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Hydrothermal synthesis of zeolites from natural stellerite①

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[Abstract] Y and P zeolites were synthesized hydrothermally from natural stellerite under different conditions and were characterized via XRD and FT-IR. The results show that the higher crystallinity of Y zeolite can be obtained in hydrothermal system with low alkalinity, low Ca^{2+}/Na^{+} ratio, and high SiO_2/Al_2O_3 ratio. The lattice space of the samples decreases as crystallization time increases. P Zeolite is prompted under condition of higher alkalinity and higher Ca^{2+}/Na^{+} ratio. The intensity and number of bands in the range of 400 cm^{-1} ~ 900 cm^{-1} increases with reaction time. Bands at 680 cm^{-1}, 760 cm^{-1} and 860 cm^{-1} corresponding to Y zeolite appear during the crystallization stage. Most of these bands shift to higher wavenumbers when SiO_2/Al_2O_3 ratio increases generally. In the hydrothermal system with reverse condition above, bands at 600 cm^{-1}, 420 cm^{-1} ~ 470 cm^{-1} hardly change as the crystallization time increases and the main crystal phase of P zeolite is obtained.

[Key words] Y zeolite; P zeolite; stellerite; crystallinity; hydrothermal synthesis
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1 INTRODUCTION

Zeolites are a family of hydrated aluminosilicate minerals which contain alkali and alkaline earth metal cations. They have a framework structure with interconnected cavities occupied by positively charged ions and water molecules. A favourable combination of physico-chemical properties is achieved by this particular structure. Zeolites are highly rated in their molecular sieving, adsorbing, catalytic and ion exchanging functions. They are used by the chemical industry as fertilizer, detergent builders, drying reagents for gases and liquids, selective molecular adsorbents for pollution abatement[1~4], etc. As this has recently led to a steep increase in demand of these products, it is obvious that zeolites synthesized from low-cost natural silica-aluminate sources is becoming increasingly interesting in the fields of chemical industries and daily application. Zeolites are usually obtained synthetically by hydrothermal growth in an aqueous (alkaline) reactant mixture. By this day, the waste solid and natural minerals rich in SiO_2 and Al_2O_3, such as flyash, tuff, pumice, kaolinite, etc., have been used as starting products for hydrothermal synthesis of zeolites[5~7]. Regarding both aspects of efficient application of natural resources and economic factor for synthesis of zeolites, for the first time, the stellerite, a natural mineral resources located in the south of China, was taken as the starting materials of zeolites in our research. Y and P Zeolites were successfully synthesized from stellerite under hydrothermal condition. The phase transformation and zeolite crystallinity were investigated via X-ray powder diffraction and IR spectrum measurements.

2 EXPERIMENTAL

The following materials were used:

Stellerite rocks were provided by Resources Administration of Ziyuan County, Guangxi province, China. Its degree of whiteness was more than 90% and it was composed of stellerite crystalline, a little of quartz. The composition mainly composed of SiO_2, Al_2O_3, CaO, as well as traces of Fe_2O_3, MgO, etc. The SiO_2/Al_2O_3 ratio is about 7. The chemical composition of stellerite rocks is listed in Table 1. $Na_2SiO_3 \cdot 9H_2O$, NaOH, $Al(OH)_3$, NaCl, HCl, obtained commercially, were also used for hydrothermal synthesis of zeolites. They were all analytical grade reagent.

Table 1 Chemical composition of stellerite (mass fraction, %)

SiO_2	Al_2O_3	Si/Al	CaO	K_2O
58.76	14.13	3.529	8.8	0.11
Na_2O	Fe_2O_3	H_2O	Volatile	Tatal
0.18	0.004	18.12	17.79	100.1

Seed preparation: Solution A was prepared by dissolving $Na_2SiO_3 \cdot 9H_2O$ into distilled water. Solution B was also prepared by dissolving $Al(OH)_3$ into concentrated NaOH solution and a diluting step followed. A gel reactant mixture for the synthesis of the

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zeolite seed was achieved as soon as solution B was slowly dropped into solution A under vigorous stirring. The composition of the mixture was (mol/mol): Na_2O: Al_2O_3: SiO_2: H_2O= 13: 1: 10: 320. The mixture was packed into a glass beaker and hydrothermally treated at 373 K for 2 h in an aqueous thermostat. The product was washed, filtered, and dried, until a white powder, the zeolite seed, was obtained.

Zeolite synthesis: Stellerite was grounded in air for 4 h by ball milling and the 85 μm powder was obtained. Then the powder was washed at room temperature for 2 h with HCl solution (100 g stellerite, 8 mL 36% HCl, 330 mL H_2O) followed by filtering and drying. The acid-washed stellerite powder was calcinated at 873 K for 4 h inside a muffle to activate the stellerite. The mixture for the synthesis of zeolites was prepared as follows: the activated stellerite, seed, NaCl, and NaOH solution were mixed together to form a homogeneous mixture in which the weight ratio of seed to stellerite was 0.25. The molar proportion of the composition is listed in Table 2. The mixture was sealed into a polytetrafluoroethylene autoclave and placed in constant temperature baking oven and aged at 323 K for 6 h, then treated hydrothermally at 373 K for different duration. The product was washed to pH= 9, and dried to obtain the zeolites. According to the chemical composition of the mixture for the synthesis of zeolites, the samples were divided into four batches: Y1x (sample Y11, Y12, Y13, Y14), Y2x (sample Y21, Y22, Y23, Y24, Y25), Y3x (sample Y31, Y32, Y33, Y34), Y4x (sample Y41, Y42, Y43, Y44, Y45).

X-ray diffraction (XRD) analysis was employed using Cu-K_α radiation on a Bruker D8 ADVANCE diffractometer. Infrared absorption spectra (FT-IR) of these samples were recorded by Bruker Vector-22 spectrometer.

3 RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of zeolite synthesized in hydrothermal system with low H_2O/Na_2O and higher Ca^{2+}/Na^+ ratios respectively. From the XRD profile, the dominant crystal phase is P zeolite, and the crystallinity of P zeolite increases with its crystallization time increased from 12 h to 48 h (Fig. 2). Y Zeolite is hardly observed in this batch. Fig. 3 shows the XRD patterns of zeolites in the second batch Y2x. For all samples Y21 to Y24, the main phase is P zeolite. Although the weak peaks of Y zeolite at 2θ= 6.4° have also detected in the profile, the intensity of Y zeolite increases slowly with crystallization time increasing. The peaks of Y zeolite gradually disappear when the intensity of P zeolite increases. It is observed that the crystallinity of Y zeolite attains its maximal value at point of 36 h by

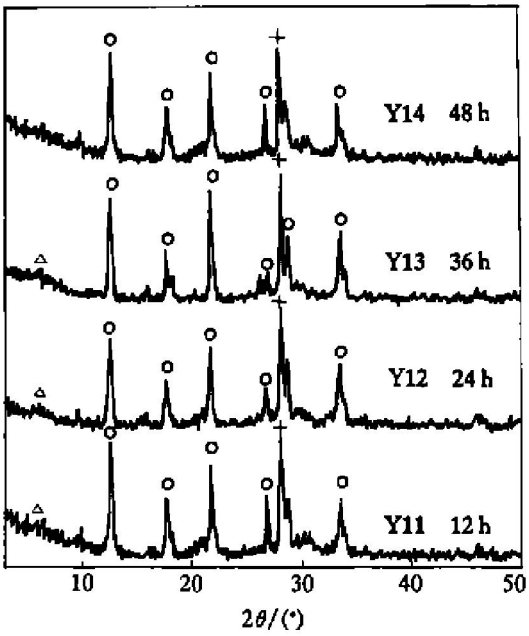

Fig. 1 XRD pattern on samples synthesized under condition of H_2O/Na_2O= 30, Ca^{2+}/Na^+ = 0.16, △—Y zeolite; ○—P zeolite; +—Quartz

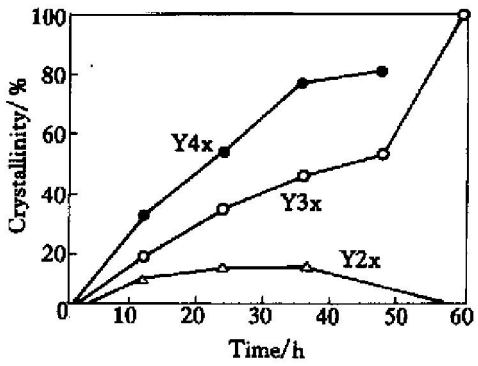

Fig. 2 Relationship between zeolite crystallinity and crystallization time

Table 2 Chemical composition of reaction mixture for Y zeolite (mole fraction, %)

Samples	Na_2O: Al_2O_3: SiO_2: H_2O	NaCl	H_2O/Na_2O	SiO_2/Al_2O_3	Ca^{2+}/Na^+
Y21, Y22, Y23, Y24, Y25	2.7: 1: 9: 125	0	46.3	9	0.21
Y31, Y32, Y33, Y34, Y35	2.85: 1: 7: 96.6	10	33.9	7	< 0.16
Y41, Y42, Y43, Y44, Y45	2.85: 1: 7: 96.6	15	33.9	7	< 0.15
Y11, Y12, Y13, Y14	4: 1.4: 10: 120	0	30	7.14	0.16

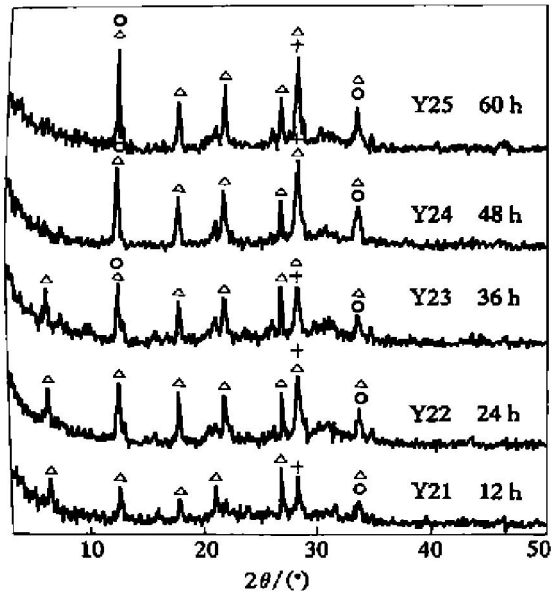

Fig. 3 XRD pattern on samples synthesized under condition of H_2O/Na_2O= 46.3, Ca^{2+}/Na^+ = 0.21, △—Y zeolite; ○—P zeolite, + —Quartz

examining the crystallinity curve in Fig. 2. The crystallization process could be described as follows: the reactant mixture → P zeolite+ Y zeolite → P zeolite. Meanwhile, a strong peak in this XRD profile is showed at 2θ= 12.8°, which is caused mainly by P zeolite for the peak in this range is the combination of the maximal unique peak of P zeolite and extremely weak peak of Y zeolite. The peak at 2θ= 6.4° is the maximal unique peak of Y zeolite, and its lattice space in the range is marked as d_0. It was found that d_0-value of Y zeolite in the batch decreases with crystallization time increasing. When the XRD analysis data are examined in details, namely, the shifts of d_0-value are 13.83037 Å (Y21) → 13.73081 Å (Y22) → 13.69625 Å(Y23) → (12.6616 Å) (Y24) → 13.13655 Å (Y25). Fig. 4 shows the XRD patterns of the samples in the third batch. Here, the H_2O/Na_2O and Ca^{2+}/Na^+ ratios are 33.9 and 0.16 respectively. From these patterns it could be found that Y and P zeolite are formed simultaneously after treated hydrothermally for 12 h. After hydrothermal treatment for 24 h, the peaks of P zeolite disappear. The peak intensity of Y zeolite increases with the crystallinity of Y zeolite increasing (Fig. 2). The shifts of d_0-value in this batch are 14.32437 Å (Y31) → 14.30741 Å (Y32) → 14.29920 Å (Y33) → 14.28428 Å (Y34). Fig. 5 shows that the crystal phase of all the samples in the fourth batch (Y4x) is only Y zeolite. The crystallinity of Y zeolite increases and the peak of the residual quarts at 2θ = 28° decreases gradually with crystallization time increasing from 12 h to 48 h. The shifts of d_0-value in the fourth batch are: (14.03359) Å (Y41) → 14.09332 Å (Y42) → 14.00330 Å (Y43) →

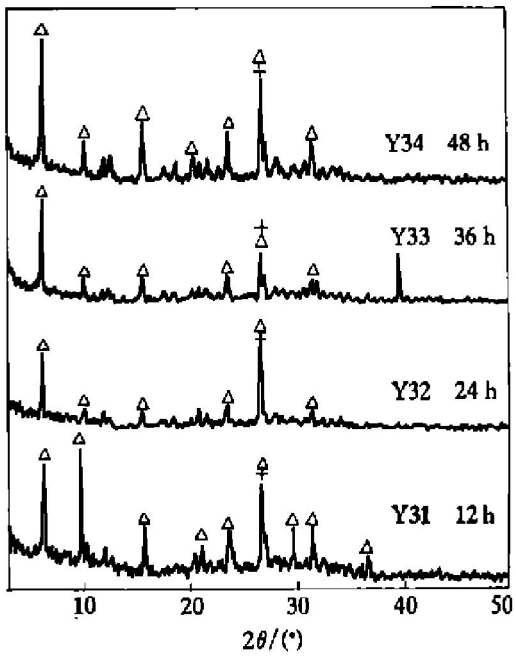

Fig. 4 XRD pattern on samples synthesized under condition of H_2O/Na_2O= 33.9, Ca^{2+}/Na^+ = 0.15, △—Y zeolite, ○—P zeolite, + —Quartz

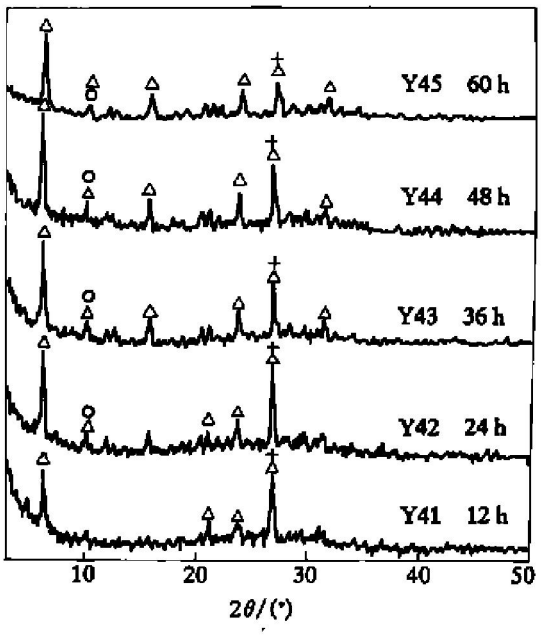

Fig. 5 XRD pattern on samples synthesized under condition of H_2O/Na_2O= 33.9, Ca^{2+}/Na^+ = 0.15, △—Y zeolite, ○—P zeolite, + —Quartz

14.13785 61 Å (Y44). The d_0-values bracketed are considered as inaccurate measurement due to device or operation.

Comparing the phase transformation of zeolites synthesized under four different hydrothermal conditions, it is apparent that the H_2O/Na_2O and Ca^{2+}/Na^+ ratios have great influence on zeolite formation. It is easier to form Y zeolite than P zeolite in hydrothermal system with low Na_2O/H_2O and low

Ca^{2+} / Na^{+} ratios. The crystallinity of zeolite increases and its lattice space decreases with crystallization time increasing, meanwhile, the SiO_2/ Al_2O_3 ratio is increased.

Fig. 6 shows the IR spectra of the samples in the first batch (Y1x). It is seen that the intensities and locations of the bands at 432 cm^{-1}, 450 cm^{-1} and 603 cm^{-1} have not changed observably. The bands at 432 cm^{-1} and 450 cm^{-1} are associated with structure-insensitive T-O bonding modes of tetrahedral TO_4 units (T = Si or Al)[8]. The band at 603 cm^{-1} was assigned to structural elements of six-rings[9,10] that may act as precursors for the nucleation events. Although the band at 603 cm^{-1} is clearly detected, Y zeolite is not observed by XRD (Fig. 1). These phenomena are attributed to the fact that the growth of Y zeolite is restrained by overwhelming growth of P zeolite in hydrothermal system with higher alkalinity. Bands at 670 cm^{-1} ~ 700 cm^{-1} and 742 cm^{-1} are associated with inter-bonding vibration of O-Si(Al)-O or O-Si-O. The intensity of the former band increases and it shifts to higher wavenumbers, namely, the shift of the bands is 680 cm^{-1} → 680.7 cm^{-1} → 682.7 cm^{-1} → 690.4 cm^{-1}. The bands at 1 020 cm^{-1} ~ 1 034.5 cm^{-1} and 970 cm^{-1} which are regarded as antisymmetric stretching of O-Si(Al)-O moved to higher wavenumber (1 020 cm^{-1} → 1 023 cm^{-1} → 1 032.5 cm^{-1} → 1 034.5 cm^{-1}) and the intensity also increases with crystallization time increasing. The other bands at 1 490 cm^{-1} and 1 641.1 cm^{-1} are due to rudimental $CaCO_3$ in stellerite and adsorbed water[11]. The IR spectrum of batch Y2x show (Fig. 7) that the number of IR absorption peaks in the range of 900 cm^{-1} ~ 400 cm^{-1} increases with crystallization time increasing. The intensity of band around 600 cm^{-1} and the complexity of the spectral

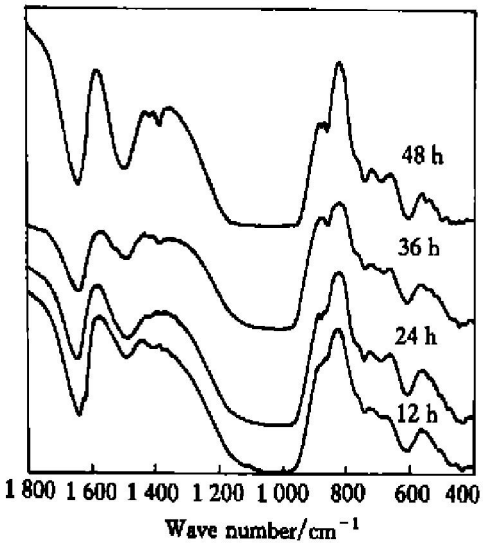

Fig. 6 IR spectrum of samples synthesized under condition of H_2O/ Na_2O= 30, Ca^{2+} / Na^{+} = 0.16

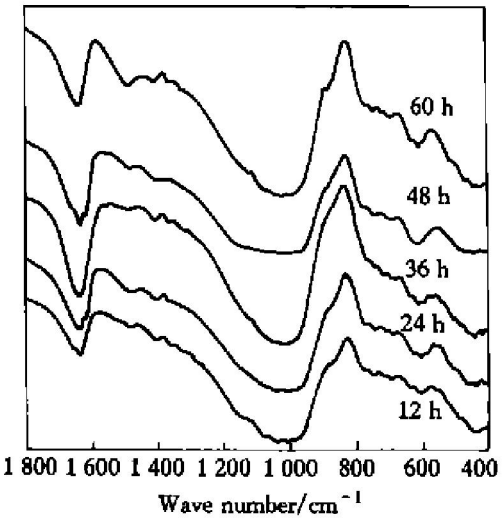

Fig. 7 IR spectrum of samples synthesized under condition of H_2O/ Na_2O= 46.3, Ca^{2+} / Na^{+} = 0.21

lines in the range of 900 cm^{-1} ~ 400 cm^{-1} attains their maxima after hydrothermal treatment for 36 h. The result is uniform that detected by XRD as shown in Figs. 2 and 5. The IR spectral profile is very different between batches Y3x, Y4x and Y1x, Y2x. Although the number and the shape of IR absorption peaks in batch Y3x and Y4x are approximately same under same crystallization time, and the intensities of these peaks in batch Y3x (Fig. 8) are weaker than that in batch Y4x (Fig. 9). This difference between Y3x and Y4x is caused by different Ca^{2+} / Na^{+} ratio in their hydrothermal system. It is considered that the growth process of Y zeolite is accelerated in hydrothermal system containing higher content of Na^{+}. The changes of absorption peaks in batch Y4x from Y41 to Y45 is as follows: (12 h) 466.7 cm^{-1}, 603.6 cm^{-1}, 864 cm^{-1} → (24 h) 462.8 cm^{-1}, 597.8

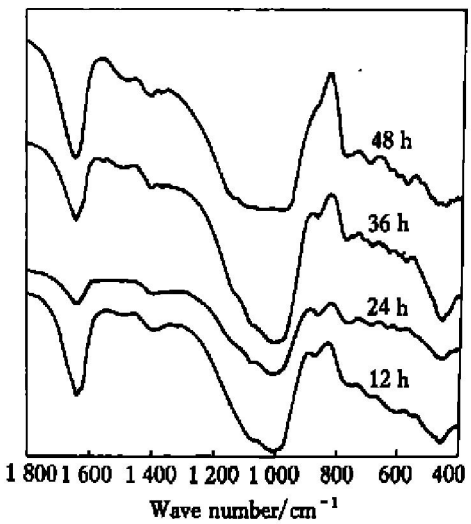

Fig. 8 IR spectrum of samples Y3x synthesized under condition of H_2O/ Na_2O= 33.9, Ca^{2+} / Na^{+} = 0.15

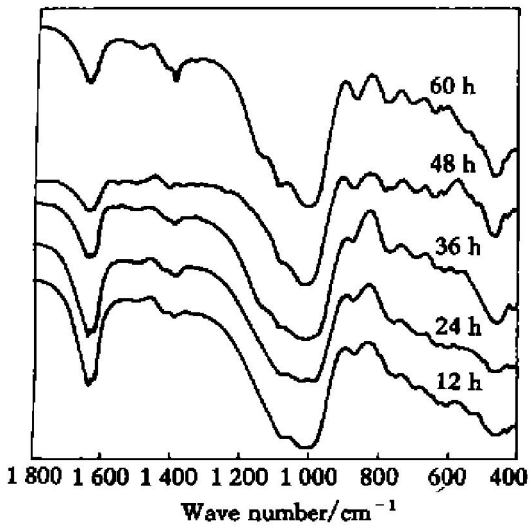

Fig. 9 IR spectrum of samples Y4x synthesized under condition of H_2O/Na_2O= 33. 9, Ca^{2+}/Na^+ = 0. 15

cm^{-1}, 628. 7 cm^{-1}, 748. 2 cm^{-1}, 867. 8 cm^{-1} → (36 h) 457 cm^{-1}, 607. 5 cm^{-1}, 682. 7 cm^{-1}, 767. 5 cm^{-1}, 867. 8 cm^{-1} → (48 h) 462. 8 cm^{-1}, 603. 6 cm^{-1}, 680. 7 cm^{-1}, 775. 2 cm^{-1}, 864 cm^{-1} → (60 h) 460. 9 cm^{-1}, 607. 5 cm^{-1}, 692. 3 cm^{-1}, 771. 4 cm^{-1} and 860 cm^{-1}. The appearance of bands at 682. 7 cm^{-1}, 767. 5 cm^{-1} and the rise of their intensities are related to the formation and crystallinity increasing of Y zeolite. It was verified that the SiO_2/Al_2O_3 ratio in zeolites increased as the new bands at 682. 7 cm^{-1} and 767. 5 cm^{-1} moved to higher wavenumber.

3 CONCLUSIONS

Y and P zeolite were successfully synthesized hydrothermally from natural stellerite. The results showed that the higher crystallinity of Y zeolite can be obtained in hydrothermal system with low alkalinity, low Ca^{2+}/Na^+ and higher SiO_2/Al_2O_3 ratios. The lattice space is decreased with crystallization time increasing. P zeolite is prompted under condition of higher alkalinity and Ca^{2+}/Na^+ ratio. IR spectrum measurement show that the intensity and number of bands in the range of 400 cm^{-1} ~ 900 cm^{-1} increase obviously with crystallization time increasing. Bands 680 cm^{-1}, 760 cm^{-1} and 860 cm^{-1} corresponding to Y zeolite appear during later crystallization stage. Most of these bands move to higher wavenumber, meanwhile, SiO_2/Al_2O_3 ratio increases generally. In hydrothermal system with reverse condition above, bands 600 cm^{-1} and 420 cm^{-1} ~ 470 cm^{-1} hardly change with crystallization time increasing.

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