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Supplementary information

Fine-tuning the chemical state and acidity of ceria incorporated in hierarchical zeolites for ethanol dehydration

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Materials

All chemicals were of analytical grade and used as received without further purification. Aluminium isopropoxide (Sigma-Aldrich, ≥98.0%), tetraethyl orthosilicate (TEOS, Sigma-Aldrich, ≥99.0%), sodium hydroxide (NaOH, Carlo Erba, ≥98.0%) were used as aluminium source, silica source, and mineralizing agent, respectively. Tetrapropylammonium hydroxide (TPAOH, 1.0 M in H_2O) and tetrabutylphosphonium hydroxide (TBPOH, Sigma-Aldrich, 40% in H_2O) were used as structure-directing agents (SDAs) for conventional zeolites and hierarchical zeolites, respectively. Cerium (III) acetate (TCI, >98.0%) was used as a precursor for cerium oxide. To study the catalytic activity, ethyl alcohol (Sigma-Aldrich, ≥99.0%) was used as a reactant.

Catalyst preparation

Synthesis of conventional ZSM-5 zeolite (ZSM5-CON)[1]

The conventional ZSM-5 zeolite was synthesized with the molar composition of $10SiO_2$: $0.05Al_2O_3$: 1TPAOH: 1.03NaOH: $400H_2O$. After mixing TEOS (7 g) and TPAOH (3.42 g) as a silica-SDA solution, the sodium hydroxide (0.14 g) mixed with DI-water was slowly added into the silica-SDA solution, and it was then stirred at room temperature for 2 hours. After the aging process, the obtained gel was transferred to the lined hydrothermal synthesis reactor and heated to 180 °C for 3 days. After that, the prepared sample was washed with DI-water, filtered and dried at 110 °C. Finally, the ZSM5-CON was calcined at 650 °C for 6 hours to remove SDA.

Synthesis of hierarchical Silicalite-1 (Silicalite1-HIE) and ZSM-5 zeolites (ZSM5-HIE)[1]

The hierarchical Silicalite-1 and ZSM-5 with different Si/Al ratios were synthesized with the molar composition of $60SiO_2$: xAl_2O_3: 18TBPOH: 0.75NaOH: $600H_2O$, where x was 0 and 0.3, denoted as Silicalite1-HIE and ZSM5-HIE, respectively. Firstly, TEOS, and aluminium isopropoxide were mixed together to prepare as a silica-alumina solution. The second solution containing TBPOH (8.62 g), sodium hydroxide (0.02 g) and DI-water was slowly added into a silica-alumina solution, then stirred at room temperature for 12 hours. After the aging process, the obtained gel was transferred to the lined hydrothermal synthesis reactor and heated to 130 °C for 2 days. After that, the prepared sample was washed with DI-water, filtered and dried at 110 °C. Finally, the Silicalite1-HIE and ZSM5-HIE zeolite were calcined at 650 °C for 6 hours to remove SDA.

Preparation of ceria supported on zeolites using ion-exchange method (Exc)

The prepared zeolites were mixed with the desired amount of cerium (III) acetate and DI-water at 80 °C for 2 hours, and then filtered and washed with DI water, finally dried at 100 °C overnight. The prepared catalysts were calcined at 550 °C for 4 hours denoted as yCe(Exc)-ZSM5-HIE, and yCe(Exc)-ZSM5-CON for the hierarchical ZSM-5 and the conventional ZSM-5, respectively (y = 0, 1, 5, 10 and 20 wt% of CeO_2).

Preparation of ceria supported on zeolites using impregnation method (Imp)

The synthesized zeolites were mixed with the desired amount of cerium (III) acetate and DI-water at room temperature for 24 hours using an impregnation method. Subsequently, the solvent was evaporated by rotary evaporator, and the obtained materials were finally dried at 100 °C overnight. The prepared catalysts were calcined at 550 °C for 4 hours, denoted as yCe(Imp)-Silicalite1-HIE, yCe(Imp)-ZSM5-HIE for the hierarchical silicalite-1, and the hierarchical ZSM-5, respectively (y = 5 wt% of CeO_2).

It should be noted that all samples are denoted as *y*Ce(*M*)-zeolite supports, where y is the CeO_2 content. *M* refers to the preparation method (Exc = ion-exchange method; Imp = impregnation method).

Characterization

The powder X-ray diffraction (XRD) patterns of the prepared catalysts were investigated using Bruker D8 ADVANCE instrument with CuKα radiation (40 kV, 40 mA) in the 2θ range of 5 ° to 60 ° with the step size of 0.02° and the scan rate of 1° min^{-1}.

To study the morphology of the catalysts, scanning electron microscopy (SEM) images and transmission electron microscopy (TEM) images were obtained from JEOL JSM-7610F microscope, and JEOL JEM-ARM200F microscope at 200 kV, respectively.

The textural properties of all the prepared catalysts were determined by a N_2 adsorption-desorption measurement at −196 °C operated on a MicrotracBEL, BELSORP-max model, and all the prepared samples were degassed at 350 °C for 24 hours before the measurement. The specific surface area (SBET), micropore surface area and pore volume were calculated by the Brunauer–Emmett–Teller (BET) method, and *t*-plot method, respectively.

The elemental analysis was studied by using wavelength-dispersive X-ray fluorescence spectrometer (WDXRF) performed on Bruker S8 TIGER ECO instrument and scanning electron microscope and energy dispersive X-ray spectrometer (SEM-EDS) obtained from JEOL JSM-7610F microscope.

The surface properties were investigated including acidity performed by NH_3 temperature programmed desorption (NH_3-TPD), basicity performed by CO_2 temperature programmed desorption (CO_2-TPD), and reducibility performed by H_2 temperature programmed reduction

(H_2-TPR). The measurements were conducted using a BELCAT II instrument equipped with thermal conductivity detectors (TCD). Prior to the NH_3-TPD and CO_2-TPD measurements, the samples (0.05 g) were pre-treated typically at 300 °C for 1 hour under the flow of He to completely remove molecules adsorbed on the samples, and then cooled down to 100 °C, together with saturated in the gas mixture of NH_3 gas (5 vol% in He) or CO_2 gas for 30 min (50 mL min^{-1}), and flushed with He flow (50 mL min^{-1}) for 30 min at 100 °C. The desorption steps of both techniques were recorded from 100 to 800 °C with the heating rate of 10 °C.min^{-1}. In case of H_2-TPR, the samples were pre-treated typically at 300 °C for 1 hour with the heating rate of 10 °C min^{-1} under the flow of Ar and then cooled down to 50 °C. After that, the measurement was performed from 50 °C to 900 °C with the heating rate of 5°C min^{-1} in a flow of 2 v/v% of H_2 in Ar (50 mL min^{-1}).

The oxidation state of Ce was carefully characterized by using X-ray absorption near-edge structure (XANES) and all samples were pre-treated typically at 350 °C for 2 hours under the flow of N_2 to remove molecules adsorbed on the samples. The Ce L3-edge XANES spectra were obtained in transmission mode at the BL5.2 station at Siam Photon Laboratory (Synchrotron Light Research Institute (Public Organization), SLRI), Thailand.

Catalytic activity test

The catalytic performance in ethanol dehydration was obtained using a fixed-bed reactor. Firstly, the prepared catalysts (0.1 g) were pretreated at 350 °C under the flow of N_2 (5 mL.min^{-1}) for 2 hours. Then, the reaction was performed under N_2 flow at 350 °C with the $WHSV_{EtOH}$ of 5 h^{-1}. The quantification of products was analyzed by a gas chromatograph (GC, Agilent 7890B) equipped with a flame ionization detector (FID) and PoraBOND Q capillary column (25 m x 0.32 mm) at a certain time interval of 1 hour. Subsequently, the conversion of ethanol (X_{EtOH}) and the product selectivity (S_i) were estimated by following equation:

$$X_{EtOH} = \left(\frac{(n_{EtOH})_0 - (n_{EtOH})_t}{(n_{EtOH})_t} \right) \times 100\%$$

$$S_i = \left(\frac{n_i}{(\sum n)_t} \right)$$

Where $(n_{EtOH})_0$, $(n_{EtOH})_t$, n_i, Σn are the initial number of moles of ethanol, the number of moles of ethanol at a certain time, the number of moles of the desired product i, and the total number of moles of all the products, respectively.

Reference

[1] Wannapakdee, W., Yutthalekha, T., Dugkhuntod, P., Rodponthukwaji, K., Thivasasith, A., Nokbin, S., ... & Wattanakit, C. (2019). Dehydrogenation of propane to propylene using promoter-free hierarchical Pt/Silicalite-1 nanosheets. Catalysts, 9(2), 174.

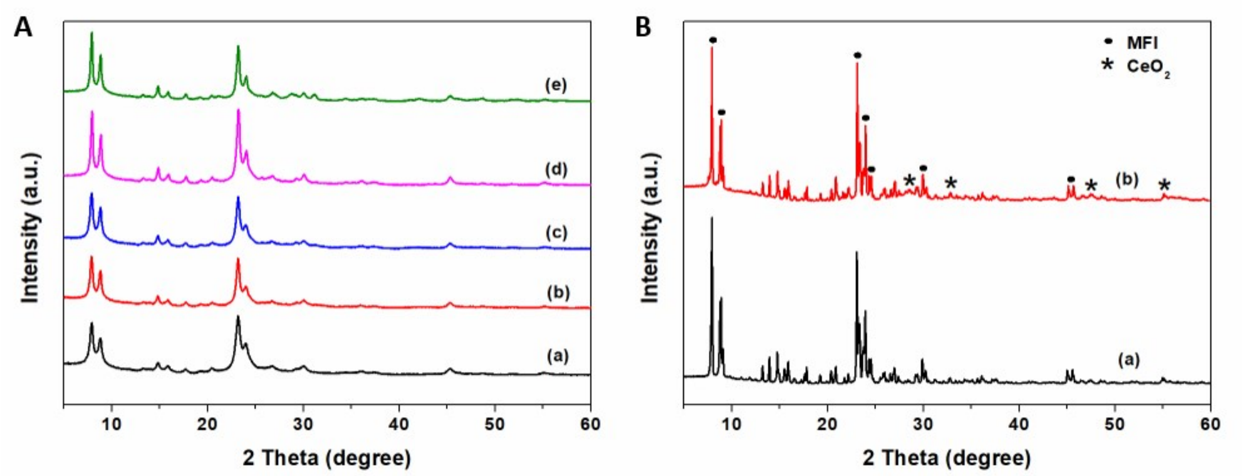

Fig. S1 XRD patterns of (A) hierarchical zeolite supports: (a) ZSM5-HIE, (b) 5Ce(Imp)-ZSM5-HIE, (c) 5Ce(Exc)-ZSM5-HIE, (d) Silicalite1-HIE, and (e) 5Ce(Imp)-Silicalite1-HIE, and (B) conventional zeolite supports: (a) ZSM5-CON and (b) 5Ce(Exc)-ZSM5-CON.

Table S1 Relative crystallinity of all the prepared catalysts.

Tag	Catalyst	Relative crystallinity (%)*
A-(a)	ZSM5-HIE	100.0
A-(b)	5Ce(Imp)-ZSM5-HIE	91.2
A-(c)	5Ce(Exc)-ZSM5-HIE	95.4
A-(d)	Silicalite1-HIE	100.0
A-(e)	5Ce(Imp)-Silicalite1-HIE	95.2
B-(a)	ZSM5-CON	100.0
B-(b)	5Ce(Exc)-ZSM5-CON	87.2

* The relative crystallinity of all the prepared catalysts before and after CeO_2 modification calculated by using the integrated data of the three most intense peaks at Theta (2θ) of 7.8º, 8.9º and 23.2º. The sample before CeO_2 modification was used as the reference to calculate the relative crystallinity of the CeO_2samples.

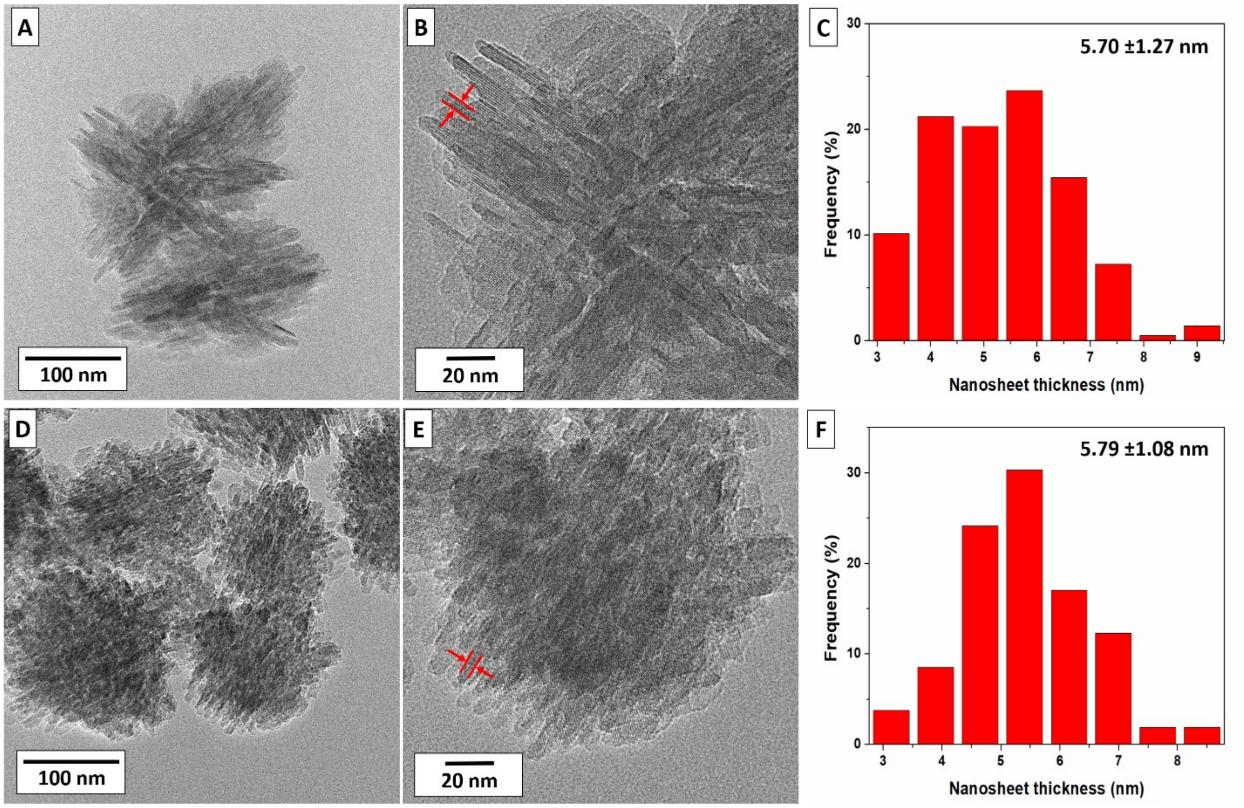

Fig. S2 TEM images and nanosheet thickness distribution of (A-C) Silicalite1-HIE and (D-F) ZSM5- HIE.

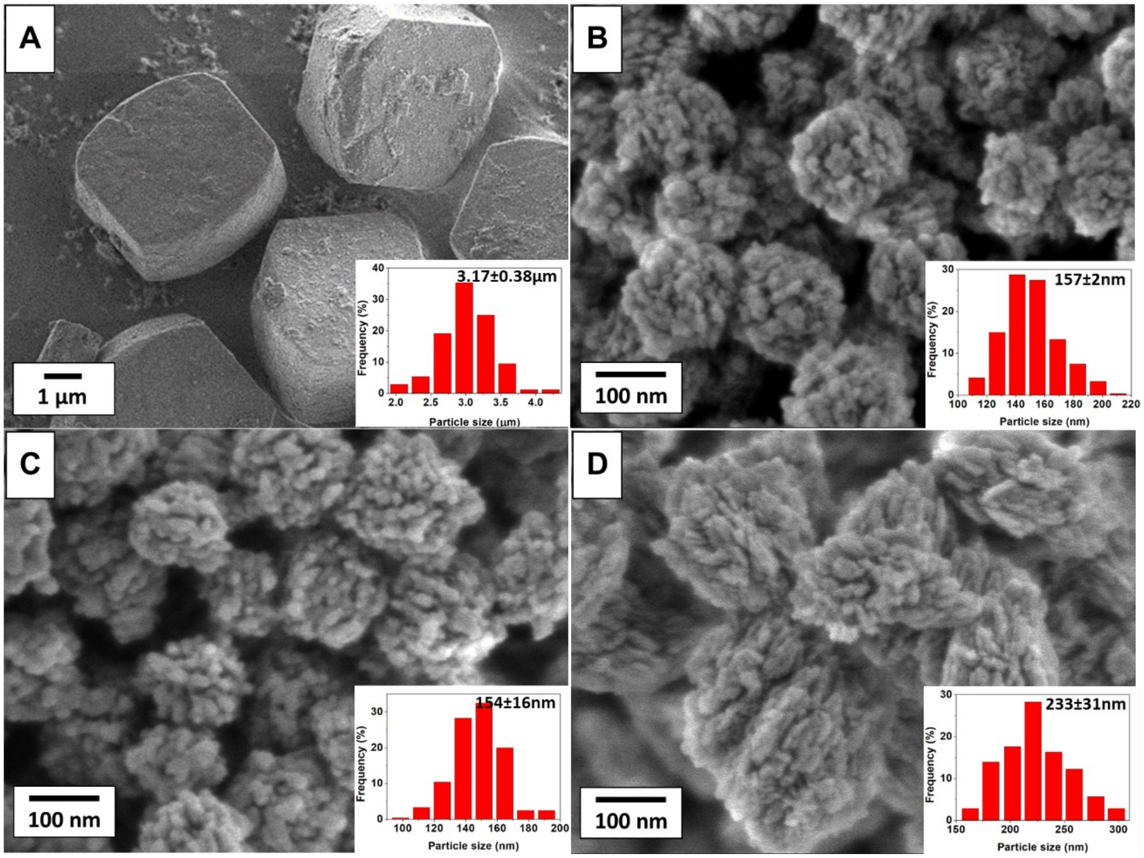

Fig. S3 SEM images and zeolite particle size distribution of (A) 5Ce(Exc)-ZSM5-CON, (B) 5Ce(Exc)-ZSM5-HIE, (C) 5Ce(Imp)-ZSM5-HIE and (D) 5Ce(Imp)-Silicalite1-HIE.

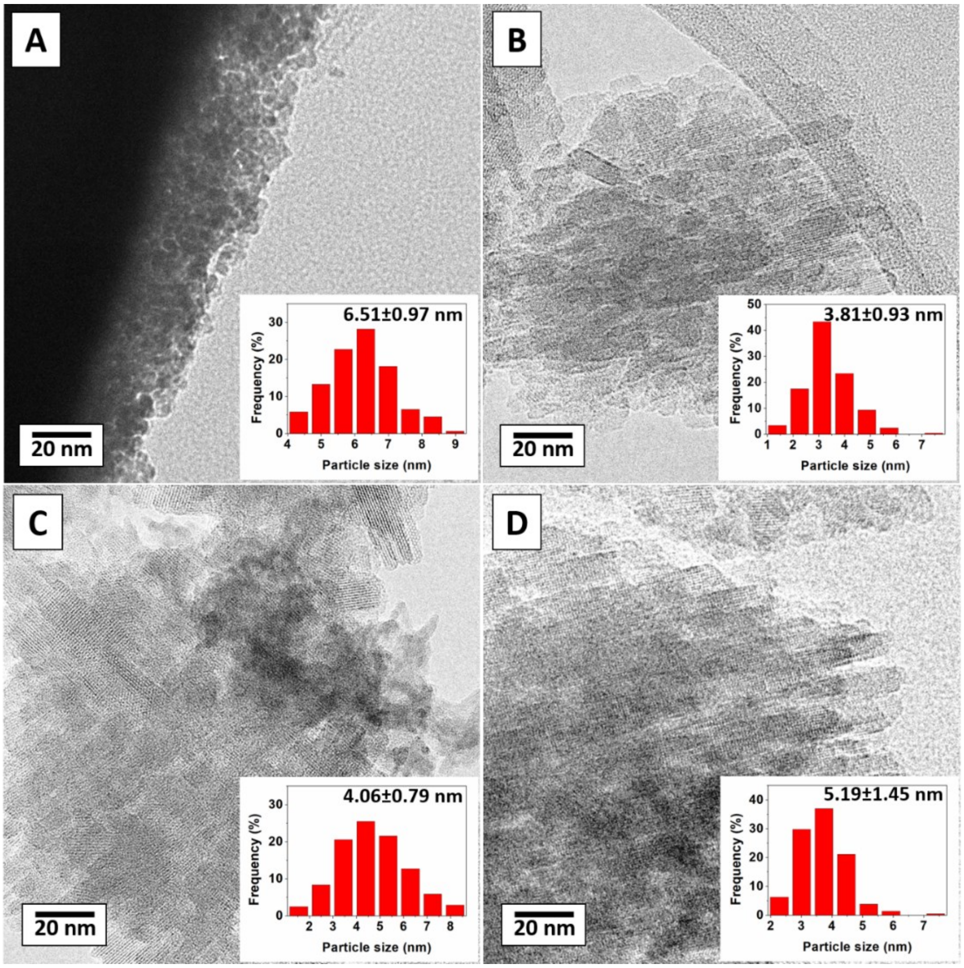

Fig. S4 TEM images and CeO_x particle size distribution of (A) 5Ce(Exc)-ZSM5-CON, (B) 5Ce(Exc)-ZSM5-HIE. (C) 5Ce(Imp)-ZSM5-HIE, and (D) 5Ce(Imp)-Silicalite1-HIE.

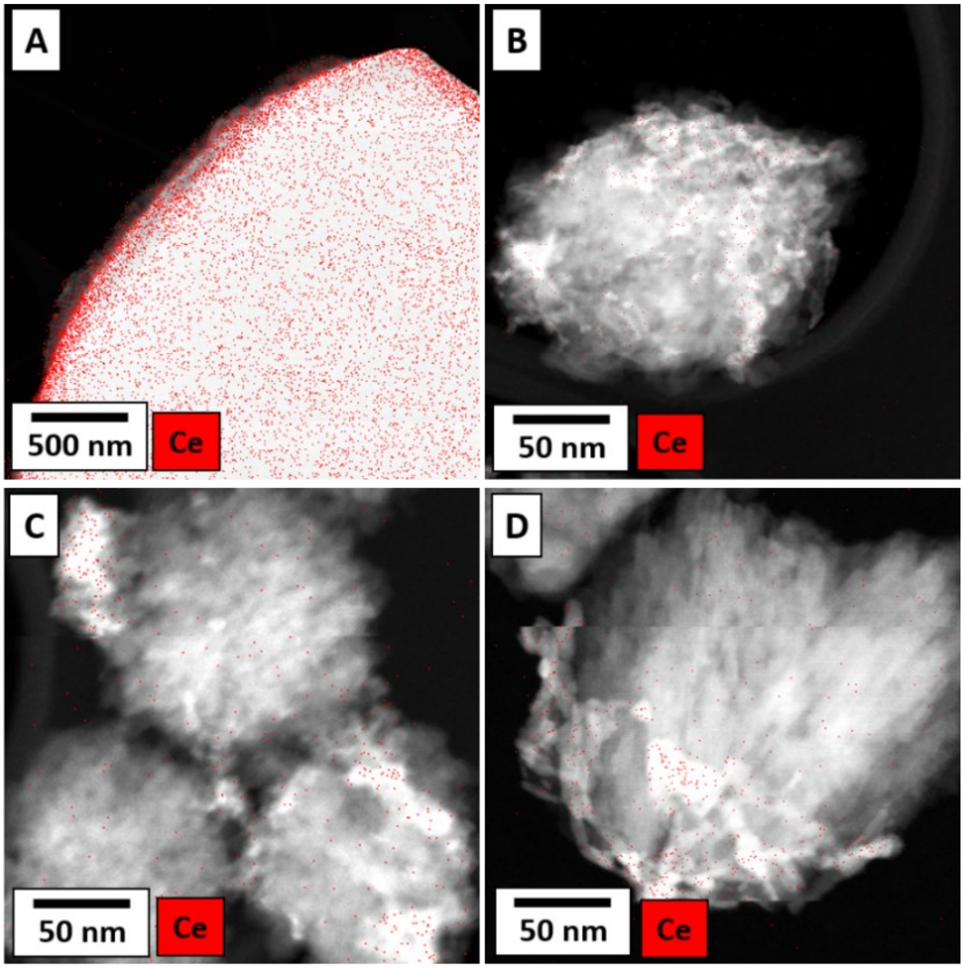

Fig. S5 STEM-EDS images of (A) 5Ce(Exc)-ZSM5-CON, (B) 5Ce(Exc)-ZSM5-HIE, (C) 5Ce(Imp)-ZSM5-HIE and (D) 5Ce(Imp)-Silicalite1-HIE.

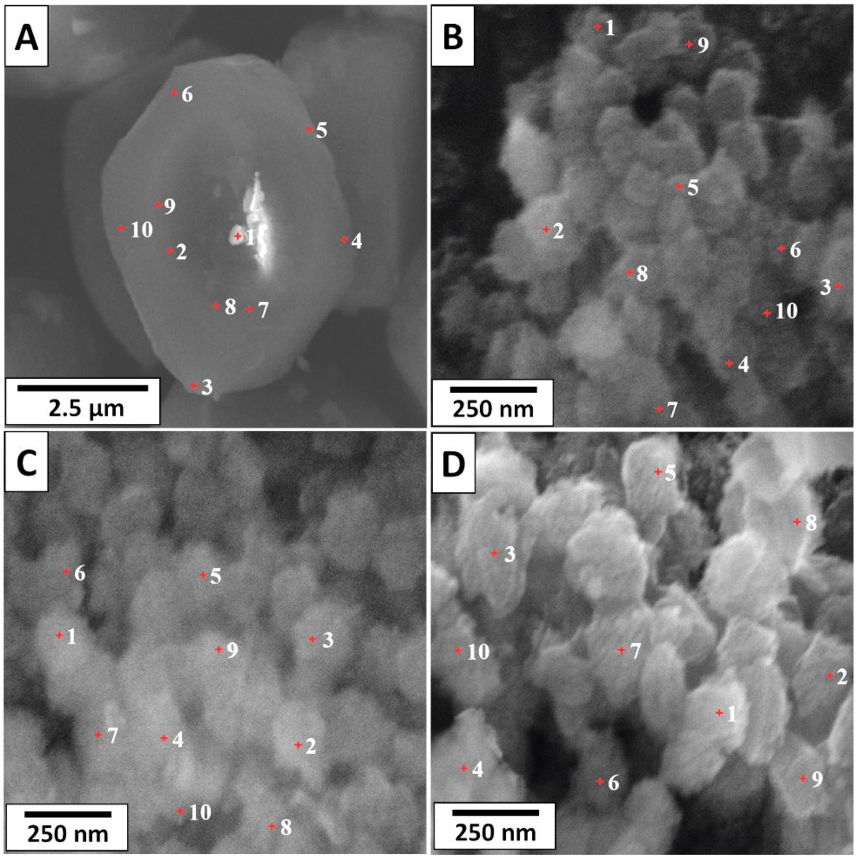

Fig. S6 SEM-EDS elemental points analysis of (A) 5Ce(Exc)-ZSM5-CON, (B) 5Ce(Exc)-ZSM5-HIE, (C) 5Ce(Imp)-ZSM5-HIE and (D) 5Ce(Imp)-Silicalite1-HIE.

Table S2 Elemental points analysis

Point	**Ce/Si ratio**			
	5Ce(Exc)-ZSM5-HIE	**5Ce(Exc)-ZSM5-CON**	**5Ce(Imp)-Silicalite1-HIE**	**5Ce(Imp)-ZSM5-HIE**
1	1.24	7.18	8.59	6.57
2	1.39	10.39	8.65	8.56
3	1.05	22.70	8.16	5.99
4	1.67	7.45	8.46	7.74
5	1.11	13.58	4.77	5.90
6	0.78	16.02	7.93	5.76
7	0.89	14.69	9.76	6.48
8	1.80	10.87	9.02	8.91
9	0.78	15.20	7.12	8.86
10	1.45	24.56	9.05	7.83
Average	1.22 ±0.36	14.26 ±5.82	8.15 ±1.39	7.26 ±1.26

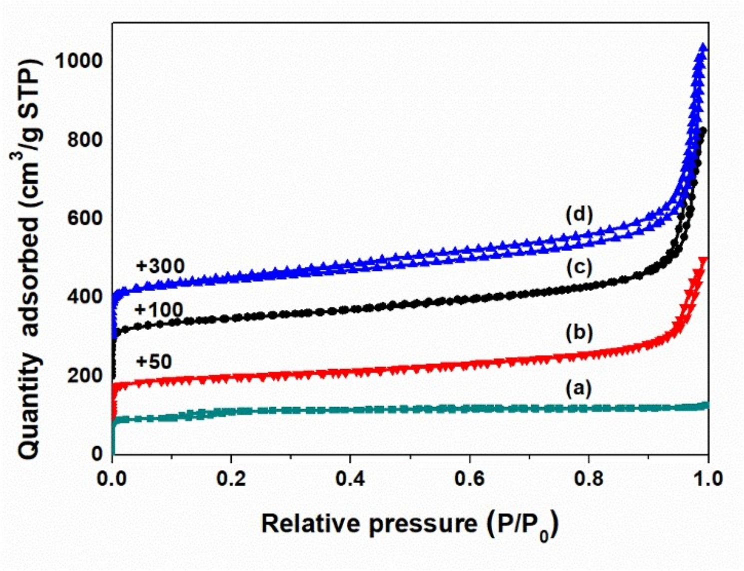

Fig. S7 N_2 adsorption/desorption isotherms of (a) 5Ce(Exc)-ZSM5-CON, (b) 5Ce(Imp)-ZSM5-HIE, (c) 5Ce(Exc)-ZSM5-HIE, and (d) 5Ce(Imp)-Silicalite1-HIE.

Table S3 Textural properties of all the prepared catalysts

Catalysts	**Si/Al**[a]	**S_{BET}**[b] **(m^2g^{-1})**	**S_{ext}**[c] **(m^2g^{-1})**	**S_{micro}**[d] **(m^2g^{-1})**	**V_{total}**[e] **(cm^3g^{-1})**	**V_{micro}**[f] **(cm^3g^{-1})**	**V_{ext}**[g] **(cm^3g^{-1})**
5Ce(Exc)-ZSM5-HIE	60.7	464	206	258	0.956	0.147	0.809
5Ce(Exc)-ZSM5-CON	97.6	383	5	378	0.191	0.177	0.014
5Ce(Imp)-ZSM5-HIE	58.4	356	139	217	0.604	0.104	0.500
5Ce(Imp)-Silicalite1-HIE	∞	475	196	279	0.877	0.112	0.765

[a] Si/Al determined by wavelength dispersive x-ray fluorescence.

[b] S_{BET}: Specific surface area (m^2g^{-1}) determined by BET method.

[c] S_{ext}: External surface area (m^2g^{-1}).

[d] S_{micro}: micropore surface area (m^2g^{-1}), determined by t-plot method.

[e] V_{total}: total pore volume (cm^3g^{-1}) obtained at $P/P_0=0.99$.

[f] V_{micro}: micropore volume (cm^3g^{-1}), determined by t-plot method.

[g] V_{ext}: external pore volume (cm^3g^{-1}), $V_{ext}=V_{total}-V_{micro}$.

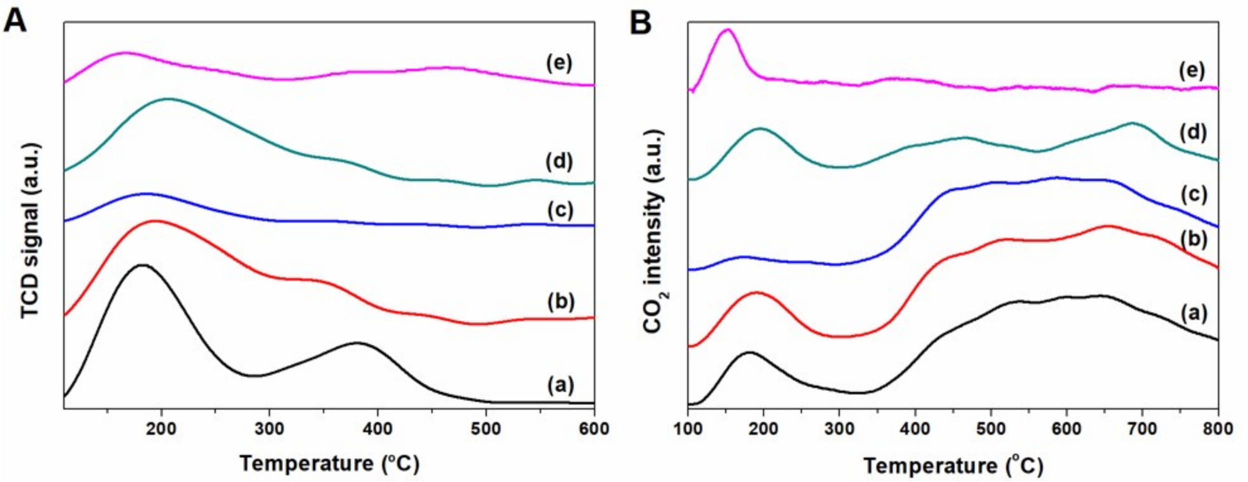

Fig. S8 Chemisorption profiles of (A) NH_3 TPD and (B) CO_2 TPD for (a) 5Ce(Exc)-ZSM5-HIE, (b) 5Ce(Imp)-ZSM5-HIE, (c) 5Ce(Imp)-Silicalite1-HIE, (d) 5Ce(Exc)-ZSM5-CON, and (e) commercial CeO_2 nanoparticles.

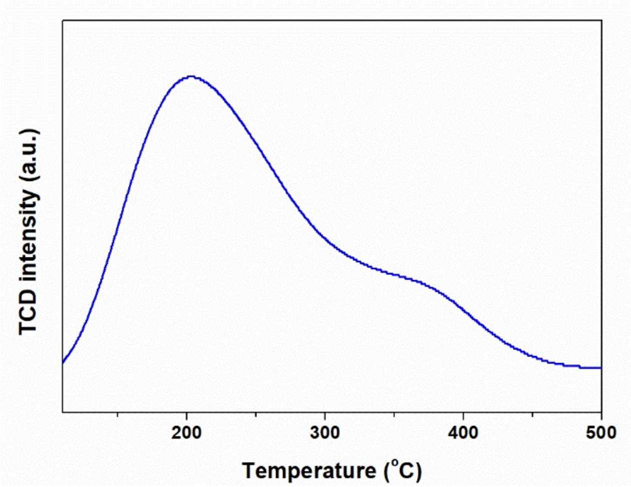

Fig. S9 Chemisorption profiles of NH_3 TPD for ZSM5-HIE.

Table S4 Acid density of all the prepared catalysts obtained from NH_3-TPD measurement.

Catalysts	Acidity amount (μmol g^{-1})		Total acid density (μmol g^{-1})
	Weak (180-200°C)	Strong (350-400°C)	
ZSM5-HIE	79	34	113
5Ce(Imp)-ZSM5-HIE	73	39	112
5Ce(Imp)-Silicalite1-HIE	24	4	28
5Ce(Exc)-ZSM5-HIE	95	57	152
5Ce(Exc)-ZSM5-CON	71	21	92
CeO_2	23	12	45

Table S5 Basic density of all the prepared catalysts obtained from CO_2-TPD measurement.

Catalysts	Basicity amount (µmol g^{-1})			Total basic density (µmol g^{-1})
	Weak (150-200°C)	Moderate (450-500°C)	Strong (600-700°C)	
5Ce(Imp)-ZSM5-HIE	37	101	247	385
5Ce(Imp)-Silicalite1-HIE	8	95	171	273
5Ce(Exc)-ZSM5-HIE	35	146	169	350
5Ce(Exc)-ZSM5-CON	33	60	77	170
CeO_2	21	19	2	42

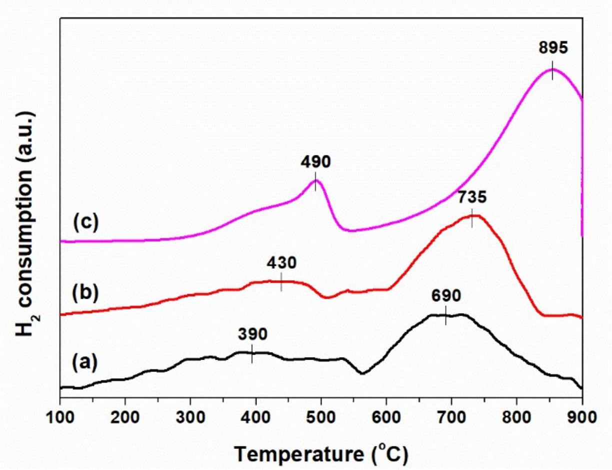

Fig. S10 Chemisorption profiles of H_2 TPR for (a) 5Ce(Exc)-ZSM5-HIE), (b) 5Ce(Imp)-ZSM5-HIE and (c) commercial CeO_2 nanoparticles.

Table S6 Reducibility of all the prepared catalysts obtained from H_2-TPR measurement.

Catalysts	H_2 consumption (mmol g^{-1})		Total H_2 consumption (mmol g^{-1})
	Surface oxygen	bulk	
5Ce(Imp)-ZSM5-HIE	0.002	0.003	0.005
5Ce(Exc)-ZSM5-HIE	0.002	0.003	0.005
CeO_2	0.002	0.007	0.009

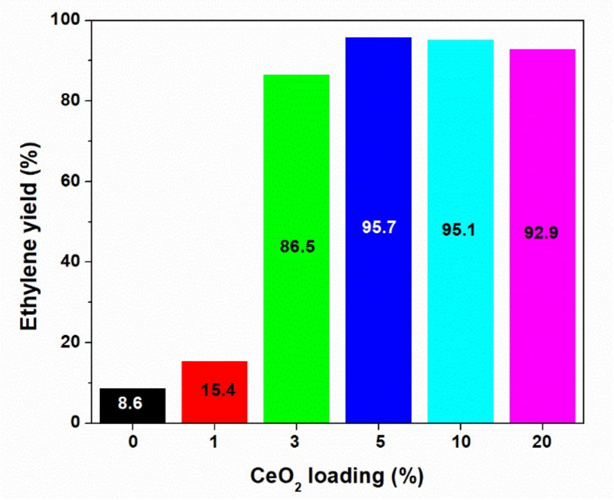

Fig. S11 Catalytic activity in term of ethylene yield over different CeO_2 loading on ZSM5-HIE prepared by ion-exchange method: Reaction condition at 350°C after 12h of reaction time.

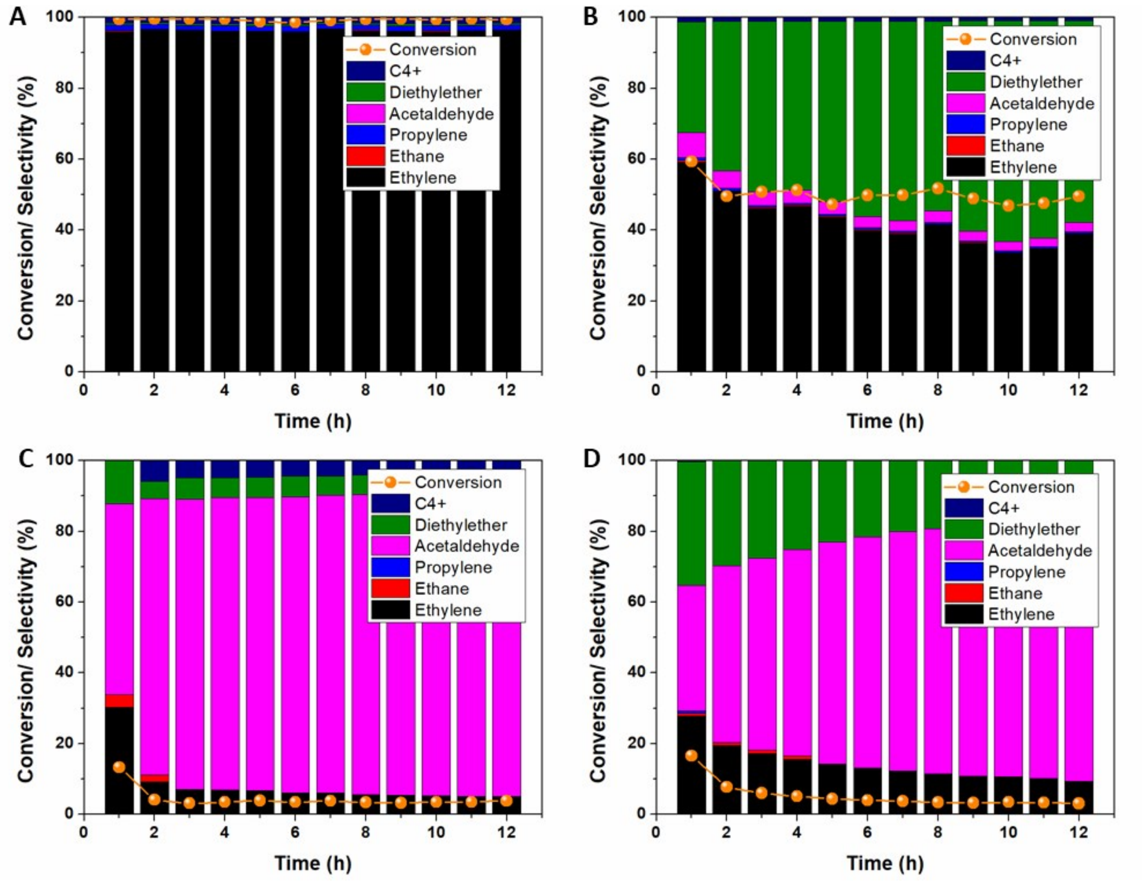

Fig. S12 Catalytic performance in term of ethanol conversion and product selectivity of (A) 5Ce(Exc)-ZSM5-HIE, (B) 5Ce(Imp)-ZSM5-HIE. (C) 5Ce(Imp)-Silicalite1-HIE and (D) 5Ce(Exc)-ZSM5-CON.

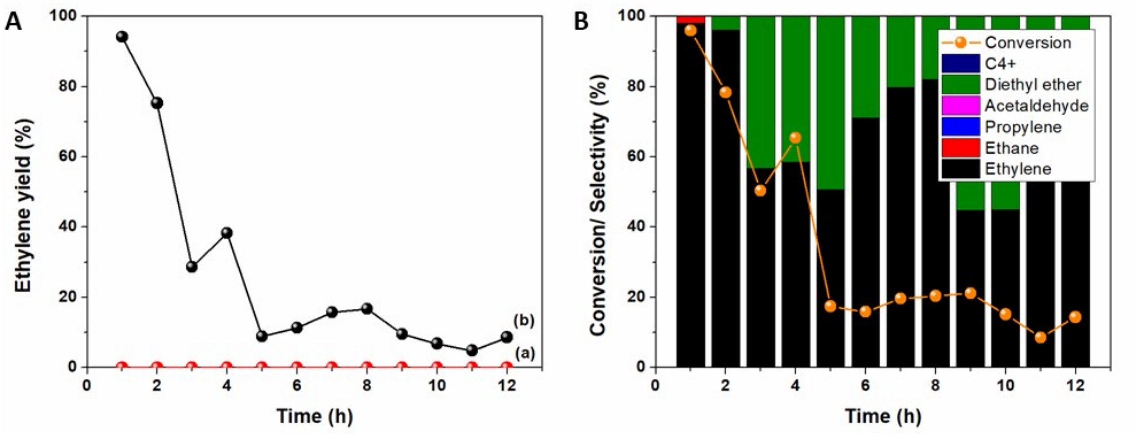

Fig. S13 Catalytic performance in term of ethanol conversion and product selectivity over hierarchical zeolites: (A) Catalytic activity of (a) Silicalite1-HIE and (b) ZSM5-HIE and (B) Product distribution over ZSM5-HIE.

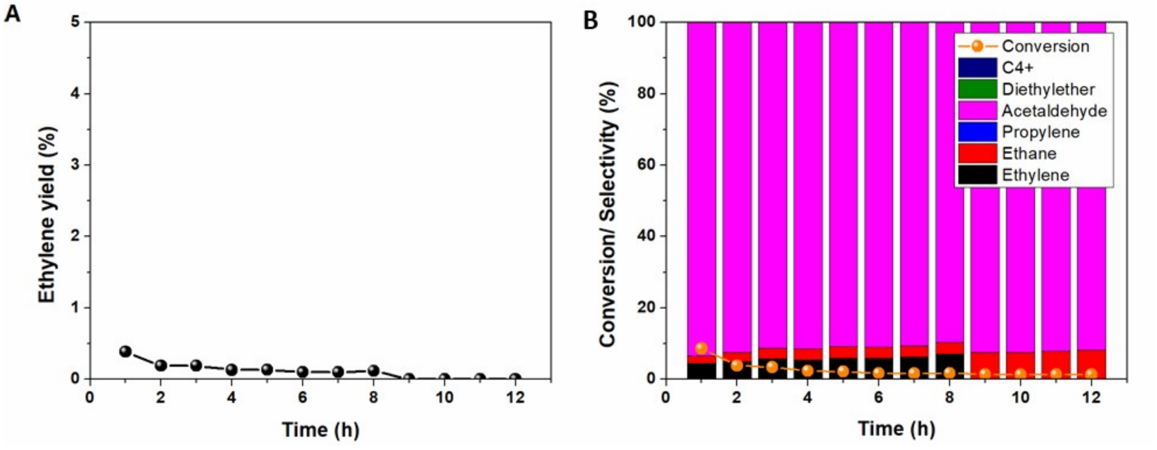

Fig. S14 Catalytic performance in term of ethanol conversion and product selectivity of commercial CeO_2 nanoparticles: (A) Catalytic activity, and (B) Product distribution.

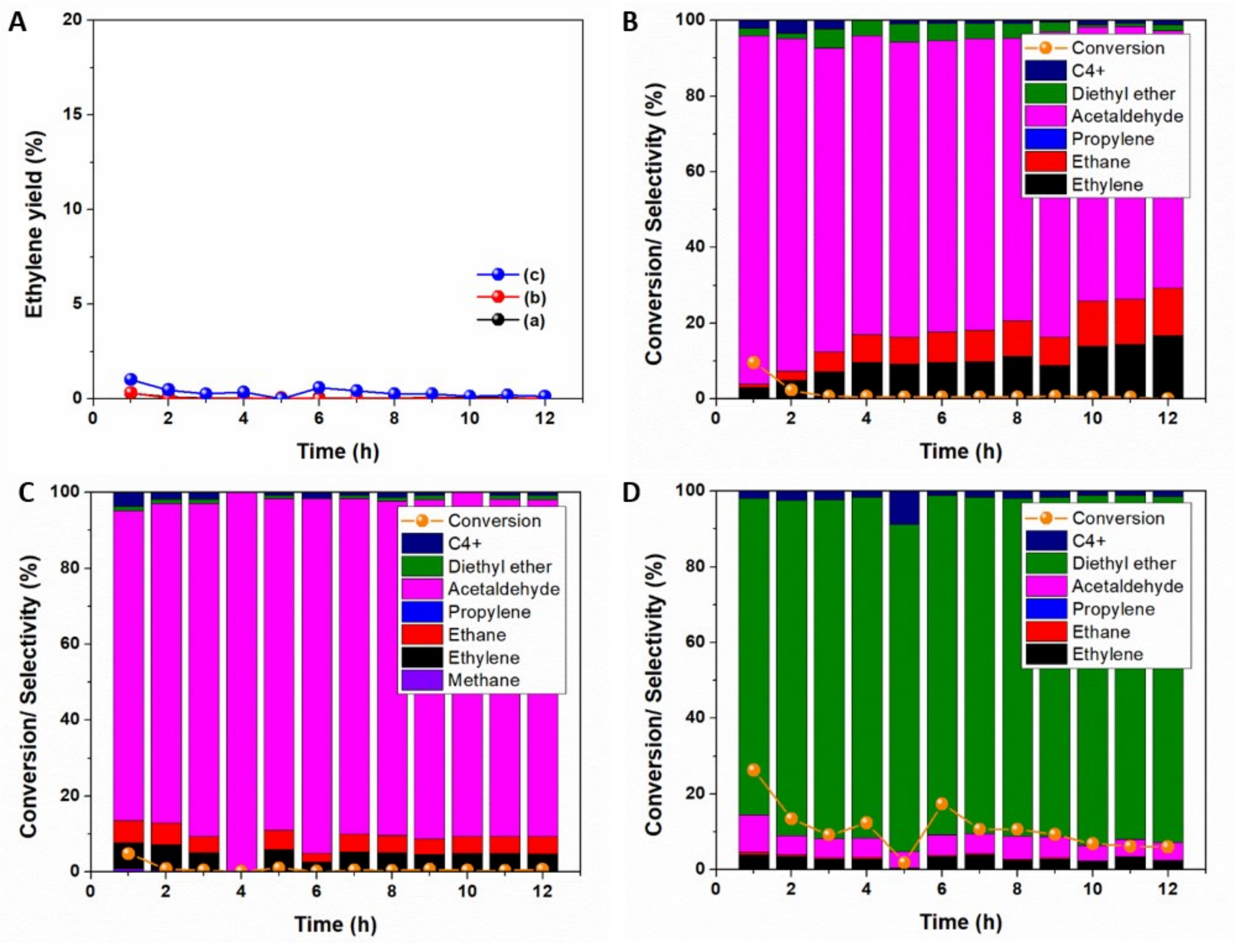

Fig. S15 Catalytic performance in term of ethanol conversion and product selectivity: (A) Catalytic activity of (a) 5Ce(Imp)-ZSM5-CON, (b) 5Ce(Imp)-SiO_2 and (c) 5Ce(Imp)-Al_2O_3 and product distribution of (B) 5Ce(Imp)-ZSM5-CON, (C) 5Ce(Imp)-SiO_2 and (D) 5Ce(Imp)- Al_2O_3.