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Preparation of nanosized NaA zeolite and its surface modification by KH-550

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Nanosized NaA zeolite was successfully synthesized by hydrothermal method using tetraethyl orthosilicate (TEOS) and aluminum isopropoxide (AIP) as the main raw materials. The surface modification of NaA zeolite was carried out by silane coupling agent 3-aminopropyltriethoxysilane (KH-550). The effects of silane coupling agent dosage, reaction temperature, reaction time, hydrolysis time and pH value on grafting rate of NaA zeolite were investigated in detail. The zeolites were characterized by XRD, SEM-EDS, FT-IR and TG-DTA. The results showed that the surface of NaA zeolite was modified successfully by KH-550. The optimal modification conditions obtained were as follows: the dosage of coupling agent in 95 % ethanol – 1.6 %, reaction temperature – 70 °C, reaction time – 2 h, hydrolysis time – 20 min, and pH value – 3.5. Under these conditions, the grafting rate of modified NaA zeolite was 3.95 %.

Keywords: *modified zeolite; silane coupling agent; grafting rate; characterization*

1. Introduction

Zeolites are silicate crystalline materials with regular pore size and structure [1]. They are characterized by thermal stability, acid properties, as well as adsorption and ion-exchange capacities. Therefore, they have been frequently used as ion-exchangers, catalysts, and adsorbents in practical applications [2–5]. Preparation and modification studies have developed rapidly because of the wide applications in many fields. Zeolite-organic composite materials, prepared by filling zeolite into a polymer, have been widely used in gas separation, pervaporation, etc. [6–9]. The poor compatibility between organic and inorganic phases often cause the interface defects to form, which leads to deteriorating of some properties of composite materials. Coupling agents were often used to enhance the interaction between inorganic and organic phases, to improve the microstructure of composite materials [10, 11]. Silane as a kind of coupling agent has been widely used at present. It is the most effective modifier for inorganic particles with hydroxyl groups. It is very suitable for surface modification of zeolite because the surface of zeolite has a lot of hydroxyl groups. The structure of silane is $R_1Si(OR_2)_3$ (where R_2 is alkyl and R_1 is other reactive group). The siloxane bonds are formed by condensation reaction between silicon hydroxyls produced by hydrolysis of coupling agent and hydroxyls on the surface of inorganic particles. Thus, the covalent bonds are established between the coupling agent and inorganic phase. In addition, R_1 can produce physical or chemical effects with organic components. Connections between inorganic and organic phases are eventually formed [12].

In this paper, nanosized NaA zeolite was firstly synthesized by hydrothermal method. The surface modification of NaA zeolite was carried out by silane coupling agent 3-aminopropyltriethoxysilane (KH-550). The effects of modification conditions on grafting rate of NaA zeolite were investigated in detail. The synthesized zeolites were characterized by XRD, SEM-EDS, FI-IR and TG-DTA.

2. Experimental

2.1. Materials

Chemical reagents included tetraethyl orthosilicate (TEOS, A.R. Aladdin), aluminum isopropoxide (AIP, A.R. Aladdin), tetramethylammonium

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hydroxide (TMAOH, 25 wt.%, Aladdin), sodium hydroxide (NaOH, A.R. Shanghai Sinopharm Chemical Reagent Co., Ltd.), glacial acetic acid (CH_3COOH, A.R. Shanghai Sinopharm Chemical Reagent Co,. Ltd.), ethanol (CH_3CH_2OH, A.R. Shanghai Sinopharm Chemical Reagent Co., Ltd.), 3-aminopropyltriethoxysilane (KH-550, C.P. Nanjing Capatue Chemical Co., Ltd.).

2.2. Preparation of nanosized NaA zeolite

NaA zeolite was prepared from a synthetic solution by dissolving AIP in TMAOH. The mixture was stirred for several hours at room temperature until a clear solution was obtained. Then, NaOH and TEOS were respectively added to the mixture and the final mixture was stirred for 24 hours. The molar composition of the resulting synthetic solution was as follows: Na_2O:2 Al_2O_3:15 SiO_2:30 TMAOH:1350 H_2O. Finally, the solution was heated to reflux for 10 days at 50 °C. After the hydrothermal treatment, NaA zeolite was recovered, washed with deionized water, freeze-dried, dried in vacuum at 60 °C for 24 hours, and then calcined at 550 °C for 9 hours.

2.3. Modification of NaA zeolite

6.0 g NaA zeolite was added to 50 mL 95 % ethanol. The pH of the solution was adjusted with glacial acetic acid. Silane coupling agent (KH-550) was added to the solution and the solution hydrolysis was conducted for a period of time. The solution was heated to reflux for some time, and then cooled and centrifuged. The modified NaA zeolite was recovered, washed with ethanol and deionized water, respectively, freeze-dried, and dried in vacuum at 60 °C for 24 hours.

2.4. Calculation of grafting rate

The effect of silane coupling agent on the surface modification of NaA zeolite was investigated by calculating the grafting rate. The modified zeolite dried to a constant weight was calcined at 550 °C for 9 hours. The grafting rate was calculated according to the weight loss of the modified zeolite. The grafting rate was defined as the mass ratio of total organic components in the modified zeolite (i.e. mass loss) to unmodified zeolite. The equation for grafting rate is as follows [13]:

$$g = \frac{m_1}{m_0} \times 100\% \quad (1)$$

where g stands for the grafting rate; m_1 is the mass of total organic components in the modified zeolite; m_0 is the mass of unmodified zeolite.

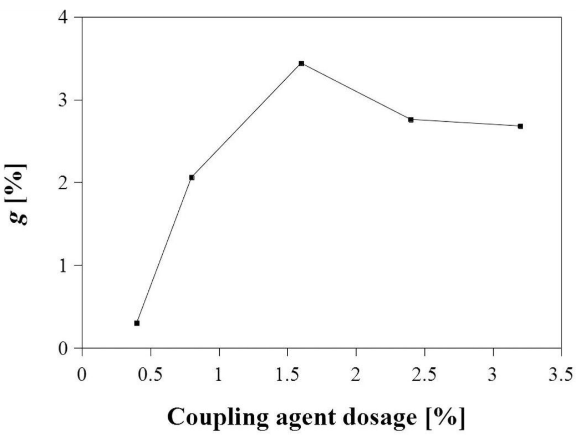

Fig. 1. Effect of silane coupling agent dosage on grafting rate of NaA zeolite.

2.5. Characterization

The crystal structure of NaA zeolite was identified by X-ray diffraction (XRD, D8-Advance, German Bruker) using, CuKα radiation with λ = 1.5406 Å. Scanning electron microscopy (SEM) investigation was carried out on a field-emission scanning electron microanalyzer (S-4800, Japan Hitachi, 5.0 kV). The IR spectra of unmodified and modified NaA zeolites were studied by Fourier transform infrared spectrometer (FT-IR, Tensor 27, German Bruker) using KBr pellets. The mass losses of NaA zeolites were tested by thermogravimetric analyzer (TG, HCT-1, China Beijing). The carbon content was tested by elementary analyzer (Vario EL III, Elemental, Germany). Elemental analyses of Si, Al and O were carried out by energy dispersion spectroscopy (EDS, E-max, Japan Hitachi).

3. Results and discussion

3.1. Effect of modification conditions on grafting rate of NaA zeolite

(1) Effect of silane coupling agent dosage

A series of experiments with different dosages of silane coupling agent were performed to test the grafting rate. Fig. 1 shows the effect of silane dosage on the grafting rate. The mass fraction of coupling agent in 95 % ethanol was 0.4 %, 0.8 %, 1.6 %, 2.4 % and 3.2 %, respectively. The results show that the grafting rate increased with the increase of the coupling agent dosage and reached the maximum value when the dosage was 1.6 %. After that, the grafting rate began to decrease with the increase of coupling agent dosage. The amount of coupling agent was too small to achieve modification. But excessive dosage not only increased the cost, but also caused self-polymerization reaction and decrease in grafting rate.

(2) Effect of reaction temperature

Fig. 2 shows the effect of reaction temperature on the grafting rate. The reaction temperature was set at 50 °C, 60 °C, 65 °C, 70 °C and 75 °C, respectively. The results showed that the grafting rate increased with the increase of reaction temperature and decreased when the temperature was above 70 °C. The solubility and reactivity of coupling agent could be improved by increasing the reaction temperature of the solution, hence, shortening the reaction time and improving the modification effect. Excessive temperature could result in self-polymerization or decomposition of the coupling agent, which was detrimental to the main reaction.

(3) Effect of reaction time

Fig. 3 shows the effect of reaction time on the grafting rate. The reaction time was 0.5 h, 1 h, 2 h, 3 h and 4 h, respectively. The results show that the grafting rate increased with the increase of reaction time. The grafting rate began to decrease after the reaction time reached 2 h, which might be attributed to the decomposition and adsorption of the grafted modifier.

(4) Effect of hydrolysis time

Fig. 4 shows the effect of hydrolysis time on the grafting rate. The hydrolysis time was tested

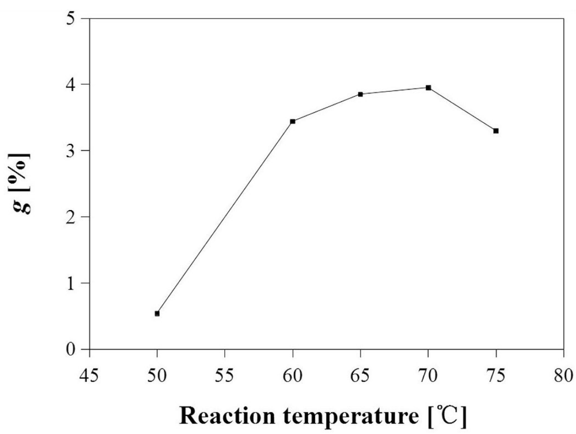

Fig. 2. Effect of reaction temperature on grafting rate of NaA zeolite.

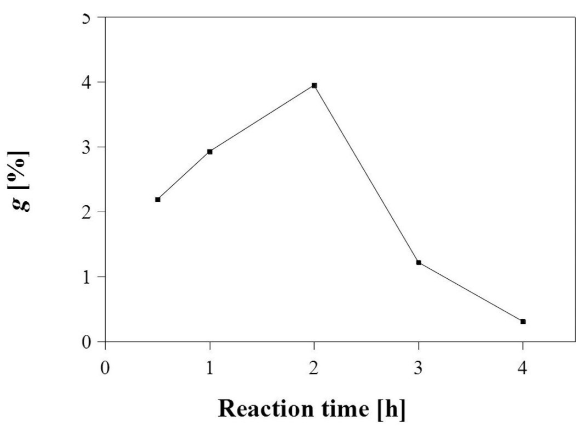

Fig. 3. Effect of reaction time on grafting rate of NaA zeolite.

at 5 min, 10 min, 20 min, 30 min and 40 min, respectively. The results show that the grafting rate increased with the increase in hydrolysis time. It began to decrease after the hydrolysis time reached 20 min, which might be due to the accelerated condensation of hydrolysis product of coupling agent, thereby causing the coupling agent to partially lose its coupling activity.

(5) Effect of pH value

Fig. 5 shows the effect of pH value on the grafting rate. The pH was set to 3, 3.5, 4 and 5, respectively. The results show that the grafting rate was the best when the pH value of the solution was 3.5. The hydrolysis and condensation rate of coupling agent were faster when the acidity of the solution

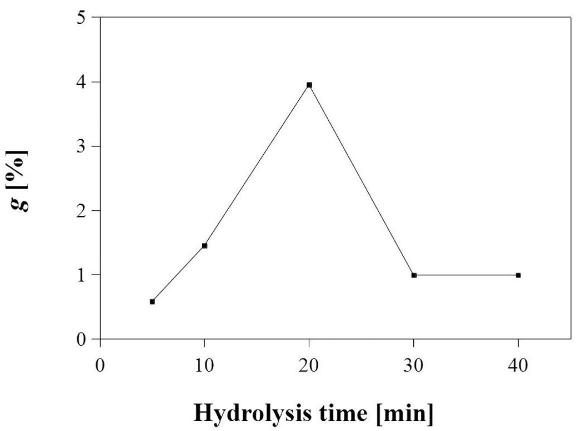

Fig. 4. Effect of hydrolysis time on grafting rate of NaA zeolite.

was too large or tended to decrease, which was unfavorable to the main reaction with zeolite. The pH of 3.5 was the optimum condition for the acidity of the solution.

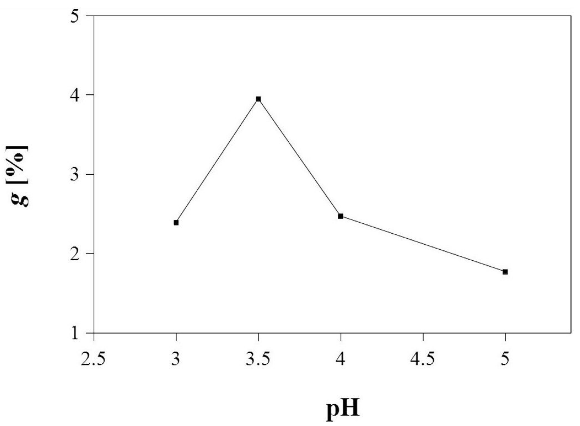

Fig. 5. Effect of pH on grafting rate of NaA zeolite.

3.2. Characterization of NaA zeolite

The XRD pattern of the synthesized NaA zeolite shown in Fig. 6 was analyzed. The diffraction peaks at 12.30 Å, 8.69 Å, 7.09 Å, 5.49 Å, 4.10 Å, 3.71 Å, 3.28 Å, 2.98 Å and 2.62 Å correspond to the characteristic peaks of NaA zeolite. The result indicates that the synthesized zeolite is NaA zeolite.

The morphology of the synthesized NaA zeolite was observed by SEM. Fig. 7 shows the SEM

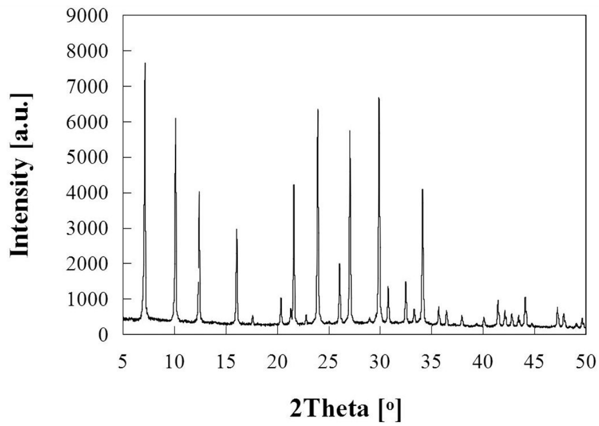

Fig. 6. XRD pattern of NaA zeolite.

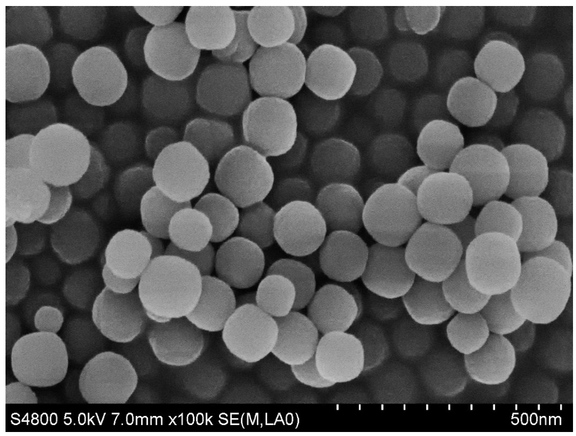

Fig. 7. SEM image of NaA zeolite.

image at magnification of 100,000 times. The NaA zeolite particles exhibit sphere-like shape. The particle sizes are between 80 nm to 150 nm.

IR spectra of the zeolites were measured before and after modification in order to investigate the influence of silane coupling agent on the structure of modified zeolite. The results are shown in Fig. 8. The peak of the modified zeolite at 3445 cm^{-1} which is characteristic of hydroxyl groups is weaker than that of the unmodified zeolite. It indicates that the numbers of hydroxyl group on the zeolite surface was reduced. This can be attributed to the reaction of the silicon hydroxyl groups in KH-550 with the hydroxyl groups on the zeolite surface. In addition, a new characteristic peak appeared near 1390 cm^{-1}, which corresponds to the vibration of the C–H bond in KH-550.

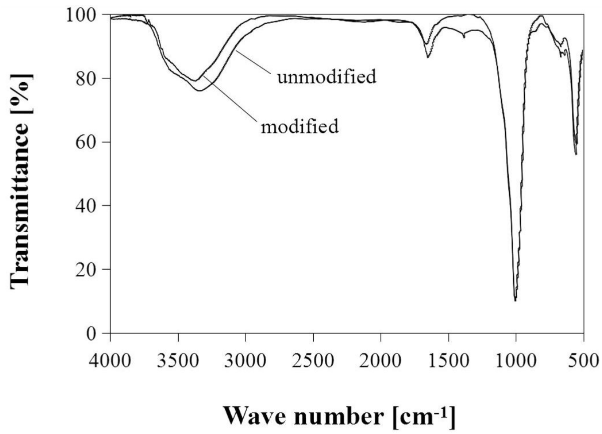

Fig. 8. IR spectra of unmodified and modified zeolite.

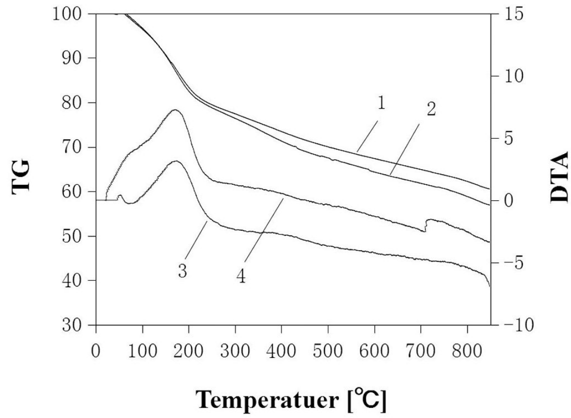

Fig. 9. TG-DTA curves of unmodified zeolite (curves 1 and 3) and modified zeolite (curves 2 and 4): 1 and 2 are TG curves before and after modification, respectively; 3 and 4 are DTA curves before and after modification, respectively.

The zeolites were analyzed by TG-DTA before and after modification in order to investigate the influence of silane coupling agent on the structure of the modified zeolite. The results are shown in Fig. 9. The mass loss of modified zeolite is greater than that of the unmodified zeolite because the surface of the former was grafted with some hydrocarbon groups. Zeolites mainly lose the adsorbed water before 175 °C. The modified zeolite had an additional mass loss after 175 °C, which may be connected with decomposition of the hydrocarbon chain grafted on the modified zeolite surface. The mass losses of unmodified and modified zeolite at 600 °C were 32.2 % and 35.9 %, respectively.

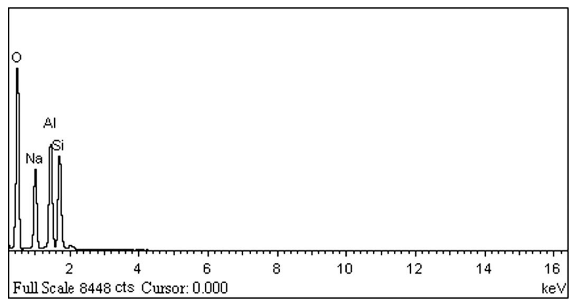

Fig. 10. EDS of unmodified zeolite.

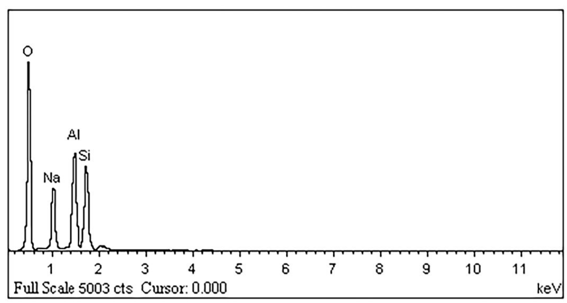

Fig. 11. EDS of modified zeolite.

The zeolites were analyzed by EDS before and after modification in order to investigate the influence of silane coupling agent on the structure of the modified zeolite. The results are shown in Fig. 10 and Fig. 11. The Si/Al ratio and O/Al ratio of modified zeolite are larger than those of unmodified zeolite. The carbon content determined by elementary analysis is 2.78 wt.%. The results indicate that KH-550 was successfully grafted on the surface of NaA zeolite.

4. Conclusions

Nanosized NaA zeolite was successfully synthesized by hydrothermal method. The effects of KH-550 dosage, reaction temperature, reaction time, hydrolysis time and pH value on grafting rate of NaA zeolite were investigated in detail. The results showed that the surface of NaA zeolite was successfully grafted with KH-550. The optimal modification conditions obtained were as follows: the coupling agent dosage – 95 % ethanol – 1.6 %, reaction temperature – 70 °C, reaction time – 2 h, hydrolysis time – 20 min, and pH value – 3.5. Under these conditions, the grafting rate of modified NaA zeolite was 3.95 %.

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