Synthesis of A Single-Phase Superfine Na-Y Zeolite from Coal Fly Ash

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Abstract. The process for the synthesis of flyash-based superfine zeolites-Y (FAZ) were presented, which basically included the alkaline fusion treatment of fly ash (FA), the gels formation by dissolved and aged, following hydrothermal crystallization. A detailed investigation was carried out to determine the effects of conditions of synthesis superfine zeolite-Y. The crystallization structure of zeolite-Y was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The experimental results show that the optimized conditions: Fly ash by alkali fusion (NaOH: fly ash ratio 1.2:1), and dissolved of 60 C using distilled water and aged of 25 C for 22h. The following, at conditions of 2.2 M NaOH solution, liquid:solid=6.5, the slurry was hydrothermal crystallized at 100 C for 24 h. Synthesis of particles exhibits completely grown crystals of zeolites-Y and cubic morphology with approximate dimensions of 400 mm. The crystalinity of zeolite-Y was 88.7%. At the advantage of this paper was to synthesize superfine Y zeolite that using only flyash as a raw materia and without using any other silicon and aluminum source and any template addition under mild conditions.

Introduction

Coal ash is generated by combustion of coal in a power station as a waste product. It has been established that FA is mainly composed of amorphous material (alumino-silicate glasses) can be converted to zeolites in alkali solutions by hydrothermal treatment. There are many reports for synthesis of zeolite from FA, for example, faujasite, Na-A zeolite, phillipsite and hydroxysoodalite. The zeolite-Y has be used in received much attention. It is also reported that use of zeolite-Y can improve catalytic cracking selectivity, reduce coke formation, increase the yield of diesel oil and promote gasoline quality; it can also be used in the fine chemical industry. In the syntheses of zeolite-Y, silica source such as sodium silicate solution and Source of aluminum are currently used and this requires the addition of seeds or initial solution to provide nuclei[1~4]. The aim of this paper was to synthesize a single-phase superfine zeolite-Y from FA. And any source of silicon and aluminum source and any organic template without additional. The products thus obtained were characterized by XRD and SEM. The formation condition and process of a single-phase zeolite-Y are discussed in this article.

Experiment

Zeolite synthesis

A homogenous mixture was prepared by proper grinding and mixing of flyash and caustic soda in 1:1.2 ratio. This mixture was heated at about 750 C for about 2h. Then, the fusion sample was cooled, milled and mixed thoroughly using distilled water in a breaker. The breaker was kept in a...
water bath and stirred constantly for a few hours. The slurry was subjected to ultrasonic and aging for a few hours. This amorphous alumino-silicate gel was formed. This gel was then subjected to crystallization between 40°C~ 100°C for about 10~30 h in specially designed stainless alloy autoclaves with thin walls which allow a fast heat transfer. The solid crystalline product was recovered by filtration and washed with distilled-deionized water thoroughly until the filtrate pH was 11, and dried at 80 °C for 24 h in an air oven.

Characterization.

The materials obtained were characterized by various conventional methods. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku X-ray diffractometer using Ni-filtered Cu KR radiation (30 kV, 16 mA). Particle morphology was observed by an Hitachi scanning electron microscope(SEM).

Results and Discussion

Influence of molar ratios SiO₂/Al₂O₃

![Fig. 1 Influence of molar ratio SiO₂/Al₂O₃ : (a) 0.9, (b) 2.0, (c)pure FA](image1)

![Fig. 2 Influence of aging temperatures : (1) 80°C, (2) 50°C and(3) 40°C for 24h](image2)

![Fig. 4 SEM spectrum of zeolite-Y at 60°C for 2h and 25°C for 22h](image4)

Figure 1 shows the XRD patterns of the synthesized samples were investigated by changing other SiO₂/Al₂O₃ ratio from 0.9 to 3.5 and the crystallization temperature at 100°C. The patterns of the material formed at SiO₂/Al₂O₃ =0.9 possesses many diffraction peaks, which can be assignable to zeolite-A . When the ratio of SiO₂/Al₂O₃ increase, new peaks of faujasite appear (pattern (b)-(c)). The synthetic faujasite type zeolite takes in two forms with the same crystal structure at different SiO₂/Al₂O₃ molar ratio. One was zeolite-X with SiO₂/Al₂O₃ =2.0 and another was zeolite-Y using only the starting materials flyash (SiO₂ and Al₂O₃ ratio of 2.5~3.5 about).

Influence of aging conditions

It has been established that the amorphous aluminosilicate in FA is easier to dissolve than the crystalline one such as R-quartz and mullite in alkali solutions. To clarify the detailed formation process of zeolite-Y, effect on the final product of crystallization were characterized under different aging conditions. In Figure 2, as can be seen, the zeolite-Y was synthesised ,but the crystallization strength reduction with temperature rise. This is because the silicon aluminum dissolved easily formation gel under high temperature, deposited on the surface of FA , further influence in which the silicon aluminum dissolved, resulted crystallization decreased. The intensity of XRD peak of the sample-(4) was highest which that it was dissolved of 60°C and aged of 25°C for 22h. So, it was used as a fixed aging condition in the following synthesis experiments.

Influence of the conditions of crystallization

Fig. 3(1) illustrates the XRD patterns of three samples synthesized from FA at the condition of 1 M, 2.2 M and 3 M NaOH solution and crystallization for 24h. According to XRD patterns of three samples obtained, only sample (2.2 MNaOH solution) was confirmed by pure-form zeolite-Y without the formation of other types of zeolites. Hui and Chao pointed out that synthesis of zeolite Y depends on the rate of gel dissolution[5], the number and distribution of nuclei in prepared initial
gel, and the crystal growth rate during hydrothermal treatment. The structural formation of zeolite Y may be explained in turn depend on other factors such as synthesis temperature, crystallization time, composition molar ratios of initial gel, etc.

Fig. 3 XRD patterns of FAY in different conditions of 1) alkalinity concentration, 2) crystallization time, 3) crystallization temperatures, 4) the ratio of liquid to solid

The alumino-silicate fused mass gel obtained is amorphous and changes to the crystalline state when subjected to hydrothermal crystallization. The results presented in Fig.3(2,3) reveals that crystallization temperature and time influences zeolitic crystallinity. Percent crystallinity of zeolite-Y increases significantly until up to 100°C for 24 h. The crystallization time increases to 30h, the other peaks to formed. Therefore, crystallization conditions identified as 100°C for 24h in the experiment.

Fig. 3(4) shows the XRD patterns of samples produced using different molar ratios of liquid to solid under the same synthetic conditions. The XRD patterns indicate that all samples exhibit a zeolite-Y structure. Notably, the samples-2(liquid:solid=6.5) show significantly higher broadened diffraction peaks, with higher yield of crystallization. The relative crystallinities calculated[6] for samples -1(liquid:solid=8.5) and samples -2 are found to be 74.7% and 88.7%, respectively.

Morphological studies

The SEM photographs in Fig.3 depict the sample transformation of FA into Zeolite-Y. Samples zeolite-Y are fairly uniform in crystal size, and the individual aggregates are composed of closely packed nanocrystals, and have smaller average aggregate sizes. This is probably because less uniform crystallization occurred in gel. For the sample the average particle (aggregate) size was estimated from at least 400nm particles in the SEM images.

Conclusions

Synthesis of FAZ is directly related to extraction of silicates and aluminates form FA using sodium hydroxide. From the information presented in this paper, Si4+ and Al3+ ions are eluted from fusing FA by dissolution of amorphous material during the aging and crystallization to form a single-phase Y type zeolite in the autoclave. The Y type zeolite were characterization by XRD and SEM patterns, the following conclusions can be drawn.

A homogenous fusion mixture was prepared by proper grinding and mixing of FA and caustic soda in 1:1.2 ratio. This mixture was calcined at about 750°C for about 2h. Then sample was dissolved at 60°C and aged at 25°C for 22h, to be gel formation. The gel and water as the ratio of liquid to solid is 6.5, in 2.2 M NaOH solution to crystallization for 24h at 100°C using the autoclave. The maximum purity of zeolite-Y was obtained, crystallinity calculated for samples was 88.7%. SO, the SiO2 and Al2O3 ratio of 2.5~3.5 in FA favours formation of Zeolite-Y. On modification of the actual SiO2 and Al2O3 ratio, by increasing sodium silicate or sodium aluminate content, it was possible to synthesise zeolite-X or zeolite-A at SiO2/Al2O3 of 2.0 or 0.9 respectively. The important feature of this novel procedure is to produce superfine zeolite-Y and crystallinity 88.7% in one vessel without using any other silicon and aluminum source and any template addition. The high volume utilization of FA for zeolite production technology compared to other medium low value utilization, this production technology has advantages of value addition, offering an edge over
other flyash utilisation technologies currently used.

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References


