Mesopores in USY Zeolites
Wolfgang Lutz, Dirk Enke, Wolf-Dieter Einicke, Dirk Täschner, Rolf Kurzhals

To cite this version:


HAL Id: hal-00599885
https://hal.archives-ouvertes.fr/hal-00599885
Submitted on 11 Jun 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
### Mesopores in USY Zeolites

<table>
<thead>
<tr>
<th><strong>Journal:</strong></th>
<th>Zeitschrift für Anorganische und Allgemeine Chemie</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manuscript ID:</strong></td>
<td>zaac.201000271.R1</td>
</tr>
<tr>
<td><strong>Wiley - Manuscript type:</strong></td>
<td>Communication</td>
</tr>
<tr>
<td><strong>Date Submitted by the Author:</strong></td>
<td>06-Sep-2010</td>
</tr>
</tbody>
</table>
| **Complete List of Authors:** | Lutz, Wolfgang; BTU Cottbus, Luftchemie  
Enke, Dirk; Institute of Chemical Technology  
Einicke, Wolf-Dieter; Institute of Chemical Technology  
Täschner, Dirk; Süd-Chemie Zeolites GmbH  
Kurzhals, Rolf; Sud-Chemie Zeolites GmbH |
| **Keywords:** | zeolite, dealumination, faujasite, mesopores |
Short Communication

Mesopores in USY Zeolites

W. Lutz*[a], D. Enke*[b], W.-D. Einicke*[b], D. Täschner*[c], E. Kurzhals*[c]

[a] Brandenburgische Technische Universität Cottbus, Labor Berlin, Berlin
[b] Universität Leipzig, Leipzig
[c] Süd-Chemie Zeolites GmbH, Bitterfeld-Wolfen

Keywords: zeolite, dealumination, faujasite, mesopores

Abstract

Zeolites of type NaY synthesized by use of seed-solution and zeolite X-seeds to initialise the crystallization were compared. A different homogeneity of the internal framework structure related to the Si/Al ratio was expected. Thus, the formation of closed bulk mesopores should be influenced during treatment of NH₄NaY modification for 7 hours at 450°C and 600°C in the water steam of 1 bar. Occurrence of different mesopores was actually observed in obtained ultra-stable USY zeolites using Nitrogen adsorption. Whereas USY prepared by use of seed-solution contains only open mesopores at the crystal surface, the X-seed synthesized material contains open and closed mesopores at the surface and in the nuclei of samples, respectively.

* Wolfgang Lutz
Brandenburgische Technische Universität Cottbus, Volmerstr. 13, 12489 Berlin
Tel.: 0049 30 6392 4425
e-mail: lutz@btu-lc.fta-berlin.de
Introduction

Zeolites of NaY type with framework Si/Al ratios between 2.2 and 2.7 are suitable to be dealuminated [1]. Ion-exchanged NH$_4$NaY modification is transformed thereby into catalytically active USY (ultra-stable Y) samples [2]. The process proceeds in a steam treatment at elevated temperature [3].

Recently, the formation of two types of mesopores was reported as a result of the samples treatment for 7 hours in the steam of 1 bar water pressure at 450°C and 600°C [4]. Closed bulk mesopores were found inside the traditionally synthesized NaY$_X$-seeds crystallites surrounded by the microporous zeolite framework. Open mesopores were located near the crystallite surface. They occurred due to partial decomposition of the Aluminium-rich crystallite nuclei and corrosion of the Silicon-rich crystallites surface, respectively [5].

The non-homogeneous Si/Al distribution is typical for most NaY$_X$-seeds zeolites [6] prepared by use of silica gel, solution of sodium aluminate and, frequently, seeds of zeolite X [7, 8]. Zeolites of X and Y types are modifications of one and the same faujasite crystal type (FAU). They distinguish only in their Silicon to Aluminium ratio. While for X a Si/Al ratio of 1 to 1.2 is typical [9], Y is characterized by Si/Al values > 2.2 [1].

Crystallization of the FAU framework starts according to the traditional synthesis path-way in general from aluminosilicate gels with Si/Al distribution close to that of zeolite X composition [6]. Because of excessive consumption of aluminate ions at the beginning of the synthesis, the batch solution becomes more and more rich in silicate ions. This is the reason why crystal formation starts with an Aluminium-rich nuclei but finishes with a Silicon-rich surface.

It was found earlier that FAU zeolites, being rich in Aluminium or Silicon, show hydrothermal instability. In steam they are decomposed according to an “acid” or “alkaline” mechanisms [1]. This effect is responsible for decomposition and corrosion of parts of the
NaY\textsubscript{X}-seeds framework with non-homogeneous Si/Al distribution, too. Amorphous aluminosilicate and silica gel as siliceous extra-framework admixtures occur thereby [10].

A modified synthesis pathway for zeolite NaY\textsubscript{seed-solution} should hinder the formation of such strong gradient. This strategy uses so-called seed-solution to initialise the crystal growth of Y-type composition, already at the beginning of synthesis process [11].

Seed-solution consists of sodium silicate molecules of oligomeric chain length (5-15 Silicon atoms) in aqueous alkaline solution with some aluminate ions inside. The slightly opaque solution should favour the formation of sodalite cages as main building units of the FAU structure with a higher portion of Silicon atoms, being also in the nuclei of crystallites.

With respect to hydrothermal stability, the nuclei of such modified NaY\textsubscript{seed-solution} should be more stable than that of NaY\textsubscript{X-seed} products. Therefore, the formation of bulk mesopores should be hindered or at least minimized on this way.

**Results and Discussion**

According to unit cell composition of Na\textsubscript{53}[(AlO\textsubscript{2})\textsubscript{53}(SiO\textsubscript{2})\textsubscript{139}] and Na\textsubscript{52}[(AlO\textsubscript{2})\textsubscript{52}(SiO\textsubscript{2})\textsubscript{140}], respectively, the NaY\textsubscript{seed-solution} and NaY\textsubscript{X-seeds} samples are chemically pseudo identical. Consequently, the Si/Al ratios calculated by use of the IR double ring vibration w\textsubscript{DR} and the framework constant a\textsubscript{0} are with values of 2.6-2.7 identical. After steaming, the values preserve as very close. Dealumination changes Si/Al ratios from 3.0 - 3.3 (450°C) to 3.9 - 4.2 (600°C) (Table 1).

Micropore volume V\textsubscript{micro} and micropore surface A\textsubscript{micro} of NaY and USY samples of both series differ only to a small extent as shown in Table 2.

The greater difference of the total volumes V\textsubscript{total} between both series determined from nitrogen isotherms at p/p\textsubscript{0} = 0.9995 results from a higher free space (macropores) between crystallites of the polycrystalline NaY\textsubscript{seed-solution} particles [4]. This different sample behaviour
can be identified also by the shape of isotherms in Figure 1 and 2 (A). NaY\textsubscript{seed-solution} shows significant condensation of nitrogen inside the macropores at relative pressure higher than $p/p_0 = 0.9$. Similar tendency is observed for steamed USY samples (B, C), too.

The mesopore area $A_{\text{meso}}$ differs in opposite way. Values of NaY\textsubscript{seed-solution} are smaller for initial as well as steamed samples than those of NaY\textsubscript{X-seeds} zeolites. The difference characterizes absence of internal mesopores in NaY\textsubscript{seed-solution}. The corresponding nitrogen isotherms show no hysteresis loop for the 450°C steamed sample (Figure 1 B) and only a weak one for 600°C (C). Letter starts at $p/p_0 = 0.7$ thus characterizing the emptying of the mesopores of the outer crystallite surface. Contrary to this observation, 600°C sample of NaY\textsubscript{X-seed} (Figure 2 C) shows a second step beginning at $p/p_0 = 0.45$ resulting from emptying of the internal bulk mesopores. Thus, the different run of isotherms characterizes different mesopore systems in USY zeolites in dependence of use of seed-solution or type X-seeds for initialisation of the crystallization process.

**Experimental Section**

Zeolite of type NaY\textsubscript{seed-solution} was synthesized according to a recipe of the former Zeosorb GmbH (Bitterfeld) by homogenization of 9 mole SiO\textsubscript{2} in a solution of 1 mole Al\textsubscript{2}O\textsubscript{3}, 3.5 mole Na\textsubscript{2}O and 120 mole H\textsubscript{2}O at ambient temperature. The synthesis was carried out without aging of the aluminosilicate gel under stirring at 95°C for 36 hours. 25 g seed-solution was added to 1900 g of the batch. The composition of the seed-solution amounted to 15 mole SiO\textsubscript{2} and 1 mole Al\textsubscript{2}O\textsubscript{3} in an aqueous solution of 13 mole Na\textsubscript{2}O in 215 mole water.

For dealumination, zeolite NaY\textsubscript{seed-solution} was transferred into the ammonium modification by a three-fold ion-exchange in 0.1 M aqueous solution of NH\textsubscript{4}NO\textsubscript{3} at room temperature for 1 hour in each step and by use of a liquid/solid mass ratio of 100. The obtained NH\textsubscript{4}NaY
modification was washed with water and dried at 120°C for 1 hour. The ion exchange was limited to 79%. Under analogous conditions zeolite NaYX-seeds was ion-exchanged [4].

The hydrothermal treatment of samples of both series was performed in steam of 1bar water pressure at 450°C or 600°C for 7 hours. The heating rate of the process was equal to 10 centigrade per minute. The samples were contacted with steam after reaching the chosen temperature.

The obtained USY samples were characterized by X-ray diffraction, IR spectroscopy and nitrogen adsorption. XRD data were recorded on a Philips PW 1800 powder diffractometer equipped with a graphite monochromator and Cu Kα radiation at 40 kV and 40 mA. Measurements were performed in the 2θ range between 5 ° and 85 ° with a step of 0.03 ° and a coupling time of 1 sec count per step.

IR absorption spectra were taken on a Shimadzu FTIR 8400S spectrometer with a resolution of ± 1 cm⁻¹ by use of 30 scans. For analysis, 0.5 mg of the sample was pressed with 400 mg KBr into a pellet while spectra were registered in the IR range from 400 to 4000 cm⁻¹.

Nitrogen sorption measurements at –196°C were performed by use of a ASAP 2010 apparatus by Micromeretics. All samples were degassed at 350°C before measurement for at least 24 hours at 10⁻⁵ mbar. Adsorption and desorption isotherms were measured over a range of relative pressures (p/p₀) from 0 to 1.0. The surface area of the micropores Aₘᵢｃｒ,o, the micropore volume Vₘᵢｃｒ,o and the surface area of the mesopores Aₘₑｓₒ were determined according the t-plot method [13]. The total pore volume Vₜₐₜ₉ₐₜ was estimated from the amount of gas adsorbed at the relative pressure p/p₀ = 0.996 assuming that pores were filled.
subsequently with condensed adsorptive in the normal liquid state. Finally, the mesopore volume $V_{\text{meso}}$ was calculated according to

$$V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}} \quad (1)$$

Si/Al ratios of USY were determined by the IR spectroscopic double ring vibration $w_{\text{DR}}$ and the lattice constant $a_0$ [14] according to Equations (2) and (3)

$$x = 3.857 - 0.00619 \ w_{\text{DR}} \ (cm^{-1}) \quad (2)$$

(with Si/Al = (1-x)/x and $x = \text{Al molar fraction by use of the sensitive double-ring vibration}$) respectively

$$x = 5.348a_0 - 12.898 \quad (3)$$

(with Si/Al = (1-x)/x and $x = \text{Al molar fraction by use of the cell parameter } a_0$).

References


Table 1: Si/Al ratio of initial NaY_seed-solution and USY steamed at 450°C respectively.

600°C in comparison with NaY_X-seeds and USY samples of Reference [4]

<table>
<thead>
<tr>
<th>sample</th>
<th>IR $w_{DR}$, cm$^{-1}$</th>
<th>Si/Al acc. to Eq. (2)</th>
<th>XRD $a_0$, nm acc. to Eq. (3)</th>
<th>Si/Al acc. to Eq. (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY_seed-solution</td>
<td>579</td>
<td>2.7</td>
<td>2.462</td>
<td>2.7</td>
</tr>
<tr>
<td>USY, 450°C</td>
<td>584</td>
<td>3.1</td>
<td>2.456</td>
<td>3.2</td>
</tr>
<tr>
<td>USY, 600°C</td>
<td>592</td>
<td>4.2</td>
<td>2.450</td>
<td>3.9</td>
</tr>
<tr>
<td>NaY_X-seeds</td>
<td>580</td>
<td>2.7</td>
<td>2.465</td>
<td>2.6</td>
</tr>
<tr>
<td>USY, 450°C</td>
<td>586</td>
<td>3.3</td>
<td>2.458</td>
<td>3.0</td>
</tr>
<tr>
<td>USY, 600°C</td>
<td>592</td>
<td>4.2</td>
<td>2.451</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Table 2 Pore structure of initial NaY seed-solution and USY steamed at 450°C respectively 600°C in comparison with NaY X-seeds and USY samples of Reference [4]

<table>
<thead>
<tr>
<th>sample</th>
<th>(V_{\text{total}}, \text{cm}^3/\text{g})</th>
<th>(V_{\text{micro}}, \text{cm}^3/\text{g})</th>
<th>(A_{\text{micro}}, \text{m}^2/\text{g})</th>
<th>(A_{\text{meso}}, \text{m}^2/\text{g})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY seed-solution</td>
<td>0.44</td>
<td>0.35</td>
<td>863</td>
<td>19</td>
</tr>
<tr>
<td>USY, 450°C</td>
<td>0.41</td>
<td>0.30</td>
<td>742</td>
<td>30</td>
</tr>
<tr>
<td>USY, 600°C</td>
<td>0.40</td>
<td>0.27</td>
<td>682</td>
<td>34</td>
</tr>
<tr>
<td>NaY X-seeds</td>
<td>0.35</td>
<td>0.36</td>
<td>815</td>
<td>24</td>
</tr>
<tr>
<td>USY, 450°C</td>
<td>0.35</td>
<td>0.30</td>
<td>735</td>
<td>34</td>
</tr>
<tr>
<td>USY, 600°C</td>
<td>0.33</td>
<td>0.25</td>
<td>630</td>
<td>40</td>
</tr>
</tbody>
</table>
Figure 1  Nitrogen isotherms of initial NaY$_{\text{seed-solution}}$ and USY samples steamed at 450°C respectively 600°C
Figure 2  Nitrogen isotherms of initial NaY<sub>x-seeds</sub> and USY samples steamed at 450°C respectively 600°C