Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

The atomic defects on the (104) and (110) surfaces of the $MgCl_2$-supported Ziegler-Natta Catalyst: a periodic DFT study

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Table S1. Bader charges of $TiCl_4$ molecule and Ti center.

Surfaces	$TiCl_4$	Ti center
(110)		
I110	-0.22	1.74
D110-1	-0.92	1.60
D110-2	-1.64	1.34
D110-3	-0.21	1.73
(104)		
I104	-0.10	1.70
D104-1	-0.84	1.57
D104-2	-1.55	1.14
D104-3	-0.02	1.71

Table S2. Adsorption energies (kcal mol^{-1}) for the $TiCl_4$ on the C110 and C104 surfaces.

Surfaces	$TiCl_4$
C110	-14.2
C104	-26.8

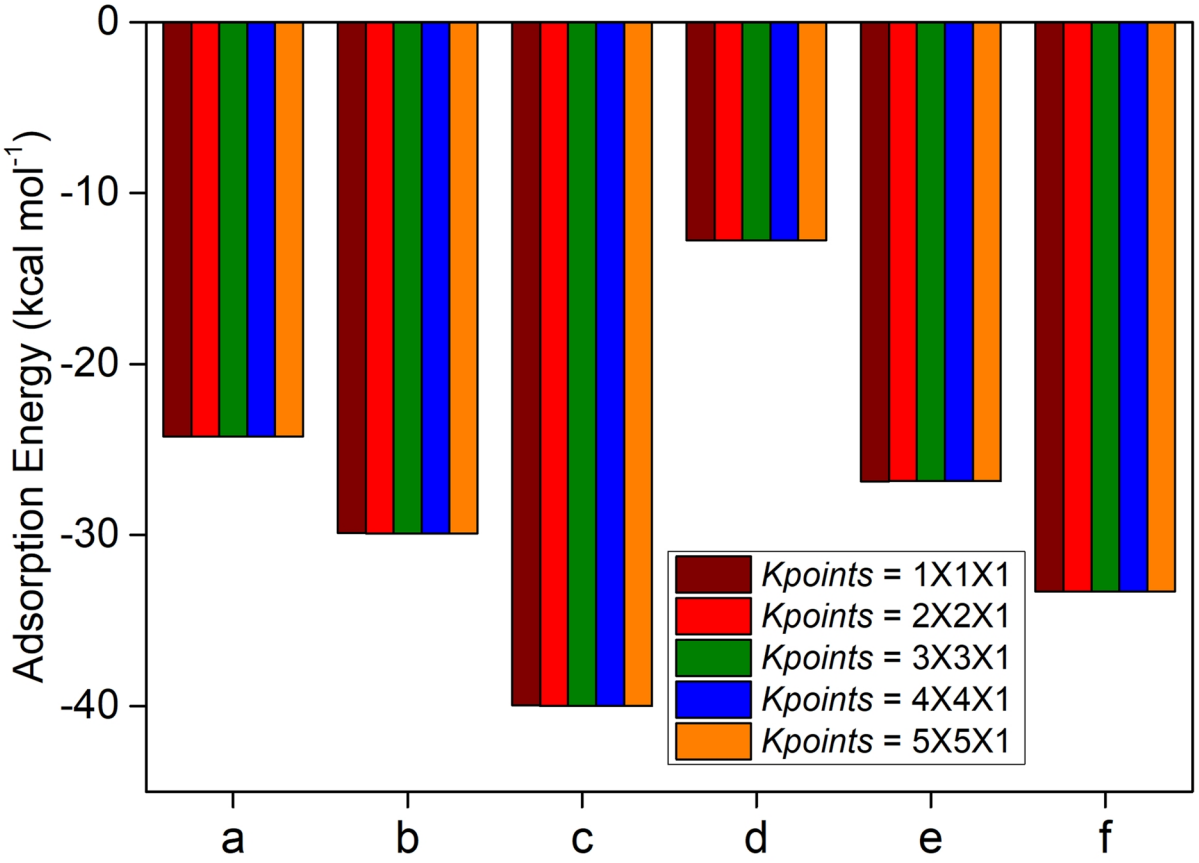

Fig. S1 Adsorption energy for (a) $TiCl_4/MgCl_2(110)$, (b) $EB/MgCl_2(110)$, (c) $DMDOMe/MgCl_2(110)$, (d) $TiCl_4/MgCl_2(104)$, (e) $EB/MgCl_2(104)$, and (f) $DMDOMe/MgCl_2(104)$ under different k point meshes.

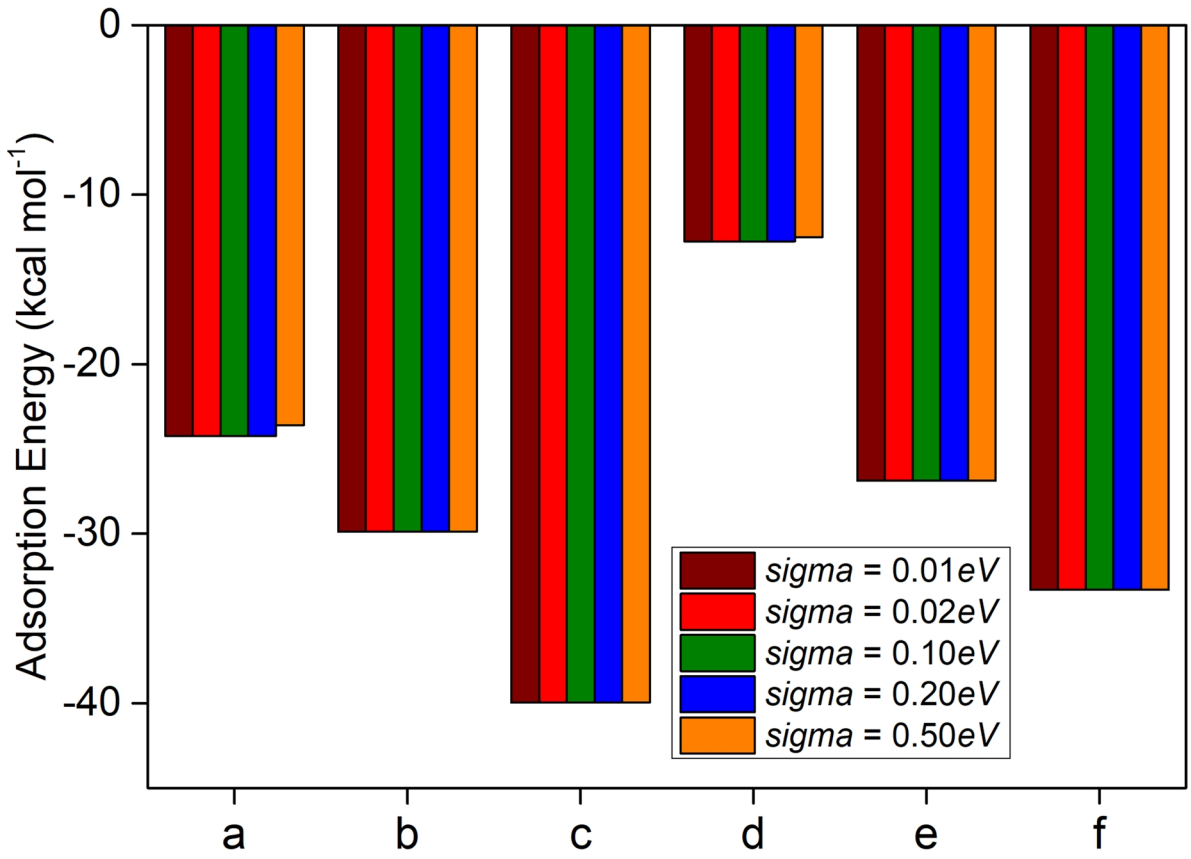

Fig. S2 Adsorption energy for (a) $TiCl_4/MgCl_2(110)$, (b) $EB/MgCl_2(110)$, (c) $DMDOMe/MgCl_2(110)$, (d) $TiCl_4/MgCl_2(104)$, (e) $EB/MgCl_2(104)$, and (f) $DMDOMe/MgCl_2(104)$ under different smearing methods.

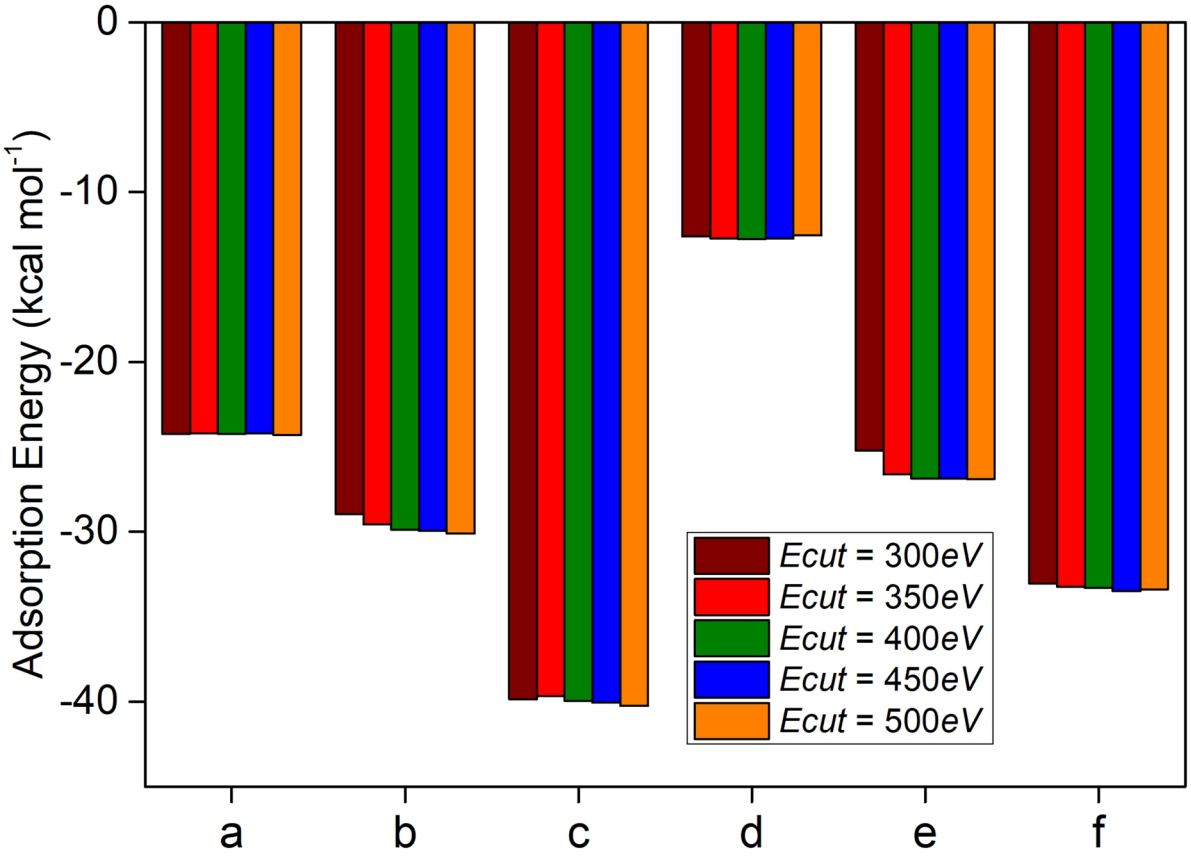

Fig. S3 Adsorption energy for (a) $TiCl_4/MgCl_2(110)$, (b) $EB/MgCl_2(110)$, (c) $DMDOMe/MgCl_2(110)$, (d) $TiCl_4/MgCl_2(104)$, (e) $EB/MgCl_2(104)$, and (f) $DMDOMe/MgCl_2(104)$ under different cutoff energies.

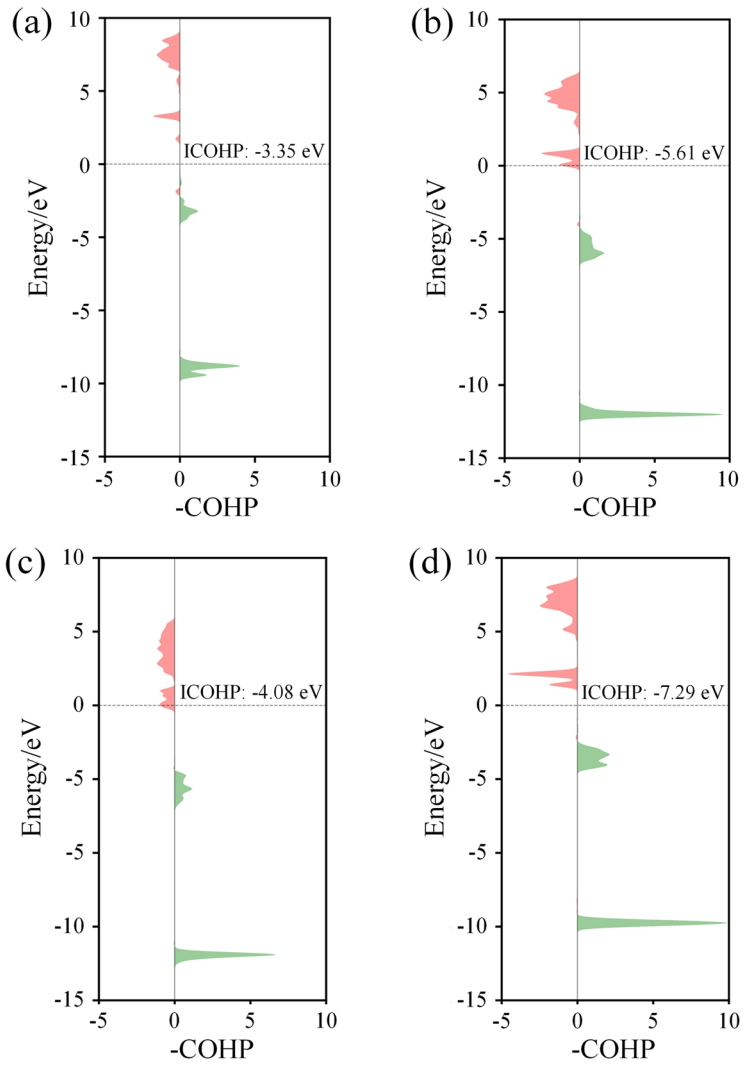

Fig. S4 The crystal orbital Hamilton population (COHP) analysis of the $(Ti\text{-}Cl)_5$ bond in (a) the I104 surface, (b) the D104-1 surface, (c) the D104-2 surface, and (d) the D104-3 surface. The Colour code for the COHP curves is as follows: green, bonding contributions; and red, antibonding contributions.

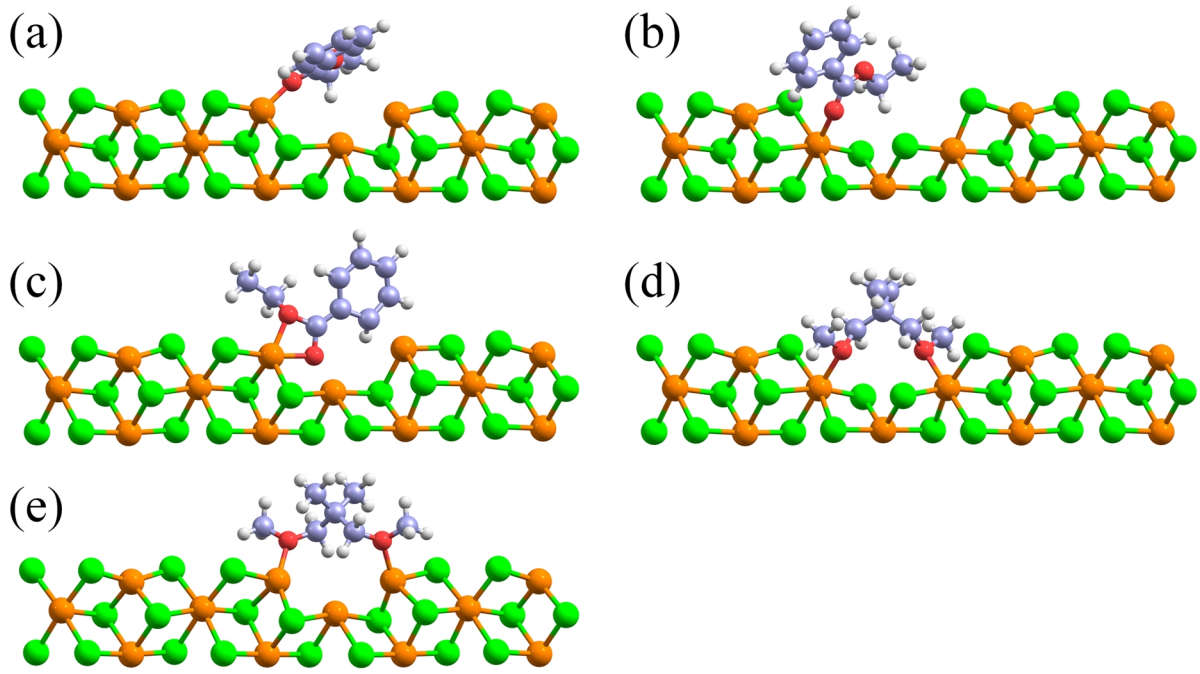

Fig. S5 The binding modes for EB and DMDOMe on: (a), (c), and (e) the D110-2 surface, and (b), and (d) the D110-3 surface. Colour code: orange, Mg; green, Cl of the $MgCl_2$; blue, C; red, O; and light gray, H. Only the relaxed atoms are shown for clarity.

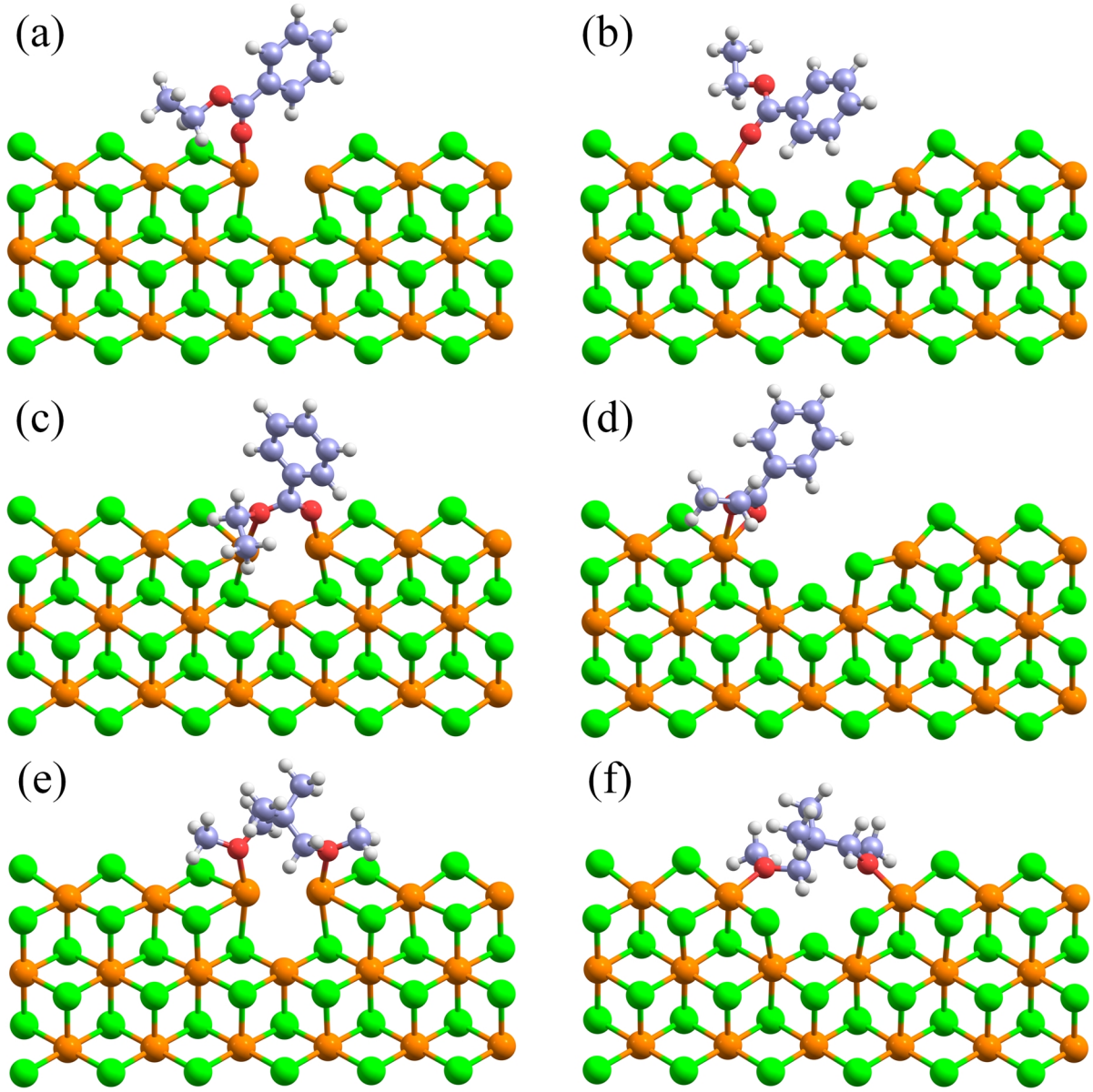

Fig. S6 The binding modes for EB and DMDOMe on: (a), (c), and (e) the D104-2 surface, and (b), (d), and (f) the D104-3 surface. Colour code: as mentioned above. Only the relaxed atoms are shown for clarity.

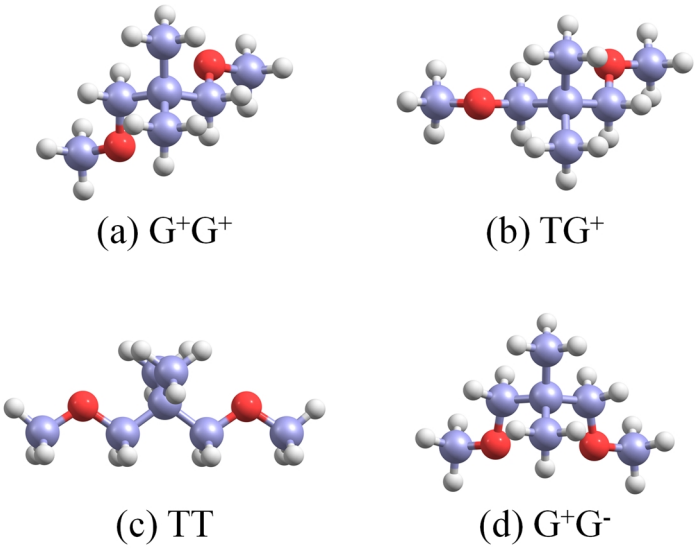

Fig. S7 Optimized structures of DMDOMe at four energy minima. Colour code: as mentioned above.

The conformational analysis of 2,2-methyl-1,3-dimethoxypropane (DMDOMe) shows that DMDOMe has four conformational minima corresponding to (G^+G^+), (TG^+), (TT) and (G^+G^-). The related conformational energies of the four molecule structures in Fig. S8 are 0.0 kcal mol^{-1}, 0.5 kcal mol^{-1}, 1.3 kcal mol^{-1}, 3.6 kcal mol^{-1}, respectively.

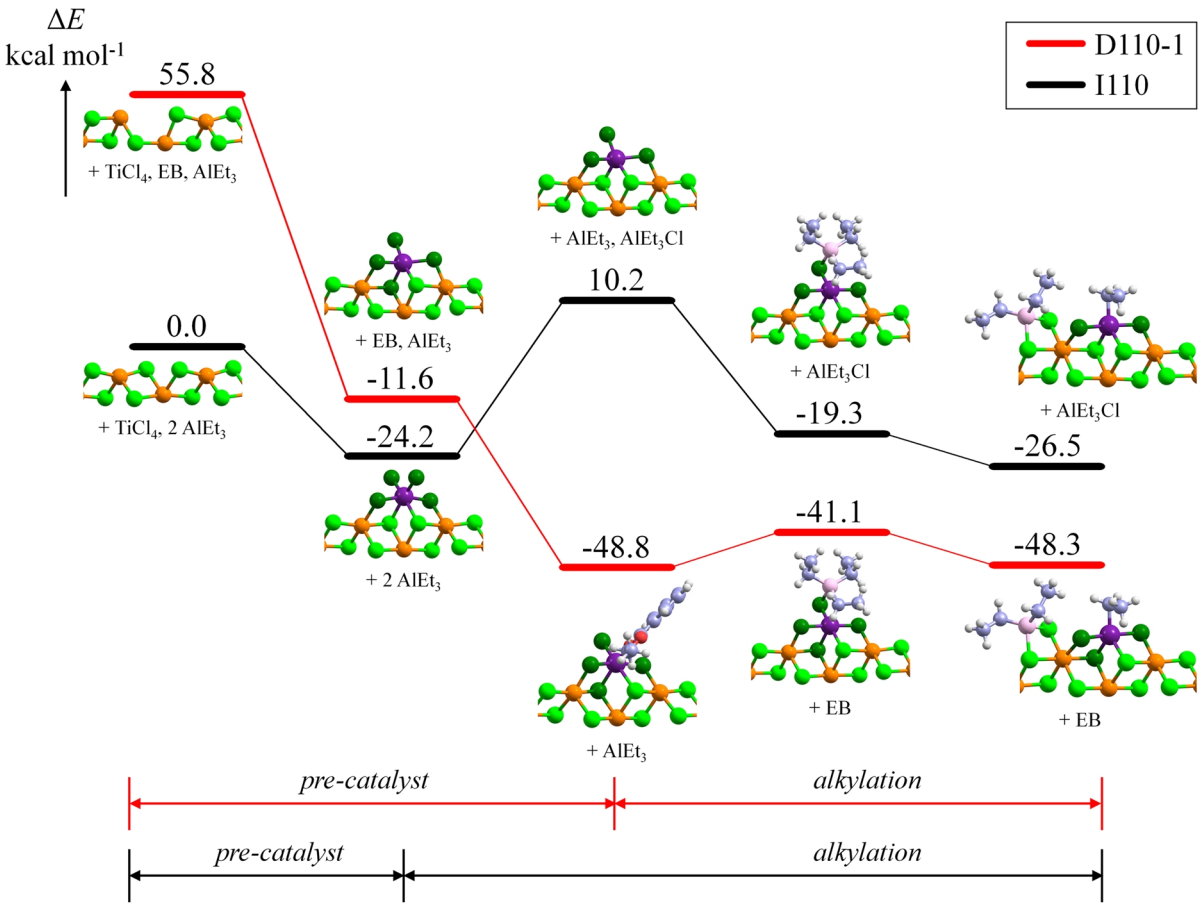

Fig. S8 The energy profile for a comparative study of forming the DEAC coordinated Ti active site on the I110 and D110-1 surfaces. Colour code: violet, Ti; dark green, Cl of the $TiCl_4$; pink, Al; and others as mentioned above.

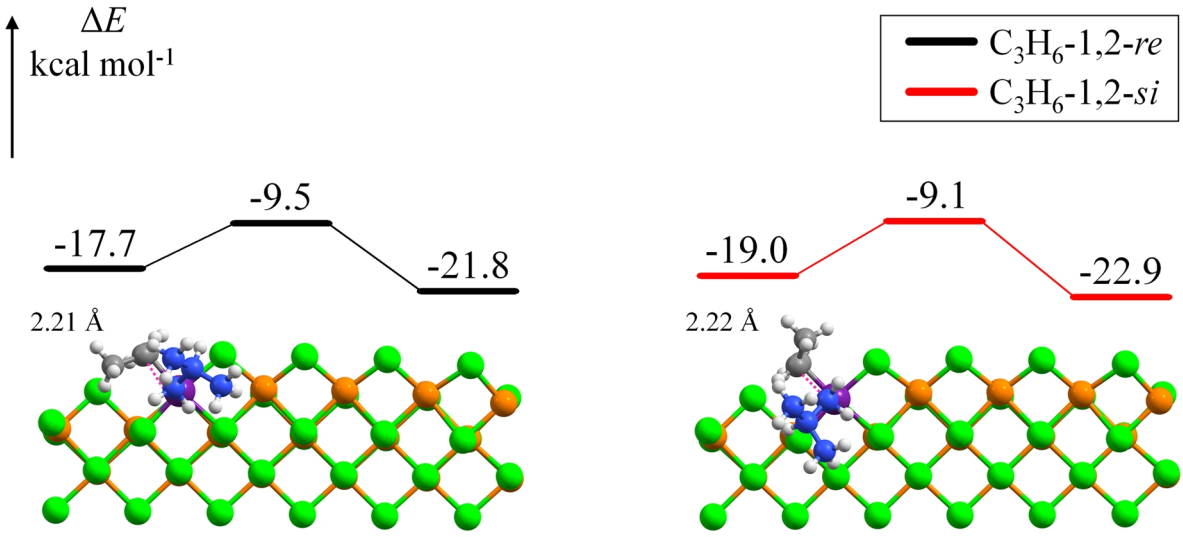

Fig. S9 The energy profile of propylene 1,2-insertion into the Ti-*i*Bu chain on the C104 surface and top view of transition states. Colour code: dark blue, C of the growing chain; dark gray, C of propylene; and others as mentioned above.