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**Mesopores in USY Zeolites**

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**Short Communication****Mesopores in USY Zeolites**

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**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 NH<sub>4</sub>NaY 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.

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## Introduction

Zeolites of NaY type with framework Si/Al ratios between 2.2 and 2.7 are suitable to be dealuminated [1]. Ion-exchanged  $\text{NH}_4\text{NaY}$  modification is transformed thereby into catalytic 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  $\text{NaY}_{\text{X-seeds}}$  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  $\text{NaY}_{\text{X-seeds}}$  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

1  
2  
3 NaY<sub>X-seeds</sub> framework with non-homogeneous Si/Al distribution, too. Amorphous  
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5 aluminosilicate and silica gel as siliceous extra-framework admixtures occur thereby [10].  
6  
7

8 A modified synthesis pathway for zeolite NaY<sub>seed-solution</sub> should hinder the formation of such  
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10 strong gradient. This strategy uses so-called seed-solution to initialise the crystal growth of Y-  
11  
12 type composition, already at the beginning of synthesis process [11].  
13  
14

15 Seed-solution consists of sodium silicate molecules of oligomeric chain length (5-15 Silicon  
16  
17 atoms) in aqueous alkaline solution with some aluminate ions inside. The slightly opaque  
18  
19 solution should favour the formation of sodalite cages as main building units of the FAU  
20  
21 structure with a higher portion of Silicon atoms, being also in the nuclei of crystallites.  
22  
23

24 With respect to hydrothermal stability, the nuclei of such modified NaY<sub>seed-solution</sub> should be  
25  
26 more stable than that of NaY<sub>X-seed</sub> products. Therefore, the formation of bulk mesopores  
27  
28 should be hindered or at least minimized on this way.  
29  
30  
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## 36 **Results and Discussion**

37

38 According to unit cell composition of Na<sub>53</sub>[(AlO<sub>2</sub>)<sub>53</sub>(SiO<sub>2</sub>)<sub>139</sub>] and Na<sub>52</sub>[(AlO<sub>2</sub>)<sub>52</sub>(SiO<sub>2</sub>)<sub>140</sub>],  
39  
40 respectively, the NaY<sub>seed-solution</sub> and NaY<sub>X-seeds</sub> samples are chemically pseudo identical.  
41  
42 Consequently, the Si/Al ratios calculated by use of the IR double ring vibration  $w_{DR}$  and the  
43  
44 framework constant  $a_0$  are with values of 2.6-2.7 identical. After steaming, the values preserve  
45  
46 as very close. Dealumination changes Si/Al ratios from 3.0 - 3.3 (450°C) to 3.9 - 4.2 (600°C)  
47  
48 (Table 1).  
49  
50  
51

52 Micropore volume  $V_{micro}$  and micropore surface  $A_{micro}$  of NaY and USY samples of both  
53  
54 series differ only to a small extent as shown in Table 2.  
55  
56

57 The greater difference of the total volumes  $V_{total}$  between both series determined from  
58  
59 nitrogen isotherms at  $p/p_0 = 0.9995$  results from a higher free space (macropores) between  
60  
crystallites of the polycrystalline NaY<sub>seed-solution</sub> particles [4]. This different sample behaviour

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3 can be identified also by the shape of isotherms in Figure 1 and 2 (A).  $\text{NaY}_{\text{seed-solution}}$  shows  
4  
5 significant condensation of nitrogen inside the macropores at relative pressure higher than  
6  
7  
8  $p/p_0 = 0.9$ . Similar tendency is observed for steamed USY samples (B, C), too.  
9

10 The mesopore area  $A_{\text{meso}}$  differs in opposite way. Values of  $\text{NaY}_{\text{seed-solution}}$  are smaller for  
11  
12 initial as well as steamed samples than those of  $\text{NaY}_{\text{X-seeds}}$  zeolites. The difference  
13  
14 characterizes absence of internal mesopores in  $\text{NaY}_{\text{seed-solution}}$ . The corresponding nitrogen  
15  
16 isotherms show no hysteresis loop for the 450°C steamed sample (Figure 1 B) and only a  
17  
18 weak one for 600°C (C). Letter starts at  $p/p_0 = 0.7$  thus characterizing the emptying of the  
19  
20 mesopores of the outer crystallite surface. Contrary to this observation, 600°C sample of  
21  
22  $\text{NaY}_{\text{X-seed}}$  (Figure 2 C) shows a second step beginning at  $p/p_0 = 0.45$  resulting from emptying  
23  
24 of the internal bulk mesopores. Thus, the different run of isotherms characterizes different  
25  
26 mesopore systems in USY zeolites in dependence of use of seed-solution or type X-seeds for  
27  
28 initialisation of the crystallization process.  
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### 39 **Experimental Section**

40  
41 Zeolite of type  $\text{NaY}_{\text{seed-solution}}$  was synthesized according to a recipe of the former Zeosorb  
42  
43 GmbH (Bitterfeld) by homogenization of 9 mole  $\text{SiO}_2$  in a solution of 1 mole  $\text{Al}_2\text{O}_3$ , 3.5 mole  
44  
45  $\text{Na}_2\text{O}$  and 120 mole  $\text{H}_2\text{O}$  at ambient temperature. The synthesis was carried out without aging  
46  
47 of the aluminosilicate gel under stirring at 95°C for 36 hours. 25 g seed-solution was added to  
48  
49 1900 g of the batch. The composition of the seed-solution amounted to 15 mole  $\text{SiO}_2$  and 1  
50  
51 mole  $\text{Al}_2\text{O}_3$  in an aqueous solution of 13 mole  $\text{Na}_2\text{O}$  in 215 mole water.  
52  
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54  
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56

57 For dealumination, zeolite  $\text{NaY}_{\text{seed-solution}}$  was transferred into the ammonium modification by  
58  
59 a three-fold ion-exchange in 0.1 M aqueous solution of  $\text{NH}_4\text{NO}_3$  at room temperature for 1  
60  
hour in each step and by use of a liquid/solid mass ratio of 100. The obtained  $\text{NH}_4\text{NaY}$

1  
2  
3 modification was washed with water and dried at 120°C for 1 hour. The ion exchange was  
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5 limited to 79%. Under analogous conditions zeolite NaY<sub>X-seeds</sub> was ion-exchanged [4].  
6  
7  
8  
9

10 The hydrothermal treatment of samples of both series was performed in steam of 1bar water  
11  
12 pressure at 450°C or 600°C for 7 hours. The heating rate of the process was equal to 10  
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14 centigrade per minute. The samples were contacted with steam after reaching the chosen  
15  
16 temperature.  
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22 The obtained USY samples were characterized by X-ray diffraction, IR spectroscopy and  
23  
24 nitrogen adsorption. XRD data were recorded on a Philips PW 1800 powder diffractometer  
25  
26 equipped with a graphite monochromator and Cu K $\alpha$  radiation at 40 kV and 40 mA.  
27  
28 Measurements were performed in the 2 $\theta$  range between 5 ° and 85 ° with a step of 0.03 ° and  
29  
30 a coupling time of 1 sec count per step.  
31  
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34  
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36 IR absorption spectra were taken on a Shimadzu FTIR 8400S spectrometer with a resolution  
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38 of  $\pm 1 \text{ cm}^{-1}$  by use of 30 scans. For analysis, 0.5 mg of the sample was pressed with 400 mg  
39  
40 KBr into a pellet while spectra were registered in the IR range from 400 to 4000  $\text{cm}^{-1}$ .  
41  
42  
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45  
46 Nitrogen sorption measurements at -196°C were performed by use of a ASAP 2010 apparatus  
47  
48 by Micromeritics. All samples were degassed at 350°C before measurement for at least 24  
49  
50 hours at 10<sup>-5</sup> mbar. Adsorption and desorption isotherms were measured over a range of  
51  
52 relative pressures (p/p<sub>0</sub>) from 0 to 1.0. The surface area of the micropores A<sub>micro</sub>, the  
53  
54 micropore volume V<sub>micro</sub> and the surface area of the mesopores A<sub>meso</sub> were determined  
55  
56 according the t-plot method [13]. The total pore volume V<sub>total</sub> was estimated from the amount  
57  
58 of gas adsorbed at the relative pressure p/p<sub>0</sub> = 0.996 assuming that pores were filled  
59  
60

1  
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3 subsequently with condensed adsorptive in the normal liquid state. Finally, the mesopore  
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5 volume  $V_{\text{meso}}$  was calculated according to  
6

$$7 \quad V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}. \quad (1)$$

8  
9  
10  
11  
12 Si/Al ratios of USY were determined by the IR spectroscopic double ring vibration  $w_{\text{DR}}$  and  
13  
14 the lattice constant  $a_0$  [14] according to Equations (2) and (3)  
15

$$16 \quad x = 3.857 - 0.00619 w_{\text{DR}} \text{ (cm}^{-1}\text{)} \quad (2)$$

17  
18  
19  
20 (*with Si/Al = (1-x)/x and x = Al molar fraction by use of the sensitive double-ring vibration*)  
21

22 respectively  
23

$$24 \quad x = 5.348a_0 - 12.898 \quad (3)$$

25  
26  
27 (*with Si/Al = (1-x)/x and x = Al molar fraction by use of the cell parameter  $a_0$* ).  
28  
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Table 1 Si/Al ratio of initial NaY<sub>seed-solution</sub> and USY steamed at 450°C respectively 600°C in comparison with NaY<sub>X-seeds</sub> and USY samples of Reference [4]

sample	IR	Si/Al	XRD	Si/Al
	w <sub>DR</sub> , cm <sup>-1</sup>	acc. to Eq. (2)	a <sub>0</sub> , nm	acc. to Eq. (3)
	seed-solution			
NaY <sub>seed-solution</sub>	579	2.7	2.462	2.7
USY, 450°C	584	3.1	2.456	3.2
USY, 600°C	592	4.2	2.450	3.9
	X-seeds			
NaY <sub>X-seeds</sub>	580	2.7	2.465	2.6
USY, 450°C	586	3.3	2.458	3.0
USY, 600°C	592	4.2	2.451	3.9

Table 2 Pore structure of initial NaY<sub>seed-solution</sub> and USY steamed at 450°C respectively 600°C in comparison with NaY<sub>X-seeds</sub> and USY samples of Reference [4]

sample	V <sub>total</sub> , cm <sup>3</sup> /g	V <sub>micro</sub> , cm <sup>3</sup> /g	A <sub>micro</sub> , m <sup>2</sup> /g	A <sub>meso</sub> , m <sup>2</sup> /g
	seed-solution			
NaY <sub>seed-solution</sub>	0.44	0.35	863	19
USY, 450°C	0.41	0.30	742	30
USY, 600°C	0.40	0.27	682	34
	X-seeds			
NaY <sub>X-seeds</sub>	0.35	0.36	815	24
USY, 450°C	0.35	0.30	735	34
USY, 600°C	0.33	0.25	630	40

Figure 1 Nitrogen isotherms of initial NaY<sub>seed-solution</sub> and USY samples steamed at 450°C respectively 600°C

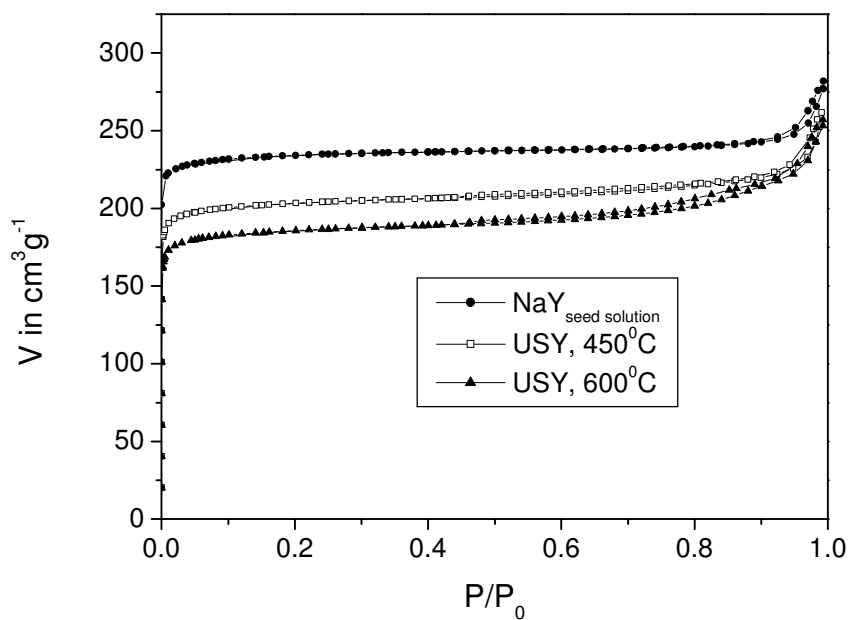


Figure 2 Nitrogen isotherms of initial  $\text{NaY}_{\text{X-seeds}}$  and USY samples steamed at  $450^\circ\text{C}$  respectively  $600^\circ\text{C}$

