

Supplementary Information

Unraveling the diffusion properties of zeolite-based multi-component catalyst by combined Gravimetric Analysis and IR spectroscopy (AGIR)

*Peng Peng^{†,‡}, Dusan Stosic[‡], Abdelhafid A. Blal[‡], Alexandre Vimont[‡], Philippe Bazin[‡],
Xin-Mei Liu[†], Zi-Feng Yan^{†*}, Svetlana Mintova^{†,‡*}, & Arnaud Travert^{‡*}*

[†]State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China

[‡]Laboratoire Catalyse et Spectrochimie (LCS), Normandie Univ, ENSICAEN, UNICAEN, CNRS, 14000 Caen, France

Preparation of the samples

Materials

All the reagents were used without further purification. The H form of parent ZSM-5 zeolite (also used as parent ZSM-5 catalyst, ZSM-5-P) with Si/Al ratio of 14 was purchased from Nankai University Catalyst Co. Sodium hydroxide (NaOH), cetyl trimethyl ammonium bromide (CTAB), sulphuric acid (H₂SO₄), and ammonium chloride (NH₄Cl) were purchased from Sinopharm Chemical Reagent Co. Ltd.

Synthesis of hierarchical single-component ZSM-5 catalyst (ZSM-5-A)

Sample ZSM-5-A was prepared using the parent zeolite ZSM-5-P (5.0 g) which was mixed with a NaOH aqueous solution (150 mL of 1.0 mol/L) at 353 K for 60 minutes. After that, the sample was filtrated, washed and dried.

Synthesis of multi-component zeolite-based catalyst (ZSM-5-AR)

Sample ZSM-5-AR was prepared from the parent zeolite ZSM-5-P firstly mixed with NaOH aqueous solution (150 mL of 1.0 mol/L) at 353 K for 60 minutes. Afterwards, cetyl trimethyl ammonium bromide (CTAB) aqueous solution (60 mL, 0.2 mol/L) was added into the mixture and stirred at 353 K for another 30 minutes. Then the pH of the mixture was adjusted to be 10.5 by dilution with H₂SO₄ (2.0 mol/L). The mixture was transferred into a Teflon-lined stainless steel autoclave and treated in an oven at 383 K for 24 hours. The sample was filtrated, washed, dried at 383K, and calcinated in a muffle furnace at 823 K for 6 hours.

Ion-exchange

In order to endow acidity into ZSM-5-A and ZSM-5-AR, the two samples were ion-exchanged three times with 0.5 mol/L NH₄Cl aqueous solution with a ratio of 30 mL/g sample at 353 K for one hour each. Then the samples were filtrated, washed, dried at 383K and calcinated at 823 K for 4 hours.

Characterization

Powder X-ray diffraction

Powder X-ray diffraction (XRD) patterns were recorded by a PANalytical X'Pert PRO MPD diffractometer equipped with Cu K α radiation (40 kV, 40 mA, $\lambda = 0.1541$ nm) in the 2θ range of 5-60° (wide-angle XRD patterns) and 2.0-10.0° (small-angle XRD patterns).

Wide-angle XRD patterns (Figure S1A) show that the intrinsic MFI framework of the samples are partially preserved upon mesopore formation for both ZSM-5-A and ZSM-5-AR catalysts. Small-angle X-ray diffraction of ZSM-5-AR shows highly ordered mesopores characteristic peaks of MCM-41 like ordered mesostructures (Figure S1B).

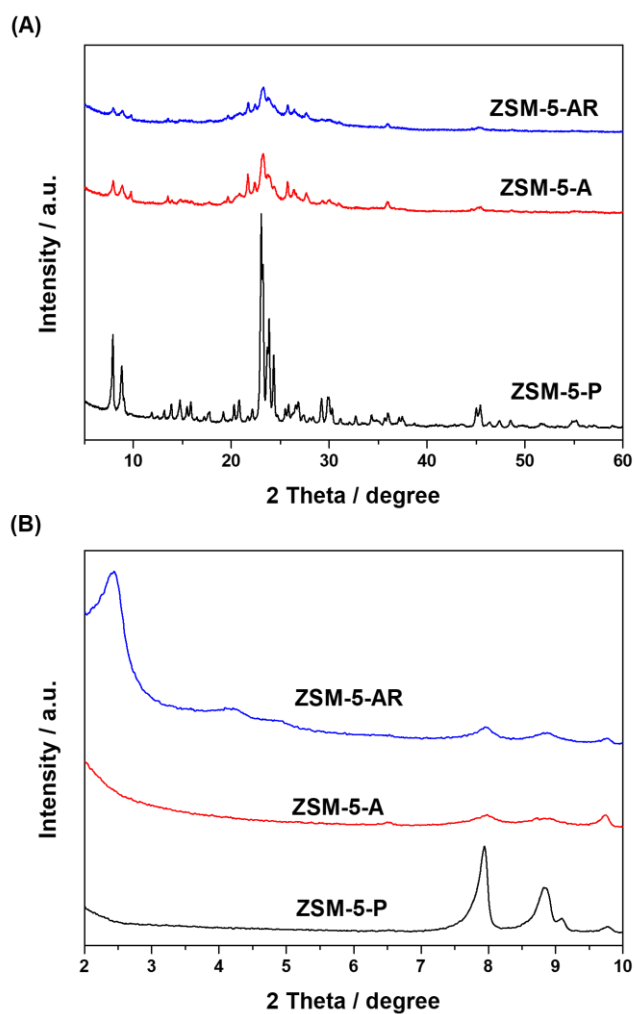


Figure S1. Wide-angle (A) and small-angle (B) XRD patterns of parent ZSM-5 catalyst (ZSM-5-P), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) and multi-component zeolite-based catalyst (ZSM-5-AR)

Nitrogen adsorption-desorption isotherms

Nitrogen adsorption-desorption isotherms were recorded on a Micromeritics ASAP2020 instrument at 77 K. Prior to analysis, samples were pre-treated at 673 K under vacuum to remove impurities. The Brunauer-Emmett-Teller (BET) equation and the adsorption data collected at $p/p_0 = 0.96$ were used for calculating total surface area (S_{total}) and total pore volume (V_{total}), respectively. Besides, mesopore surface area (S_{meso}) and micropore volume (V_{micro}) were calculated using the t -plot method. Mesopore size distribution was calculated by Barrett-Joyner-Halenda (BJH) method based on desorption branches.

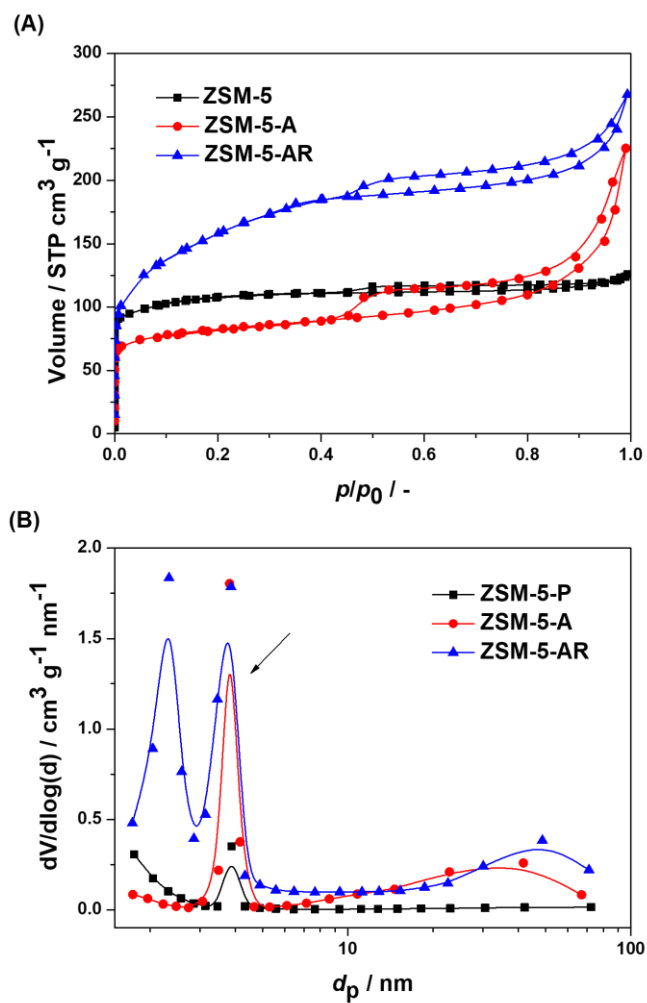


Figure S2. Nitrogen adsorption–desorption isotherm (A) and pore size distribution calculated from the BJH desorption branch of (B) parent ZSM-5 catalyst (ZSM-5-P), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) and multi-component zeolite-based catalyst (ZSM-5-AR)

Table S1. Textural properties of parent ZSM-5 catalyst (ZSM-5-P), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) and multi-component zeolite-based catalyst (ZSM-5-AR)

Sample	S_{total} /	S_{micro} /	S_{meso} /	V_{total} /	V_{micro} /	V_{meso} /
	(m ² /g)	(m ² /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)	(cm ³ /g)
ZSM-5-P	397	352	45	0.19	0.15	0.04
ZSM-5-A	309	228	81	0.25	0.09	0.16
ZSM-5-AR	623	134	489	0.48	0.04	0.44

Nitrogen adsorption-desorption isotherm of sample ZSM-5-P is of type I due to its microporous character (Figure S2A). For samples ZSM-5-A and ZSM-5-AR, N₂ isotherms reveal marked mesoporosity evidenced by an enhanced uptake at higher pressures and a distinct hysteresis loop. The mesoporosity is created at the expense of microporosity, which decreases from 0.15 cm³ g⁻¹ in the parent sample (ZSM-5-P) to 0.09 cm³ g⁻¹ and 0.04 cm³ g⁻¹ in ZSM-5-A and ZSM-5-AR, respectively (Table S1). BJH pore size distribution curves are shown in Figure S2B. The "peaks" marked by the arrow are artefacts caused by tensile strength effect¹ and do not represent real pore size distribution. Sample ZSM-5-A contains mesopores with a wide size distribution, showing that the mesopores are not ordered and not well-defined. In the case of sample ZSM-5-AR, the BJH pore size distribution curve exhibits maximum at around 2.8 nm that further confirms highly ordered mesopores.

Fourier-Transform Infrared Spectroscopy (FTIR) using pyridine as a probe molecule

Pyridine adsorption test was used to discriminate the distribution of Brønsted (B) and Lewis (L) acid sites; spectra were collected using a Thermo Nicolet 6700 Fourier-transform infrared spectrometer. The samples were pressed into self-supporting wafers (diameter: 1.6 cm, mass: 20 mg). Prior to adsorption of pyridine, all samples were pre-treated at 723 K for 4 hours under vacuum (10^{-6} Torr). Then 1 Torr of pyridine was adsorbed at 298 K to reach the equilibrium. Afterwards, the samples were evacuated at 423, 573 and 723 K and the spectra were collected. The molar extinction coefficients for B and L acid sites were based on ref. 1

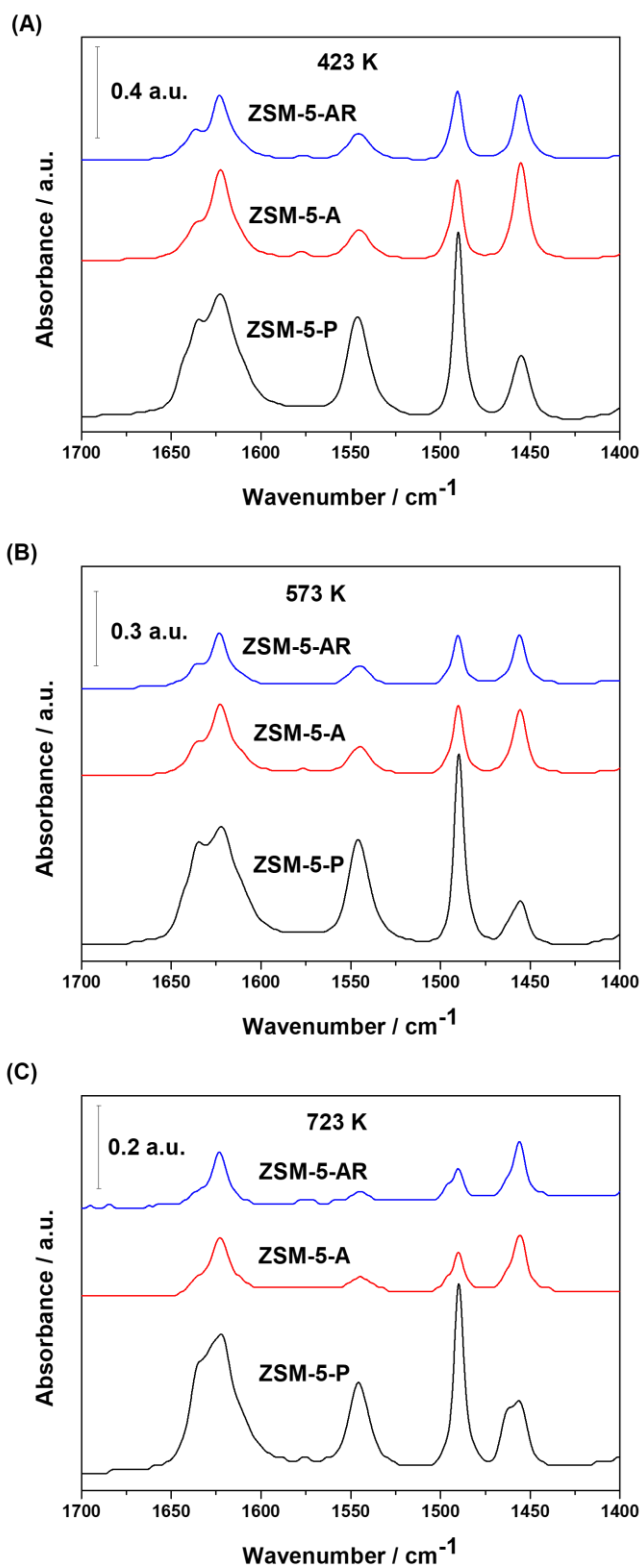


Figure S3 FTIR spectra parent ZSM-5 catalyst (ZSM-5-P), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) and multi-component zeolite-based catalyst (ZSM-5-AR) at 423 K (A), 573 K (B), and 723 K (C).

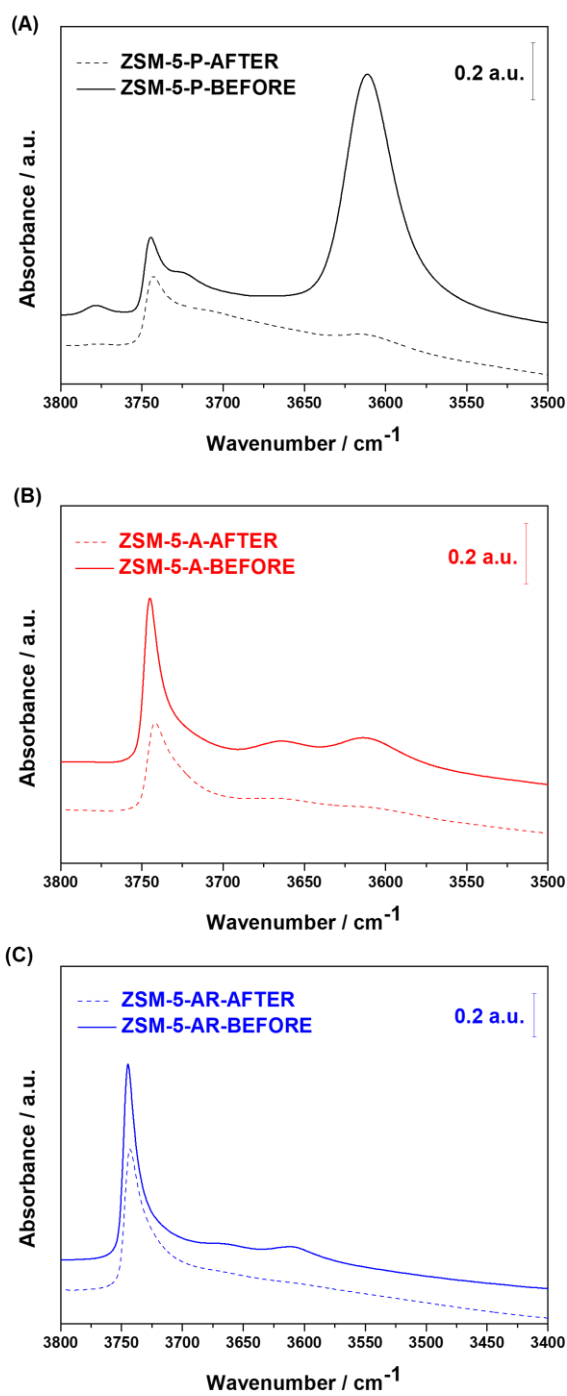


Figure S4 FTIR spectra in OH region (3800-3500 cm^{-1}) of parent ZSM-5 catalyst (ZSM-5-P) (A), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) (B) and multi-component zeolite-based catalyst (ZSM-5-AR) (C) before (solid line) and after (dash line) pyridine adsorption.

Table S2 Acidity of parent ZSM-5 catalyst (ZSM-5-P), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) and multi-component zeolite-based catalyst (ZSM-5-AR).

Samples	Brønsted acid sites / ($\mu\text{mol/g}$)			Lewis acid sites / ($\mu\text{mol/g}$)			Ratio of Brønsted and Lewis acid sites		
	423K	573K	723K	423K	573K	723K	423K	573K	723K
ZSM-5-P	403	367	169	140	85	60	2.9	4.3	2.8
ZSM-5-A	114	90	26	193	109	60	0.6	0.8	0.4
ZSM-5-AR	108	64	18	119	80	56	0.9	0.8	0.3

Fourier-Transform Infrared Spectroscopy (FTIR) using collidine as a probe molecule

Collidine adsorption test was used to detect the accessibility of Brønsted (B) and Lewis (L) acid sites; spectra were collected using a Thermo Nicolet 6700 Fourier-transform infrared spectrometer. The samples were pressed into self-supporting wafers (diameter: 1.6 cm, mass: 20 mg). Prior to adsorption, the samples were pre-treated at 723 K for 4 hours under vacuum (10^{-6} Torr). Then collidine was adsorbed at 298 K and the spectra were collected. For assess accessibility of BAS, the relative peak area at *c.a.* 3610 cm^{-1} before and after collidine adsorption were collected and calculated.

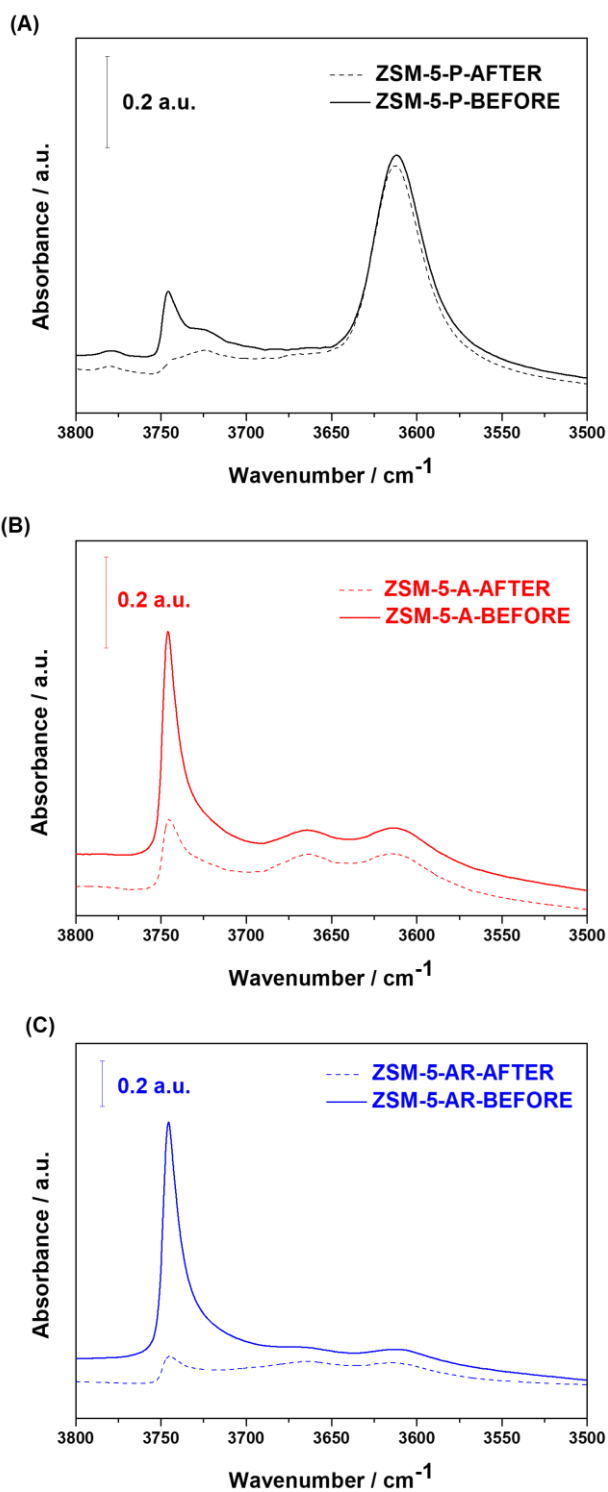


Figure S5 FTIR spectra in OH region ($3800\text{--}3500\text{ cm}^{-1}$) of parent ZSM-5 catalyst (ZSM-5-P) (A), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) (B) and multi-component zeolite-based catalyst (ZSM-5-AR) before (solid line) and after (dash line) collidine adsorption.

Fourier-Transform Infrared Spectroscopy (FTIR): acidity measurements

Acid properties of the catalysts were probed by IR using pyridine and collidine as probe molecules (Figures S3-S4 and Table S2). The kinetic diameter of pyridine (0.57 nm) is small enough to guarantee the access to all acid sites, whereas collidine is a bulky molecule (0.74 nm) used for characterizing the acid sites outside or near to the pore mouth of the micropores of ZSM-5 zeolite³. Pyridine adsorption reveals significant decrease in the amount of Brønsted acid sites (BAS) for both hierarchical catalysts, while the amount of Lewis sites is increased for ZSM-5-A and slightly decreased for ZSM-5-AR. Furthermore, the band intensities in hydroxyl region before and after adsorption of the two probe molecules are presented in Figure S5 and S6. The band at *c.a.* 3610 cm⁻¹, which reflects the stretching vibration mode of bridged hydroxyl group (Si-O(H)-Al) is associated with zeolitic BAS⁴. Pyridine adsorption on the three samples showed nearly complete disappearance of this band whereas collidine hardly titrates any of them. Therefore, we conclude that BAS are confined in the micropores of all samples.

Fourier-Transform Infrared Spectroscopy (FTIR) in OH region (3800-3500 cm⁻¹)

before and after iso-octane adsorption

The three samples were tested using combined gravimetric and infrared spectroscopy (AGIR) analysis using isooctane as a probe adsorbate. In order to collect the IR spectra in OH region (3800-3500 cm⁻¹) before isooctane adsorption, all samples were pressed into self-supporting wafers (diameter: 1.6 cm, mass: 20 mg) and purged under a flow of argon (25 mL min⁻¹) at 423 K for overnight. Then the temperature for diffusivity measurement was fixed at 423 K, and a gaseous mixture of isooctane and argon (isooctane was saturated in a saturator at 293 K, and its relative pressure was estimated by Antoine Equation) was feed into AGIR until the adsorption reached equilibrium (*i.e.* absorption bands at *c.a.* 3610 cm⁻¹ did not change).

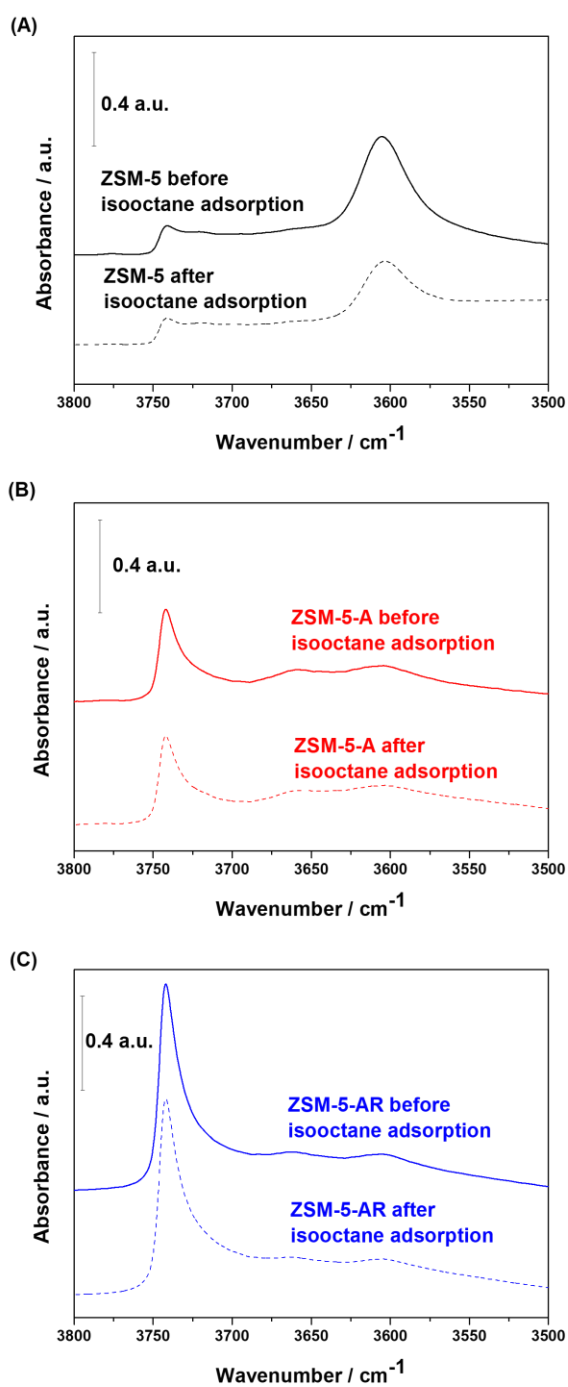


Figure S6. IR spectra in OH region (3800-3500 cm⁻¹) of parent single-component ZSM-5 catalyst (ZSM-5-P) (A), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) (B) and multi-component zeolite-based catalyst (ZSM-5-AR) (C) before and after equilibrated iso-octane adsorption.

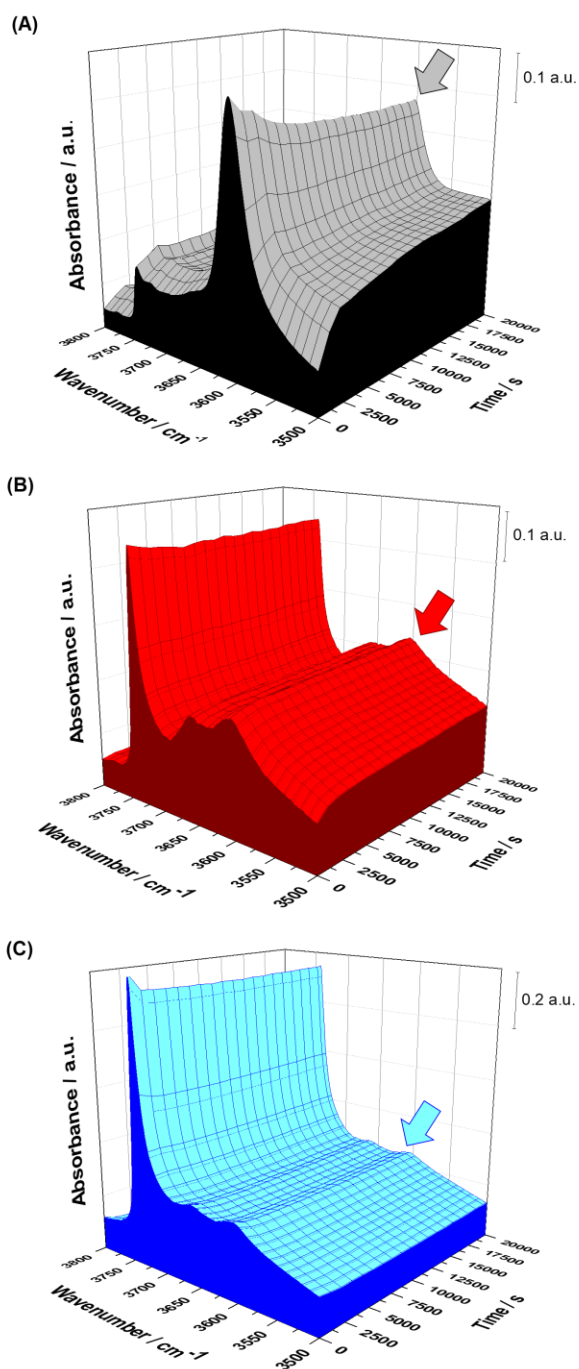


Figure S7. Absorbance change of IR spectra in OH region (3800-3500 cm⁻¹) of parent single-component ZSM-5 catalyst (ZSM-5-P) (A), hierarchical single-component ZSM-5 catalyst (ZSM-5-A) (B) and multi-component zeolite-based catalyst (ZSM-5-AR) (C) as a function of time during iso-octane adsorption. The absorption bands shown by the arrows are Si-O(H)-Al group.

Calculation of catalyst effectiveness factor

By definition, the effectiveness factor of the catalyst in conditions of mass transfer limitations is the ratio of observed reaction rate (r_o) and diffusion-free reaction rate (r_s):

$$\eta = \frac{r_o}{r_s} \quad (S1)$$

Assuming the absence of diffusion limitations, the rate-determining step of alkane cracking over zeolites is the alkane protonation leading to lower alkenes and alkanes^{5,6}.

Accordingly, the diffusion free, first-order cracking rate of isooctane is given by:

$$r_s = k N_H^+ K_{ads}^\circ \frac{P}{P^\circ} \quad (S2)$$

where k is the intrinsic cracking rate constant (s^{-1}), N_H^+ is the number of BAS per unit mass of catalyst (mol g^{-1}), K_{ads}° the alkane equilibrium adsorption constant, P the isooctane pressure (bar) and P° the pressure of the standard state (1 bar). As the diffusion free reaction rate is not known the effectiveness factor can only be assessed through the use of the Thiele modulus (ϕ) and its relationship with the catalyst effectiveness for a first-order reaction:

$$\eta = \frac{\tanh \phi}{\phi} \quad (S3)$$

For an irreversible first-order reaction, it is given by:

$$\phi = \left(\frac{L^2 k_v}{D_{eff}} \right)^{\frac{1}{2}} \quad (S4)$$

where L is the diffusion length, D_{eff} is the effective diffusion coefficient related to rate of diffusion toward the active sites, and k_v is the intrinsic kinetic constant per unit volume of catalyst ($\text{mol m}^{-3} \text{ catalyst s}^{-1}$), which can be expressed as:

$$k_v = k N_H^+ \rho \quad (\text{S5})$$

where ρ is density of the studied sample. The only type of BAS that was observed for the parent ZSM-5 and two hierarchical samples were bridged hydroxyl group Si-O(H)-Al typical of MFI framework, they can be considered as identical and homogenous for all samples and the intrinsic rate constant k is assumed to be identical too. With this assumption it can be eliminated by considering the ratio of Thiele moduli of hierarchical and parent samples. The use of the above equations yields:

$$\frac{\phi_A}{\phi_P} = \left(\frac{N_{H,A}^+}{N_{H,P}^+} \times \frac{\rho_A}{\rho_P} \times \frac{D_{\text{eff},P}/L_P^2}{D_{\text{eff},A}/L_A^2} \right)^{1/2} \quad (\text{S6})$$

where the subscripts P and A refer to the parent ZSM-5-P and hierarchical ZSM-5-A samples, respectively. A similar equation for ϕ_{AR}/ϕ_P ratio is also obtained. The first factor of the right hand side of this equation is readily obtained from the number of Brønsted acid sites measured by pyridine adsorption at 423 K (Table S2), the second one can be estimated from the pore volume derived from nitrogen adsorption-desorption isotherms (whereby the density ratio of the material is the reciprocal of density ratio of total pore volumes), and the third factor is related to the diffusion rate towards the active sites. The latter can be assessed from the effective diffusion time constants determined above based on IR spectroscopy:

$$\frac{D_{eff,P}/L_P^2}{D_{eff,A}/L_A^2} \approx \frac{\tau_{OH,P}^{-1}}{\tau_{OH,A}^{-1}} \quad (S7)$$

It is worth mentioning here that as the reaction and diffusion rate parameters used in the Thiele modulus are implicitly considered at the same temperature, we assume that the effective diffusion time constants (or effective diffusivities) have similar temperature dependence for the parent and hierarchical samples. Using these assumptions, the Thiele moduli ratios ϕ_A/ϕ_P and ϕ_{AR}/ϕ_P are 0.0516 and 0.0826, respectively.

The ratio of effectiveness factors can then be expressed as a function $f(\phi_P)$ of the Thiele modulus of the parent sample. Hence:

$$\frac{\eta_A}{\eta_P} = \frac{\tanh(0.0516 \phi_P)}{0.0516 \tanh \phi_P} = f_A(\phi_P) \quad (S8a)$$

$$\frac{\eta_{AR}}{\eta_P} = \frac{\tanh(0.0826 \phi_P)}{0.0826 \tanh \phi_P} = f_{AR}(\phi_P) \quad (S8b)$$

These functions are plotted in Figure S8. On the other hand, the actual effectiveness ratios can be readily obtained from the initial reaction rates and the number of BAS:

$$\frac{\eta_A}{\eta_P} = \frac{r_{o,A}}{r_{o,P}} \times \frac{N_{H,P}^+}{N_{H,A}^+} = 11.7 \quad (S9a)$$

$$\frac{\eta_{AR}}{\eta_P} = \frac{r_{o,AR}}{r_{o,P}} \times \frac{N_{H,P}^+}{N_{H,AR}^+} = 7.8 \quad (S9b)$$

These values can be used to estimate the Thiele modulus of the parent sample ϕ_P by numerical inversion of equations (S8a) and (S8b) which yield consistent and close estimates of $\phi_P = 9.3$ and 13.5, respectively. Such values are consistent with the fact

that the cracking on ZSM-5-P is strongly limited by internal diffusion ($\phi > 4.0$). Finally, the Thiele moduli ratios (Eqn S6) can be used to assess the Thiele moduli of the hierarchical samples, yielding for samples ZSM-5-A ZSM-5-AR of $\phi_A \approx 0.5 - 0.8$ and $\phi_{AR} \approx 0.7 - 1.1$.

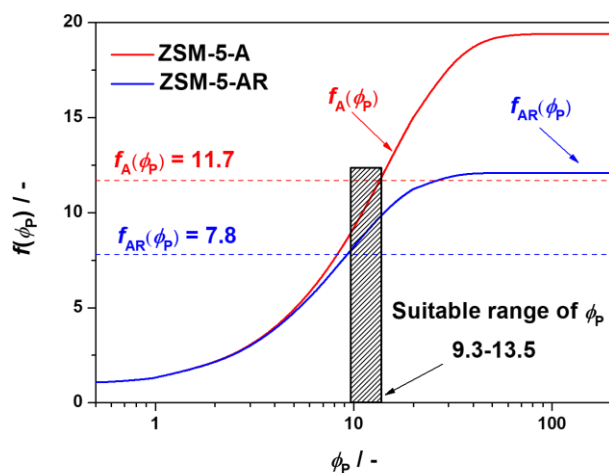


Figure S8. Assessment of the Thiele modulus of the parent single-component ZSM-5 catalyst (ZSM-5-P) from the relative efficiencies of hierarchical catalysts.

References

1. Groen, J. C., Peffer, L. A. A. & Pérez-Ramírez, J. Pore size determination in modified micro- and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis. *Microporous Mesoporous Mater.* **60**, 1-17 (2003).
2. Emeis, C. A. Determination of integrated molar extinction coefficients for infrared absorption bands of pyridine adsorbed on solid acid catalysts. *J. Catal.* **141**, 347-354 (1993).
3. Holm, M. S., Svelle, S., Joensen, F., Beato, P., Christensen, C. H., Bordiga, S., & Bjørgen, M. Assessing the acid properties of desilicated ZSM-5 by FTIR using CO and 2,4,6-trimethylpyridine (collidine) as molecular probes. *Appl. Catal. A Gen.* **356**, 23-30 (2009).
4. Zecchina, A., Bordiga, S., Spoto, G., Scarano, D., Petrini, G., Leofanti, G., Padovan, M., & Areà, C. O. Low-temperature Fourier-transform infrared investigation of the interaction of CO with nanosized ZSM5 and silicalite. *J. Chem. Soc. Faraday Trans.* **88**, 2959-2969 (1992).
5. Li, H., Kadam, S. A., Vimont, A., Wormsbecher, R. F. & Travert, A. Monomolecular Cracking Rates of Light Alkanes over Zeolites Determined by IR Operando Spectroscopy. *ACS Catal.* **6**, 4536-4548 (2016).
6. Kadam, S. A., Li, H., Wormsbecher, R. F. & Travert, A. Impact of Zeolite Structure on Entropic-Enthalpic Contributions to Alkane Monomolecular Cracking: An IR Operando Study. *Chem. - A Eur. J.* **24**, 5489-5492 (2018).