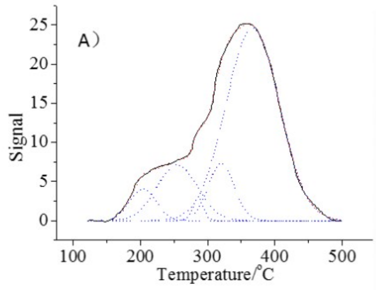
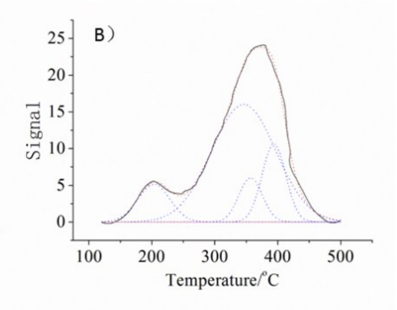
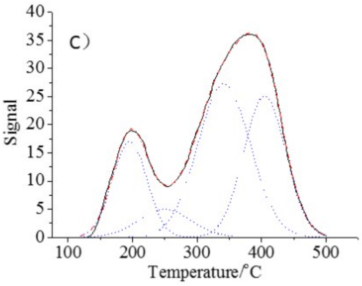
The Morphology Control of ZSM-5 and Their Application in Cracking Reaction of C4 Olefin

Jing Shi[a], Guoliang Zhao[a], Jiawei Teng[a], Yangdong Wang*[a] and Zaiku Xie*[b]

The acidities of the ZSM-5 with different morphology have been supplied in Fig. S1. It was determined by temperature programmed desorption of ammonia (NH_3-TPD) using a conventional flow apparatus equipped with a thermal conductivity detector (TCD). The load amount of sample was 100 mg with particle sizes of 20-40 mesh. After being flushed with He (25 ml min^{-1}) at 500°C for 60 min, the sample was exposed in a mixed gas of 9 vol.% of NH_3 in He at room temperature for ammonia adsorption and then flushed with pure He at 100°C until the TCD baseline remained unchanged. Afterwards, NH_3-TPD was promptly warmed at a heating rate of 10 °C min^{-1} to 500 °C. The desorbed ammonia was detected on the TCD and then trapped in a 0.01N H_2SO_4 aqueous standard solution. The amount of trapped ammonia was determined by titrating the excess of H_2SO_4 in the NH_3-trapped solution with a 0.01N standard NaOH solution to estimate the total acid quantity quantitatively. The distribution of the acidity on the samples was deconvolved by simulating the TPD plots through Gaussian curves. The temperature range for the strong acid sites was set between 300°C-500 °C.







D） Acidic properties of the samples

Samples	SiO_2/Al_2O_3 [a]	A_t [b] (mmol g^{-1})	A_s [c] (mmol g^{-1})
S-1	400	0.05	0.04
N-1	400	0.04	0.03
ST-1	400	0.09	0.06

[a] SiO_2/Al_2O_3 in the synthesis solution
[b] Total quantity of acid sites obtained from acid-base titration
[c] Strong acid sites estimated from the relative area of the deconvoluted peaks

Fig. S1 NH_3-TPD profiles of samples (A) S-1,(B) N-1 and (C) ST-1 with different morphology(solid line for experimental spectra and dotted line for deconvoluted results). (D) is the acidic properties of these samples.

It can be seen from the results that the sheet-like zeolite presented the highest quantity of acid sites and strong acid sites which may be contributed to the influence of the template applied in the synthesis. Our previous research [1] showed that the strong acid sites (A_s) play a key role in OCC reaction. For catalyst with lower $A_{s,}$ its stability was relatively better than that of catalyst with higher A_s due to the fast coking of hydrogen transfer reaction on the latter. Whereas, the sheet-like morphology zeolite displayed a best stability instead among these samples, which further proved the mass transfer advantage with morphology difference.

Reference

[1] G. Zhao, J. Teng, Z. Xie, W. Jin, W. Yang, Q. Chen and Y. Tang, *Journal of Catalysis,* **2007,** *248*, 29-37