

In situ Formation of ZSM-5 in NaY Gel and Characterization of ZSM-5/Y Composite Zeolite

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(Received May 19, 2003; CL-030432)

A novel one-pot procedure for the preparation of Y and ZSM-5 composite zeolite was developed by in situ hydrothermal crystallization of Y synthesis gel. Comparing to the mechanical mixture of ZSM-5 and Y zeolites, the composite material showed identical thermal and hydrothermal stability, better performances in dealumination and synergism advantages in catalytic cracking of heavy oil.

It is scientifically very interesting to synthesize composite molecular sieves and study their catalytic synergism.¹ Microporous-mesoporous^{2,3} and microporous-microporous⁴ composites were reported to exhibit obvious synergism in catalysis. Y and ZSM-5 are two of the most important zeolites and usually are the two major active components in fluid catalytic cracking catalysts, how about their synergism? Degnan's testing showed that there was no synergism between Y and ZSM-5 in the same particle under their conditions.⁵ Dzikh et al.⁶ observed the mixing effect of *n*-heptane transformation on the USHY+HZSM-5 mechanical mixtures compared to the corresponding predictions based on the pure zeolites results. On the other hand, Y and ZSM-5 were synthesized and purified individually by two production lines, whereas, they were mixed together when they were used in FCC catalysts. So, it is obviously advantageous to make them together when they were prepared. However, up to now, no study has been reported on the possibility of synthesizing these two zeolites in one autoclave. Here we would like to report an interesting and practical one-autoclave methodology for the preparation of Y and ZSM-5 composite and the comparison of their properties with that of mechanical mixtures.

ZSM-5/Y composite zeolites were prepared in a Teflon-lined autoclave under static hydrothermal conditions by a two-step procedure. The first step was to synthesize NaY by direct agent method. The synthesis gel, with a composition $2.9\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:8.4\text{SiO}_2:200\text{H}_2\text{O}$, was autoclaved for 24 h at 100 °C. Then go to the second step, cooling to room temperature, template $((\text{C}_2\text{H}_5)_4\text{NBr}$ and $(\text{C}_4\text{H}_9)_4\text{NBr}$) or ZSM-5 seeds were added, stirring for 30 min. The pH value was adjusted by adding diluted aq H_2SO_4 . Then it was crystallized for 24 h at 160 °C. The crystalline product was filtered off, washed with deionized water and dried at 120 °C for 4 h.

When templates were used, ZSM-5/Y composite zeolites were formed at pH range of 10.0–10.5. Seeding is also an effective method to synthesize the composite zeolites. The composite-zeolite crystallinities changed with crystallization time and temperature. It was found that the transformation of Y to P zeolite could be totally controlled until the completion of ZSM-5 crystallization. When crystallization of ZSM-5 completed, Y would begin to transform to P, and then to analcime zeolite. During the transformation process, Y, P, analcime and ZSM-5 could coexist. At last only analcime and ZSM-5, the

most stable zeolite, remained. Mertens⁷ reported that the use of an effective amount of crown ether could reduce the formation of unwanted zeolite P. In this work, we found that the transformation could completely be avoided along with the ZSM-5 formation by controlling the crystallization time and pH value. According to the powder XRD patterns as show in Figure 1, all the characteristic peaks of Y and ZSM-5 were observed and no other peaks such as P, analcime zeolite. To investigate the reliability of this methodology, the experiments were done from 100 mL to 1000 mL scale for 40 times. The ratio of ZSM-5 to Y could be controlled by adjusting the reaction conditions.

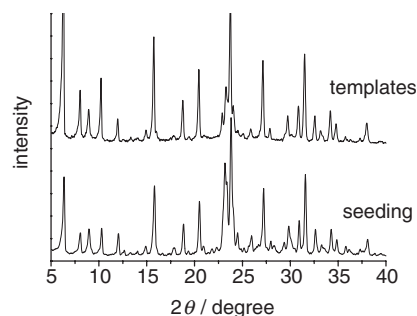


Figure 1. Powder XRD patterns of ZSM-5/Y composite zeolites.

Excess silica source is required for the conventional method of NaY synthesis. Although there are several methods for the recovery of this silica source, it seems more attractive to develop a procedure to use this silica source in situ. The present experimental data showed that, by comparison with that of NaY synthesis, the SiO_2 content of mother liquor decreased from 53.2 g L^{-1} to 7.2 g L^{-1} and the Al_2O_3 was almost digested completely. The usage percentage of the silica was increased more than 30%. And as a result, the yield of zeolite was increased by 19%.

The ²⁷Al MAS NMR spectra of calcined ZSM-5/Y indicated that the aluminum centers were in tetrahedrally coordinated sites ($\delta = 57.6\text{ ppm}$ for template method composite, and 60.0 ppm for seeding method composite), which was characteristic of aluminosilicate frameworks.

The morphology of ZSM-5/Y composites (template method, Figure 2) was not octahedral (usually NaY) and not rectangular rods (usually ZSM-5), it showed an irregular shape and appeared together with spheroid particles. The Si/Al ratio of two different particles was analysed by an X-ray microanalyzer. The Si/Al ratio of spheroid was 14 and the irregular particle was 4.3 (Si/Al ratio of pure Y zeolite gotten from the first step of crystallization was 3.4 by using the same method). This suggested that the spheroid shape particle was composed of ZSM-5 and Y zeolite, in which ZSM-5 as a binder. This indicates that Y

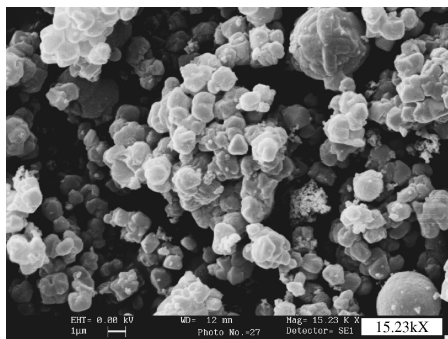


Figure 2. SEM images of ZSM-5/Y composite synthesized by templates.

particles dissolved in the course of the second step crystallization, and ZSM-5-on-Y overgrowth material⁸ may be formed by the present procedure.

When ZSM-5/Y composite was synthesized by using seeding method, the morphology as shown in Figure 3 looked like laminar cuboids spotted by some parallel rods. Only small amount of particles (looked like Y particles) were found in the SEM images. It suggested that Y zeolite was embedded in the laminar cuboids. From the SEM images at different crystallization time, we saw the agglomeration phenomena of Y particles. This was another evidence for above suggestion.

Moreover, The BET surface area analysis also supported the composite structure suggestion. The BET surface area of NaZSM-5/Y composites synthesized by templates and seeds, as well as the NaZSM-5 and NaY mixture are 539, 594, and 618 m²g⁻¹, respectively.

Si/Al ratio (obtained by Breck–Flanigen method) of NaY in the composite was identical with that in the pure NaY zeolite. The DTA analysis indicated that the thermal stability of NaZSM-5/Y composite was equivalent or a little bit better than NaY (taken from the first step).

The dealumination property of composite zeolite was analyzed by multistep-temperature-programmed (MSTP)⁹ steaming method at different temperatures. Compared to the same ZSM-5 content of mechanical mixture,¹⁰ the reserved crystallinity of Y

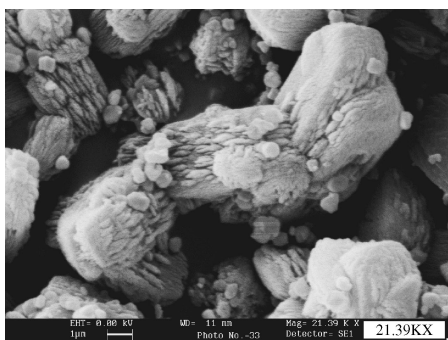


Figure 3. SEM images of ZSM-5/Y composite synthesized by seeding.

in composite was higher at 550 and 700 °C, equivalent at 830 °C. The degree of ultrastabilization was also equivalent. In the period of hydrothermal dealumination the crystallinity of ZSM-5 approximately remained constant.

The composite zeolite was ion-exchanged by the same method as NaY. The resulted zeolites were used as an active component of catalyst for catalytic cracking test at a MAT unit.¹¹ The heavy oil MAT results showed that, compared to a catalyst of mechanical mixture of ZSM-5 and Y zeolite, the composite zeolite catalyst afforded a 5.20 wt% increase in gasoline yield, 1.86 wt% decrease in light cycle oil (LCO), similar yield in LPG, and 1.09 wt% decrease in coke, i.e., the yield of light liquid (LPG + gasoline + LCO) increased by 2.94%. The composite zeolite catalyst made with templates showed similar results. This result indicated that the composite zeolite showed advantage in the heavy oil catalytic cracking reaction, it suggested that the ZSM-5 and Y zeolite in the composite exhibited a synergy effect.

References and Notes

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