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 60Cusing distilled water and aged of 25C for 22h. The following, at conditions of 2.2 MNaOH solution, liquid:solid=6.5, the slurry was hydrothermal crystallized at 100C 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 (aluminosilicate 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 hydroxysodalite. 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 750Cfor 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 40C~ 100Cfor 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 SiO_2/Al_2O_3

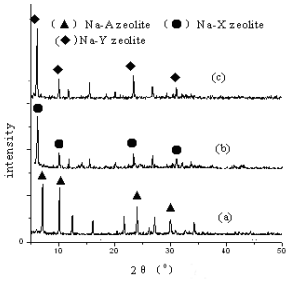

Fig. 1. Influence of molar ratio SiO_2/Al_2O_3 : (a) 0.9, (b) 2.0, (c)pure FA

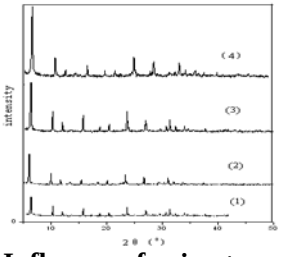

Fig. 2 Influence of aging temperatures : (1) 80C, (2) 50C and(3) 40Cfor 24h; (4) at 60C for2h and 25C for 22h

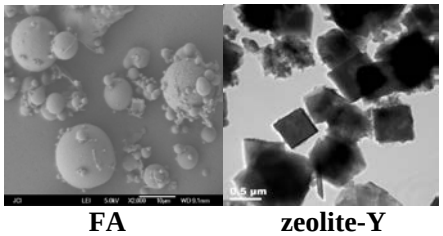

Fig. 4 SEM spectrum of zeolite-Y FA zeolite-Y

Figure 1 shows the XRD patterns of the synthesized samples were investigated by changing other SiO_2/Al_2O_3 ratio from 0.9 to 3.5 and the crystallization temperature at 100C. The patterns of the material formed at SiO_2/Al_2O_3 =0.9 possesses many diffraction peaks, which can be assignable to zeolite-A . When the ratio of SiO_2/Al_2O_3 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 SiO_2/Al_2O_3 molar ratio. One was zeolite-X with SiO_2/Al_2O_3 =2.0 and another was zeolite-Y using only the starting materials flyash (SiO_2 and Al_2O_3 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, resultd crystallization decreased. The intensity of XRD peak of the sample-(4) was highest which that it was dissolved of 60Cand aged of 25Cfor 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.

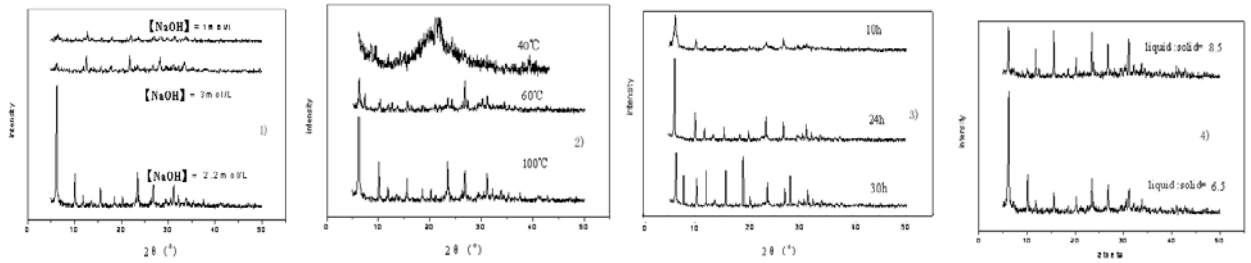

Fig. 3 XRD patterns of FAY in differentat contidions of1) alkalinity concentration, 2) crystallization time, 3) crystallization temperatures, 4) the ratio of liquid to solid

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℃for 24 h. The crystallization time increases to 30h, the other peaks to formed. Therefore, crystallization contidions identified as 100℃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 crystalinities 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, Si^{4+} and Al^{3+}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℃for about 2h. Then sample was dissolved at 60Cand aged at 25Cfor 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 100C using the autoclave. The maximum purity of zeolite -Y was obtained, crystalinity calculated for samples was 88.7%. SO, the SiO_2 and Al_2O_3 ratio of 2.5~3.5 in FA favours formation of Zeolite-Y . On modification of the actual SiO_2 and Al_2O_3 ratio, by increasing sodium silicate or sodium aluminate content, it was possible to synthesise zeolite-X or zeolite-A at SiO_2/Al_2O_3 of 2.0 or 0.9 respectively . The important feature of this novel procedure is to produce superfine zeolite-Y and crystalinity 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 mediumr 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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