Supporting information

Mass Transfer Advantage of Hierarchical Zeolites Promotes Methanol Converting into *para*-Methyl Group in Toluene Methylation

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The diffusivities of zeolite catalysts derived by "triangle method"

The intracrystalline diffusivities of zeolite catalysts were derived by "triangle method" which in heterogeneous catalyst particles under the conditions (temperature, pressure, etc.) that prevail during catalysis.[1] In this method, the graphical curve-fitting procedure was employed basing on the characteristics of the functional relationship between the degree of utilization (η) and the Thiele modulus ɸ (Figure S1).
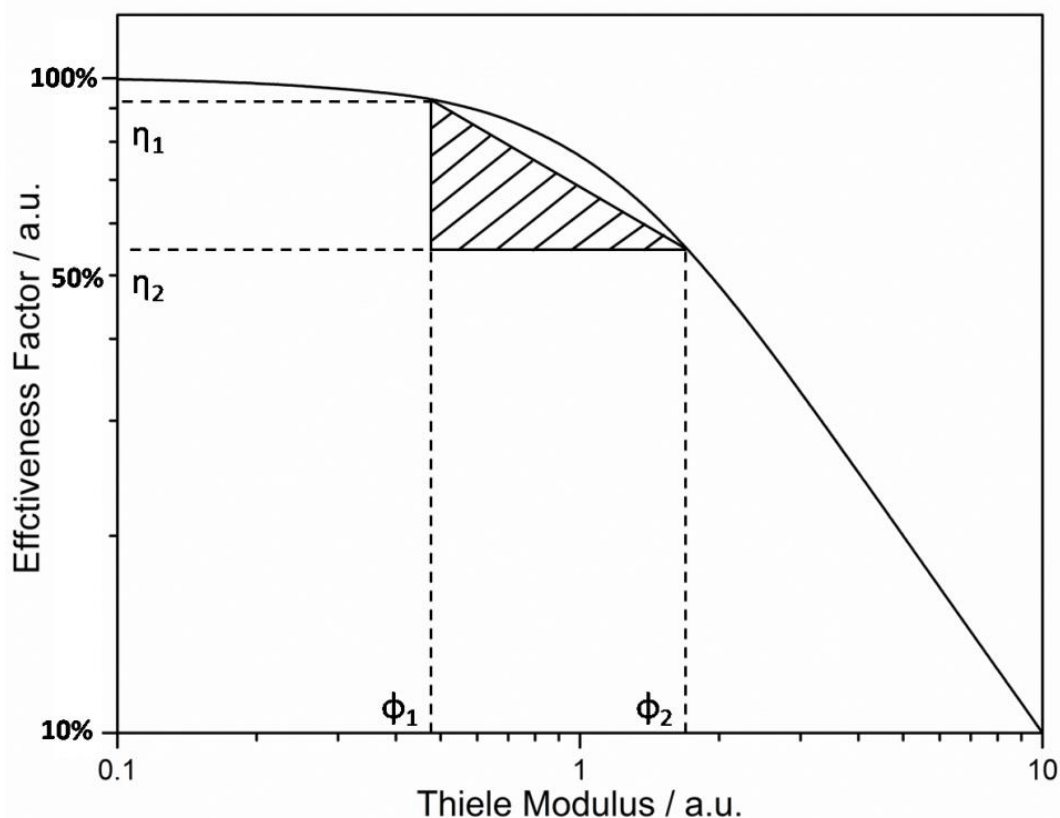

Figure S1. The graphical "triangle method" for calculating diffusivity of porous catalyst. The ratio of degree of utilization, representing a length on the logarithmic ordinate, and the ratio of Thiele modulus on the logarithmic horizontal ordinate, was fitted.

The detailed calculation was described as follows. For two catalyst samples that are characterized by different particle (crystal) sizes of known ratio, L_2/L_1, it was reasonably assumed as the report that the diffusivity [1] in all MFI microporous networks and intrinsic activity is the same. Hence, the ratio of the Thiele modulus (X_φ), φ_2/φ_1, can be derived by substituting the equation (6),

$$X_\varphi = \varphi_2 / \varphi_1 = L_2 / L_1 \quad (S1)$$

and the ratio of degree of utilization (X_η), η_2/η_1, equals to the ratio of the observed reaction rate

$$X_\eta = \eta_2 / \eta_1 = k_2 / k_1 \quad (S2)$$

If substituting equation (S1) into equation (S2), X_η can be expressed by X_φ:

$$X_\eta = \eta_2/\eta_1 = \frac{(\tanh\varphi_2)/\varphi_2}{(\tanh\varphi_1)/\varphi_1} = \frac{(\tanh X_\varphi \square \varphi_1)/(X_\varphi \square \varphi_1)}{(\tanh\varphi_1)/\varphi_1} \quad (S3)$$

For any given experimental value of X_η and the known value X_φ, equation (S3) can be employed to determine φ_1. According to the convention, $\varphi_2 > \varphi_1$ was used throughout the calculation, consequently, $\eta_2 < \eta_1$. The calculation procedure was based on the first-order reaction and slab geometry of zeolite catalyst. The derivation process and solution of zeolite catalyst with spherical geometry is similar.

This relationship between X_η and X_φ was drawn in Figure S2. It can be found the accurate result of φ_1 can be calculated when $\varphi_1 < 2$. When $\varphi_1 > 2$, it means under strict diffusion limitation, the product of η multiplied by ф (η*ф) equals 1.0. As the previous report,[1] it can be found when the fractional decrease of activity approaches the fractional increase in particle size, the product of X_η multiplied by X_φ (X_η*X_φ) equals 1.0.
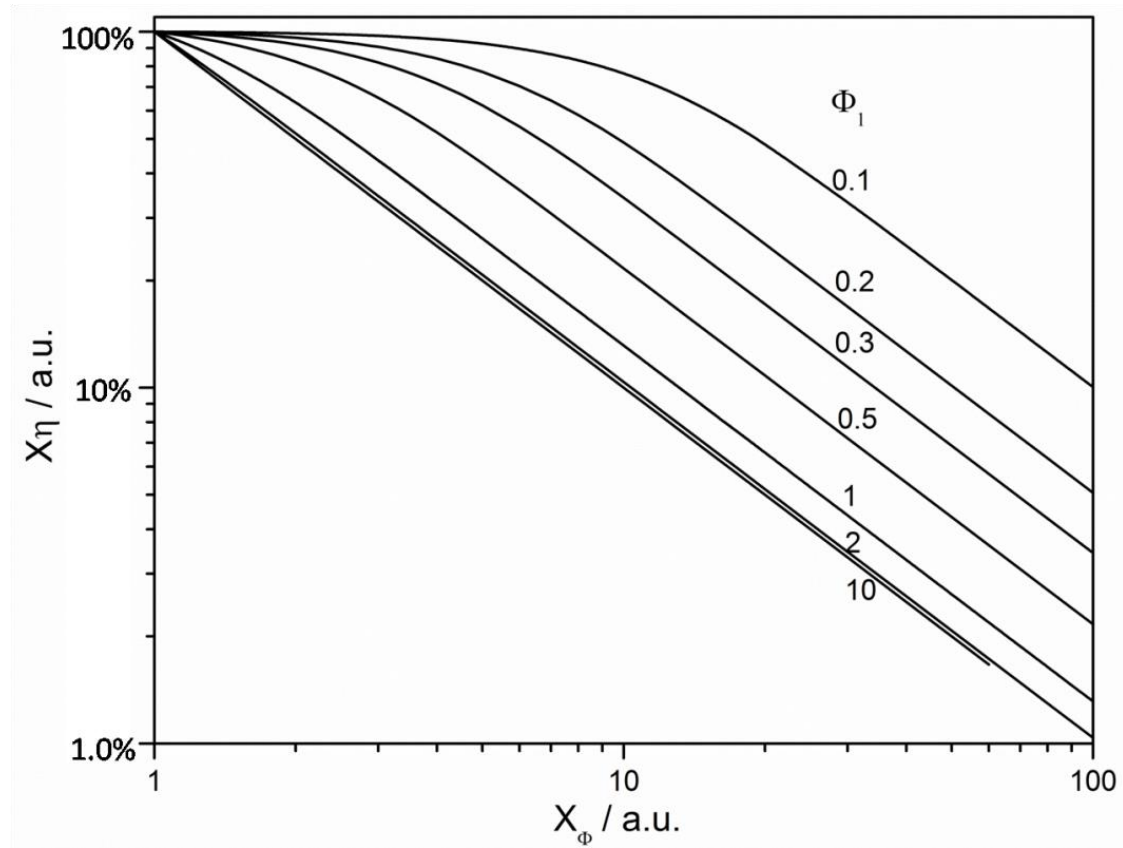

Figure S2. Solution of direct determining Thiele modulus of the catalyst with smaller particle size from the relationship between the ratio of utilization degree, X_η and the Thiele modulus ratio, X_φ for slab geometry.

We used ZSM-5 zeolites with two different crystal sizes, 150 nm (ZSM5-P) and 250 nm (ZSM5-250nm), to determine the Thiele modulus of ZSM5-P. The observed reaction rates of them were listed in Table S1 to determine the X_η. By substituting X_η and X_φ into equation (S3), the Thiele modulus of ZSM5-P can be calculated and listed in Table S1. The Thiele modulus of methylation and MTH reaction over ZSM5-P can be accurately calculated. After that, the Thiele modulus of

methylation and MTH reaction over other samples was all derived by triangle method. Constructing hierarchical structure can be considered as cutting down the effective diffusion length to improve diffusion. The change of Thiele modulus by surface modification can also be considered as the impact on diffusion.

But triangle method isn't effective to isomerization, because of the strict diffusion limitation. The Thiele modulus and degree of utilization of isomerization was calculated by equation (6) and equation (7). The characteristic diffusion length of ZSM5-P can be determined as half crystalline thickness of the zeolite crystals and as a typical slab morphology its lattice plane along (010) direction is the smallest one. The crystal size of zeolite catalysts can be reasonably considered as keeping constantly in MgO incorporation or mesopore construction. Kinetic rate constants were calculated by fitting the value of toluene and methanol conversion and yield of various products using non-linear least squares method, respectively. The diffusion rate constant (D_{eff}) of xylene was calculated from adsorption kinetics which was derived by Arrhenius equation. The Thiele modulus of isomerization over other samples was derived by the typical inversely proportional function relationship between Thiele modulus and utilization degree, $\eta*\phi = 1.0$.

Tables

Table S1. The diffusion rate coefficient calculated by normalized uptake profiles in adsorption of p-xylene and m-xylene over varied zeolite catalysts at 373 K. The pressure used in the analysis is P = 1.0 mbar.

Sample	ZSM5-P	ZSM5-H	ZSM5-P/MgO	ZSM5-H/MgO
$D_{\text{p-xylene}}$ (10^{-16} m^{2}s^{-1})	1.04	1.37	0.99	1.27
$D_{\text{m-xylene}}$ (10^{-17} m^{2}s^{-1})	2.21	1.96	1.19	1.21

Table S2. The observed reaction rate of methylation, isomerization and MTH reaction over varied zeolite samples.

Sample	$r_{\text{methylation}}$ (X 10^{-6} s^{-1})	$r_{\text{isomerization}}$ (X 10^{-3} s^{-1})	r_{MTH} (X 10^{-5} s^{-1})
ZSM5-P	6.02	1.18	2.69
ZSM5-250nm	4.51	0.71	2.47
ZSM5-H	6.22	1.25	2.74
ZSM5-P/MgO	5.16	0.87	2.39
ZSM5-H/MgO	5.95	0.89	2.51

Table S3. The Thiele modulus and utilization degree of methylation, isomerization and MTH reaction over varied zeolite samples.

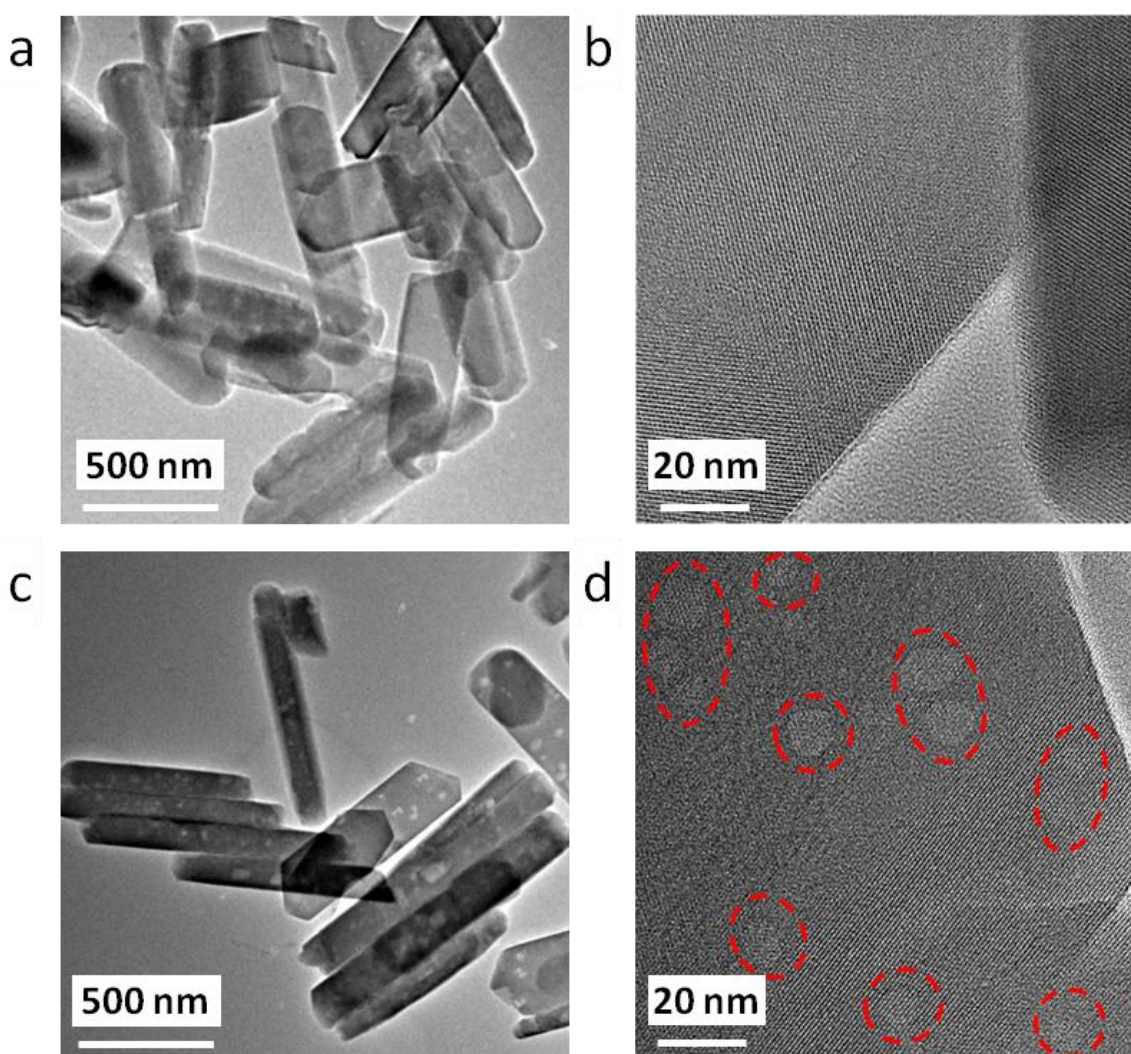| Sample	$\varphi_{methylation}$	$\varphi_{isomerization}$	φ_{MTH}	$\eta_{methylation}$ (%)	$\eta_{somerization}$ (%)	η_{MTH} (%)
ZSM5-P	0.93	3.11	0.42	78.5	32.1	94.5
ZSM5-250nm	1.55	5.22	0.70	59.0	19.0	86.3
ZSM5-H	0.85	2.89	0.35	81.3	34.3	96.1
ZSM5-P/MgO	1.26	4.20	0.75	67.5	23.8	84.1
ZSM5-H/MgO	0.95	4.12	0.62	77.9	24.3	88.7

Figures

Figure S3. TEM images of the representative particles of ZSM5-P (a and b), ZSM5-H (c and d) under different magnifications. The mesopores in Figure 2d were marked by red circle.

TEM images of the representative particles of ZSM5-P (a and b) and ZSM5-H (c and d) are given in Figure S3. Figure S3a shows the representative particles possess crystalline ZSM-5 plate-like

morphology with a dimension of ca. 200 × 600 nm. Meanwhile, Figure S3c directly reveals significant mesoporosity development in almost every particle of ZSM5-H, indicating the impact of silica etching in alkaline treatment.[2] But the influence of alkaline etching on profile and size of zeolite particles can be neglected. The HRTEM image illustrated in Figure S3b and S3d provides an insight into the detailed structure, in which the lattice fringes can be clearly seen in both of ZSM5-P and ZSM5-H, indicating perfect crystalline structure. In Figure S3d, obvious mesopores development in a representative particle of ZSM5-H, which was marked with red circles, reveals that the whole framework can be regarded as a single crystal with penetrating mesoporous network inside.
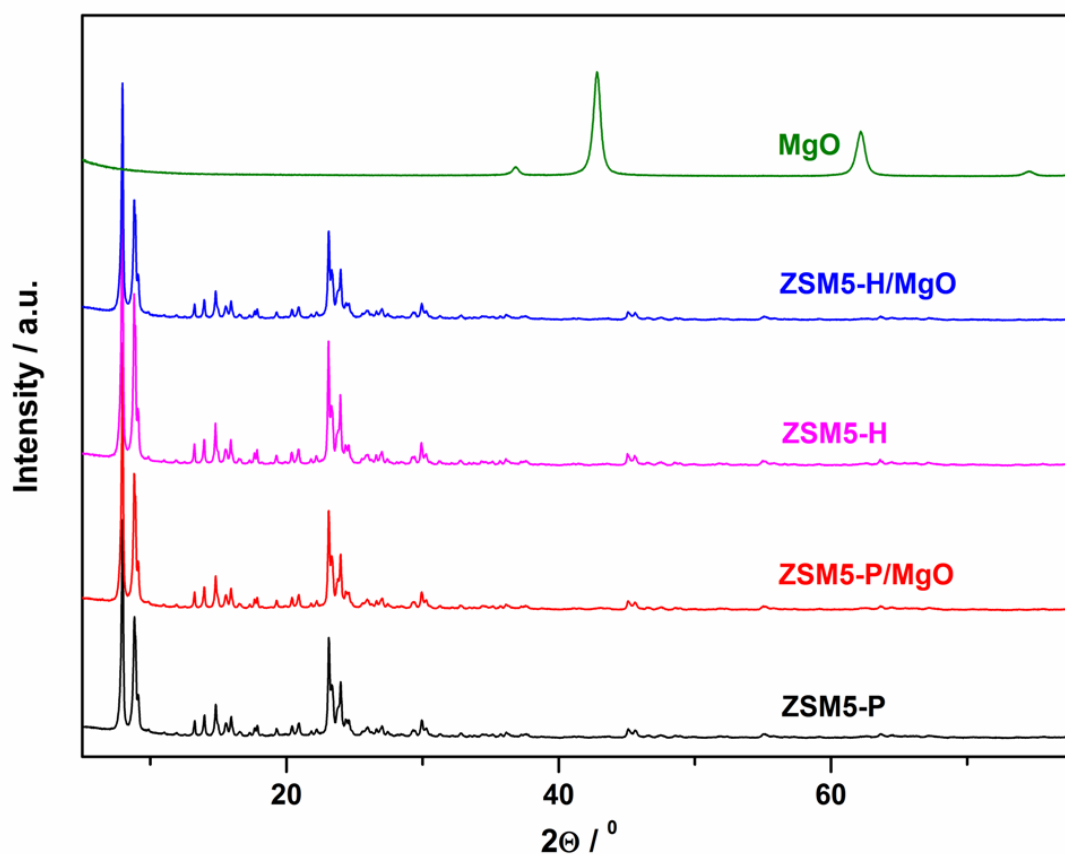

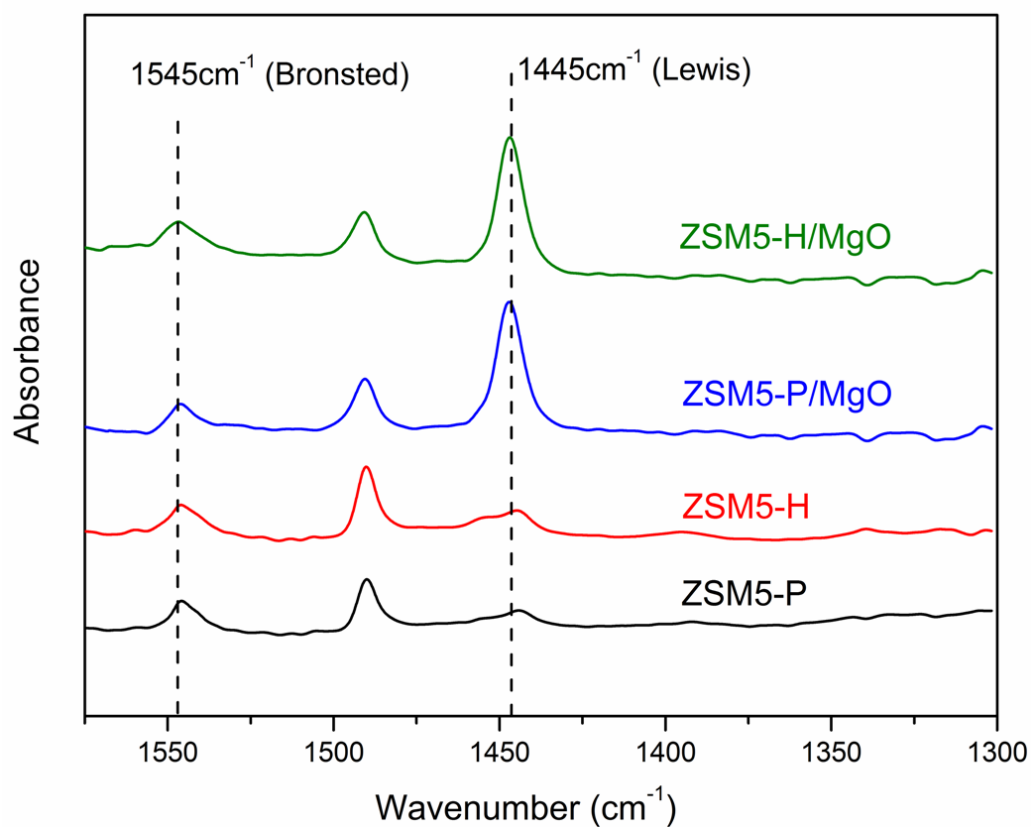**Figure S4**. XRD of parent and hierarchical ZSM-5 zeolite incorporated with different content of MgO.

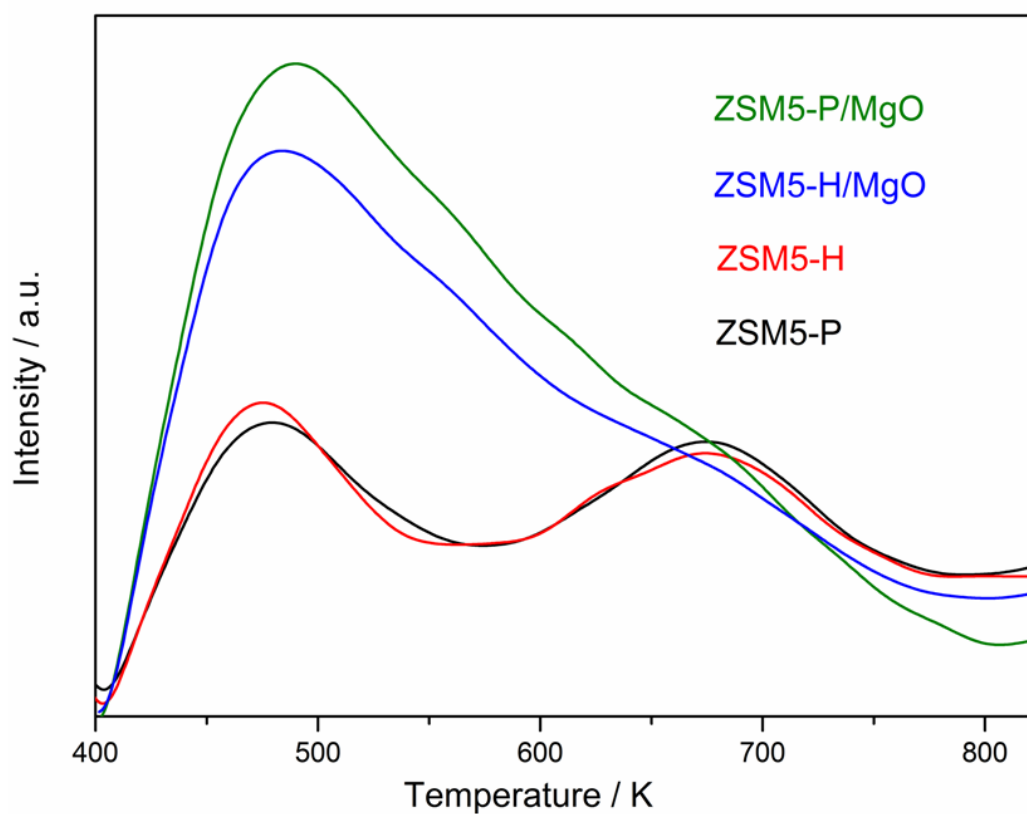**Figure S5.** Pyridine-IR of parent and hierarchical ZSM-5 zeolite incorporated with MgO.

Figure S6. NH$_3$-TPD of parent and hierarchical ZSM-5 zeolite incorporated with MgO.
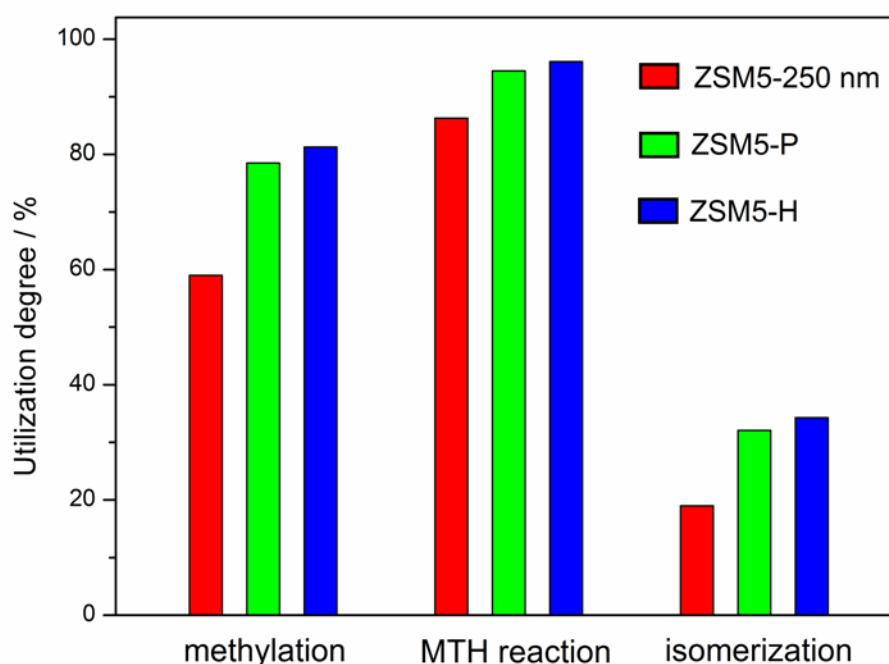
Figure S7. Utilization degree of ZSM5-250nm (red columns), ZSM5-P (green columns), and ZSM5-H (blue columns) in the methylation of toluene, MTH reaction and isomerization at 753 K, $p_{toluene}$ = 4.5 kPa, p_{MeOH} = 1.1 kPa.

Table S4. The relative amount of ^{31}P NMR peaks at different location over varied zeolite sample absorbed by TBPO.

Sample	^{31}P NMR peak/ppm relative concentration (%)	
	Peak at 74 ppm (%)	Peaks at 57-64 ppm (%)
ZSM5-P	31.7	68.3
ZSM5-P/MgO	/	100
ZSM5-H	14.5	85.5
ZSM5-H/MgO	/	100

On the basis of previous works, the confinement effect of the zeolite framework is important in determining the ^{31}P chemical shift of TMPO adsorbed on the Brønsted acid sites of zeolites.[3,4] The channel diameter of ZSM-5 is approximately 0.55−0.60 nm, which is comparable to the molecular size of TMPO with a kinetic diameter of 0.55 nm. The pore structure inside ZSM-5 facilitates the investigation of the long-range electrostatic effects from the Madelung potential of the zeolite framework (confinement effect), which is pronounced for the microporous channels of ZSM-5 zeolite.[4] Thus, the ^{31}P chemical shift can be used to characterize the integrity of the zeolite micropores. To further demonstrate the distribution of acid sites on the ZSM-5 catalysts after introduction of mesoporosity and MgO incorporation, ^{31}P NMR spectra of larger molecules, TBPO,

which only can be absorbed by acid sites on pore mouth or external surface of zeolite catalysts, were employed (Figure 3, right). The signals at 43, 50-54, 64, 68 and 74 ppm, associated with TMPO molecules adsorbed at different types of sites on the ZSM-5 catalyts.

Reference:

(1) Marshall, J. F.; Weisz, P. B. Determination of diffusivities in catalyst particles. *J. Catal.* **1988**, *111* (2), 460-463.

(2) Milina, M. ; Mitchell, S.; Crivelli, P.; Cooke, D.; Perez-Ramírez, J. Mesopore quality determines the lifetime of hierarchically structured zeolite catalysts. *Nat. Commun.* **2014**, *5*, 3922.

(3) Zheng, A. M.; Huang, S.-J.; Liu, S.-B.; Deng, F. Acid properties of solid acid catalysts characterized by solid-state 31P NMR of adsorbed phosphorous probe molecules. *Phys. Chem. Chem. Phys.* **2011**, *13* (33), 14889–14901.

(4) Zheng, A. M.; Zhang, H. L.; Lu, X.; Liu, S. B.; Deng, F. Theoretical predictions of 31P NMR chemical shift threshold of trimethylphosphine oxide absorbed on solid acid catalysts. *J. Phys. Chem. B* **2008**, *112* (15), 4496–4505.