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The synthesis of mesoporous zeolite beta aggregates without the use of second template and additive

Shu-Ping Liu, Li Chen, Yi Meng Wang*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Chemistry Department, East China Normal University, North Zhongshan Road 3663, Shanghai 200062, PR China

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ABSTRACT

Zeolite Beta Aggregates have been synthesized by the self-assembly of Beta nanoparticles without the use of second template or additive, where the large zeolitic aggregates avoided the filtration difficulties and the presence of mesopore reduced the diffusion limitation. The samples were characterized by XRD, N_2-sorption, SEM, TEM, thermogravimetric analysis, IR spectroscopy and temperature programmed desorption of ammonia. The results showed that the SiO_2/Al_2O_3 ratio played a key role on the particle size, mesopore volume and particle–particle aggregation process of zeolite Beta. The sample with SiO_2/Al_2O_3 ratio below 60 had improved textual and acidic properties and exhibited the best catalytic activity to the alkylation of phenol with tert-butanol.

1. Introduction

Zeolites are widely used as catalysts in a variety of chemical reactions in the petrochemical industry, due to the presence of strong acid sites and shape-selectivity induced by molecular-sized microporosity [1]. Beta zeolite is one of most important zeolites in industrial catalysis, exhibiting excellent properties in a series of catalytic reactions such as ethylene-benzene alkylation, isobutene-n-butene alkylation [2], alkane hydroisomerization [3,4], aromatic acylation [5,6], methyl tert-butyl ether synthesis [7], etc. Although Xiao and coworkers have reported an organotemplate-free and fast route for synthesizing Beta zeolite by the addition of calcined Beta seeds in the starting alumino-silicate gel in the absence of any organic templates [8], the synthesis of Beta zeolite normally takes for 2–7 days in the presence of organic templates (structure-directing agents, SDAs) such as tetraethylammonium (TEA^+) and others.

In general, the small size of zeolitic pore will limit the diffusion rate of the reactants and products, which will cause pore blockage and reduce yields and selectivity in catalytic applications of zeolites. The short diffusion length of nano-sized zeolites could greatly reduce the diffusion limitation. However, nano-sized zeolite powders are difficult to handle in practical applications and thus they have to be embedded into a porous matrix with a large pore size or be self-assembled into large aggregations in order to improve their thermal and mechanical stability. Nowadays, zeolites with a micro-/meso-porous hierarchical structure have attracted much attention due to their improved diffusion, catalytic activity, selectivity and lifetime [9,10].

Although the majority of studies focused on mesoporous MFI zeolites, Beta zeolites with micro-/meso-porous hierarchical structure could be synthesized by pseudomorphic crystallization by suppressing the mobility of silicates during crystallization [11], using carbon as a transitional template [12], the packing of nano-sized zeolite crystals using steam-assisted conversion techniques [13], the self-assembly of Beta nano-crystals with cationic polymers under hydrothermal condition [14], the use of organo-functionalized seeds [15], hydrothermal synthesis using polyvinyl butyral gel as the mesopore directing agent [16], a polymerization-induced colloid aggregation method [17], and desilication of zeolites for the post-synthetic generation of mesopores [18]. However, the industrial applications of these hierarchical zeolites are still limited by the complexity of their synthetic procedures and/or the cost.

By careful analysis of the literatures, we found that aggregation always occurs during the hydrothermal synthesis of zeolite beta, except for the addition of F^- source in the synthetic mixture. Many studies have postulated the mechanisms of the aggregation of particles during the zeolite nucleation and growth [19]. Much of this speculation arises from TPA-silicalite system. Recently, Hould and Lobo suggested a mechanism of Beta zeolite formation in relatively dilute solutions at a low crystallization temperature of 120 °C, where the secondary particles (Beta) selectively aggregate

* Corresponding author. Tel./fax: +86 21 62232251.
E-mail address: ymwang@chem.ecnu.edu.cn (Y.M. Wang).

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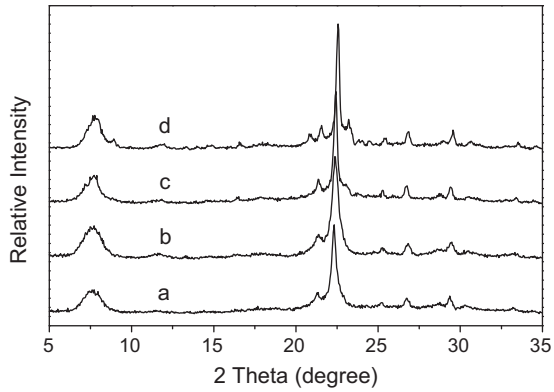

Fig. 1. XRD patterns of samples with different SiO_2/Al_2O_3 ratios synthesized at 145 °C after 6 days, (a) BEA15A, (b) BEA30A, (c) BEA60A, and (d) BEA80A.

into a tertiary particle population [20]. However, in most cases, second templates or additives were used to control the aggregation of Beta nanoparticles during the hydrothermal crystallization, which led to well-developed mesopores in microporous zeolite Beta [13–17,21,22]. Very Recently, Ryoo and coworkers reported that zeolites Beta with intercrystalline mesoporosity could be synthesized using the compound having an organic cyclic diammonium (CDM) structure without the use of additional mesopore-directing agents [11,23]. Therefore, it is possible to tune the rate of secondary particle aggregation to manipulate the alignment at the interface between the growing zeolite crystal and the secondary particle, leading to Beta zeolites with micro-/mesoporous hierarchical structure.

Noticeably, the aggregation of zeolite nanoparticles including silicalite-1 and FAU-type zeolilte was usually carried at room temperature in a diluted system [24–26]. In the study of Hould and Lobo, it takes 28 days to obtain Beta zeolites with well-shaped morphology, as the nucleation and growth rate of Beta zeolite are lower at the temperature of 120 °C than those at the conventional temperature (140–150 °C) [20]. In general, low temperature favors the formation of nano-sized zeolite [27]. With the crystallization temperature increasing, the zeolitic crystals grow larger and the secondary mesopore generated by the particle–particle assembly may disappear. Here, we reported the synthesis of mesoporous Beta aggregates without the use of any secondary-template or organic additive at elevated temperature of 145 °C, where the aggregation of Beta nanoparticles may play an important role. Our diluted synthetic mixture containing conventional tetraethylammonium as template is different from that reported by Ryoo and coworkers, where special-designed cyclic diquaternary ammoniums (CDAs) were used as template and the mixture was gelated immediately with the addition of the CDAs [11,23]. They considered that organic-silicate gel suppressed the mobility of silicates, in favorable of the maintenance of mesoporous structure. Chen also reported the synthesis of mesoporous ZSM-12 without second template under a vicious condition with H_2O/SiO_2 of 8 [28]. Our diluted synthetic mixture could be easily stirred and favor the heating transfer during the hydrothermal synthesis, which makes scaling-up synthesis easier and practical.

Table 1
Crystal size and textural properties of as-synthesized zeolite beta.

SiO_2/Al_2O_3 in gel	SBET (m^2/g)	Primary Crystal size (nm)[a]	V_{micro}[b] (cm^3/g)	V_{meso} (cm^3/g)	Crystallinity (%)	FWHM[d]
15	473.1	80	0.16	0.27	100[c]	0.518
30	583.1	50	0.18	0.41	124	0.479
60	483.7	400	0.20	0.14	182	0.274
80	494.1	340	0.21	0.22	139	0.210

[a] Estimated from SEM images.
[b] from the t-plot.
[c] Reference zeolite and crystallinity is calculated from the intensity of the most intens (302) reflection peak appearing at 22.4°.
[d] the full width at half maximum (FWHM) calculated from the most intense (302) reflection peak.

2. Experimental

2.1. Synthesis

A typical synthesis procedure of mesoporous Beta zeolite is as follows: 28.4 g of $Na_2SiO_3 \cdot 9H_2O$ were dissolved in 45 g of distilled

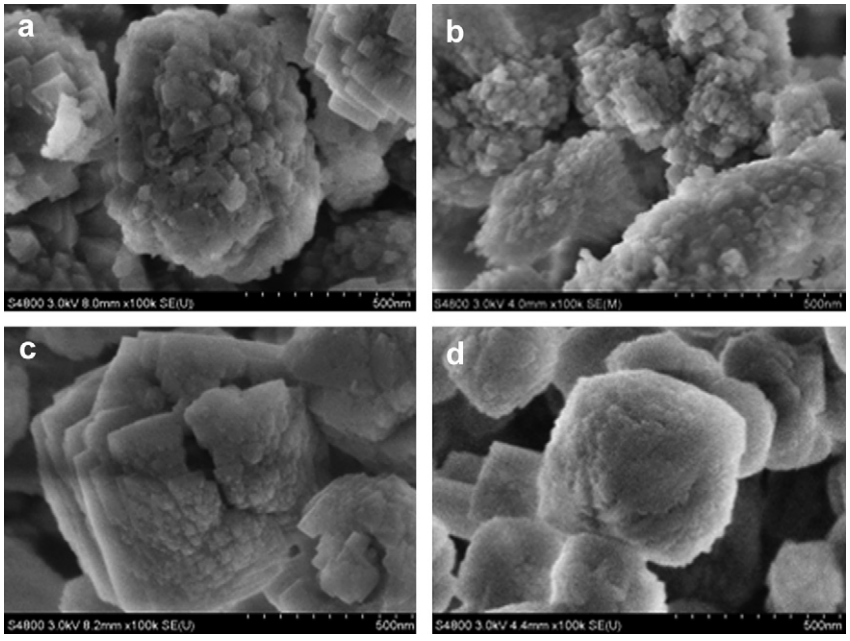

Fig. 2. SEM images of zeolite Beta samples (a) BEA15A, (b) BEA30A, (c) BEA60A, and (d) BEA80A.