Supporting Information

Synergistic construction of bifunctional and stable Pt/HZSM-5 based catalyst for efficient catalytic cracking of *n*-butane

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Supplementary Figures

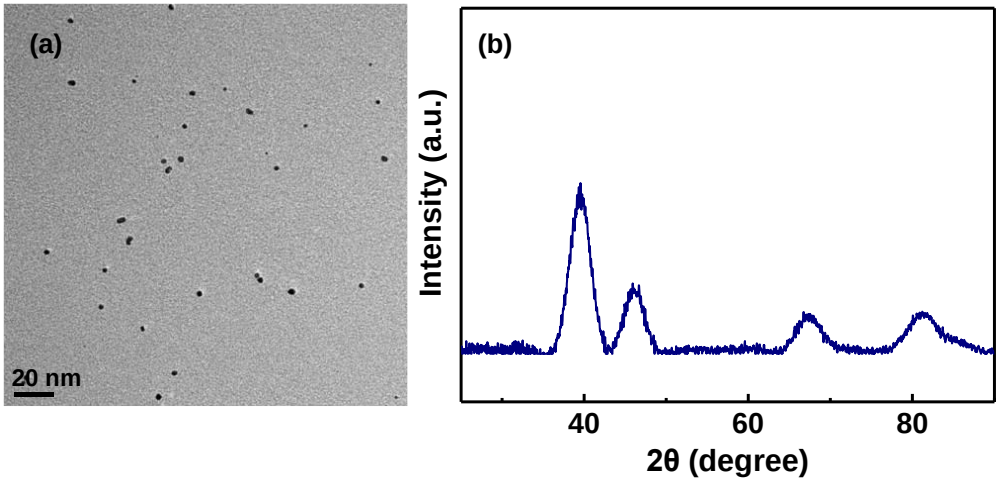

Fig. S1. (a) TEM image and (b) XRD pattern of PVP protected Pt nanoparticles

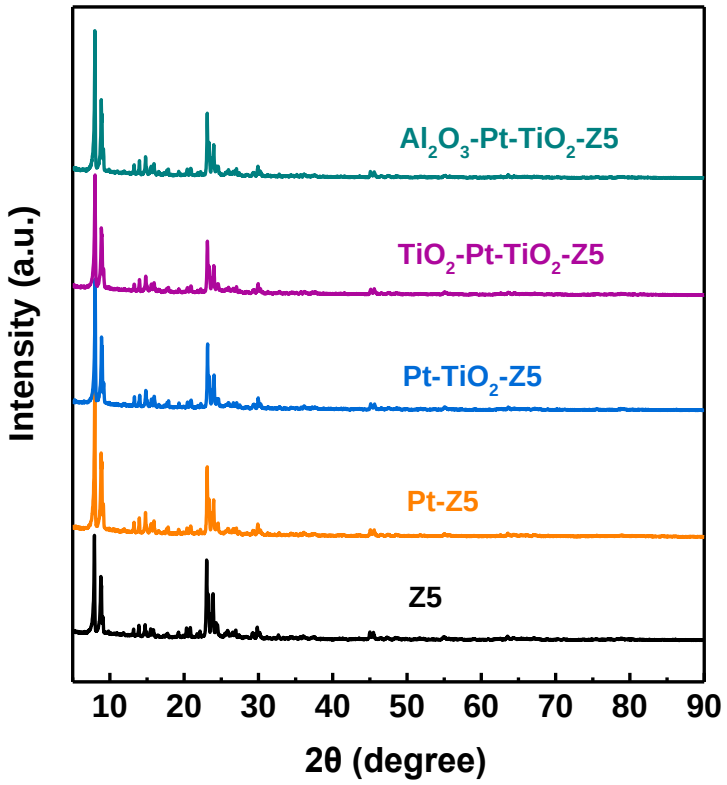

Fig. S2. X-ray diffraction patterns of catalysts

Herein, the numbers of ALD cycles of metal oxides in the first step of TiO_2-Pt-TiO_2-Z5 and Al_2O_3-Pt-TiO_2-Z5 both are 20, and in the second step are 5.

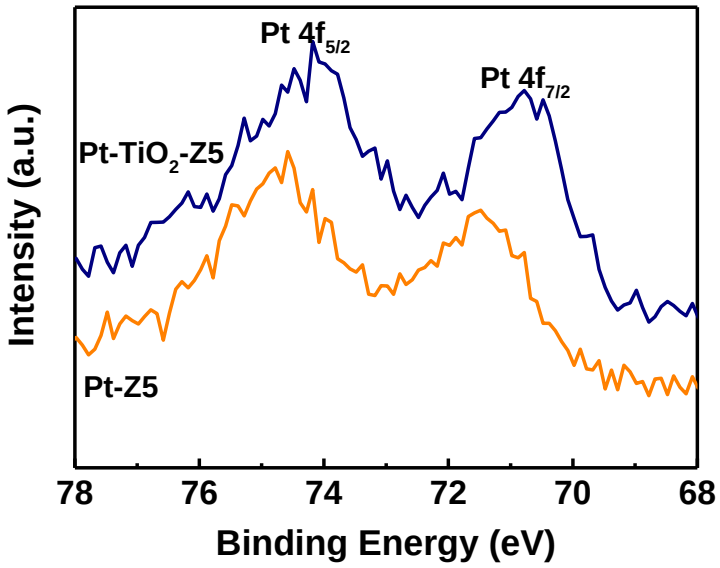

Fig. S3. XPS spectra of Pt 4f of Pt-Z5 and Pt-TiO_2-Z5 catalysts

The number of TiO_2 layers in Pt-TiO_2-Z5 is 20.

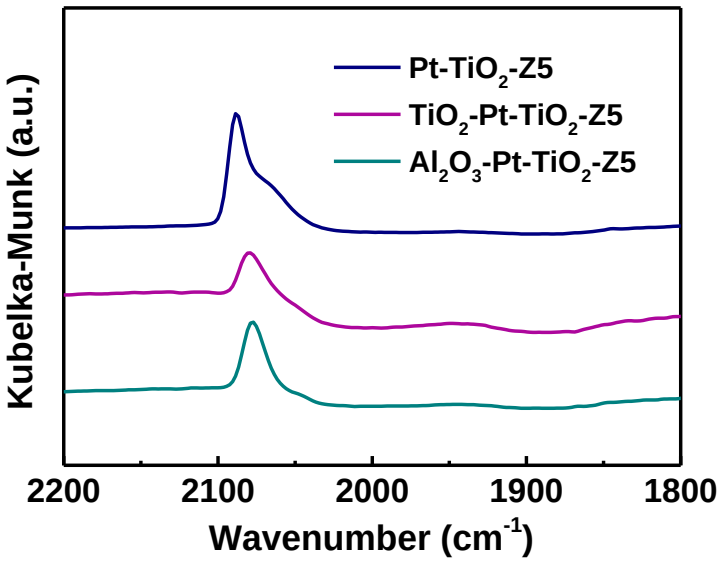

Fig. S4. CO adsorbed DRIFTS spectra of different catalysts

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 5.

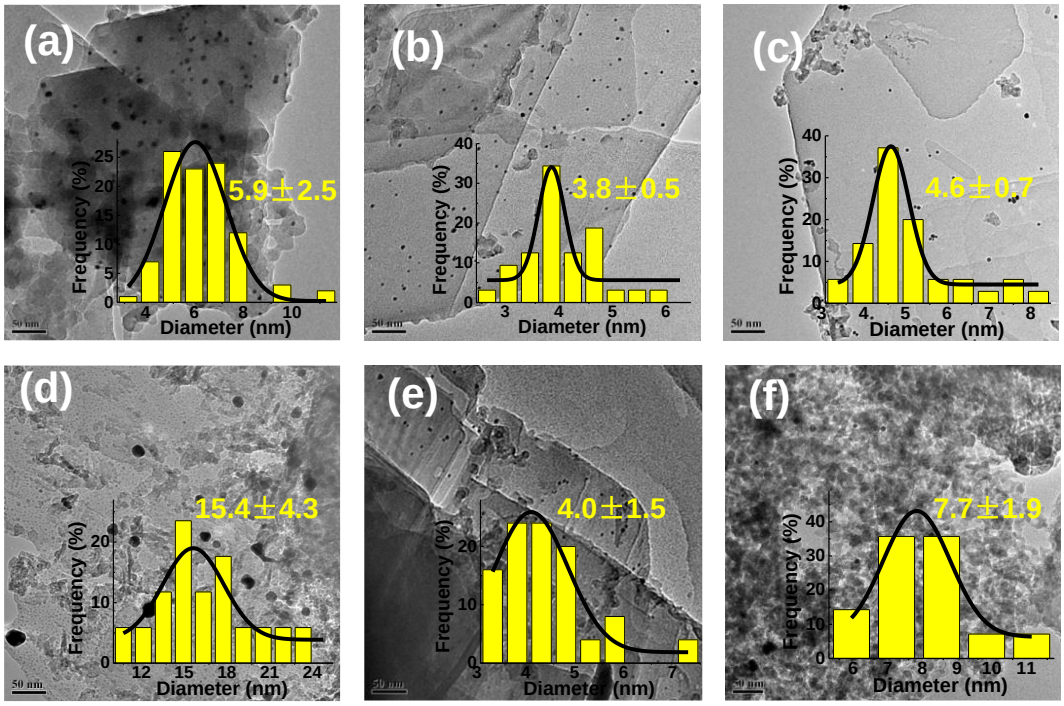

Fig. S5. TEM images of (a) Pt-Z5 before calcination at 600 ºC (b) Al_2O_3-Pt-Z5 before calcination at 600 ºC (c) TiO_2-Pt-Z5 before calcination at 600 ºC and calcinated (d) Pt-Z5 (e) Al_2O_3-Pt-Z5 (f) TiO_2-Pt-Z5 catalysts at 600 ºC in air

Herein, the numbers of TiO_2 or Al_2O_3 layers of Al_2O_3-Pt-Z5 or TiO_2-Pt-Z5 are 5.

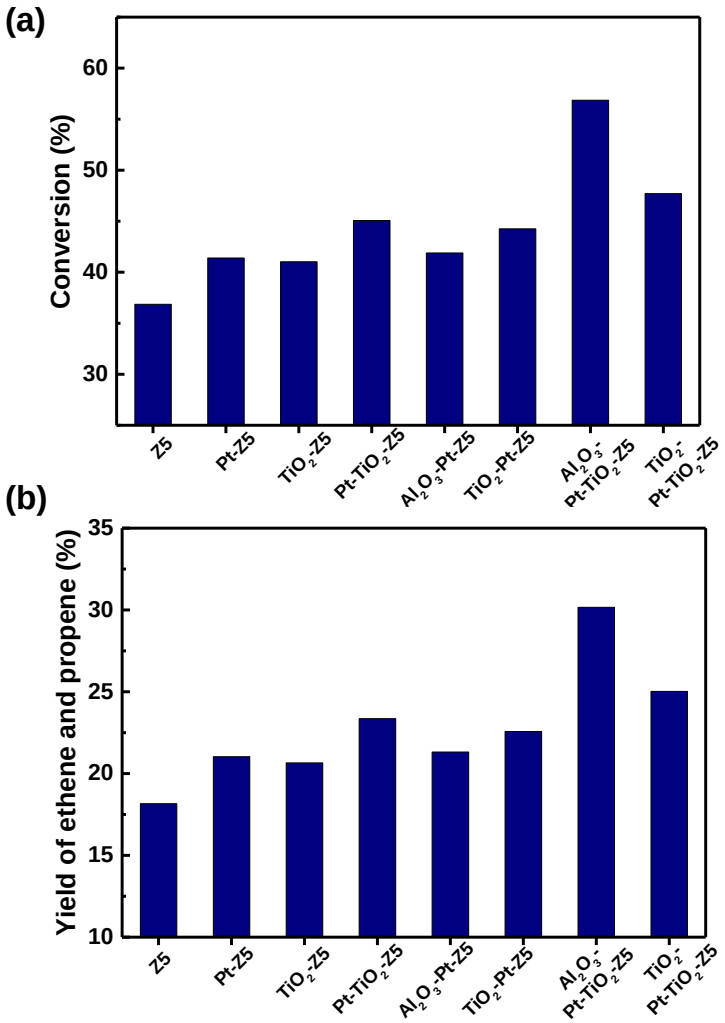

Fig. S6. The catalytic performance of the catalysts with different configurations for the catalytic cracking of n-butane at 600 °C

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 5. Tests were performed in the reactant gas of n-C_4H_{10}/N_2 (5 vol%, 40 mL·min^{-1}), and 0.2 g catalyst was used. Results show that butane conversion of Pt-TiO_2-Z5 catalyst is 9% higher than that of commercial HZSM-5. Besides, the difference in activity between Pt-TiO_2-Z5 and TiO_2-Z5 catalysts indicates that the addition of dehydrogenation component Pt could improve the catalytic performance. While catalysts (Pt-TiO_2-Z5, TiO_2-Pt-Z5 and Al_2O_3-Pt-Z5) with only one ALD step faded next to catalysts (TiO_2-Pt-TiO_2-Z5 and Al_2O_3-Pt-TiO_2-Z5) with two ALD step in catalytic cracking of n-butane reaction, which proved the superiority of the former catalysts.

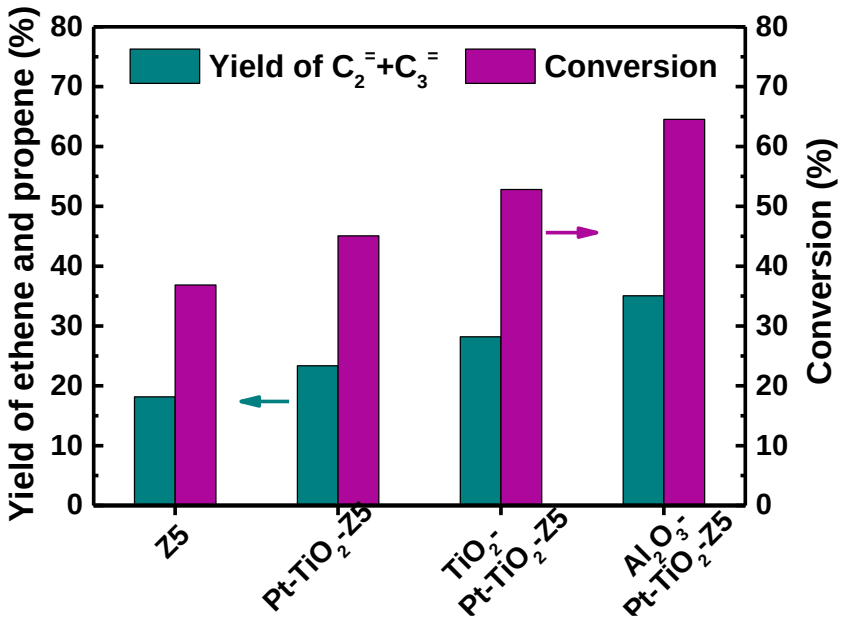

Fig. S7. Conversion and yield of ethene plus propene of catalysts in catalytic cracking of n-butane at 600 ºC

Tests were performed in the reactant gas of n-C_4H_{10}/N_2 (5 vol%, 40 mL·min^{-1}), and 0.2 g catalyst was used. Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

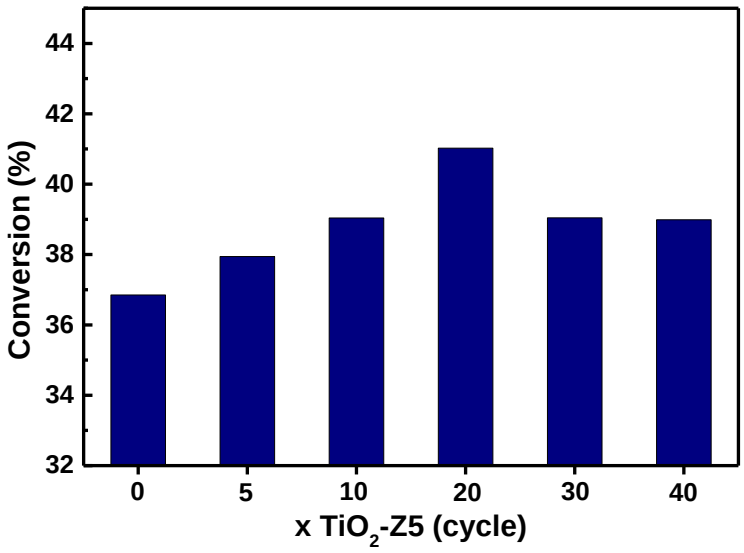

Fig. S8. The conversion of n-butane on the catalysts with various cycles in the first ALD step for the catalytic cracking of n-butane at 600 °C

Tests were performed in the reactant gas of n-C_4H_{10}/N_2 (5 vol%, 40 mL·min^{-1}), and 0.2 g catalyst was used. x TiO_2-Z5 represents that the catalyst was prepared by a x-cycle TiO_2 by ALD on commercial HZSM-5 (x=0, 5, 10, 20, 30, 40).

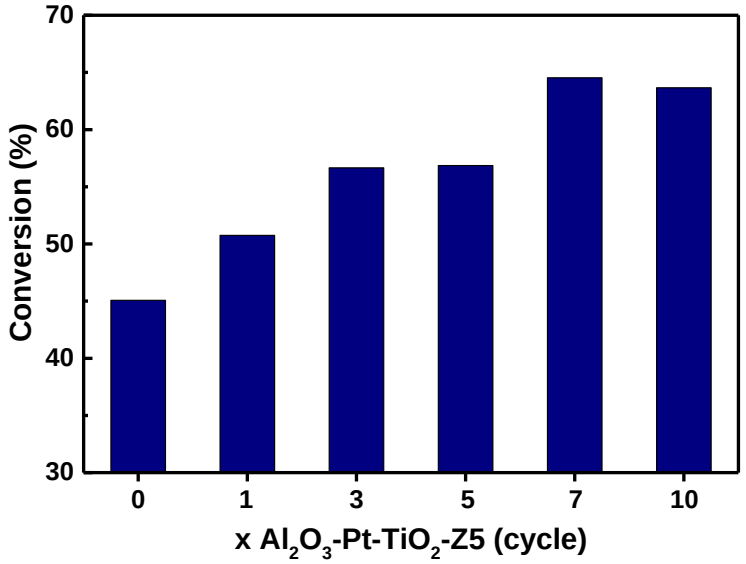

Fig. S9. The conversion of n-butane on the catalysts with different cycles in the second ALD step of Al_2O_3 in the catalytic cracking of n-butane at 600 °C

Tests were performed in the reactant gas of n-C_4H_{10}/N_2 (5 vol%, 40 mL·min^{-1}), and 0.2 g catalyst was used. Herein, the number of TiO_2 layers during the first ALD step is 20.

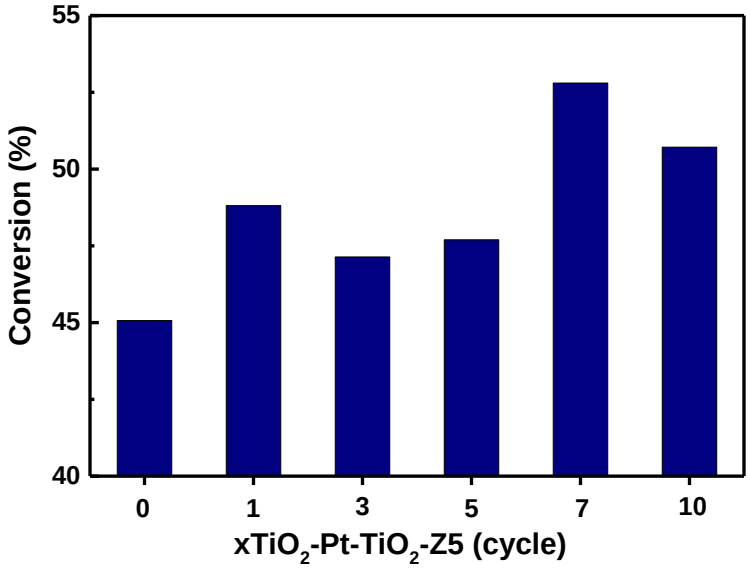

Fig. S10. The conversion of n-butane on the catalysts with different cycles of TiO_2 in the second ALD step for the catalytic cracking of n-butane at 600 °C

Tests were performed in the reactant gas of n-C_4H_{10}/N_2 (5 vol%, 40 mL·min^{-1}), and 0.2 g catalyst was used. Herein, the number of TiO_2 layers during the first ALD step is 20.

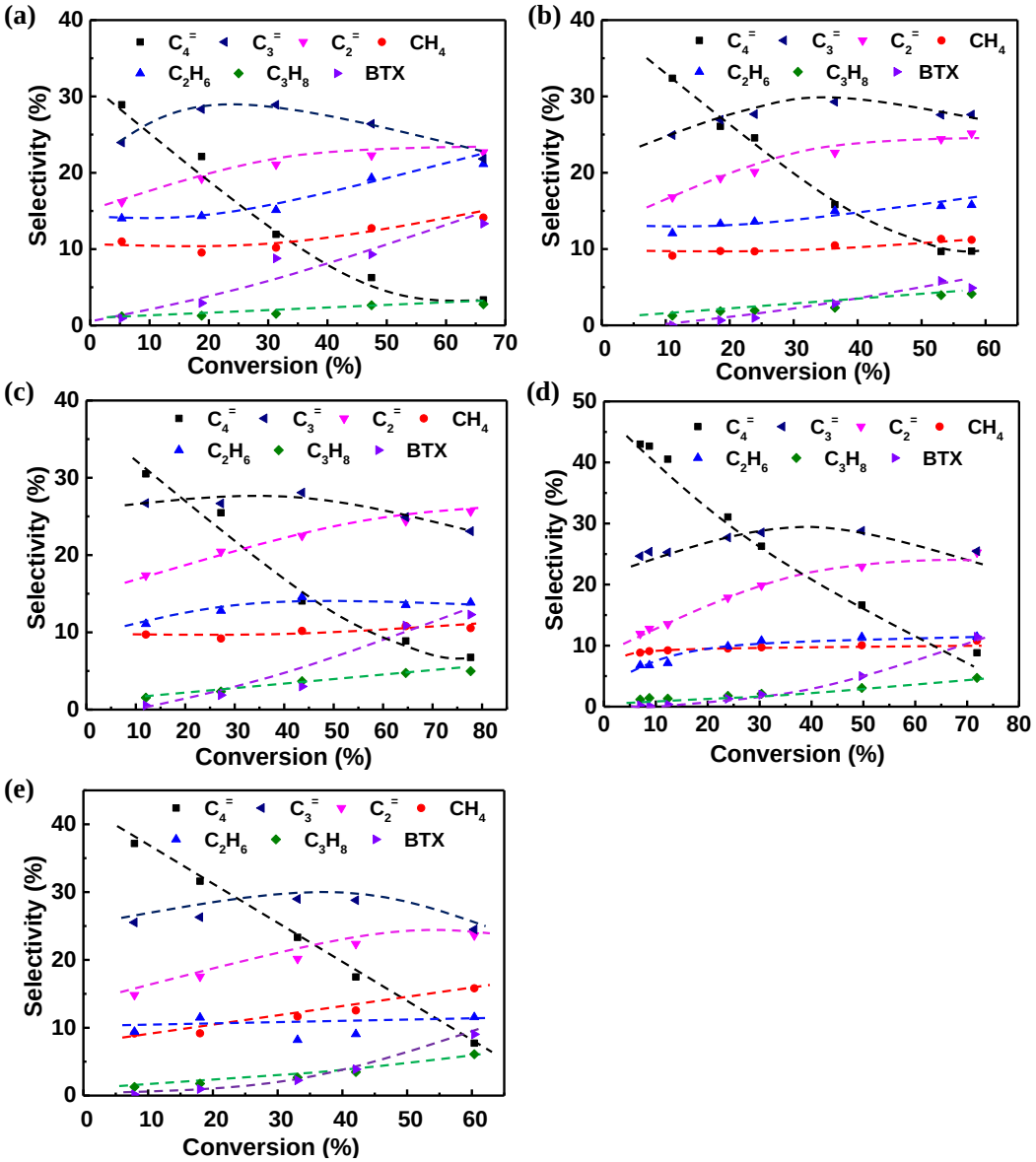

Fig. S11. The relationship between selectivity and conversion of series of catalysts (a) Z5 (b) Pt-Z5 (c) Pt-TiO_2-Z5 (d) TiO_2-Pt-TiO_2-Z5 (e) Al_2O_3-Pt-TiO_2-Z5 at 600 °C

Tests were all performed in the reactant gas of n-C_4H_{10}/N_2 (5 vol%), and the space velocity was changed during the tests. Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

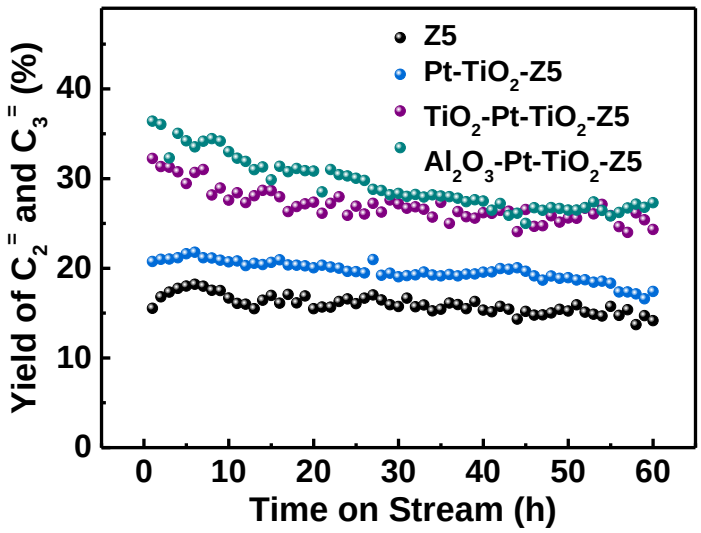

Fig. S12. Yield of ethene plus propene of catalysts for 60 h performance test in catalytic cracking of n-butane at 600 ºC

Test was performed in the reactant gas of *n*-C_4H_{10}/N_2 (5 vol%, 40 mL·min^{-1}), and 0.2 g catalyst was used. Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

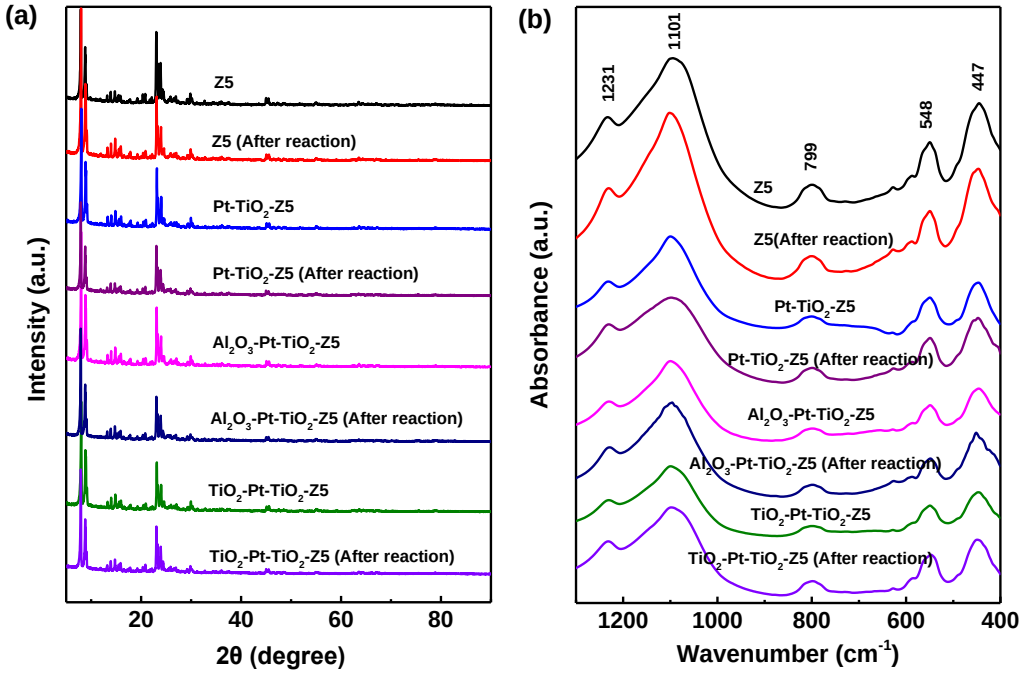

Fig. S13. (a) X-ray diffraction patterns and (b) Infrared spectra of fresh and spent catalysts

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

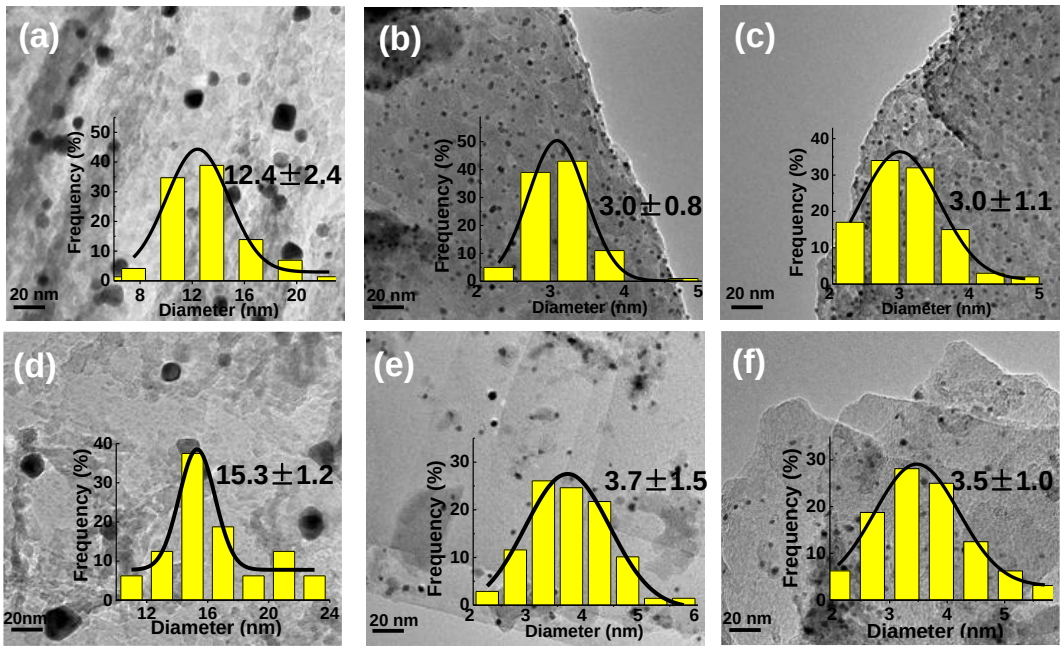

Fig. S14. TEM images of fresh catalysts (a) Pt-TiO_2-Z5 (b) Al_2O_3-Pt-TiO_2-Z5 (c) TiO_2-Pt-TiO_2-Z5 and spent catalysts (d) Pt-TiO_2-Z5 (e) Al_2O_3-Pt-TiO_2-Z5 (f) TiO_2-Pt-TiO_2-Z5 after 60 h time-on-stream reaction

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

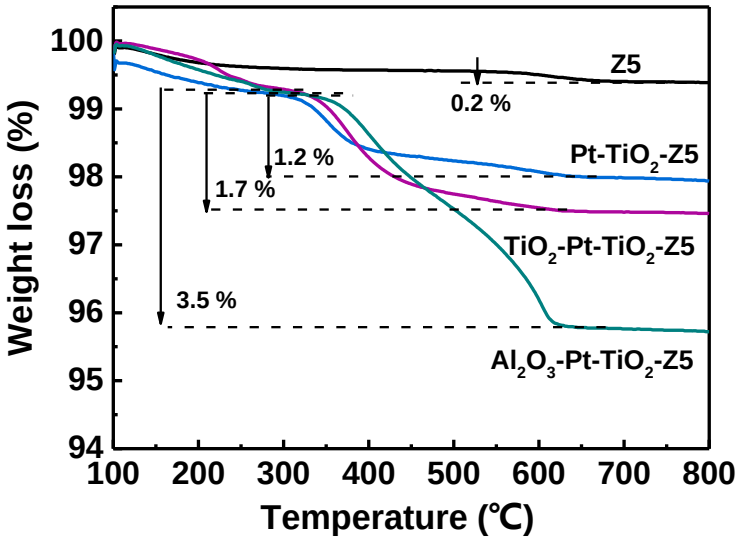

Fig. S15. TG curves of carbon deposition analysis on spent catalysts after 60 h reaction

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

The TG results show the weight losses of Al_2O_3-Pt-TiO_2-Z5, TiO_2-Pt-TiO_2-Z5, Pt-TiO_2-Z5 and Z5 are 3.5 wt.%, 1.7 wt.%, 1.2 wt.% and 0.2 wt.%, respectively, indicating the catalyst with Al_2O_3 overcoat has the highest coke amount, which is probably resulting from its high conversion.

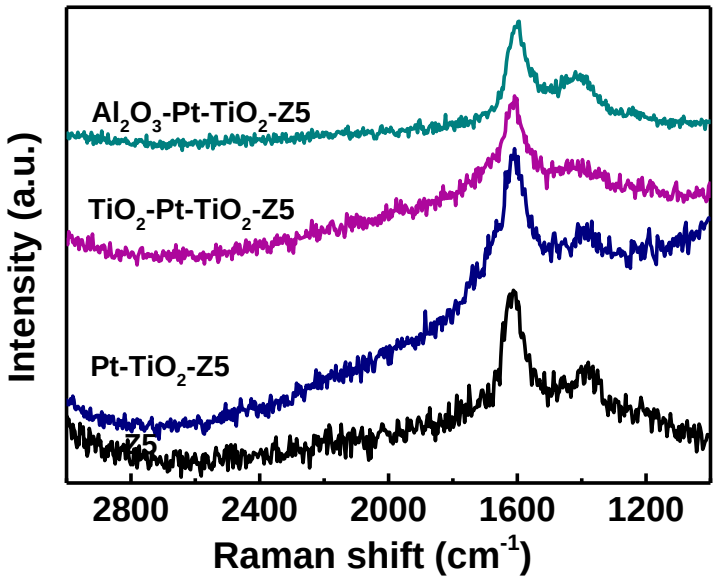

Fig. S16. Raman spectra of the spent catalysts after 60 h reaction

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

Results indicate that all the catalysts show two carbon deposition peaks, as D band (1370-1410 cm^{-1}) and G band (1590-1620 cm^{-1}), correspond to disordered structure and sp^2-hybridized graphite carbon species, respectively[S1]. From the results, Al_2O_3-Pt-TiO_2-Z5 has the highest proportion of I_D/I_G, indicating highest proportion of disorderly carbon. A lower Raman shift observed on Al_2O_3-Pt-TiO_2-Z5 catalyst in Raman spectra also means a higher disordered degree. In addition, Pt-TiO_2-Z5 has the largest coke particles size as the half peak width in G band is the widest.

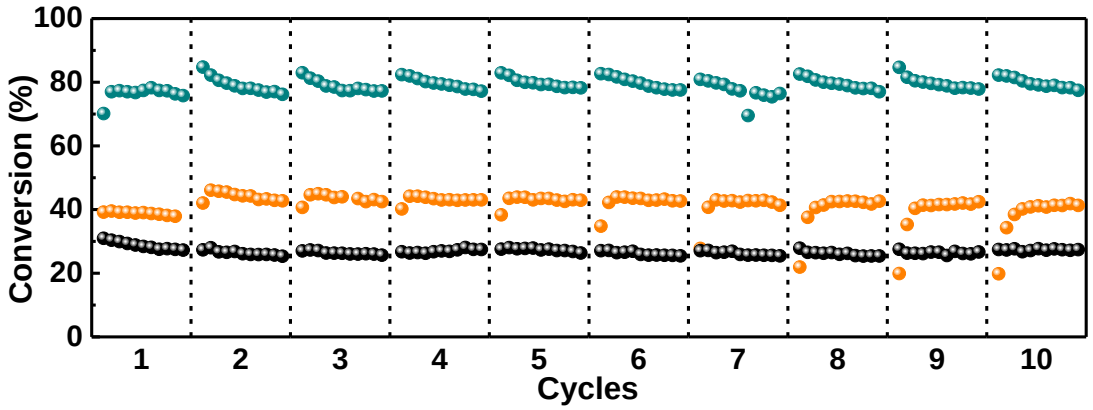

Fig. S17. Regeneration behavior of typical Al_2O_3-Pt-TiO_2-Z5 (■), Pt-Z5 (■) and Z5 (■) catalysts at 600 °C

Tests were performed in a feed of 5% C_4H_{10} in N_2. Every cycle maintains 400 minutes. Herein, the number of TiO_2 layers during the first ALD step is 20, and the number of Al_2O_3 layers during the second ALD step is 7.

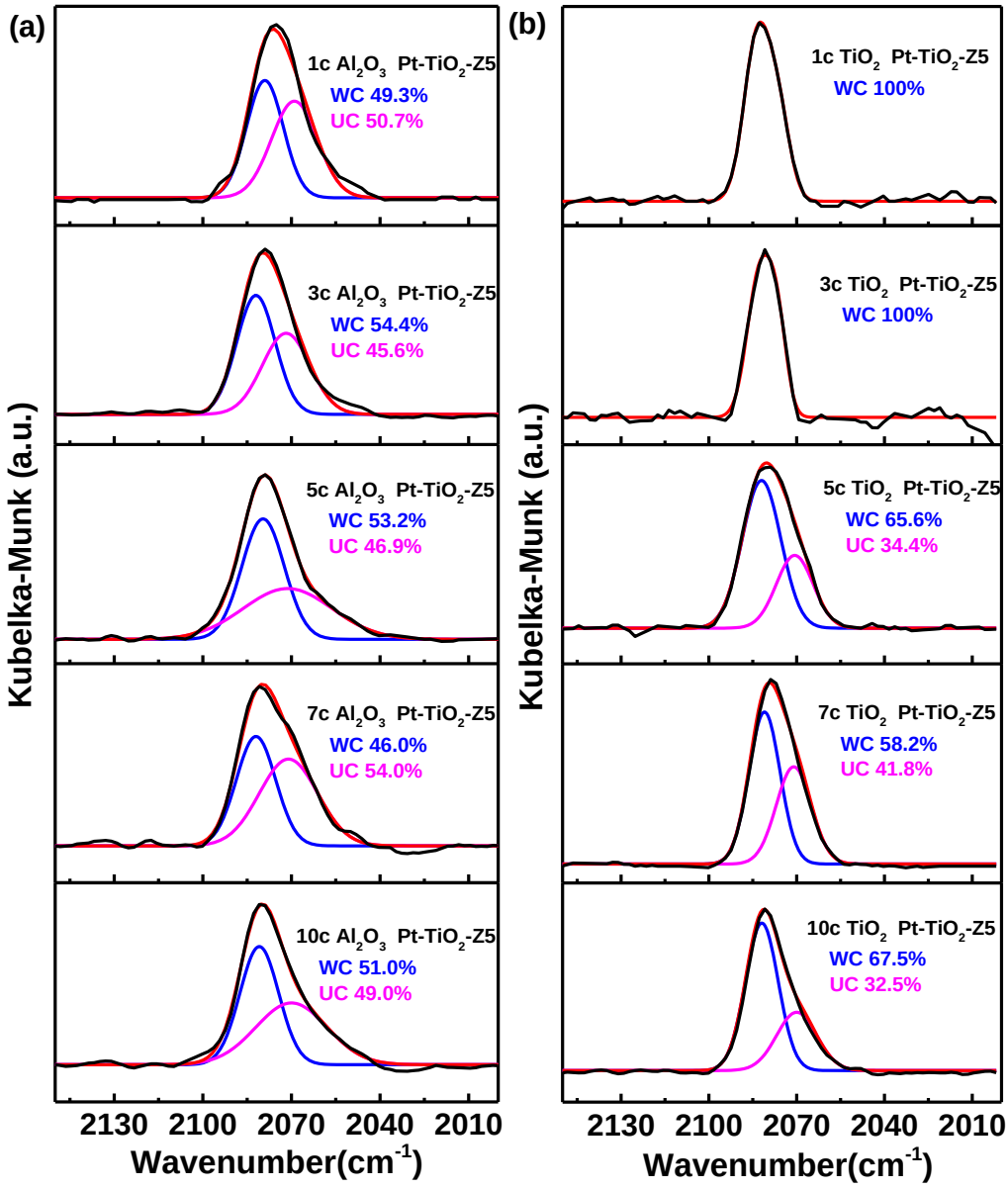

Fig. S18. DRIFT spectra of CO molecules adsorbed on catalysts with a series of (a) Al_2O_3 and (b) TiO_2 overcoats

The sintering-resistance ability of Al_2O_3 under 3-cycle overcoat is better than that of TiO_2. Sintering occurred on 1c TiO_2 Pt-TiO_2-Z5 and 3c TiO_2 Pt-TiO_2-Z5 catalysts, while not on 1c Al_2O_3 Pt-TiO_2-Z5 and 3c Al_2O_3 Pt-TiO_2-Z5 catalysts. This is due to island growth mechanism in ALD early stage[S2], where Al_2O_3 has a better property to extend and form a membrane than TiO_2 during calcination process. Herein, the number of TiO_2 layers during the first ALD step is 20.

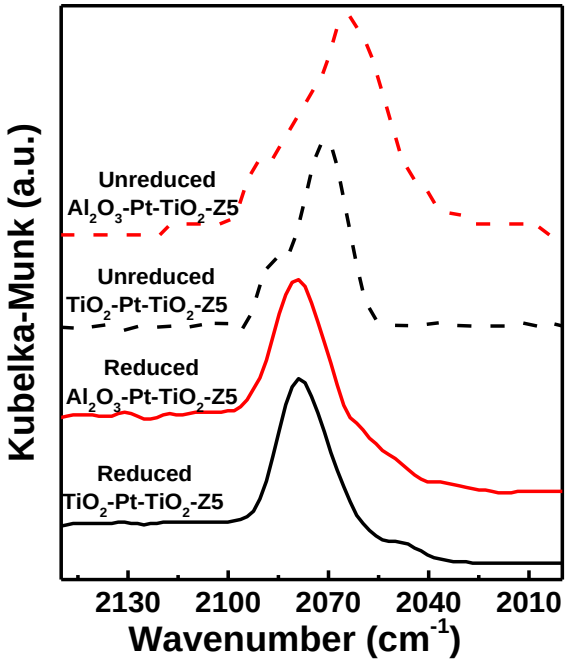

Fig. S19. DRIFTS spectra of CO molecules adsorbed on catalysts before and after reduction process in H_2/N_2 (5 vol%) at 500 °C for 1 h

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers introduced in the second ALD step of TiO_2-Pt-TiO_2-Z5 and Al_2O_3-Pt-TiO_2-Z5 are both 7.

Supplementary Tables

Tables S1. Textural properties of different catalysts

Sample	S_{BET} m^2/g	V_{ads} cm^3/g	V_{des} cm^3/g	D_{ads} nm	D_{des} nm
Z5	309.3	0.15	0.14	5.7	6.2
TiO_2-Z5	303.5	0.12	0.13	5.1	5.8
Pt-TiO_2-Z5	281.5	0.11	0.09	4.9	8.6
TiO_2-Pt-TiO_2-Z5 (before calcination)	252.8	0.11	0.11	5.3	5.2
TiO_2-Pt-TiO_2-Z5 (after calcination)	280.5	0.12	0.12	4.9	5.2
Al_2O_3-Pt-TiO_2-Z5 (before calcination)	246.4	0.10	0.10	4.8	4.7
Al_2O_3-Pt-TiO_2-Z5 (after calcination)	283.6	0.11	0.11	4.7	4.9

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 5.

Table S2. Assignments for the IR bands of HZSM-5

Assignment	Wavenumber (cm^{-1})
Terminal Si-OH	3745
-OH in B acid	3610
Skeletal vibration	1880 1885 2010
Inner ν_{as} T-O-T	1101
Outside ν_{as} T-O-T	1231
Outside ν_sT-O-T	799
penta-cycles	548

Table S3. Raman results of spent catalysts

Sample	D band		G band		I_D/I_G
	Intensity	position/cm^{-1}	Intensity	position/cm^{-1}	
Z5	75.6	1370	211.7	1612	0.357
Pt-TiO_2-Z5	73.4	1391	195.3	1604	0.376
Al_2O_3-Pt-TiO_2-Z5	74.0	1413	162.0	1597	0.457
TiO_2-Pt-TiO_2-Z5	74.4	1408	321.4	1612	0.231

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

Table S4. ICP results of different catalysts

Sample	Pt Content (%)	Ti Content (%)	Al Content (%)	Si Content (%)
Pt-Z5	0.31	0	0.64	43.2
Pt-TiO_2-Z5	0.32	3.1	0.59	39.7
TiO_2-Pt-TiO_2-Z5	0.29	3.7	0.64	37.9
Al_2O_3-Pt-TiO_2-Z5	0.29	2.9	1.57	40.6

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

Table S5. NH_3-TPD results of different catalysts

Sample	Weak Acid Peak Area	Strong Acid Peak Area
Z5	1268	734
Pt-TiO_2-Z5	1279	832
TiO_2-Pt-TiO_2-Z5	1178	684
Al_2O_3-Pt-TiO_2-Z5	1203	778

330 ^oC was picked as the boundary between strong acid and weak acid.

Herein, the number of TiO_2 layers during the first ALD step is 20, and the numbers of TiO_2 or Al_2O_3 layers during the second ALD step are 7.

Supplementary References

[S1] N. R. Ostyn, J. A. Steele, D. M. Prins, S. P. Sree, C. V. Chandran, W. Wangermez, G. Vanbutsele, G. W. Seo, M. B. J. Roeffaers, E. Breynaert and J. A. Martens, *Nanoscale Adv.*, 2019, **1,** 2873-2880.

[S2] B. Gong and G. N. Parsons, *J. Mater. Chem.*, 2012, **22**, 15672-15682.