Enhanced accessibility and utilization efficiency of acid sites in hierarchical MFI zeolite catalyst for the effective diffusivity advance

Jian Zhou, Zhicheng Liu, Yangdong Wang, Huanxin Gao, Liyuan Li, Weimin Yang, Zaiku Xie, and Yi Tang*

Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai 201208, P. R. China;

Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

E-mail: xiezk2009@gmail.com

Experimental section

Materials, Ion-exchange manipulation, characterization and catalysis

Materials: The conventional ZSM-5 zeolite (ConvZ) was synthesized by the common hydrothermal technique with the Si/Al ratio of 120. The fabrication of process of hierarchical ZSM-5 zeolite involves two key steps: the precursors of zeolites and mesoporous copolymer template were first transformed into homogeneous gels, followed by the steam-assisted crystallization (SAC) treatment.[1] In details, F127 (BASF, MW = 12600), aluminium isopropoxide, tetraethoxysilane (TEOS) and tetrapropyl ammonium hydroxide (TPAOH, 25%) was added dropwise to distilled water under continuous stirring to get a homogeneous sol. The molar ratio of the resultant sol was 0.5 Al_2O_3: 120 SiO_2: 1.2 F127: 12 TPAOH: 4800 H_2O. Stirring was continued to form a solidified gel. The resultant wet gel was aged and then dried at 363 K until the mass became unchanged. Then, this as-prepared gel was crystallized by SAC method at 443 K for 18 h. After the steps of washing, filtration, drying and calcination et al, the obtained white product was labelled as Hierarchical ZSM-5 (abbreviated to HierZ).

Ion-exchange manipulation: Z-(H)-H series samples were made by ion-exchanging with NH_4NO_3 (0.5 M) aqueous solution at 333 K for three times and then calcination at 673 K. Ion-exchanging manipulation of Z-(Na)-Na series samples were performed by NaCl (0.5 M) aqueous solution at 333 K for three times and then dried at 423 K. Using the above Z-(Na)-Na samples, Z-(Na)-H series samples can be obtained by ion-exchanging with the aqueous solution of tetrapropyl ammonium Bromide (0.2 M) at 333 K for three times and then calcinating at 773 K.

Characterization: XRD patterns were recorded on a Bruker D8 Advance diffractometer using Cu K_α radiation at 40 kV and 40 mA with the scanning rate 4 °min^{-1}.

The N_2 adsorption/desorption isotherms were measured on a Micromeritics ASAP 2010 porosimeters at 77 K. The mesopore specific surface area, pore volume and the pore size distribution were determined using the BET and BJH methods, respectively. The micropore specific surface area and volume were calculated from the t-plots of the N_2 adsorption data.

FE-SEM images were obtained on Hitachi S4800 electron microscopes.

The Al and Na contents analysis of various catalysts was performed by ICP-AES with a Varian Vista AX ICP-AES spectrometer.

The measurement of cumene diffusion in ZSM-5 zeolites was performed using a computer-controlled intelligent gravimetric analyzer (IGA, Hiden Analytical Ltd., Warrington, UK), similar with the reports.[2,3] A sensitive microbalance (resolution of 0.1 μg) was mounted in a thermostated enclosure to remove thermal coefficients of the weighing system and thus provide high stability and accuracy. The sample was degassed under a vacuum of less than 10^{-3} Pa at 673 K for 2 h prior to the adsorption measurement. The temperature change of sample was regulated within 0.1 K. The pressure was determined using two high accuracy Baratron pressure transducers and increased gradually to obtain the entire equilibrium adsorption isotherm. For each step, the amount of absorbate introduced in the system was kept small enough to keep the adsorption process isothermal. The increase of weight was continuously recorded.

NH_3-TPD was performed on a homemade apparatus. The sample (150 mg) was pre-treated at 823 K for 1 h and then cooled down to 323 K in He flow. The gas mixture of NH_3-He with mole ratio 10%-90% was injected until adsorption saturation followed by the flow of pure He at 373 K for 2 h to remove the physically adsorbed ammonia. Then, the temperature was raised from 373 K to 773 K under He flow with a heating rate of 10 $Kmin^{-1}$ and the desorbed ammonia was monitored by a gas chromatography equipped with a TCD detector.

The pyridine in-situ IR (abbreviated to Py-IR as follows) experiments were performed on a homemade vacuumed adsorption system followed by testing of FTIR. In detail, the tabletted samples were firstly activated at 673 K and then vacuumed to less than 10^{-1} Pa in a sealing system. Adsorption was proceeded at 473 K in the saturated atmosphere of Pyridine for 15 min, followed by degassed to less than 10^{-1} Pa again. The in-situ FTIR spectra were recorded with a resolution of 2cm^{-1} at 573 K.

Catalysis: The catalytic activities of the samples toward cumene cracking were tested in a stainless micro-catalytic-reactor. The sample load was 0.12 g which was diluted into a well-distributed mixture with 4.0 g quartz sand. Then the mixture was preheated at 773 K for 1 h under N_2 flow before reaction. In the reaction, the cumene was uniformly pumped into a preheating device to transform the liquid into vapour and then the cumene vapour was mixed with the N_2 flow which was used as the carrier gas. The ratio of cumene and N_2 was kept as 1: 80 mol /mol. The contact time was adjusted by changing the flow rate of gas mixture. The catalytic activities of the zeolites were detected at different temperatures. The products were analyzed by an on-line gas chromatograph (Agilent 6820) equipped with a flame ionization detector. Before the catalysis test, the elimination of external diffusion was identified by detecting the conversion-contact time curves over different amounts of catalysts.

Figures

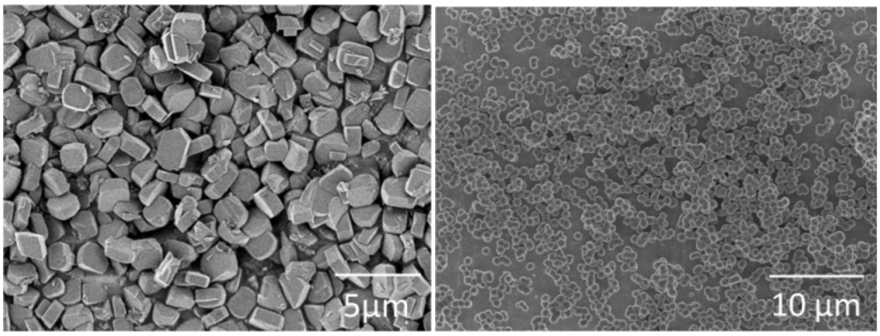

Fig. S1. Low magnification SEM images of ConvZ (left) and HierZ (right). It provided SEM images of conventional and hierarchical ZSM-5 zeolites at low magnification which indicating uniform particle sizes in the whole samples.

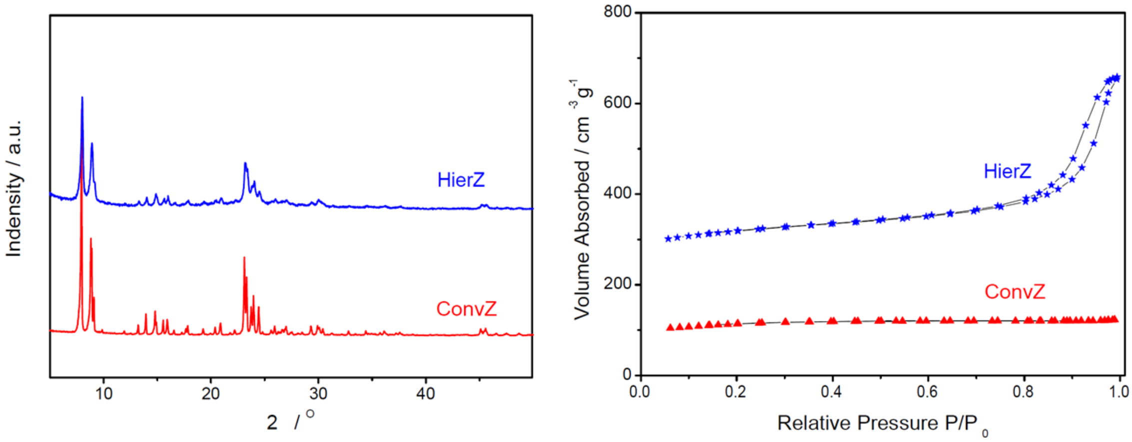

Fig. S2. XRD patterns and N_2 sorption isotherms of ConvZ and HierZ. The isotherm of HierZ was offset by 200 cm^3g^{-1}.

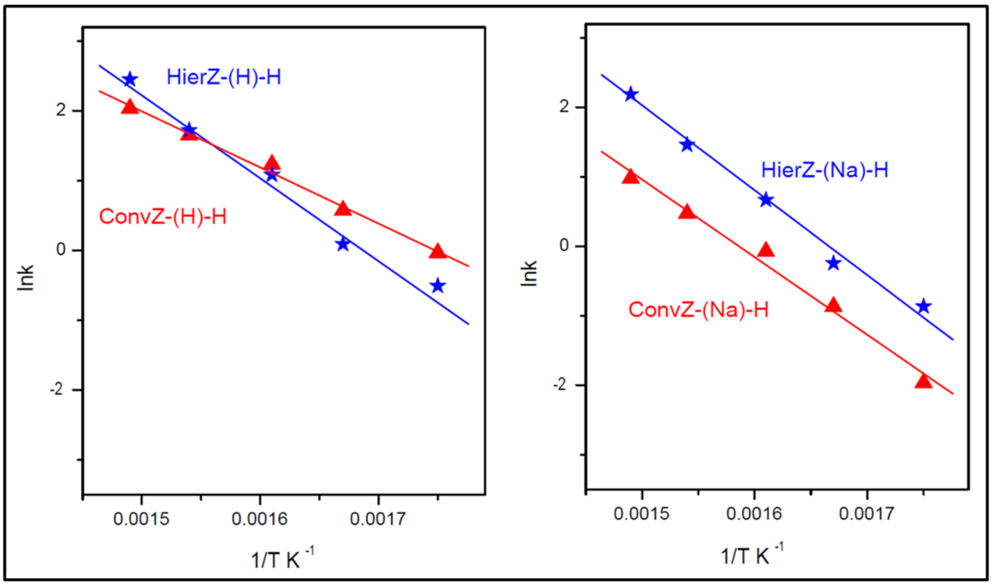

Fig. S3 Arrhenius fittings of cumene cracking reaction over the synthesized Z-(H)-H series(a) and Z-(Na)-H series (b) catalysts: ConvZ (▲) and HierZ (★).

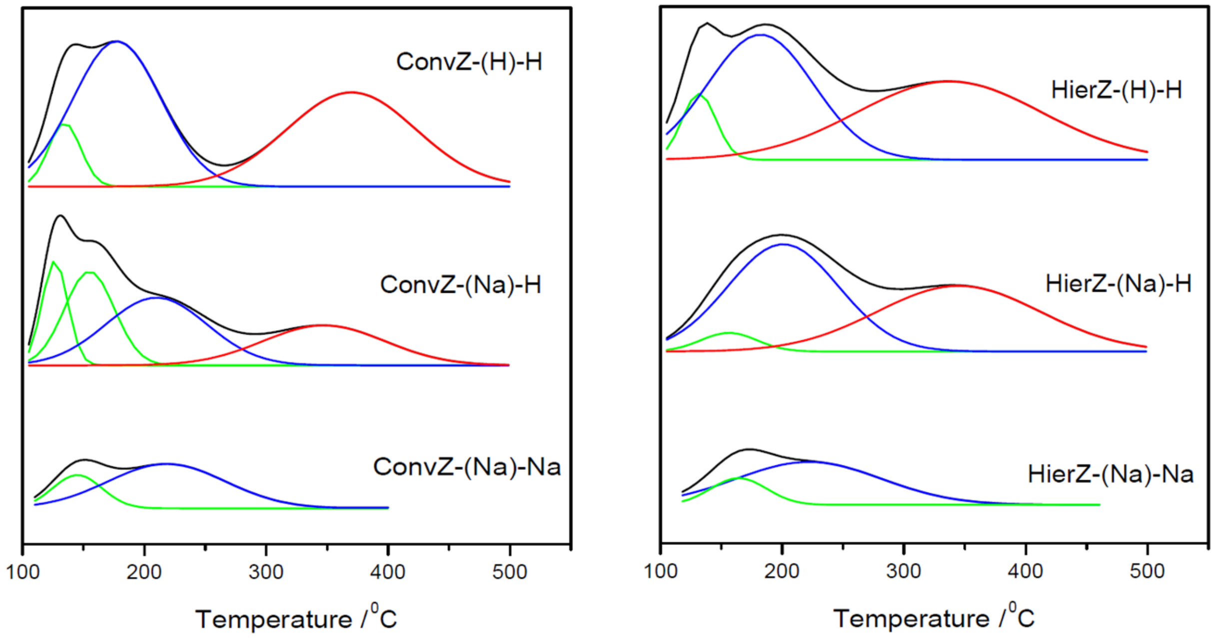

Fig. S4 NH_3-TPD of ConvZ-(H)-H, ConvZ-(Na)-H, ConvZ-(Na)-Na, HierZ-(H)-H, HierZ-(Na)-H and HierZ-(Na)-Na.

It can be found ConvZ-(H)-H possess more stronger acids than ConvZ-(Na)-H, indicating the stronger acid sites are most located in the micropore in ConvZ. Comparatively, the curves of HierZ-(Na)-H is very similar with HierZ-(H)-H; in other words, the deactivation of internal acid sites has neglectable effect on concentration of total acids. Therefore, most acid sites are located on the external surface of hierarchical ZSM-5 zeolite, which are more accessible in the cracking reaction.

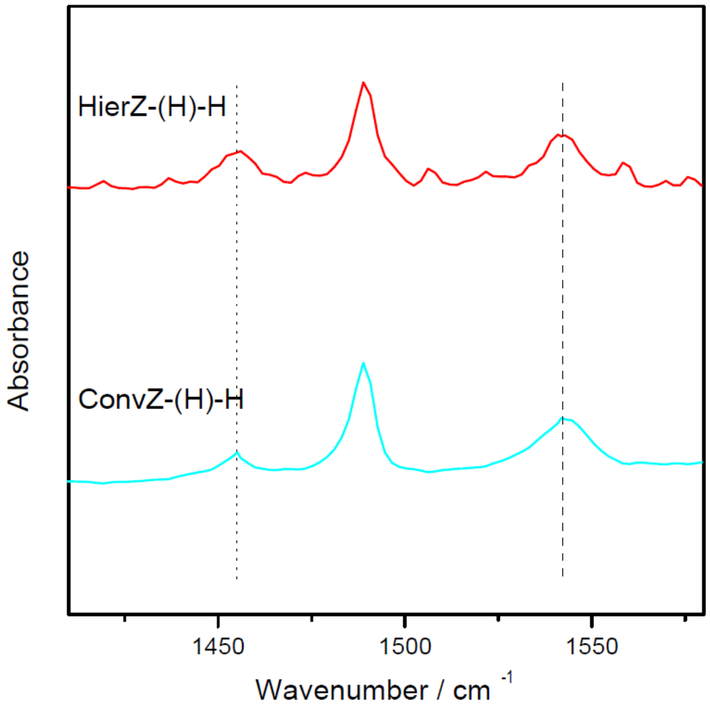

Fig. S5 Pyridine-absorbed IR spectra of ConvZ-(H)-H and HierZ-(H)-H.

More Lewis acid / Bronsted acid ratio of HierZ-(H)-H than ConvZ-(H)-H can be found for more Al atoms were exposed on the external surface.

Tables

Table S1. Textural properties of conventional and hierarchical ZSM-5 zeolites.

Sample	S_{BET}[a]/ m^2g^{-1}	S_{micro}[b] / m^2g^{-1}	$S_{external}$[b] / m^2g^{-1}	V_{micro}[b] / cm^3g^{-1}	V_{pore}[c] / cm^3g^{-1}	D_{pore}[c] / nm
ConvZ	387	250	137	0.12	0.19	-
HierZ	412	175	237	0.08	0.71	11.8

a: surface area by BET method; b: micropore and external surface areas and micropore volumes by t-plot method; c: total pore volumes at $P/P_o = 0.99$ and adsorption average pore diameter by BJH method.

Table S2 Chemical properties of conventional and hierarchical ZSM-5 zeolites with different surface acid deactivation.

Sample	Al[a] [mol%]	Na[a] [mol%]	Na/Al [mol/mol]	Percentage of external acids
ConvZ-(Na)-H	0.61	0.38	0.62	38%
HierZ-(Na)-H	0.62	0.08	0.13	87%
ConvZ-(Na)-Na	0.58	0.60	1.03	-

[a] determined by ICP-AES method.

Additional References

1. J. Zhou, Z. L. Hua, Z. C. Liu, W. Wu, Y. Zhu, J. L. Shi, *ACS Catal.* **2011**, *1*, 287.

2. Z. P. Liu, W. M. Fan, J. H. Ma, R. F. Li, *Adsorption* **2012**, *18*, 493.

3. L. Zhao, B. J. Shen, J. S. Gao, C. M. Xu, *J. Catal.* **2008**, *258*, 228.