peak is usually attributed to Si(4Al) species in zeolites.

Linde Type N zeolite synthesised using microwave method without OSDA (Table 2, sample 7) showed a relatively simple spectrum. Only two major local Si environments were observed at -85.3 ppm and -86.3 ppm (silanol species at -83.7 ppm).

27Al and 23Na MAS NMR spectra of zeolite samples synthesised hydrothermally with no OSDA at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C (Table 2, sample 1-5) show only one Al and one Na local environment respectively. This indicates that Al were tetrahedrally coordinated in the framework associated...
with Na ions. Sodalite (Table 2, sample 6) and Linde Type
N zeolite (Table 2, sample 7), however, showed an extra broad
signal. Although this signal is also tetrahedral framework Al,
we were not able to explain such broadening.

For single phase zeolites, we were able to calculate the
Si/Al ratio by using equation (1). Table 3 shows the Si/Al
ratio of selected as-synthesised zeolite samples. For zeolite
sample synthesised hydrothermally with no OSDA at 50°C
and 95°C, the estimated ratio was 1.4 and 1.2 respectively.
The estimated Si/Al ratio of the Linde Type N zeolite was 1.1.

\[
\left( \frac{Si}{Al} \right)_{framework} = \frac{\left( \sum_{n=0}^{4} I_{Si(nAl)} \right)}{\left( \sum_{n=0}^{4} 0.25nI_{Si(nAl)} \right)}
\]

where \( I_{Si(nAl)} \) is the relative intensity of the \( Si(OAl)_{n}(OSi)_{4-n} \).

Table 3 Si/Al ratio of single phase as-synthesised zeolite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Si/Al ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>Zeolite A</td>
<td>1.4</td>
</tr>
<tr>
<td>1e</td>
<td>Sodalite</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>Linde Type N</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The suggested Si/Al ratio for zeolite A with no OSDA, and
for sodalite, is 1. The as-synthesised zeolite A with no
OSDA had a slightly higher Si/Al ratio, while as-synthesised
sodalite is close to the suggested value.

4.3 Scanning Electronic Microscopy (SEM)

The SEM micrographs of selected as-synthesised zeolite sam-
ple are shown in Figure 5. When we synthesise zeolite A
hydrothermally with no OSDA at different temperatures, we
saw the change of morphology from the formation of zeolite A
at low temperature to sodalite at high temperature. Although
the powder pattern of the zeolite sample synthesised at 50°C
showed a single phase, aggregates of small crystals less than
0.2 \( \mu \)m without defined shape were observed. At tempera-
tures of 70°C (figure 5(a)) and 80°C, we saw a mixture of
cubic zeolite A crystals, as well as sodalite crystals with un-
defined shape. Sodalite crystals with hexagonal faces formed
at 95°C, with average size of 1 \( \mu \)m as shown in figure 5(b).

Figure 6 shows the zeolite samples synthesised using mi-
crowave method without using OSDA. Linde Type N zeo-
lite crystals with various morphology at different tempera-
tures were observed. At 60°C, Linde Type N zeolite formed as
truncated cubes associated with spheres with rough surface (figure
6(a)). The truncated cubic crystals grow into aggregates and
eventually to 2 \( \mu \)m spheres with smooth surface at 90°C. Uniform
sodalite crystal with size 3 \( \mu \)m were observed when the
temperature increased above 100°C, as shown in figure
6(b).

5 Conclusions

Linde Type N zeolite, with an LTN framework, has been syn-
thesized without structure directing agents at 60°C in an hour
using a microwave method. This is a lower temperature syn-
thesis compared to the hydrothermal method described by
Duecker et al. This zeolite has a very complex structure and
is considered as one of the most complex zeolites among the
216 known today.

We found that both zeolite A and Linde Type N zeolite
can be crystallized at relatively low temperatures (40–50°C)
in pure form. At higher temperatures, competing sodalite
phase appears during the crystallization. However, when
synthesising Linde Type N zeolite hydrothermally, no so-
dalite phase is observed at 100°C. We also studied some of
the as-synthesised zeolites using Solid State MAS NMR and
SEM. NMR helped us to determine the Si/Al ratios of the
as-synthesised zeolites and we attempted to rationalize their
chemical shifts. SEM helped us to see their crystal morphol-
ogy and size.
Fig. 6 SEM micrographs of as-synthesised zeolite samples using microwave method with no OSDA at different temperatures (a) Linde Type N zeolite at 60°C (b) Sodalite at 100°C

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References