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Short Communication

Mesopores in USY Zeolites

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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_4NaY 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 NH_4NaY 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

NaY_{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_{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_{seed-solution} should be more stable than that of NaY_{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 Na₅₃[(AlO₂)₅₃(SiO₂)₁₃₉] and Na₅₂[(AlO₂)₅₂(SiO₂)₁₄₀], respectively, the NaY_{seed-solution} and NaY_{X-seeds} samples are chemically pseudo identical. Consequently, the Si/Al ratios calculated by use of the IR double ring vibration w_{DR} and the framework constant a_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_{micro} and micropore surface A_{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_{total} between both series determined from nitrogen isotherms at $p/p_0 = 0.9995$ results from a higher free space (macropores) between crystallites of the polycrystalline NaY_{seed-solution} particles [4]. This different sample behaviour

can be identified also by the shape of isotherms in Figure 1 and 2 (A). $\text{NaY}_{\text{seed-solution}}$ 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_{meso} differs in opposite way. Values of $\text{NaY}_{\text{seed-solution}}$ are smaller for initial as well as steamed samples than those of $\text{NaY}_{\text{X-seeds}}$ zeolites. The difference characterizes absence of internal mesopores in $\text{NaY}_{\text{seed-solution}}$. 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 $\text{NaY}_{\text{X-seed}}$ (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 $\text{NaY}_{\text{seed-solution}}$ was synthesized according to a recipe of the former Zeosorb GmbH (Bitterfeld) by homogenization of 9 mole SiO_2 in a solution of 1 mole Al_2O_3 , 3.5 mole Na_2O and 120 mole H_2O 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_2 and 1 mole Al_2O_3 in an aqueous solution of 13 mole Na_2O in 215 mole water.

For dealumination, zeolite $\text{NaY}_{\text{seed-solution}}$ was transferred into the ammonium modification by a three-fold ion-exchange in 0.1 M aqueous solution of NH_4NO_3 at room temperature for 1 hour in each step and by use of a liquid/solid mass ratio of 100. The obtained NH_4NaY

modification was washed with water and dried at 120°C for 1 hour. The ion exchange was limited to 79%. Under analogous conditions zeolite NaY_{X-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 K α radiation at 40 kV and 40 mA. Measurements were performed in the 2 θ 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 $\pm 1 \text{ cm}^{-1}$ 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 Micromeritics. 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/p_0) from 0 to 1.0. The surface area of the micropores A_{micro} , the micropore volume V_{micro} and the surface area of the mesopores A_{meso} were determined according the t-plot method [13]. The total pore volume V_{total} was estimated from the amount of gas adsorbed at the relative pressure $p/p_0 = 0.996$ assuming that pores were filled

subsequently with condensed adsorptive in the normal liquid state. Finally, the mesopore volume V_{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_{DR} and the lattice constant a_0 [14] according to Equations (2) and (3)

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

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

respectively

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

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

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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]

sample	IR w _{DR} , cm ⁻¹	Si/Al acc. to Eq. (2)	XRD a ₀ , nm	Si/Al acc. to Eq. (3)
	seed-solution			
NaY _{seed-solution}	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 _{X-seeds}	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_{seed-solution} and USY steamed at 450°C respectively 600°C in comparison with NaY_{X-seeds} and USY samples of Reference [4]

sample	V _{total} , cm ³ /g	V _{micro} , cm ³ /g	A _{micro} , m ² /g	A _{meso} , m ² /g
	seed-solution			
NaY _{seed-solution}	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 _{X-seeds}	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_{seed-solution} and USY samples steamed at 450°C respectively 600°C

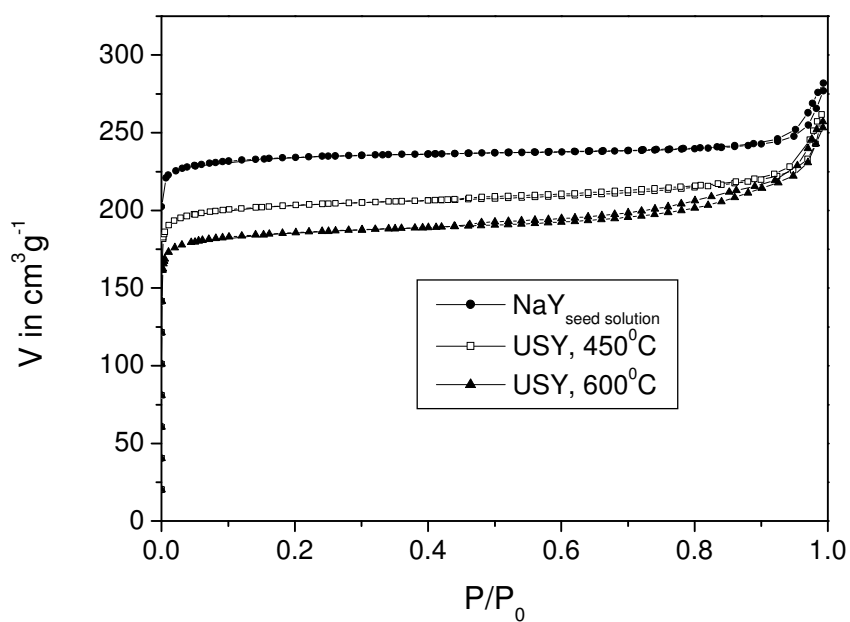


Figure 2 Nitrogen isotherms of initial NaY_{X-seeds} and USY samples steamed at 450°C respectively 600°C

