

Electronic Supplementary Information

Steering interface effect of H-ZSM-5 zeolites with tailored surface barriers to improve their catalytic performances

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1. Experimental details

1.1 Synthesis of the pristine H-ZSM-5 zeolite

The H-ZSM-5-*p* zeolite sample was prepared by hydrothermal synthesis according to previously reported method.¹ Typically, tetraethyl orthosilicate (TEOS), NaAlO₂, 25% tetrapropylammonium hydroxide (TPAOH) and urea were dissolved in distilled water with a molar ratio of SiO₂: Al₂O₃: TPAOH: H₂O: urea = 1: 0.0017: 0.4: 45: 0.2. Then the mixture was transferred into a Teflon-lined autoclave, and kept for 4 days at 180 °C. After washed and filtered for several times, the products were collected, centrifuged, filtered and dried, and then calcined in air at the oven for 6 h at 550 °C to remove the organic template. Finally, the Na-forms ZSM-5 samples were treated by NH₄-exchange with 0.1 M NH₄NO₃ solution at 80 °C for 3 h, and calcined at 550 °C for 6 h to obtain H-form ZSM-5 zeolites. The NH₄-exchange and calcination processes were repeated three times.

1.2 The surface decoration of H-ZSM-5 zeolite

The pristine H-ZSM-5 zeolite was further modified by conventional chemical liquid deposition (CLD) of tetraethoxysilane (TEOS). Typically, 1.0 g of H-ZSM-5-*p* zeolites were dispersed in 20.0 mL of ethanol solvents and heated to reflux under magnetic stirring at 60 °C. Then, 0.3 mL TEOS were added and the mixture was continuously stirred for 2 h. After washed, filtered and drying, the sample was calcined at 550 °C for 6 h. This procedure was repeated four times until the desired surface permeability was achieved. The obtained H-ZSM-5 zeolites were denoted as H-ZSM-5-*m*.

1.3 Characterizations of H-ZSM-5 catalysts

The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 5.1540589$ nm) as X-ray source generated at 40 kV and 40 mA. The scanning rate was performed at 1° min⁻¹ over a 2 θ range of 5-50°. The Ar physisorption was performed on a Micromeritics TriStar3000 Surface Area Analyzer at -198 °C. The pyridine and the di-tert-butyl-pyridine (DTBPy) adsorption analysis of the H-ZSM-5 samples were implemented by *in situ* IR cell with

CaF₂ windows. Firstly, the H-ZSM-5 samples were pressed into a self-supporting wafer with a weight of 15 mg at the pressure of 30 MPa. Then, the *in situ* IR cell was degassed at 400 °C for four hours under an ultrahigh vacuum, then cooled down to 200 °C. Subsequently, the pyridine or the DTBPy steams were introduced into the IR cell for 30 min, and the physical adsorption pyridine molecules in zeolite samples were wiped out by degassing for 30 min. Finally, the IR spectra were recorded on a Nicolet 6700 instrument equipped with an MCT detector at a resolution of 4 cm⁻¹. The NH₃ temperature-programmed desorption (NH₃-TPD) was performed on a homemade instrument. Typically, the zeolite sample (0.1 g) was pretreated in a quartz reactor with a high-purity N₂ flow (30 mL min⁻¹) at 500 °C for 2 hours, then cooled down to room temperature. NH₃ adsorption was performed at room temperature in a 10 vol% NH₃-N₂ mixture (20 mL min⁻¹) for 1 h, followed by TPD in a pure N₂ flow (30 mL min⁻¹) by raising the temperature to 600 °C at a ramp rate of 10 °C min⁻¹. The Scanning electron microscopy (SEM) analysis was performed on a Hitachi S-4800 electron microscope. Before data collections, the sample was dispersed ultrasonically in ethanol for 30 min and then dropped onto a silicon pellet, followed by drying in an oven for 60 min. The TEM images were carried out on a Tecnai 20 STWIN electron microscope at an acceleration voltage of 200 kV.

1.3 Coke analysis

The coke contents of the used H-ZSM-5 zeolite catalysts after time on stream for 100 h were investigated by employing the TGA technique (SDT Q600 V20.9 Build 20). During the TGA experiments, the temperature was increased to 850 °C under a flowing air of 100 mL min⁻¹ at a constant ramping rate of 10 °C min⁻¹. Then, the weight loss of the curves between 400 and 800 °C was used to evaluate the total coke content of zeolite catalysts. It should be noted that the coke density in zeolite catalysts was regarded as similar to the coal of 1.22 g cm⁻³.^{2,3} Then, the content of internal coke species could be calculated with the decrease of micropore volumes compared to that of the fresh zeolite, and the content of external coke species was determined by the total coke content subtracting the internal one. Finally, the micropore blockage degree

was evaluated by the proportion of micropore volume decrease to the micropore volume of the corresponding fresh zeolite.

1.4 Catalytic cracking process

The OCC reactions were performed in a stainless catalytic reactor. The catalyst (0.30 g) with grain sizes of 20-40 mesh was loaded in the reactor and was pretreated in high-purity N₂ flow at 550 °C for 2 h. Then, C₄⁼/C₄⁰ (60% / 40% volume ratio) mixtures with WHSV of 30⁻¹ h was introduced into the reactor with a laboratory-scale piston pump for reactants input. The pressure of reactant was typically regulated at 1.6 bar. Products were analyzed by an online gas chromatography (Agilent 7860). The calculation of C₄⁼ conversion was based on the moles of C₄⁼ at inlet and outlet gases, the product selectivity was calculated on a molar carbon basis.

1.5 Measurements of diffusivity

The diffusivity of the analytic H-ZSM-5 samples were measured by a home-made time-resolved *in situ* FT-IR spectroscopy with a Nicolet 6700 instrument equipped with an MCT detector at a resolution of 4 cm⁻¹, the detailed experimental steps were described in our previous work.⁴ Firstly, the H-ZSM-5 sample was pressed into a self-supporting wafer and placed inside a gold sample holder surrounded by a heating wire. The sample holder was fixed in the *in situ* IR cell connected to a gas control system. Before measurement, H-ZSM-5 sample was pretreated with a pure N₂ flow at high temperature. Subsequently, the sample was cooled down to the test temperature. For a typical measurement, the guest molecules (C₄⁼ or cyclohexane) was introduced into the IR cell, and the IR spectra were collected. Finally, the diffusion rates were calculated using the following formula for sheet like zeolite^{5,6}:

$$\frac{m_t}{m_{(t \rightarrow \infty)}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(- (2n+1)^2 \frac{\pi^2 D_{eff}}{L^2} t\right) \quad (1)$$

Where m_t is the amount adsorbed at time t (s), m_{∞} is the amount adsorbed at equilibrium coverage, D_{eff} represents the apparent diffusion coefficient, and L represents the diffusion length of H-ZSM-5 crystal. In this work, the diffusion rate, D_{eff}/L^2 was chosen for evaluated the diffusion properties of H-ZSM-5 samples.

It is worth noting that these apparent diffusion rates of ZSM-5 zeolites reflect the molecular diffusivities not only in their intracrystalline pores but also on their surface structures.^{7,8} Recently an approach that can directly quantify the surface permeability (α/L) via fitting the initial uptake curves of the relevant zeolite was successfully exploited:⁹

$$\left. \frac{M_t}{M_\infty} \right|_{\sqrt{t} \rightarrow 0} \cong \frac{\alpha}{L}(\sqrt{t})^2 + O(\sqrt{t^3}) \quad (2)$$

And the intracrystalline diffusivity (D_{int}/L^2) can be fitted by the following approximation:^{10,11}

$$\frac{L^2}{D_{eff}} = \frac{L^2}{D_{int}} + \frac{3L}{\alpha} \quad (3)$$

2. Supplementary tables and figures

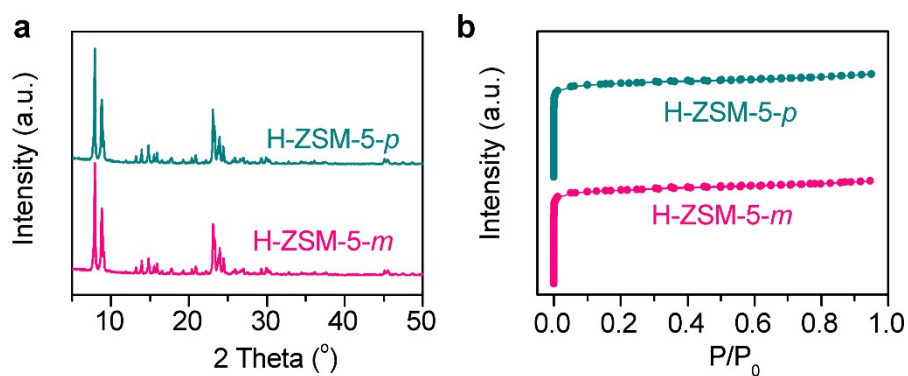


Fig. S1 **a** The X-ray diffraction patterns and **b** The Ar physisorption isotherms of H-ZSM-*p* and H-ZSM-5-*m* zeolites.

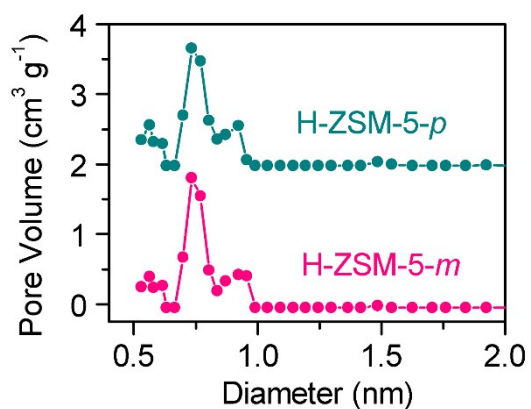


Fig. S2 The micropore size distributions of H-ZSM-*p* and H-ZSM-5-*m* zeolites.

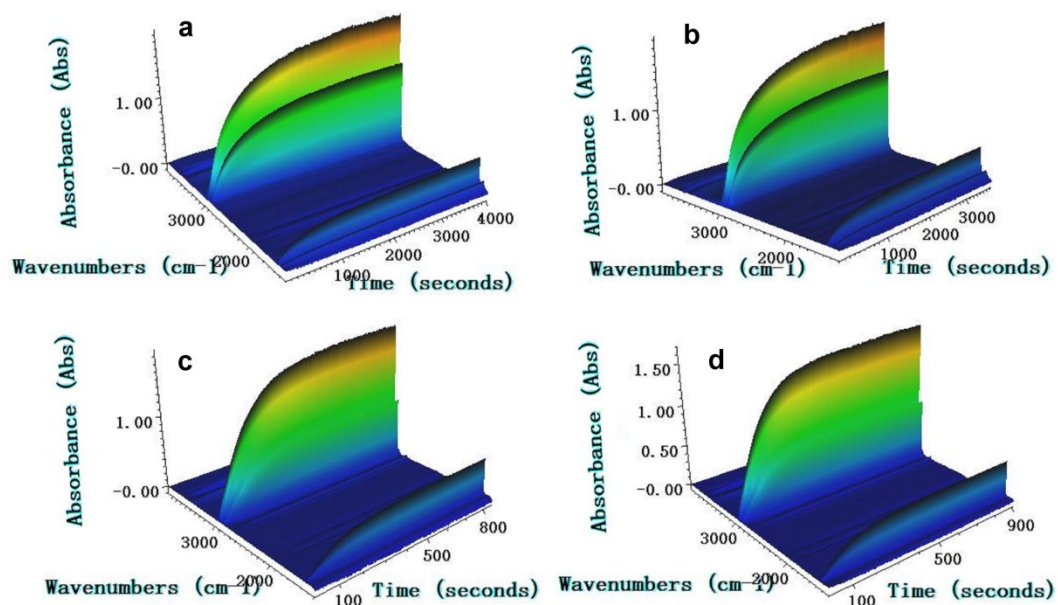


Fig. S3 The original uptake curves of H-ZSM-5-*p* and H-ZSM-5-*m* zeolites. **a, b** The C₄= molecules over H-ZSM-5-*p* and H-ZSM-5-*m*, respectively; **c, d** The cyclohexane molecules over H-ZSM-5-*p* and H-ZSM-5-*m*, respectively. The normalized areas of the IR bands of butene and propene molecules at 2750-3150 cm⁻¹ were used to quantify the relative concentrations of adsorbate in the zeolites.

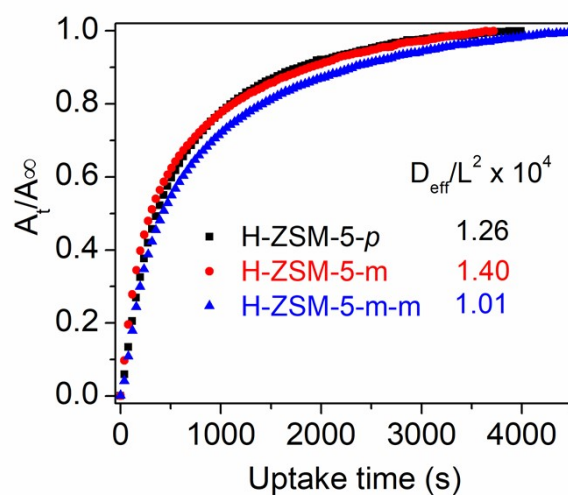


Fig. S4 The diffusion behaviors of 1-butene molecules in H-ZSM-5-p, H-ZSM-5-m and H-ZSM-5-m-m zeolites. The corresponding apparent diffusion rates fitted by Eq. S1.

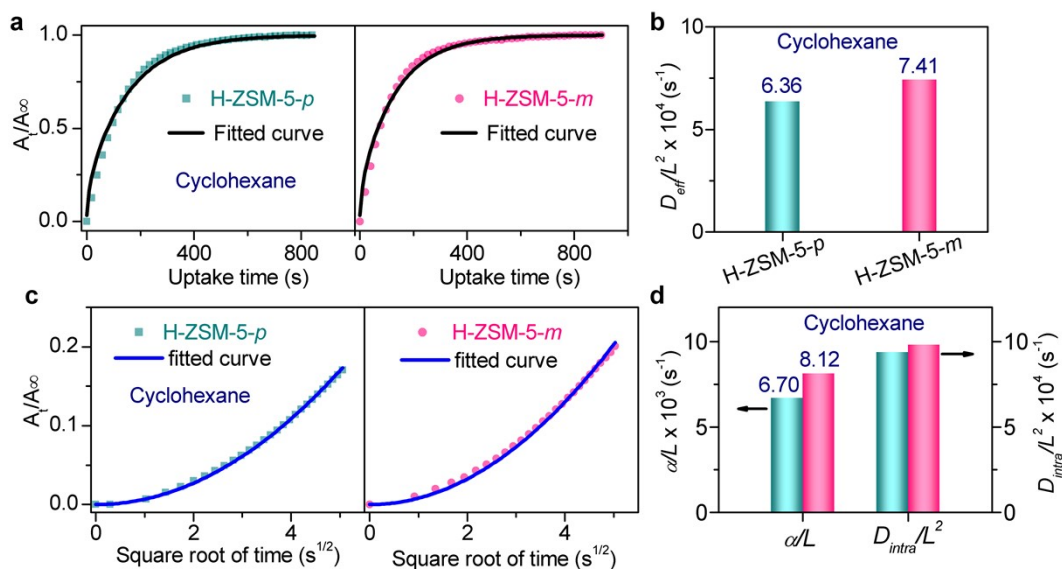


Fig. S5 The diffusion behaviors of cyclohexane molecules in H-ZSM-5-*p* and H-ZSM-5-*m* zeolites. **a** The normalized uptake curves of cyclohexane molecules over different H-ZSM-5 zeolites. **b** The corresponding apparent diffusion rates fitted by Eq. S1. **c** Initial uptake curves of cyclohexane molecules over H-ZSM-5 zeolites. **d** Surface permeability (α/L) and intracrystalline diffusivities (D_{intra}/L^2) of cyclohexane molecules derived by the uptake curves of H-ZSM-5 samples fitted by Eqs. S2 and S3.

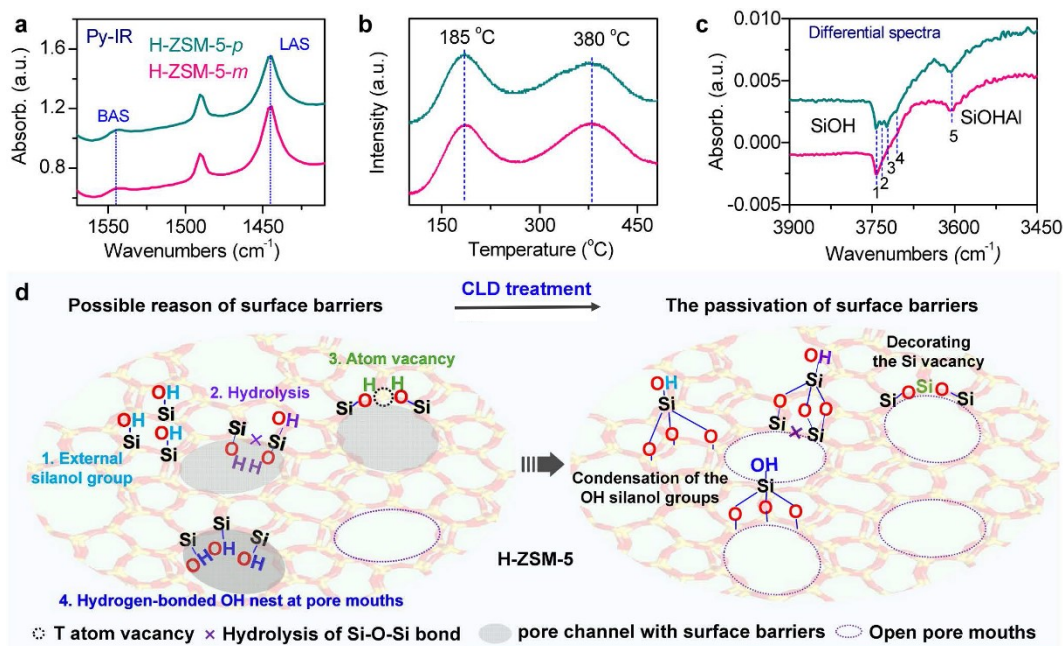


Fig. S6 **a** The Pyridine-adsorption IR spectra of ZSM-5 zeolites. **b** The NH_3 temperature-programmed desorption (NH_3 -TPD) curves of H-ZSM-5-p and H-ZSM-5-m zeolites. The high-temperature peak existing at around 380 $^{\circ}\text{C}$ arises from the strong acid sites, and the low-temperature peak at around 185 $^{\circ}\text{C}$ belongs to the weak acid sites. **c** The Differential IR spectra before and after di-tert-butyl-pyridine (DTBPy) adsorption: 1-4 bands (3742, 3732, 3723, and 3706 cm^{-1}) represent the external Si-OH nests on the surface or near the micropores; 5 band (3606 cm^{-1}) represents the external Si-OH-Al bridging hydroxyl groups. **d** The possible mechanism of surface diffusion barriers over the high silica H-ZSM-5 zeolites and the passivation of the surface barriers by CLD treatment with TEOS molecules.

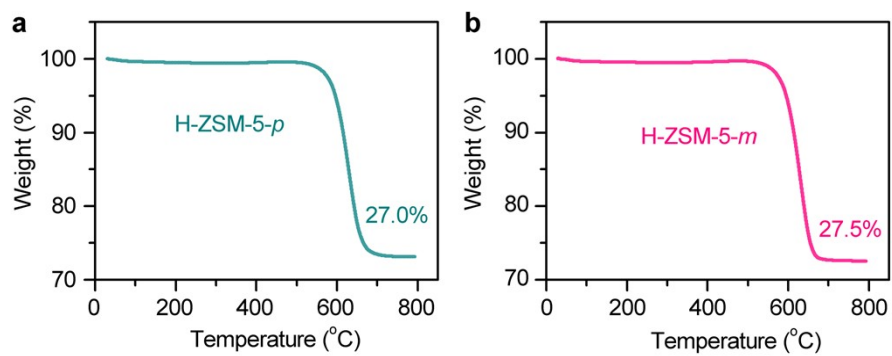


Fig. S7 The TGA curves of the H-ZSM-5-*p* and H-ZSM-5-*m* zeolite catalysts after reaction for 100 h. **a** H-ZSM-5-*p*; **b** H-ZSM-5-*m*.

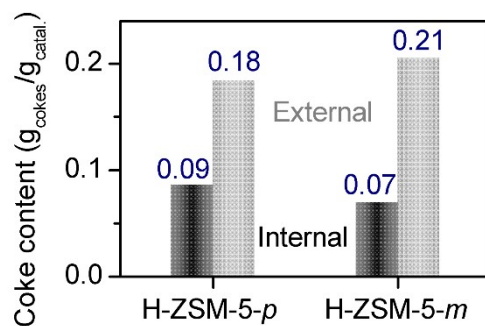


Fig. S8 The distributions of coke depositions after 100 h of OCC reactions over H-ZSM-5 zeolite catalysts with various surface diffusion barriers.

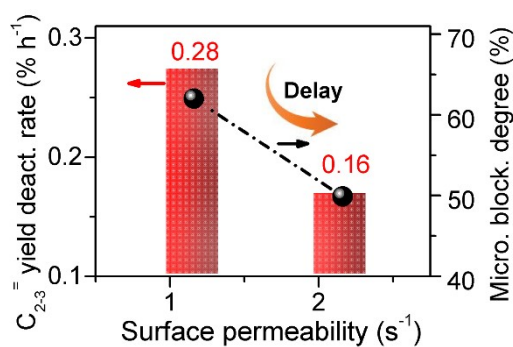


Fig. S9 Correlation of C₂₋₃ yield deactivation rate with the surface permeability of 1-butene molecules in H-ZSM-5 crystals. The deactivation rates were calculated on the basis of the catalytic performances displayed in Fig. 3a. The data between 20 h and 100 h were chosen due to the actual deactivation time.

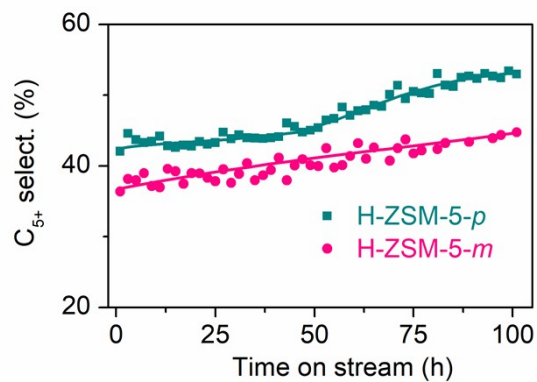


Fig. S10 The C₅₊ selectivity of H-ZSM-5-p and H-ZSM-5-m zeolites in the OCC reactions. Reaction conditions: M (catalyst) = 0.3 g; P = 0.6 Bar; T = 550 °C; F = 15 mL h⁻¹; C₄⁼ / (C₄⁼ + C₄⁰) × 100% (weight%) = 60%; Time on stream, 100 h.

Table S1 The structural and compositional parameters of the H-ZSM-5 zeolites.

zeolites	$S_{\text{BET}}^{\text{a}}$ [cm ² g ⁻¹]	$S_{\text{micro}}^{\text{b}}$ [cm ² g ⁻¹]	$V_{\text{total}}^{\text{c}}$ [cm ³ g ⁻¹]	$V_{\text{micro}}^{\text{d}}$ [cm ³ g ⁻¹]	Si/Al ratio ^e [%]	Brønsted acid sites ^f [umol g ⁻¹]
H-ZSM-5- <i>p</i>	363.3	330.7	0.169	0.139	301	26.6
H-ZSM-5- <i>m</i>	366.1	332.3	0.170	0.140	303	25.5

^a BET surface area; ^b Micropore area evaluated by the t-plot method; ^c Single point desorption total pore volume of pores less than 43.9605 nm diameter at $P/P_0 = 0.950000000$; ^d Pore volume for micropores evaluated by the t-plot method; ^e Determined by ICP analysis; ^f Determined by the area of Pyridine-adsorption IR spectra at 1545 cm⁻¹. The extinction coefficient of $\epsilon_{\text{B}} = 1.67 \pm 0.1$ cm mol⁻¹ was employed. ¹²

Table S2 The structural parameters of the H-ZSM-5 samples after working for 100 h.

samples	S _{BET} ^a [cm ² g ⁻¹]	S _{micro} ^b [cm ² g ⁻¹]	S _{meso} ^c [cm ² g ⁻¹]	V _{total} ^d [cm ³ g ⁻¹]	V _{micro} ^e [cm ³ g ⁻¹]	V _{meso} ^f [cm ³ g ⁻¹]
H-ZSM-5- <i>p</i>	188.6	165.3	19.4	0.0907	0.0684	0.0205
H-ZSM-5- <i>m</i>	193.6	177.1	15.0	0.107	0.0828	0.0175

^a BET surface area; ^b Micropore area evaluated by the t-plot method; ^c BJH desorption method; ^d Single point desorption total pore volume of pores less than 43.9605 nm diameter at P/P₀ = 0.950000000; ^e Pore volume for micropores evaluated by the t-plot method; ^f Pore volume for mesopores evaluated by BJH desorption.

3. References

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