

Supplementary material

Hydrothermal synthesis of mixtures of NaA zeolite and sodalite from Ti-bearing electric arc furnace slag

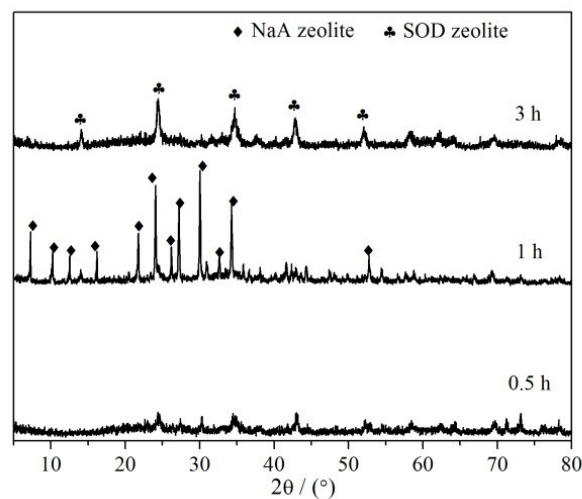


Fig. S1 XRD patterns of samples synthesized at different hydrothermal time.

$(n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)=2.0:1, n(\text{H}_2\text{O})/n(\text{Na}_2\text{O})=100:1, T=160^\circ\text{C})$

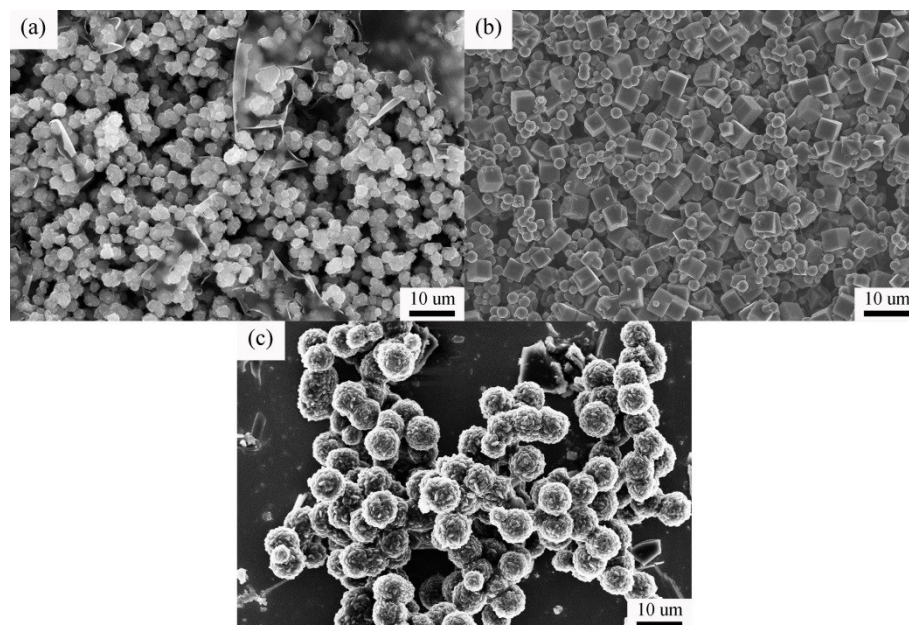


Fig. S2 SEM images of samples synthesized at different hydrothermal time. (a) 0.5 h, (b) 1 h,

(c) 3 h $(n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)=2.0:1, n(\text{H}_2\text{O})/n(\text{Na}_2\text{O})=100:1, T=160^\circ\text{C})$

Fig. S1 showed that some poor crystal substance could be synthesized at 0.5 h and well crystallized NaA zeolite generated at 1 h when the hydrothermal temperature was fixed at 160°C. However, they would convert to SOD zeolite with the hydrothermal time prolonging to 3 h. The SEM images shown in Fig. S2 confirmed the results of XRD patterns illustrated in Fig. S1. A lot of loosely packed, incomplete crystallization samples with irregular shapes were observed in Fig. S2a. It might be ascribed to the nuclei of zeolite wrapped by amorphous mass. After 1 h hydrothermal crystallization, a large number of bigger cubic with well-developed faces were the main fraction of the products (Fig. S2b). When the further prolongation of hydrothermal time up to 3 h, most of the cubic particles disappeared and new large spherule crystals composed of lamellar generated (Fig. S2c).

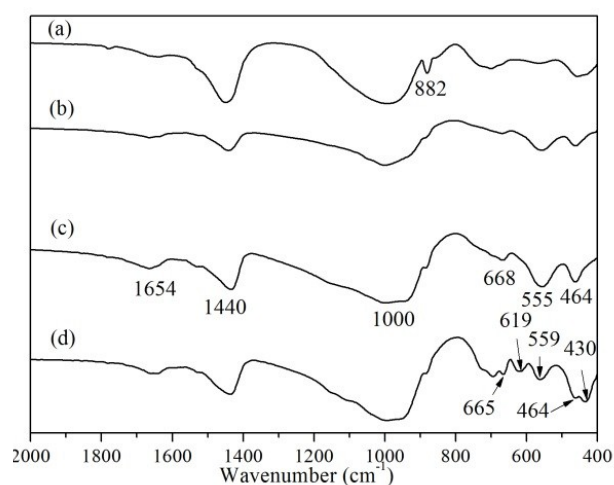


Fig. S3 FT-IR spectra of samples synthesized at different hydrothermal time. (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h ($n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)=2.0:1$, $n(\text{H}_2\text{O})/n(\text{Na}_2\text{O})=100:1$, $T=120^\circ\text{C}$)

A complementary FT-IR study was performed on the samples synthesized at 120°C for different time and the results were shown in Fig. S3. Similar results were obtained: the intensity of absorption band at about 555 cm^{-1} increased with the hydrothermal time prolonging from 3 to 9 h, suggesting that the amount of [D4R] increased during this period, namely, NaA zeolite begin to

generate from amorphous aluminosilicates. However, the absorption band at about 555 cm^{-1} became weak whilst some obvious absorption bands at about 616 and 662 cm^{-1} appeared, indicating that [D4R] existed in NaA zeolite disassembled and left β -cages joined via [S4R] to form SOD zeolite. The FT-IR spectra were in good agreement with the XRD results as shown in Fig. 9.

Fig. S4 are the SEM images of intermediate phases formed during the transformation from NaA zeolite to SOD at different reaction temperatures. As shown in Fig. S4(a), cubic particles with surface corrosion (part A) and some imperfect spherical particles (part B) were coexisted in the obtained sample. Detail with enlarged scale was shown in Fig. S4(b), it can be seen that the well-developed surface of some cubic particles were corroded by the flakes developed within their centers. The broken cubes did show regular edges, and the cubic morphology was partially maintained in the particle (part A). With the reaction time prolonging, the number of flakes increased obviously and dispersed on the face of cubic particles uniformly (Fig. S4(c)), indicating that the nucleation of SOD with imperfect spherical structure was formed in the center of cubic particles rather than in the aluminosilicate gel. Further prolonging the reaction time, all the face of cubic particles were corroded and converted to spherical structure, proving that the formation mechanism of SOD was nucleation in the NaA zeolite cubic shells and growth at the expense of rupturing the structure of NaA zeolite following the Ostwald ripening rule.

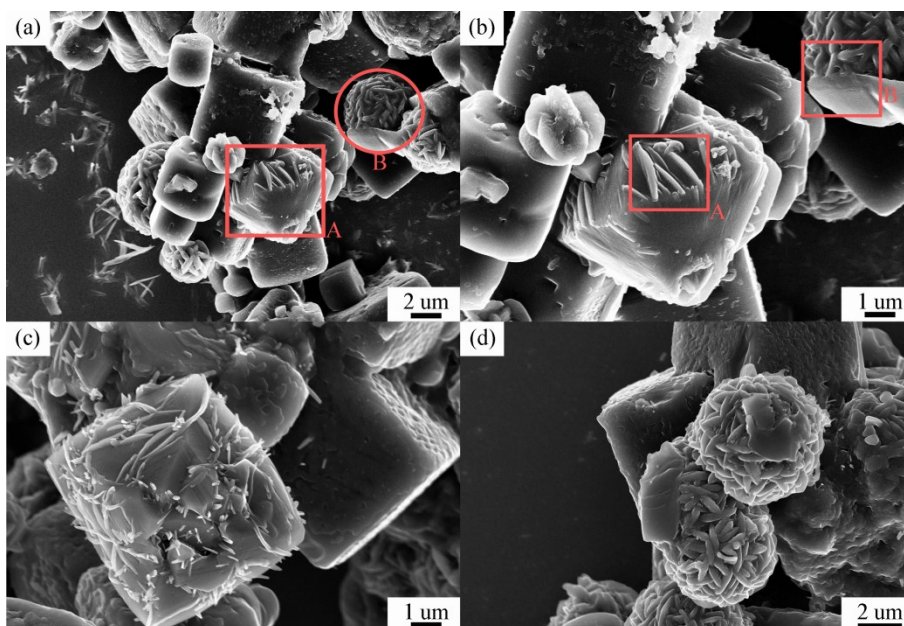


Fig. S4 SEM images of intermediate obtained with NaA zeolite converted to SOD zeolite at different reaction temperatures (a, b) 9 h, (c) 10 h, (d) 11 h ($n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)=2$, $n(\text{H}_2\text{O})/n(\text{Na}_2\text{O})=100$, $T=120^\circ\text{C}$)

In order to confirm the transformation from NaA to SOD zeolite was a spontaneous behaviour rather than the influence of other impurity elements, the elementary analysis of synthesized zeolites was made by ICP and the results showed that the main compositions of obtained zeolites were only Na, Al, Si, O and trace of Ti, indicating that the other elements existed in Ti-bearing EAF slag nearly did not involve in the synthesis of zeolite.

The removal of Cu^{2+} by prepared zeolite was a synergistic action of adsorption and ion exchange according to our analysis. In order to investigate the ion exchangeable ability of synthesized zeolites accurately, 0.1 g zeolite sample was added into the beaker containing 100 mL KCl solution (0.1 mol/L) at room temperature with acute stirring for 6 h. Then the

solution was centrifugalized and the content of Na^+ in the upper solution was analyzed by ICP-AES. The ion exchangeable ability of synthesized zeolite can be measured by calculating the change of Na^+ concentration since Na^+ in zeolite would dissolve in the solution during the ion exchange process. The results showed that ion exchange ability of zeolites synthesized at 120°C , 140°C and 160°C were 1.471, 0.828 and 0.638 mmol/g, respectively, indicating that the ion exchange property of NaA zeolite was better than that of SOD zeolite.