Supplementary materials

Catalytic cracking of n-pentane over CLD modified HZSM-5 zeolites

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Table S1 Experiment parameters for the CLD strategy

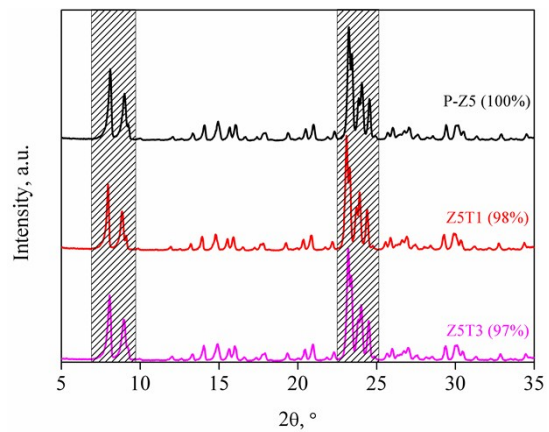| Precursors	Code	Catalyst (g): Ethanol (mL): Precursor (μL))
Tetraethyl orthosilicate, TEOS	S	1:25:150
Tetrabutyl orthotitanate, TBOT	T	1:25:175
Tetrabutyl orthosilicate, TBOS	B	1:25:240

Fig. S1 XRD patterns of the parent and TiO$_2$-CLD modified HZSM-5 zeolites.
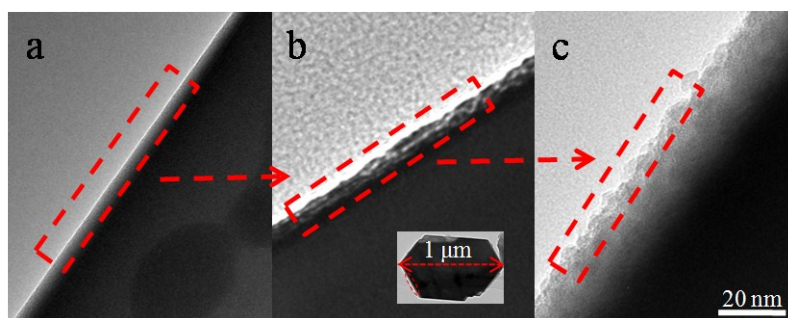
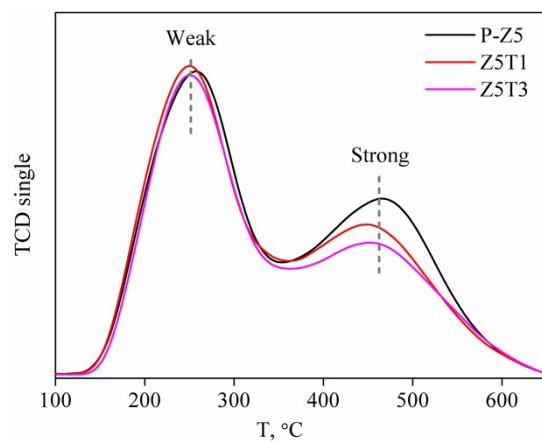Fig. S2 TEM images of (a) P-Z5, (b) Z5T1, and (c) Z5T3.

Fig. S3 NH$_3$-TPD profiles of the parent and TiO$_2$-CLD modified HZSM-5 zeolites.

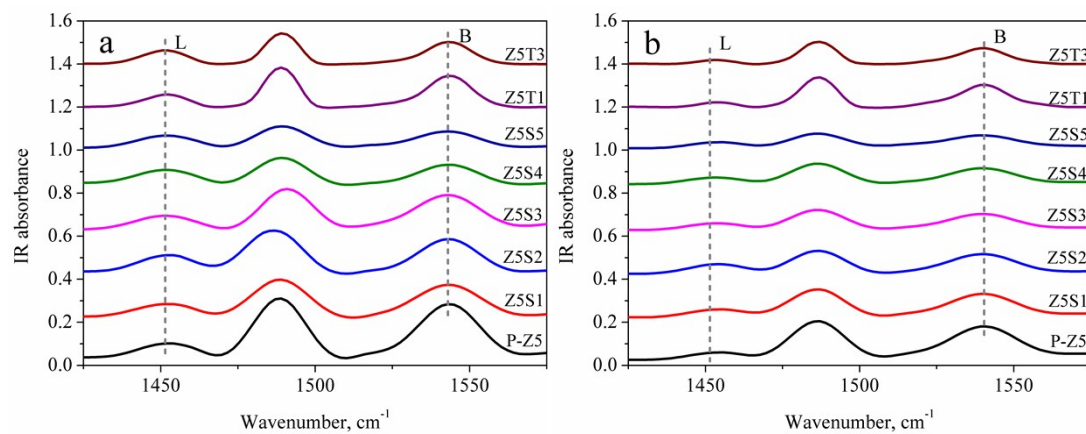Fig. S4 Py-IR spectra of the parent and CLD modified HZSM-5 zeolites: (a) 200 °C and (b) 350

°C.

S1 Blank experiments

Blank experiments were carried out in an empty reactor and a reactor loaded with diluents (SiC, 1 g) under the reaction conditions: n-pentane, 1.2 mL·h^{-1}; partial pressures, 2 kPa; temperature, 500-550 °C, respectively. The results indicated that n-pentane can hardly cracking under these conditions, and the conversion was zero.

S2 Mass balance

During n-pentane cracking, the products heavier than C5 may be generated on the traceable level, and it was not given in the Micro 490GC. Based on the element balance analysis at 500 °C (Fig. S5), it was figured out that both H/C (equation S1) and N/C (equation S2) atom ratio were approximately equal to the theoretical values 2.4 and 18.8, indicating that the heavy products was of insignificance in n-pentane cracking, and it was feasible to investigate n-pentane cracking on this experiment apparatus.

$$\frac{H}{C} = \frac{\sum m \cdot (i)}{\sum n \cdot (i)} \quad \text{(S1)}$$

$$\frac{N}{C} = \frac{2 \cdot (N_2)}{\sum n \cdot (i)} \quad \text{(S2)}$$

where (i) is the corresponding mole fraction of species i. (N_2) is the mole fraction of N_2 in product. Letter "m" and "n" refer to the number of hydrogen and carbon atom in species i, respectively.

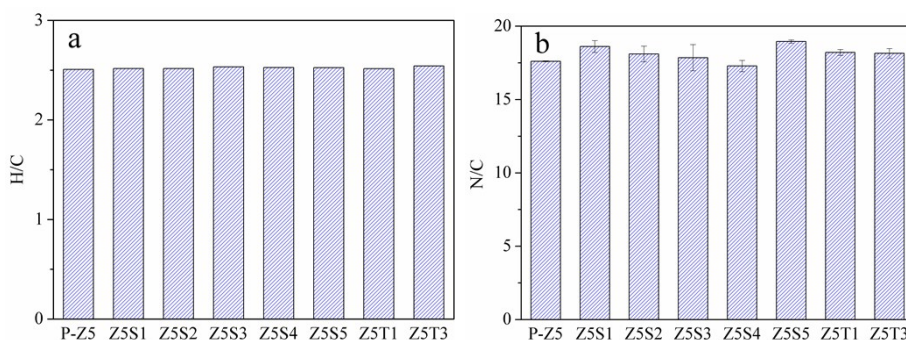

Fig. S5 Element balance analysis of the products for n-pentane cracking at 500 °C: (a) H/C atom ratio and (b) N/C atom ratio.

S3 Influence of precursor size

In order to explore the influence of precursor size, TBOS (tetrabutyl orthosilicate) was selected to replace TEOS in the CLD strategy, and the achieved catalyst was labeled as Z5B1. As shown in Table S2, the two catalysts with 1-cycle CLD modification, Z5S1 and Z5B1, exhibited the similar physical and chemical properties. As presented in Fig. S6, in the stability test, negligible difference was detected between the two catalysts, indicating that the size of CLD precursor can hardly influence the porous layer and the final catalytic performance in the scope of investigation.
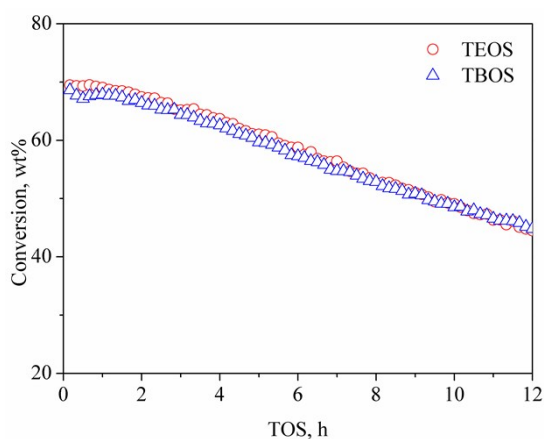

Fig. S6 Stability test for the Si$_2$O-CLD modified HZSM-5 catalysts with different precursor sizes

(T, 550 °C).

Table S2 Properties of Z5S1 and Z5B1

Catalyst	SiO$_2$-loading[a] (wt%)	S$_{BET}$[b] (m^2·g^{-1})	S$_{mic}$[c] (m^2·g^{-1})	S$_{ext}$[c] (m^2·g^{-1})	V$_t$[d] (cm^3·g^{-1})	V$_{mic}$[c] (cm^3·g^{-1})	V$_{mes}$ (cm^3·g^{-1})	Acid sites amount[e] (mmol·g^{-1})	S/W[e]	B$_T$/L$_T$[f]	B$_S$/L$_S$[g]
Z5S1	4	368.5	323.9	44.6	0.172	0.133	0.039	2.823	0.90	4.0	8.5
Z5B1	4	365.4	320.8	44.7	0.172	0.131	0.041	2.802	0.90	3.9	8.2

[a] The theoretical loading amount. [b] Estimated by BET method. [c] Estimated by t-plot method. [d] Calculated from N$_2$ uptake at P/P$_0$=0.99. [e] Determined by NH$_3$-TPD (S and W represent strong and weak acid sites). [f] Determined by Py-IR at 200 °C (B, L and T represent Brønsted, Lewis and total acid sites). [g] Determined by Py-IR at 350 °C.

S4 Verification of equation (8)

As shown in equation (8), the apparent reaction rate per B acid site (R_{app}) was positively linear with the reactant partial pressure (P_{par}), and the influences of acid strength and conversion level were not reflected. Thus, it is feasible to verify equation (8) though adjusting experiment conditions. The first experiment (No. 1) was designed by adjusting the P_{par} of reactant in the gas phase. And it was found that compared with the parent experiment (No. P), the half P_{par} led to a half R_{app} value. The other two experiments (No. 2 and 3) were designed by adjusting SiO_2/Al_2O_3 of HZSM-5 zeolite and WHSV value to tailor the acid strength and conversion level, respectively. It was found that the two factors resulted in a slight influence on the R_{app} value. Thus, it can be concluded that within the experimental uncertainties, equation (8) was feasible to describe the reaction kinetic of n-pentane cracking under the reaction condition in this paper.

Table S3 Experiment plans and results

No.	Catalyst	WHSV (h^{-1})	P_{par} (kPa)	X (%)	R_{app} (g(n-pentane)·mmol(BAS)$^{-1}$·h^{-1})
P	P-Z5	3.7	2	32.6	0.56
1	P-Z5	3.7	1	18.0	0.28
2	Z5(50)[a]	3.7	2	20.0	0.50
3	P-Z5	7.4	2	16.5	0.52

[a] The properties of Z5(50) was shown in Table S4.

Table S4 Acid properties of P-Z5 and Z5(50)

Catalyst	Acid sites amount[a] ($mmol·g^{-1}$)	S/W[a]	B_T/L_T[b]	B_S/L_S[c]
P-Z5	3.054	0.88	5.5	10.8
Z5(50)	2.011	0.91	4.9	9.7

[a] Determined by NH_3-TPD (S and W represent strong and weak acid sites). [b] Determined by Py-IR at 200 °C (B, L and T represent Brønsted, Lewis and total acid sites). [c] Determined by Py-IR at 350 °C.