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Synthesis of Nanosized NaY Zeolite by Confined Space Method

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Abstract: Nanosized NaY crystals have been prepared from metakaolin and sodium silicate by confined space synthesis with starch additive. It is found that the product has a narrow crystal size distribution (50-100 nm), high Si/Al ratio (Si/Al=4.6-6.1), high surface area (1090 m^2/g) and the average diameter of nanosized NaY (75 nm) synthesized is 30 nm, it is smaller than that of without starch additive.

Keywords: Confined space synthesis, zeolite, nanosized NaY, crystals, metakaolin.

Traditional methods of the synthesis of NaY zeolite involve crystallization from a gel or a clear solution under hydrothermal conditions[1,2], which lead to form much wastewater. In recent years much attention has been focused on preparation of nanosized zeolite crystals[3-5] and some synthetic methods of nanosized NaY zeolite crystals have been reported, however, none of these methods can control the crystal size and distributions of the size of the resulting crystal well. Furthermore, isolation of the small zeolite crystals is not simple due to the colloidal properties of these materials. Therefore, with the inspiration of ZSM-5 synthesis in the presence of carbon black materials[6], we have attempted a novel method for the preparation of nanosized NaY zeolite crystals. With this new method nanosized NaY zeolite crystals were simply isolated from metakaolin. The synthetic method involves crystallization of the nanosized NaY zeolite in the sealed stainless steel autoclave in an oven, by use of starch as the additive material which was easily removed by pyrolysis after the nanosized NaY zeolite recovered.

Table 1 gives details of the pore structure of the samples obtained from N_2 adsorption and desorption isotherms. The significantly larger pore volume of nanosized NaY has the larger NaY surface area, which results in the smaller crystal content in the sample. It is also found that the average pore radius of the sample with higher Si/Al ratio is about twice of the lower Si/Al sample.

Figure 1 illustrates the X-ray diffractions of the synthesized zeolite and metakaolin. It seems that the sample contains highly crystalline NaY as judged from the diffraction line width and contrast to metakaolin.

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Table 1 Selective properties of nanosized NaY

Sample	Si/Al	d_{pore} [a] nm	Pore volume [a] cm^3/g	Surface area [a] m^2/g	Destroy temp. [b] ℃
Sample[c] 0	5.2	18.8	2.2	360	1100
Sample 1	4.6	25.6	2.4	480	1020
Sample 2	5.4	29.5	3.2	670	960
Sample 3	5.8	43.2	3.9	850	950
Sample 4	6.0	48.4	4.2	985	950
Sample 5	6.1	56.1	4.5	1090	960

a. BJH method (desorption); b. DSC method; c. Sample 0 were prepared without starch additive.

Compare the crystal sizes and crystal morphology of the NaY with/without starch additive, apparently, the starch is favorable to nanosized NaY zeolite synthesis with narrow particle distribution of 50-100 nm related to 50-210 nm, moreover, with starch additive the average diameter of nanosized NaY is about 75 nm, it is 30 nm smaller than that of no starch additive (**Figure 2**). It may be concluded that starch is a good support or induction material, which lead to the direct reaction and confine the space of reactant because of its viscosity, so starch can be applied in confined space in the synthesis of nanosized NaY.

Figure 1 XRD pattern of (a)nanosized NaY zeolite(Sample 4) and (b)metakaolin

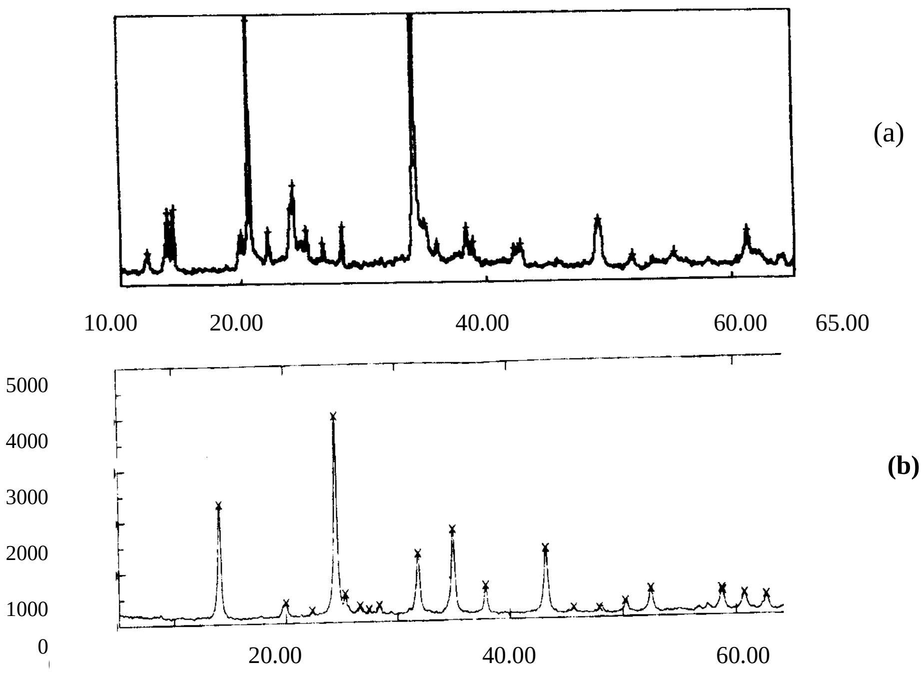
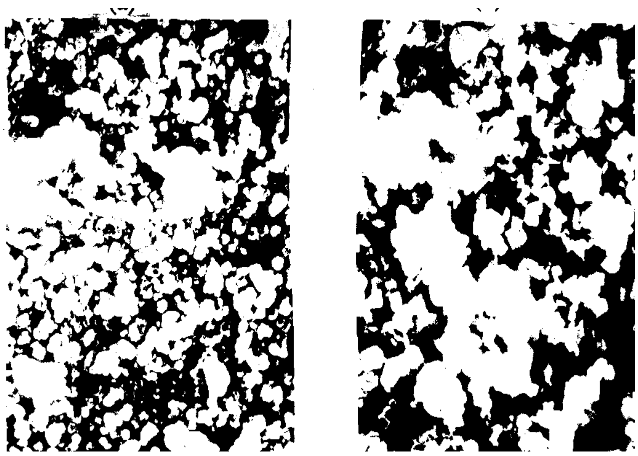


Figure 2 SEM image of nanosized NaY (a) Sample 4; (b) Sample 0

(a) **(b)**



Sample **4** has a total BET surface area of 985 m^2/g with an external surface area of 312.0 m^2/g. In addition to the pore volume inside the NaY crystals the material had an additional pore volume of 1.82 mL/g with an average pore radius of 16 nm. This mesopore system resulting from the packing of nanosized NaY crystals seems to provide excellent possibilities for diffusion of reactants and products, which is of significant importance in heterogeneous catalysis. However, Sample **0** only has a total BET surface area of 360 m^2/g with an external surface area of 76.0 m^2/g and NaY zeolite produced in industry has a total BET surface area of 250 m^2/g with an external surface area of 30.0 m^2/g.

The confined space synthesis, due to reducing reaction chance and consolidating directive reaction, is possible to prepare zeolites with a given crystal size distribution and very small zeolite crystals. Currently, the studies on reducing the size and narrow are in progress, the particle distribution of crystalline NaY crystals by the reported method from metakaolin.

Experimental

X-ray diffraction(XRD) were recorded by slow scanning on a D/max-rB vertical goniometer equipped with a θ-compensating divergence slit and a diffracted beam graphite monochromator utilizing Cu-Kα radiation. Crystal sizes were calculated by XRPD line broadening using the Scherrer equation. Particle distribution was analyzed by LS800 Laser particle sizer and verified by XRPD and SEM. The Si/Al ratio was also determined by X-ray diffraction[7] according to the following relationship:

$$SiO_2/Al_2O_3 = (25.858-a_0)\times 2/ (a_0-24.191)$$

Solid morphology were determined by scanning electron micrographs (SEM; Hitachi

H-700 instrument), a gold film was sputtered onto the sample *prior to* observation (ISI-DS130) [8]. The elemental composition was obtained by ICP. Thermal analysis (TG and DTA) was performed using Perkin-Elmer equipment consisting a DTA 1700 differential thermal analyzer. The heating rate was maintained at 10 ℃/min in a flowing air atmosphere of 50 mL/min. N_2 adsorption-desorption isothermals were obtained at liquid N_2 using a ASAP 2000 instrument and surface area and pore size distribution of the samples were calculated by the BdH method [9] .

Synthesis of Sample

Starch ($M_{wt.}$ 80, 000) of analytic grade was used in the experiments. The starch was dried at 100℃ for 2 h *prior to* use. All other reagents, metakaolin (≤1.0 μm, Na_2O: 0.5%, K_2O: 0.2%, Al_2O_3: 43.5%, SiO_2: 53.8%, H_2O: 2.0wt%), sodium silicate (analytic grade), sodium hydroxide (NaOH, 97wt%) and distilled water, were used as received.

Typical procedure, 5 g of starch was suspended in clear solution of Na_2SiO_3, H_2O and NaOH, and subsequently the metakaolin was introduced. The composition of the synthetic gel (molar basis) was xAl_2O_3: 0.1 starch: 5.2 Na_2O: 8 SiO_2: 120 H_2O($0 \leq x \leq$ 0.5-1.0). After aging for 1 h at room temperature the mixture was transferred into a stainless steel autoclave and heated in an oven at 100℃ for 12 h. After cooling the autoclave to room temperature the product was suspended in water, filtered by suction, resuspended in water, and filtered again. It was repeated three times and finally the product was washed with distilled water and dried at 110℃ for 3 h, the starch additive was removed by pyrolysis in a muffle furnace at 550℃ for 2 h or washed with water, because starch can be hydrolysized by concentrated base after reaction and easily dissolved in water. Five nanosized NaY zeolite samples with different Si/Al ratio were prepared using the reported method.

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