ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

One-pot synthesis of mesoporous beta zeolite directly using waste petroleum coke as template

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Highlights

- A clean and efficient strategy for conversion of waste petroleum coke (PC) was proposed.
- PC can be directly used as template and doesn't need to be converted to active carbon first.
- Hierarchical beta zeolite was successfully synthesized directly using PC as template.
- The formation mechanism of hierarchical beta zeolite by petroleum coke was analyzed.

1. Introduction

Beta is a large pore zeolite presenting a three dimensional interconnected channel system with 12-membered openings. This zeolite is of particular interest as a catalyst for petrochemical reactions such as C_4 alkylation, aromatic acylation, alkane hydroisomerization, etc[1-2]. However, the only presence of micropores in the materials usually imposes intracrystalline diffusion limitations, rendering low utilization of the zeolite active volume in catalyzed reactions[3-4]. Therefore, synthesizing hierarchical beta zeolite is of particular scientific meanings. Petroleum coke is a waste by-product of heavy oil refining and upgrading processes. Nowadays, petroleum coke is mainly used for power generation and electrodes manufacture for alumina industry, etc. In order to avoid petroleum coke accumulation, various alternative utilizations need to be established [5]. In this paper, the petroleum coke was employed as the carbon source to directly synthesis the mesoporous beta zeolite. In particular, the petroleum coke does not need to be converted to active carbon first. This method is of great essential to the synthesis of hierarchical zeolite and efficient utilization of petroleum coke.

2. Methods

Mesoporous beta zeolite was successfully synthesized by high pressure hydrothermal method. The tetraethyl ammonium ions (TEA^+), aluminum sulfate and silica sol were used as the template, Al source and Si source, respectively. The solution molar ratios were $n(SiO_2):n(Al_2O_3)$: $n(TEA^+)$: $n(H_2O)=1:0.02:0.7:16$. The milled petroleum coke was added into above solution and crystalized at 413K for four days. The as-obtained zeolite was centrifuged, washed and finally calcined at 550°C for 5 h.

3. Results and discussion

The X-ray diffraction (XRD) patterns (Fig.1) of the samples show intense reflections at 7.8° and 22.5° which are typical diffraction peaks of beta zeolite. The N_2 physisorption isotherm (Fig. 2) of beta zeolite is a typical type IV isotherm with a hysteresis loop corresponding to the capillary condensation at relative pressure between 0.4 and 1.0, which indicates the presence of the mesopores. The presence of mesopores is

also confirmed by the transmission electron microscope (TEM) images in Fig.3. It is clear that the nanocrystals was surrounded by the mesoporous matrix.

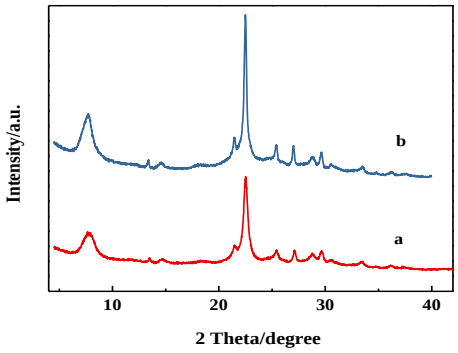

Figure 1. XRD patterns of beta zeolites. (a) with petroleum coke and (b) normal beta zeolite.

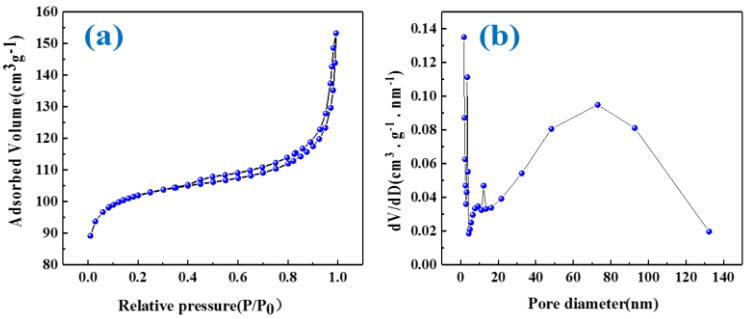

Figure 2. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of beta zeolites with petroleum coke

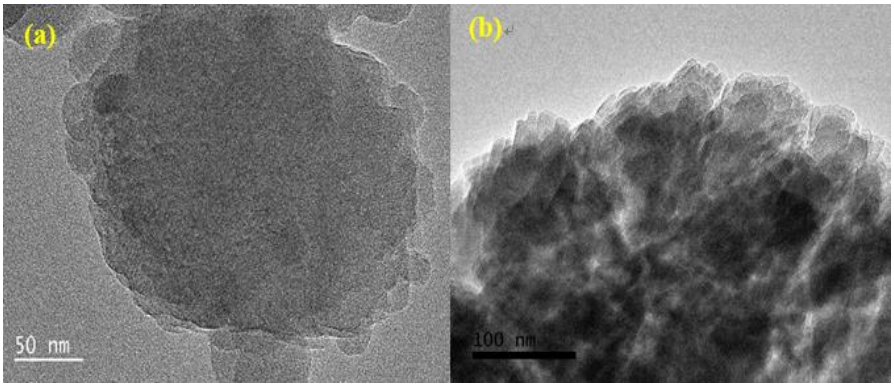

Figure 3. TEM images of conventional beta zeolite (a) and mesoporous beta zeolite (b).

Moreover, the coke content and physico-chemical properties of coke are further characterized by multi-techniques such as UV-Raman, TGA-DTG, ^{13}C NMR and FT-IR. The detailed formation mechanism of mesoporous beta zeolite is further proposed.

4. Conclusions

In this paper, the mesoporous beta zeolite was successfully synthesized using the milled petroleum coke (um scale) as template. Interestingly, the petroleum coke does need to be converted to active carbon first. The hard templating which uses petroleum as the carbon source can form a multi-structured beta zeolite. Moreover, the physico-chemical properties of coke are further determined by UV-Raman, TGA-DTG, ^{13}C NMR and FT-IR, and formation mechanism of mesoporous beta zeolite is analyzed.

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Keywords
One-pot synthesis, mesoporous, beta, petroleum coke.