Synthesis of Zeolite Beta from Low-Cost Natural Aluminosilicate Minerals and Its Catalytic Application for Esterification

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Abstract: Herein, a cheap and green route for synthesizing zeolite beta from natural aluminosilicate minerals via a nanoscale depolymerization-reorganization approach is reported. The physicochemical and catalytic properties of the synthesized zeolite beta were systematically characterized and assessed, respectively. The results indicate that the resulting zeolite beta has more Brönsted acid sites compared with the reference one, and thus exhibits higher catalytic activity in the esterification of acetic acid with ethanol. This methodology demonstrates great perspective for the low-cost and eco-friendly synthesis of zeolite beta that avoids the use of aluminum- and silicon-containing chemicals and reduces the usage of the organic template.

Keywords: Zeolite beta, Natural aluminosilicate minerals, Esterification.

1. Introduction

Zeolite beta, an important catalytic material, has been widely used in many major chemical processes (such as esterification process) due to its unique pore structure and catalytic properties. However, its high cost greatly limits its practical application. Thus, the research on the innovation of zeolite beta preparation to reduce its production cost has received much attention, mainly including the employment of cheap silica and alumina sources to substitute for the synthetic silicon- and aluminum-containing chemicals which are relatively expensive and the reduction of the usage of organic template (such as tetraethylammonium hydroxide, TEAOH) which accounts for more than 70% of the overall cost. Recently, the use of natural clay minerals (e.g. kaolin, rectorite, and diatomite) as the low-cost starting materials for the synthesis of zeolites is a field of current interest. Our group have successfully developed a novel nanoscale depolymerization-reorganization approach to synthesize zeolites Y and ZSM-5 from natural aluminosilicate minerals without using any aluminum- and silicon-containing inorganic chemicals[1, 2]. In this work, we attempted to synthesize zeolite beta with high crystallinity and purity with the aim to reduce its production cost and pollution emission via using such a nanoscale depolymerization-reorganization approach.

2. Experimental

The natural rectorite was depolymerized via a submolten salt (SMS) system at a temperature of ca. 250 °C, and the natural diatomite was treated through the thermal activation method, as described by our previous study[1, 2]. Zeolite beta was synthesized from the SMS depolymerized rectorite and thermally activated diatomite by the conventional hydrothermal crystallization with a molar composition of 7 Na_2O:1 K_2O:1 Al_2O_3:50 SiO_2:6.5 $(TEA)_2O$:750 H_2O. In detail, the thermally activated diatomite, SMS depolymerized rectorite, KCl, NaOH, TEAOH and deionized water were mixed together, and the resulting mixture was stirred at room temperature for 2 h; then the thus-obtained precursor was hydrothermally crystallized at 160 °C for 60 h; finally, the crystallization product was filtered, washed thoroughly with deionized water, dried at 120 °C overnight, calcined at 550 °C for 6 h in dry air to remove the organic template, and ion-exchanged with NH_4Cl solution to yield H-form zeolite beta.

Esterification of acetic acid with ethanol was performed under the conditions of atmospheric pressure, 120 °C, and weight hourly space velocity (WHSV) of 1.5 h^{-1} in a homemade continuous flow tubular fixed bed microreactor. The reaction products were collected and analyzed using an SP3420A gas chromatograph.

3. Results and discussion

Fig. 1A shows the X-ray diffraction (XRD) patterns of the synthesized and reference samples. The characteristic reflections at 2θ = 7.6, 21.4 and 22.5° associated with BEA structure can be clearly visualized, with no other unidentified reflection being observed, suggesting that both the synthesized and reference samples are pure-phase zeolite beta. The crystallinity of the synthesized sample is 90%, indicating that high quality zeolite beta can be synthesized by using silicon and aluminum species derived from the two natural minerals. Field-emission scanning electron microscopy (FESEM) image (Fig. 1B) exhibits that the synthesized sample has the spherical morphology with uniform crystal size (ca. 200-300 nm). The nitrogen adsorption-desorption isotherms (Fig. 1C) of the synthesized and reference samples reveal a steep increase in the adsorption amount within the relative pressure (P/P_0) range from 10^{-6} to 0.01, which is characteristic of Langmuir adsorption due to the filling of nitrogen in micropores and thereby suggests that they are typical microporous materials. The specific surface area and micropore volume of the synthesized beta are 521 m^2/g and 0.20 cm^3/g, respectively, very close to those (550 m^2/g and 0.21 cm^3/g, respectively) of the reference sample and thereby further suggesting the high crystallinity of the synthesized zeolite beta.

The results of the pyridine adsorption experiments followed by Fourier transform infrared (FTIR) measurements show that the amount of Brönsted acid (0.81 mmol/g) in the synthesized zeolite is much higher than that (0.59 mmol/g) in the reference zeolite, suggesting the former may be more suitable for esterification reactions. From the catalytic results shown in Fig. 1D, it can be seen that at a reaction temperature of 120 °C, the conversion of acetic acid over the synthesized zeolite beta is ca. 80%, much higher than that over the reference one (ca. 70%); meanwhile, the selectivity to ethyl acetate over the former is ca. 7% higher than that over the latter.

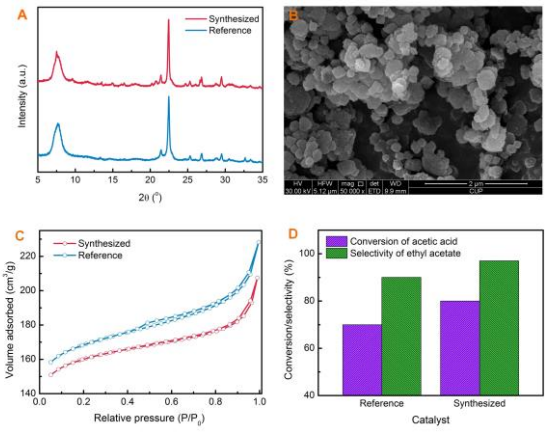

Figure 1. XRD patterns, FESEM image, nitrogen adsorption-desorption isotherms and catalytic results of the samples.

4. Conclusions

In summary, we have successfully synthesized pure-phase zeolite beta by employing a SMS depolymerized aluminum-rich rectorite and a thermally activated silicon-rich diatomite as the starting materials without adding any silicon- or aluminum-containing chemicals and using less template via a nanoscale depolymerization-reorganization approach. The resulting pure-phase zeolite beta with more Brönsted acid sites exhibits excellent catalytic performance in the esterification of acetic acid with ethanol. Specifically, the conversion of acetic acid and the selectivity to ethyl acetate increased by ca. 10% and ca. 7%, respectively, over the synthesized zeolite than over the reference one.

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References

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