



# A novel approach to synthesize in-situ crystallized zeolite/kaolin composites with high zeolite content



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## ABSTRACT

We present an alkali solution aided (ASA) activation approach to activate kaolin microspheres and its application to synthesize in-situ crystallized zeolite/kaolin composite materials. Compared with conventional thermal activation methods, the ASA activation can high-effectively convert silicon and aluminum species in kaolin microspheres into active silica and alumina for synthesizing zeolite/kaolin composites, leading to a successful synthesis of zeolite/kaolin composites with high zeolite content and outstanding attrition resistance. When used as a fluid catalytic cracking catalyst, the resulting zeolite Y/kaolin composite gave high conversion efficiency of vacuum oil and high selectivity to valuable products.

## 1. Introduction

In the petroleum refining industry, fluid catalytic cracking (FCC) is a predominant process to convert heavy crude oil into valuable products such as gasoline, diesel, ethylene and propylene (Buurmanslunge et al. 2011). With the ever increasing demand for vehicle fuels and light olefins, considerable efforts have been made to prepare FCC catalysts with high conversion efficiency of heavy crude oil and high selectivity to valuable products (Corma et al. 2006; Tan et al. 2007). Generally, FCC catalysts are microspheres with an average diameter of ca. 70  $\mu\text{m}$  that contain zeolitic materials (such as zeolites Y or/and ZSM-5) as well as matrix components (such as clay, alumina and silica). In FCC processes, the reactions occurring on zeolite tend to be selective, resulting in the formation of valuable products such as gasoline and diesel, whereas the reactions taking place on matrix are usually non-selective, giving rise to the formation of undesirable products such as coke and dry gas (Corma 1989). Generally, coke deposited on catalyst decreases with the increasing zeolite/matrix ratio (Furimsky 2007). Hence, to increase the selectivity of FCC processes to valuable products, catalysts with high zeolite content is highly desirable. However, ordinary FCC catalysts manufactured by mechanically binding zeolite and kaolin matrix in a proper mass proportion with a binder such as alumina or/and silica usually have a zeolite content of no higher than 40%, because further increasing zeolite content may decrease catalyst attrition resistance and thereby deteriorate the operation of FCC units and increase catalyst consumption (Liu et al. 2006). For this reason, the

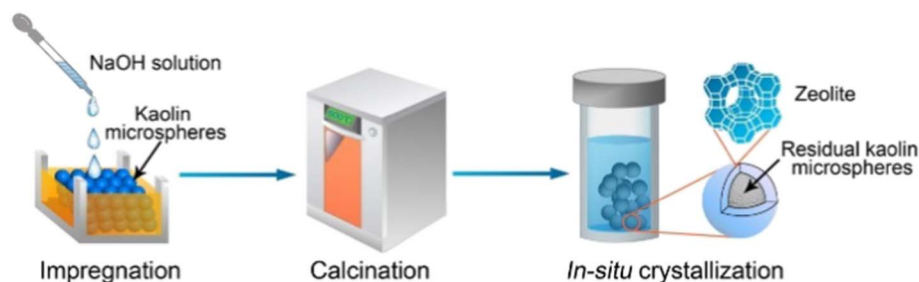
former Engelhard Corporation (now acquired by BASF) developed the well-known in-situ crystallization method by overgrowing zeolite Y on kaolin microspheres. By this way, zeolite Y/kaolin composites with a zeolite content higher than 40% could be obtained, and the resulting in-situ crystallized FCC catalysts possessed outstanding resistance to attrition because of the strong chemical bonding between the zeolite and the matrix (Brown et al. 1983; Zhang and Xiong 2012). Compared with conventional FCC catalysts fabricated by mechanically binding preformed zeolite crystals and kaolin powders with alumina/silica, in-situ crystallized FCC catalysts exhibited extremely high stability to steam at high temperature, outstanding accessibility of active sites to bulky crude oil molecules, and excellent tolerance to contaminant metals and thereby superior catalytic activity (Wei et al. 2010).

A typical in-situ crystallization strategy involves the pre-activation of kaolin microspheres and hydrothermal synthesis of zeolite Y/kaolin composites using the pre-activated kaolin microspheres and water glass as the main providers of alumina and silica, respectively. However, kaolin, a cheap aluminosilicate clay mineral with abundant reserves in the earth (Belver et al. 2002; Shen et al. 2008), in its natural state is inactive, and even after thermal activation at a temperature up to 900  $^{\circ}\text{C}$  only part of the aluminum-oxygen bonds in the mineral are destroyed, with the silicon-oxygen bonds being intact (Lee et al. 1999; White et al. 2010a).

Herein we report a novel approach to effectively pre-activate kaolin microspheres and synthesize in-situ crystallized FCC catalyst with high zeolite content, as illustrated in Scheme 1. In our approach, kaolin

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Scheme 1. Preparation of in-situ crystallized zeolite/kaolin composites.

microspheres that were made by spraying-drying were first impregnated with a NaOH solution, then dried at 100 °C for 10 h, and finally calcinated at 600 °C for 2 h, which here is called alkali solution aided (ASA) activation. Thereafter, the ASA activated kaolin microspheres, the structure-directing agent (SDA), the silica source (silica sol) and deionized water were mixed in a suitable proportion, and after pH adjustment the above mixture was aged and crystallized under the conventional hydrothermal conditions. Following this proposed route, zeolite/kaolin composites with high zeolite contents from ASA activated microspheres can be obtained.

## 2. Experimental

### 2.1. Materials

Silica sol (containing 25.0 wt% SiO<sub>2</sub>) was purchased from Qingdao Haiyang Chemical Company, Ltd. (China). Aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O, 99.0 wt%), sodium hydroxide (96.0 wt%) and sodium aluminate (containing 45.0 wt% Al<sub>2</sub>O<sub>3</sub>) were purchased from the market. Kaolin microspheres (40–120 μm) were kindly provided by Lanzhou PetroChemical Company, PetroChina Company, Ltd.

### 2.2. Pre-activation

Pre-activated kaolin microspheres were prepared by two methods. One was to directly heat kaolin microspheres to 780 °C at a ramp rate of 3 °C and then calcine them at this temperature for 4 h to produce high temperature thermally (HTT) activated kaolin microspheres. The other was to impregnate kaolin microspheres with a NaOH solution (3 wt%) for 2 h first, then dry them at 100 °C for 10 h, and finally heat them to 600 °C at a ramp rate of 3 °C and calcine them at this temperature for 2 h to produce ASA activated kaolin microspheres.

### 2.3. In-situ synthesis

The synthesis of zeolite Y/kaolin composites was performed under typical hydrothermal conditions. Initially, a SDA with the molar ratio of Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:H<sub>2</sub>O = 17.5:1:17.6:310 was prepared upon the addition of NaOH, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O and deionized water into silica sol. This solution was aged for 2 days at room temperature. NaY/kaolin composites were prepared by mixing 6.0 g of pre-activated kaolin microspheres, 11.2 g of silica sol, 7.6 g of SDA, and 5.8 g of NaOH with 34 mL of deionized water while stirring. Then, the resulting mixture with the molar ratio of Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:H<sub>2</sub>O at 4.04:1.0:10.6:130.6 was aged at 60 °C for 12 h, then transferred into an autoclave, and finally crystallized at 100 °C for 13 h. Finally, the crystallization product was recovered by ultrasonic washing with deionized water and drying at 110 °C. The NaY/kaolin composites synthesized from HTT and ASA activated kaolin microsphere were named as CHTT and CASA, respectively.

### 2.4. Characterizations

X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 Advance X-ray diffractometer with monochromatized Cu Kα radiation (40 kV, 40 mA). The relative crystallinity of the samples was determined according to the ASTM D-3906/03 standard using a commercial zeolite (provided by Nankai University Catalyst Company, Tianjin) as the reference sample whose crystallinity was taken as 100%. The NaY contents in the NaY/kaolin composites were estimated by comparing the peak areas of the characteristic diffraction peaks (2θ at 15.7° ± 0.2°, 18.7° ± 0.2°, 20.4° ± 0.3°, 23.7° ± 0.4°, 27.1° ± 0.5°, 30.8° ± 0.5°, 31.5° ± 0.5° and 34.2° ± 0.6°) of NaY in the composites to those of an internal standard NaY sample using a working curve. The working curve was obtained by plotting the peak areas of these NaY characteristic diffraction peaks versus the mass fractions of NaY in a series of NaY and kaolin mechanical mixtures with known contents of NaY.

Field-emission environmental scanning electron microscopy (FESEM) images were obtained on a FEI Quanta 200F machine. The high resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken on a FEI Tecnai F20 (200 kV) microscope with the sample mounted onto a C-flat TEM grid. Digital diffractograms of the BF image and Fourier-filtered image were achieved by using the standard image processing method (Digital Micrograph Program from Gatan Inc.).

The <sup>27</sup>Al and <sup>29</sup>Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy characterizations were performed with a Bruker DSX 500 MHz spectrometer operated at 14 kHz spinning rate with 1 ms of π/8 pulse. Before measurement, the samples were dehydrated for 3 h at 110 °C. Further deconvolution of the MAS NMR spectra was performed by applying Gaussian and Lorentzian simulation at the characteristic peaks and using the proper area relation between two neighboring peaks. The species content was calculated as the ratio between the area of the characteristic peak and the sum of areas of all the peaks.

N<sub>2</sub> isotherms were measured with a Micromeritics ASAP 2020 apparatus at −196 °C. The samples were vacuum-degassed at 350 °C for 5 h prior to the measurement. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas of the samples. The micropore volumes (V<sub>micro</sub>) were estimated using the de Boer t-plot method, the pore size distributions were calculated from the adsorption data using the Barrett-Joyner-Halenda (BJH) approach, and the values of mesoporous specific surface areas (S<sub>meso</sub>) and volumes (V<sub>meso</sub>) were obtained from the adsorption branches according to the ASTM D-4365/95 standard.

The attrition indexes of zeolite/kaolin composites were determined according to the ASTM D-5757/00 standard.

### 2.5. Catalytic performance tests

The tests were conducted in a bench-scale cracking reactor under the conditions typical for FCC units: temperature 520 °C, mass ratio of

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