

# Growth of ultrafine zeolite Y crystals on metakaolin microspheres

Mingcan Xu, Mojie Cheng and Xinhe Bao\*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R. China. E-mail: xhbao@ms.dicp.ac.cn

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Ultrafine zeolite Y crystals (*ca.* 100–200 nm) have been successfully grown on metakaolin microspheres (< 100  $\mu\text{m}$ ) for which good hydrothermal stability was observed; products were characterized by powder X-ray diffraction, scanning electronic microscopy and transmission electronic microscopy.

Zeolite Y is the most widely used catalyst in petroleum cracking and reforming processes.<sup>1</sup> In order to increase the yield of diesel oil in FCC (fluid catalytic cracking), improve the catalytic selectivity and reduce coke formation,<sup>2,3</sup> fine and even ultrafine zeolite Y crystals are desirable. Although ultrafine zeolite Y crystals have been synthesized in the laboratory,<sup>4,5</sup> there are still two key problems remaining. One is the difficulty of production in large quantities for industry since separation of ultrafine crystals by centrifugation is not viable on such a scale. The other drawback of such crystals is their low hydrothermal stability.<sup>5,6</sup> *In situ* Crystallization of ultrafine zeolite Y on supports may solve these problems. In an early report zeolite Y was crystallized on shaped kaolin pellets.<sup>7</sup> Here, we report a method to grow ultrafine zeolite Y crystals on metakaolin microspheres. At the same time, better hydrothermal stability of the ultrafine crystals was observed after growth on the support.

The synthesis was performed under hydrothermal conditions. Initially, a clear aqueous solution with composition (molar ratio) of 16:16:283:1 ( $\text{SiO}_2:\text{Na}_2\text{O}:\text{H}_2\text{O}:\text{Al}_2\text{O}_3$ ) was prepared upon addition of NaOH,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and deionized water to silica sol (30%). This solution was aged for 3 days at room temperature. Uniform metakaolin microspheres (GSS600) of *ca.* 40–100  $\mu\text{m}$  diameter were prepared by flotation with deionized water from kaolin microspheres (GSS), and then calcined at 600  $^\circ\text{C}$  for 3 h. 2.8 g sodium citrate was then added to the above aged solution and stirred for 2 h until dissolution was complete. Then, 6 g GSS600 was added under strong stirring. After 6 h, aqueous sulfuric acid was added dropwise with agitation leading to a gel mixture with final composition (molar ratio) 1:16:7.8:400 ( $\text{Al}_2\text{O}_3:\text{SiO}_2:\text{Na}_2\text{O}:\text{H}_2\text{O}$ ) excluding the kaolin microspheres. Finally the mixture was maintained at 100  $^\circ\text{C}$  for 10 h. Two products were separated by flotation, which were filtered off and washed. One product (KYAOLIN) consisted of spherical particles with a similar diameter as the kaolin microspheres while the other product (NNY) was a fine white powder. Both were dried at 120  $^\circ\text{C}$ .

The powder X-ray diffraction (XRD) pattern [Fig. 1(a)] of NNY is typical for zeolite Y, and no peaks from any other crystalline substances were present. Clearly NNY consists of zeolite Y crystals that did not grow on the metakaolin microspheres. This result suggests that zeolite Y is the only crystalline product present in this synthesis system. Fig. 1(b) shows the XRD pattern of GSS600; besides peaks attributed to mica and quartz impurities, only a broad background, characteristic of amorphous material, was observed. Kaolin-type clay is essentially an aggregation of book-shaped units of the clay mineral kaolinite.<sup>8</sup> Upon calcination at 600  $^\circ\text{C}$  GSS600 transformed into metakaolin<sup>9</sup> and all the kaolinite peaks disappeared. Fig. 1(c) shows the XRD pattern of KYAOLIN, which reveals a clear XRD pattern of zeolite Y above the background of the metakaolin microspheres (GSS600); no other crystalline peaks were identified. The above analysis of the

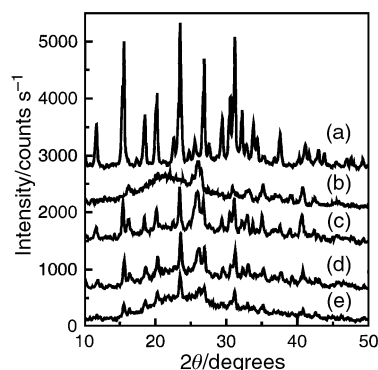


Fig. 1 XRD patterns of NNY (a), GSS600 (b), KYAOLIN (c), hydrothermally treated KYAOLIN (HKYAOLIN) (d) and hydrothermally treated NNY (HNNY) (e) obtained on a Rigaku D/MAX- $\gamma\text{b}$  diffractometer using Cu-K $\alpha$  radiation.

XRD patterns undoubtedly indicates that zeolite Y crystals were synthesized on the metakaolin microspheres.

On the surface of GSS600 [Fig. 2(a)], only irregular flakes can be seen. In comparison to GSS600, scanning electronic microscopy (SEM) of KYAOLIN [Fig. 2(b)] revealed many closely packed cubic crystals on the surface of the metakaolin microspheres. Fig. 3 shows a transmission electronic microscopy (TEM) image of a KYAOLIN section. The region shown

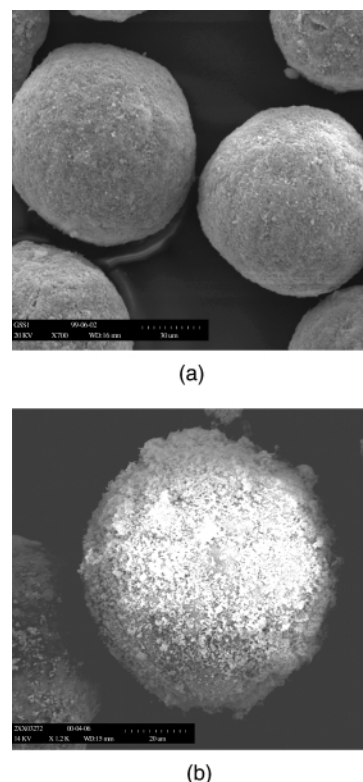
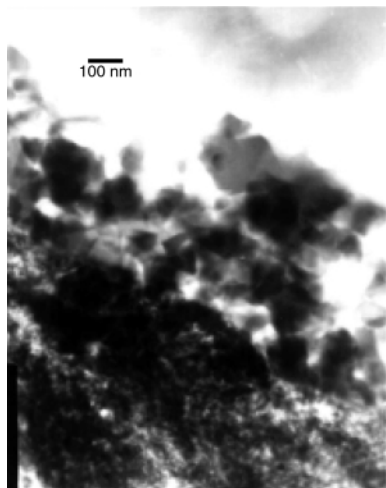


Fig. 2 SEM image of GSS600 (a) and KYAOLIN (b) obtained on a S3200N (HITACHI) scanning electronic microscope.



**Fig. 3** TEM picture of a section (40–70 nm thickness) of KYAOLIN obtained on a JEM-2000EX, 100 kV instrument.

is part of a metakaolin microsphere section and was found to be homogeneous. A layer of cubic crystals, distinctly different from the metakaolin microspheres, were spread along the surface of the metakaolin microspheres. It is also observed that the crystals with sizes in the range 100–200 nm grow out of the metakaolin microspheres. The electronic microscope images and the XRD patterns unequivocally show that ultrafine zeolite Y crystals are grown on metakaolin microspheres.

HKYAOLIN [Fig. 1(d)] and HNNY [Fig. 1(e)] are, respectively, the products KYAOLIN and NNY treated with 100% water vapour at 650 °C for 2 h. In the XRD pattern of HKYAOLIN, clear peaks from the zeolite Y crystals are still present. Compared with KYAOLIN [Fig. 1(c)], the corresponding peaks from zeolite Y crystals in HKYAOLIN are somewhat

broadened and reduced in intensity. This indicates that the crystalline structure of zeolite Y crystals grown on metakaolin microspheres are degraded to some extent during the hydrothermal treatment. As seen in Fig. 1(e), the intensities of peaks from zeolite Y crystals in HNNY are much weaker than those of the product NNY [Fig. 1(a)], and some amorphous substance was evident, *i.e.* during the hydrothermal treatment, the crystalline structure of the zeolite Y crystals is largely destroyed and changed into amorphous materials. The difference in decrease of the relative intensity of the HKYAOLIN and HNNY demonstrates that the hydrothermal stability of the ultrafine zeolite crystals is improved after growth on the metakaolin microspheres. The reasons for this improved hydrothermal stability upon growth on metakaolin spheres are, as yet, unclear, and require further investigation.

All the information obtained from XRD patterns, SEM and TEM images demonstrates that ultrafine zeolite Y crystals have been successfully grown on metakaolin microspheres and that they show good hydrothermal stability. The ultrafine zeolite Y crystals grown on metakaolin microspheres may have potential use in FCC processes.

## Notes and references

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