



## Research paper

# Pure-phase zeolite beta synthesized from natural aluminosilicate minerals and its catalytic application for esterification



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## ABSTRACT

The use of natural aluminosilicate minerals as the low-cost starting materials for zeolite synthesis is a field of current interest. However, impurities existing in these minerals greatly affect the purity of final products. Herein, we describe a cheap and green route for synthesizing pure-phase zeolite beta from natural aluminosilicate minerals via a modified nanoscale depolymerization-reorganization approach. The physicochemical and catalytic properties of the synthesized zeolite beta were systematically characterized and assessed, respectively. The results indicate that the resulting zeolite beta possesses more moderate Brønsted 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 environmentally-benign synthesis of zeolite beta that avoids the use of aluminum- and silicon-containing inorganic chemicals, eliminates the interference of impurities, and reduces the usage of the organic template.

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## 1. Introduction

Zeolite beta is one of the commodity catalytic materials in petrochemical and fine chemical industries due to its three-dimensional 12-ring channel system ( $6.6 \times 6.7 \text{ \AA}^2$  along *a*- and *b*-axes and  $5.6 \times 5.6 \text{ \AA}^2$  along *c*-axis) with tunable acidity, high thermal and hydrothermal stabilities, and outstanding catalytic properties (Higgins et al., 1988; Treacy and Newsam, 1988; Cambor et al., 1992; Kamimura et al., 2010b). Particularly, zeolite beta is considered to be a promising catalytic material in the esterification reaction of acetic acid and ethanol for the production of ethyl acetate which is an industrially important organic chemical material as well as a common green solvent (Inui et al., 2002; Kirumakki et al., 2006; Pattanaik and Mandalia, 2011; Nielsen et al., 2012; Löser et al., 2014). Although zeolite beta exhibits superior performance in diverse acid-catalyzed reactions, its practical application is greatly limited by its high cost (Matsukata et al., 2002; Shen et al., 2008; Xie et al., 2008). Therefore, much efforts have been devoted to reducing its production cost (Shen et al., 2008; Xie et al., 2008; Majano et al., 2009; Kamimura et al., 2010a, 2010b; Li et al., 2010; Duan et al., 2011), mainly include two aspects. One is to decrease or even eliminate the use of organic structure-directing agents such as

tetraethylammonium hydroxide (TEAOH), because not only their price accounts for more than 70% of the overall cost but also their removal from the product zeolite via calcination incurs partial structural collapse, high energy consumption and serious pollution to environment (Xie et al., 2008; Majano et al., 2009; Kamimura et al., 2010a, 2010b). Another one is to search for inexpensive silica and alumina sources to substitute for the synthetic silicon- and aluminum-containing chemicals such as sodium silicate and aluminum sulfate which are commonly used as the feedstocks for synthesizing zeolite beta in industry. The reason is that these chemicals are produced from natural aluminosilicate/silicate minerals through complicated reactions and separation processes associated with huge energy and material consumptions and severe pollutant emissions (Shen et al., 2008; Li et al., 2010; Duan et al., 2011).

Recently, natural aluminosilicate minerals (e.g. kaolinite, rectorite, and diatomite) with abundant reserves in the earth had been explored as low-cost starting materials for preparing zeolites by several research groups (Caballero et al., 2007; Shen et al., 2008; Li et al., 2010; Wei et al., 2010; Duan et al., 2011; Holmes et al., 2011; Li et al., 2012; Ding et al., 2013; Liu et al., 2014; Yue et al., 2014; Liu et al., 2015; Yue et al., 2015). Particularly, silicon-rich diatomite, a material of fine-grained biogenic siliceous sediment consisting of amorphous silica derived from opalescent skeletons and diatoms, after thermal activation has shown great potential as makeup silica source for synthesizing zeolites with higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios such as zeolites Y and ZSM-5. Unfortunately, both literature results and our previous works showed that, when using thermally activated diatomite as the starting material for

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**Table 1**  
The chemical compositions of the natural rectorite and diatomite and the synthesized H-beta zeolite.

Component, wt%	Rectorite	Diatomite	H-beta
Na <sub>2</sub> O	1.03	0.09	0.09
Al <sub>2</sub> O <sub>3</sub>	37.20	2.13	6.28
SiO <sub>2</sub>	43.20	96.20	92.46
P <sub>2</sub> O <sub>5</sub>	3.05	0.02	–
SO <sub>3</sub>	0.07	0.06	–
MgO	0.23	0.05	0.03
K <sub>2</sub> O	1.03	0.53	0.02
CaO	7.05	0.18	0.62
TiO <sub>2</sub>	5.94	0.10	0.18
Fe <sub>2</sub> O <sub>3</sub>	0.51	0.52	0.23

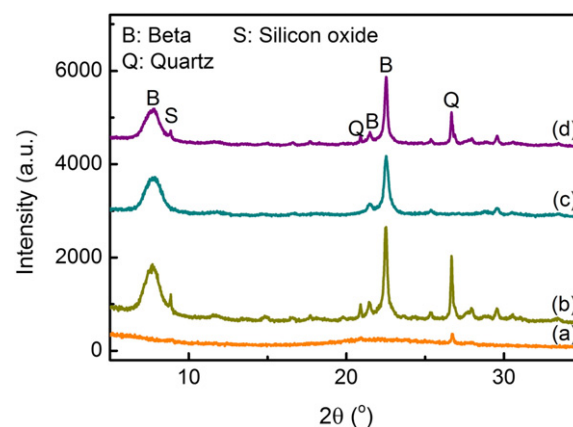
synthesizing zeolites, it is hard to obtain pure-phase zeolite product without containing quartz impurity (Wang et al., 2002; Chaisena and Rangriwatananon, 2005; Du et al., 2011; Li et al., 2012; Hung and Hai, 2013; Yue et al., 2014; Li et al., 2015; Yue et al., 2015). The presence of quartz impurity is detrimental to many catalytic processes, particularly in a harsh condition, and thereby influences the application of products (Holmes et al., 2011). Taking fluid catalytic cracking process as an example, the existence of quartz can damage the reactor badly due to its high wear resistance. Therefore, an improved route to synthesize pure-phase zeolite beta without quartz from natural diatomite is desirable.

Herein we report a novel strategy to synthesize zeolite beta with high crystallinity and purity from two natural aluminosilicate minerals without adding any silicon- and aluminum-containing chemicals via a modified nanoscale depolymerization-reorganization approach. Very importantly, by using this improved methodology, not only the product purity increases, but also the production cost and pollution emission greatly reduce. In addition, the synthesized zeolite beta exhibits superior catalytic performance in the esterification of acetic acid with ethanol.

## 2. Experimental

### 2.1. Materials

The natural aluminum-rich rectorite (Hubei Celebrities Rectorite Technology Co., Ltd., P. R. China) and silicon-rich diatomite (Qingdao

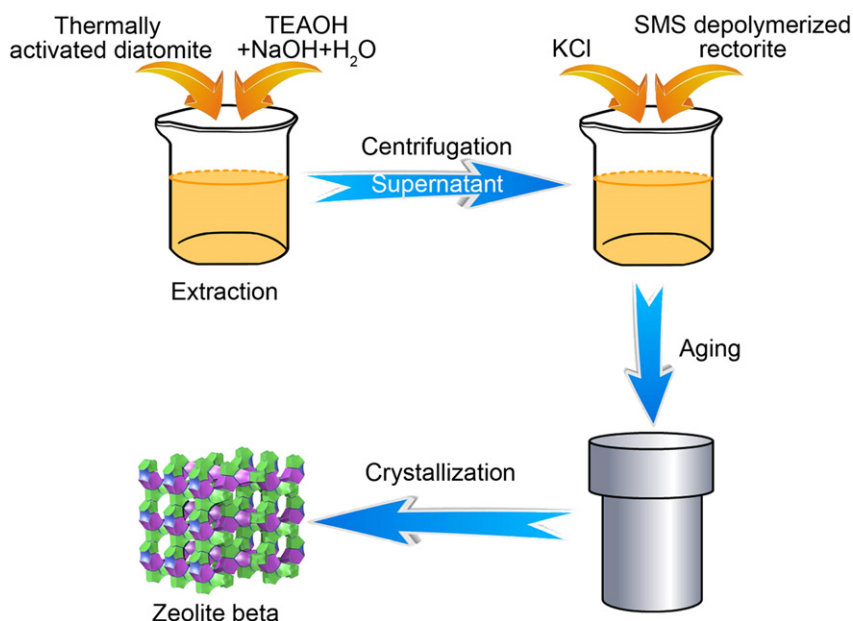


**Fig. 2.** XRD patterns of the thermally activated diatomite (a) and the product synthesized with no extraction step from diatomite (b), white carbon black (c) and the mixture of 10 wt% diatomite and 90 wt% white carbon black (d).

Chuanyi Diatomite Co., Ltd., P. R. China) used in the present study were commercial grade products and their chemical compositions are given in Table 1. TEOAH (25 wt% in water) was purchased from Zhejiang Kente Chemical Co., Ltd., P. R. China. Sodium hydroxide (NaOH), potassium chloride (KCl), ammonium chloride (NH<sub>4</sub>Cl) and white carbon black were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., P. R. China. The zeolite H-beta with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 40 used as the reference was a commercial product of the Catalyst Plant of Nankai University, P. R. China.

### 2.2. Synthesis of zeolite beta

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 Yue et al. (2014, 2015). It must be noted that the temperature of the SMS activation is much lower than that of the conventional thermal treatment (ca. 800 °C), and all NaOH used in the depolymerization process will take part in the followed zeolite synthesis with no necessity to be removed from the activated product.



**Fig. 1.** Schematic diagram showing the synthesis of zeolite beta from the thermally activated diatomite and SMS depolymerized rectorite through a modified nanoscale depolymerization-reorganization approach.

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