Supplementary information

Unravelling Selective Growth Mechanism of Al_2O_3 with Dimethylaluminum Isopropoxide as Precursor in Atomic Layer Deposition: A Combined Theoretical and Experimental Study

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1. The structure of different Pt facets and particle size and distribution of Pt nanoparticles

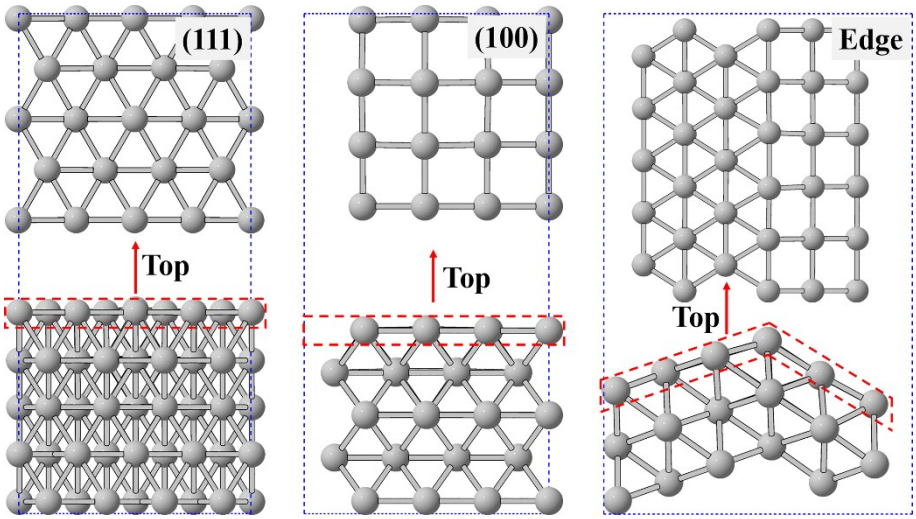

Figure S1.The detailed structures of Pt (111), (100) and Edge for theoretical simulation.

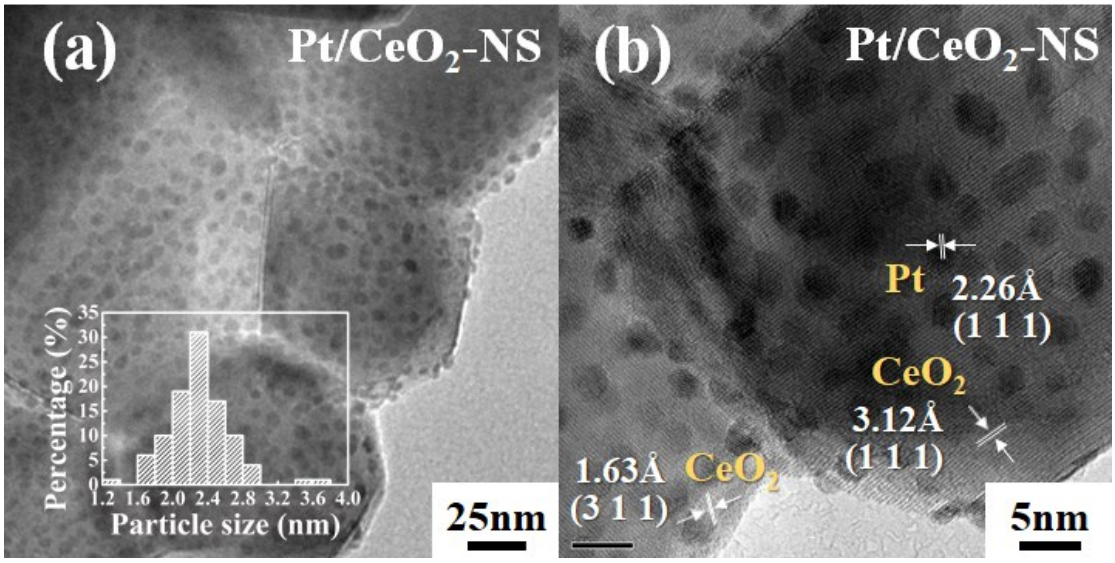

Figure S2. Particle size and distribution of 2 ALD cycles Pt nanoparticles at CeO_2 nanospheres (NS).

2. DMAl decomposition on Pt facets with double hydroxyls

2.1. Pt (111) with double hydroxyls

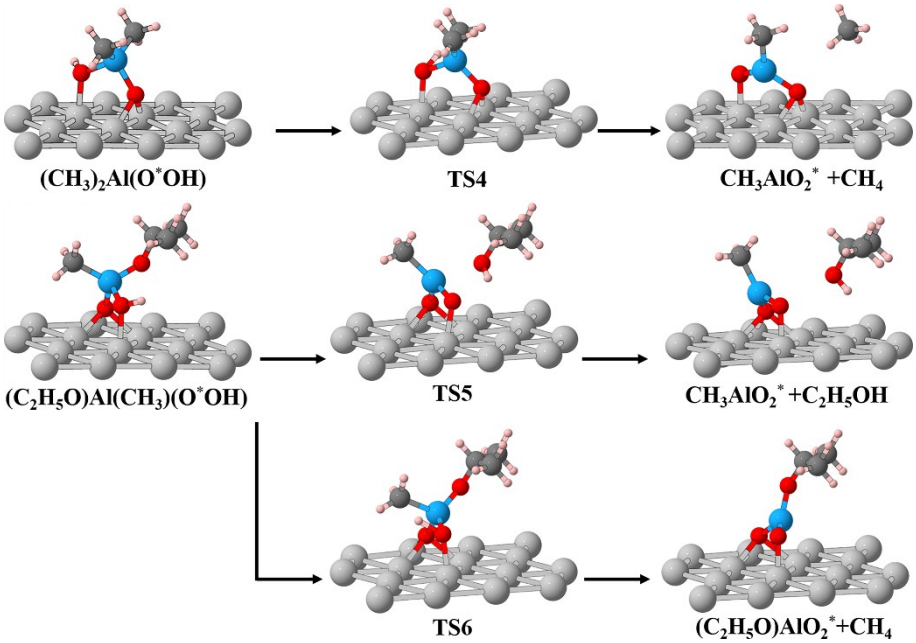

Figure S3. The configurations of intermediates in further decomposition of residual precursors.

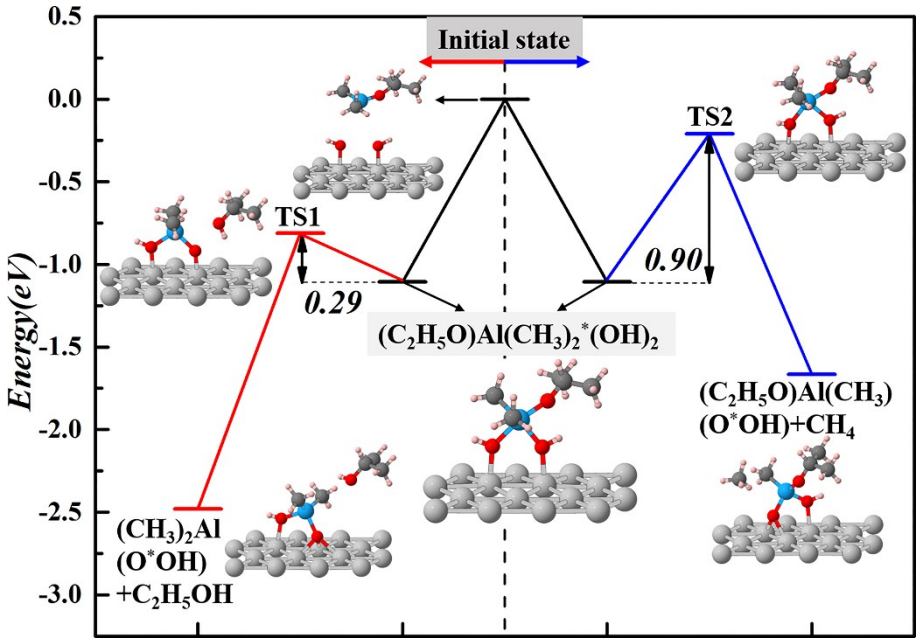

Figure S4. DMAI adsorption and decomposition on Pt (111) facet with t-t binding hydroxyls.

2.2. Pt(100) with double hydroxyls

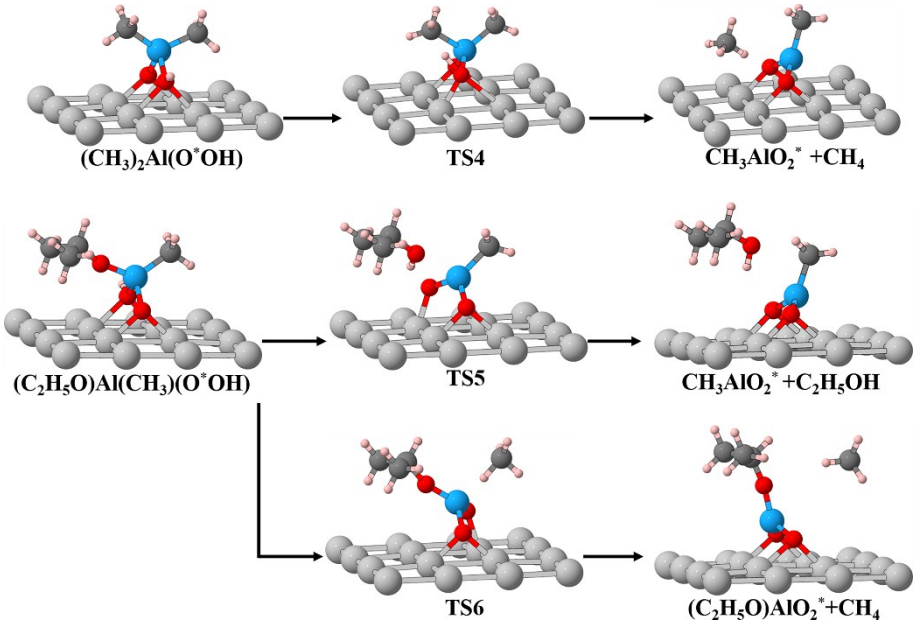

Figure S5. The configurations of intermediates in further decomposition of residual precursors.

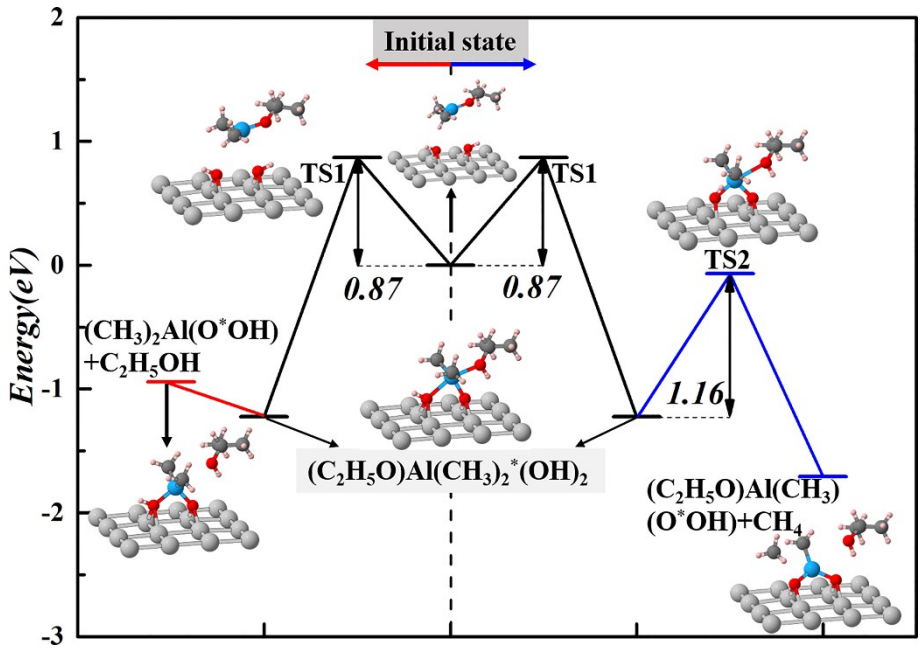

Figure S6. DMAI adsorption and decomposition on Pt (100) slab with b-b binding hydroxyls.

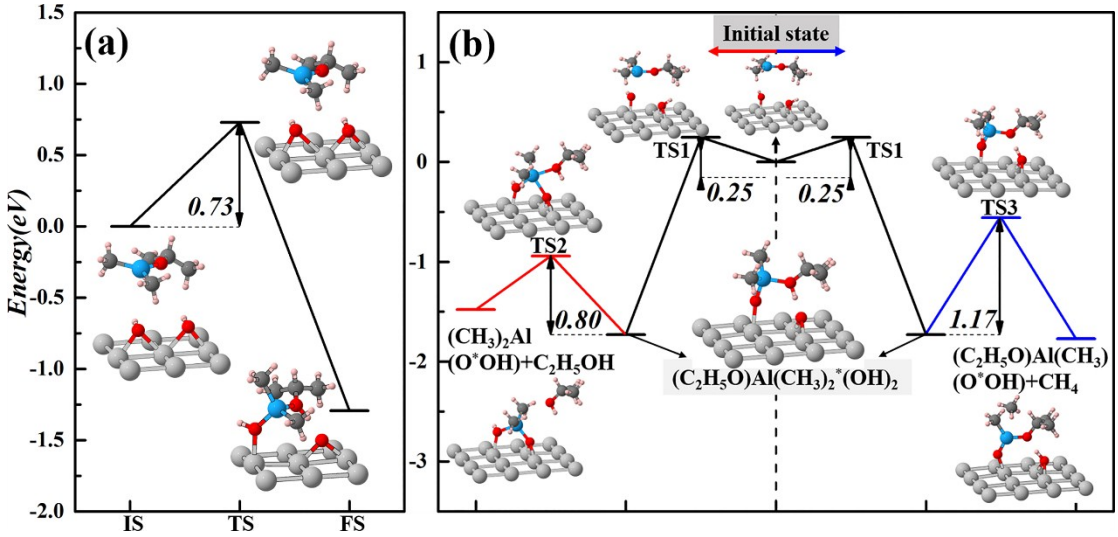

Figure S7. DMAI adsorption and decomposition on Pt (100) slab with b-b (a) and t-b (b) binding hydroxyls.

2.3. Pt edge sites with double hydroxyls

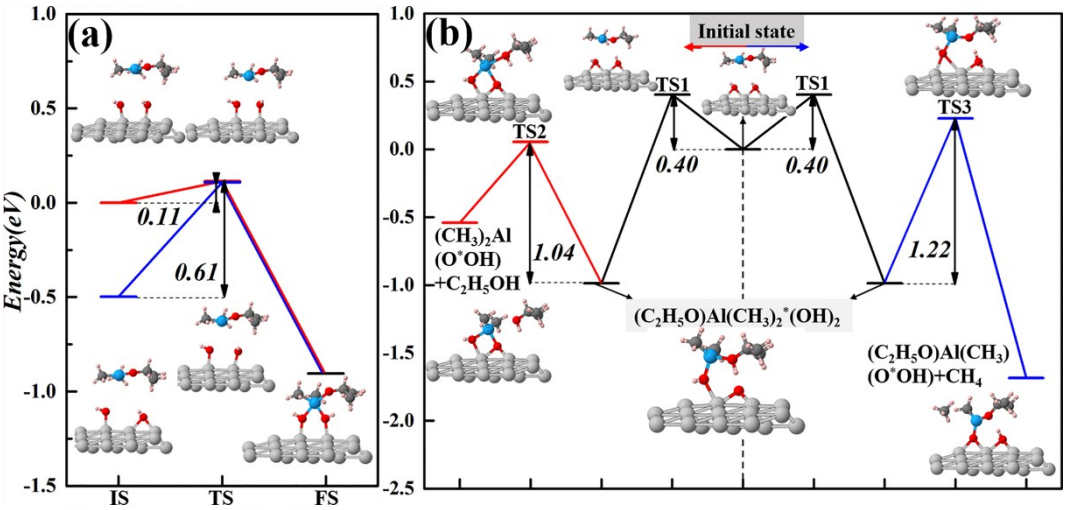

Figure S8. (a) DMAI adsorption on Pt edge sites with t-t and t-b type structure; (b) DMAI adsorption and decomposition on edge sites with b-b binding structure.

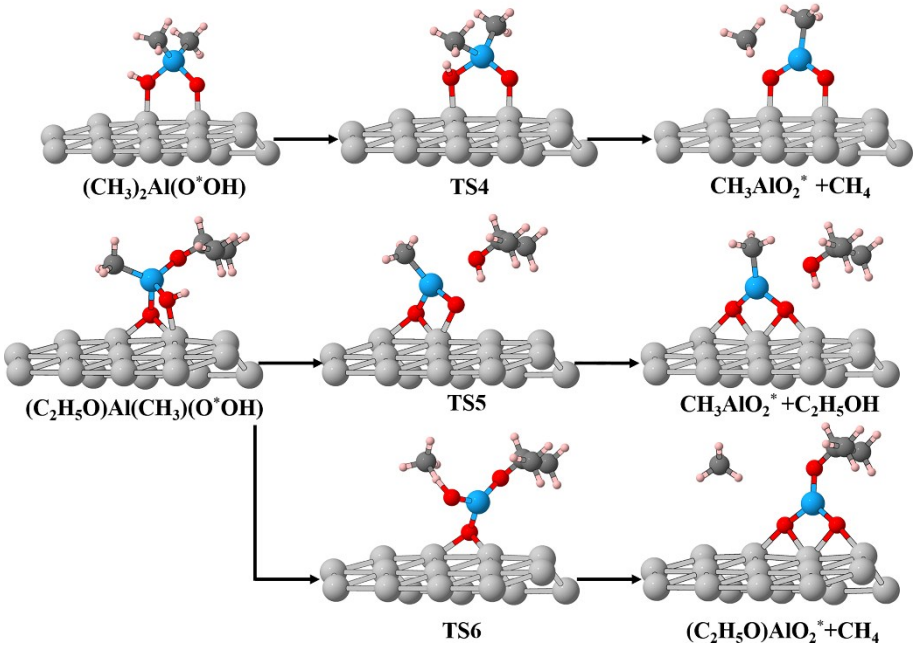

Figure S9. The configurations of intermediates in further decomposition of residual precursors.

3. DMAI decomposition on Pt facets with isolate hydroxyls

The DMAI adsorption and dissociation over Pt slabs with one hydroxyl are also studied. The mechanisms are shown in **Scheme S1**. Firstly, one DMAI molecule binds with the hydroxyl at slabs. Later, the isopropanol and methane are formed via Al-O and Al-C bonds breakage and recombination in ES2 and ES3, respectively. The corresponding reaction diagrams are shown in Figure S9.

Scheme S1 DMAI dissociation mechanism on Pt slabs with 1OH

$$ES1:(C_2H_5O)Al(CH_3)_2+{}^*OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_2H_5O)Al(CH_3)_2{}^*OH$$

$$ES2:(C_2H_5O)Al(CH_3)_2{}^*OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_2H_5OH+(CH_3)_2AlO^*$$

$$ES3:(C_2H_5O)Al(CH_3)_2{}^*OH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CH_4+(C_2H_5O)(CH_3)AlO^*$$

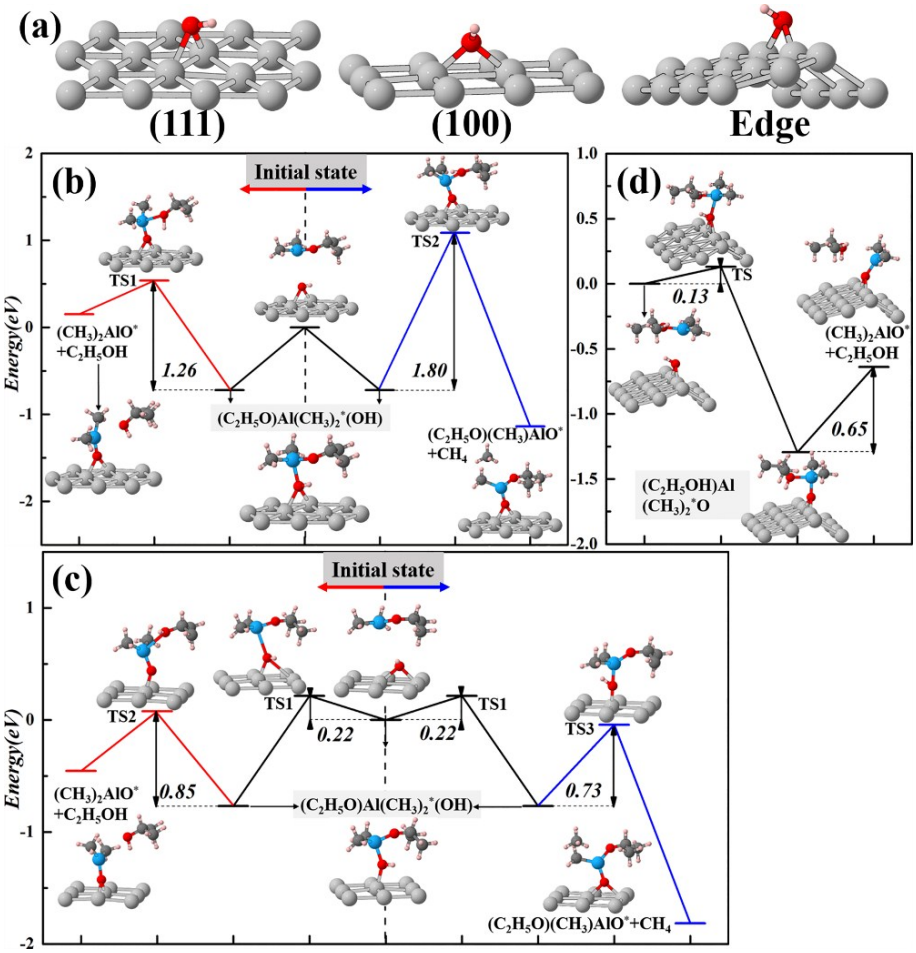

Figure S10. The configurations of (a) Pt (111), (100) and edge sites with isolate OH and the DMAI dissociation pathways on these facets: (b) (111), (c) (100) and (d) edge sites.

4. HRTEM image of AlOx decorated Pt NPs.

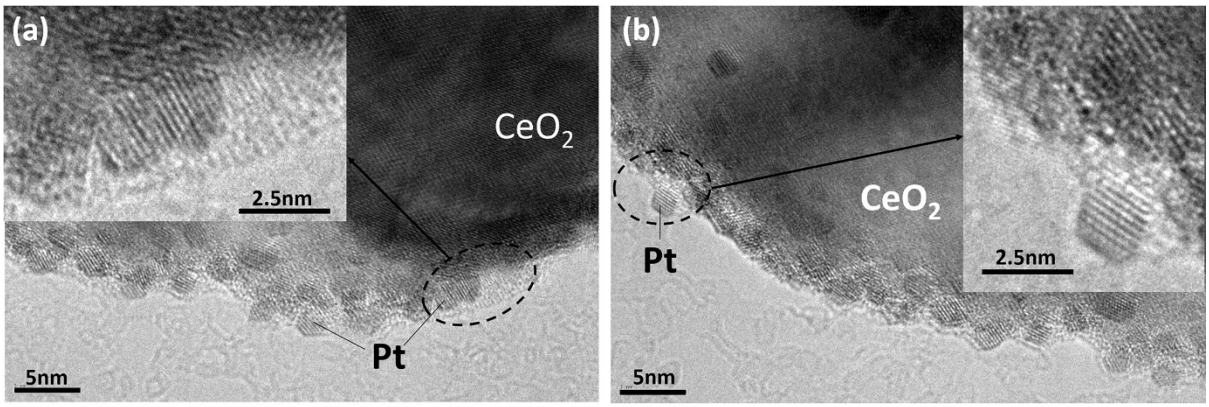

Figure S11. HRTEM image of the sample with 3 cycles AlOx on Pt NPs.

5. TMA decomposition on Pt slabs with double hydroxyls

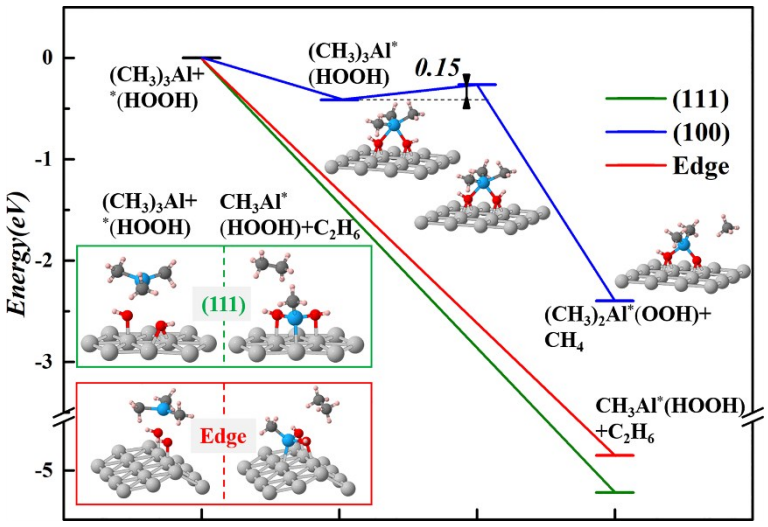

Figure S12. Trimethylaluminum (TMA) decomposition mechanism at Pt slabs with double hydroxyls.

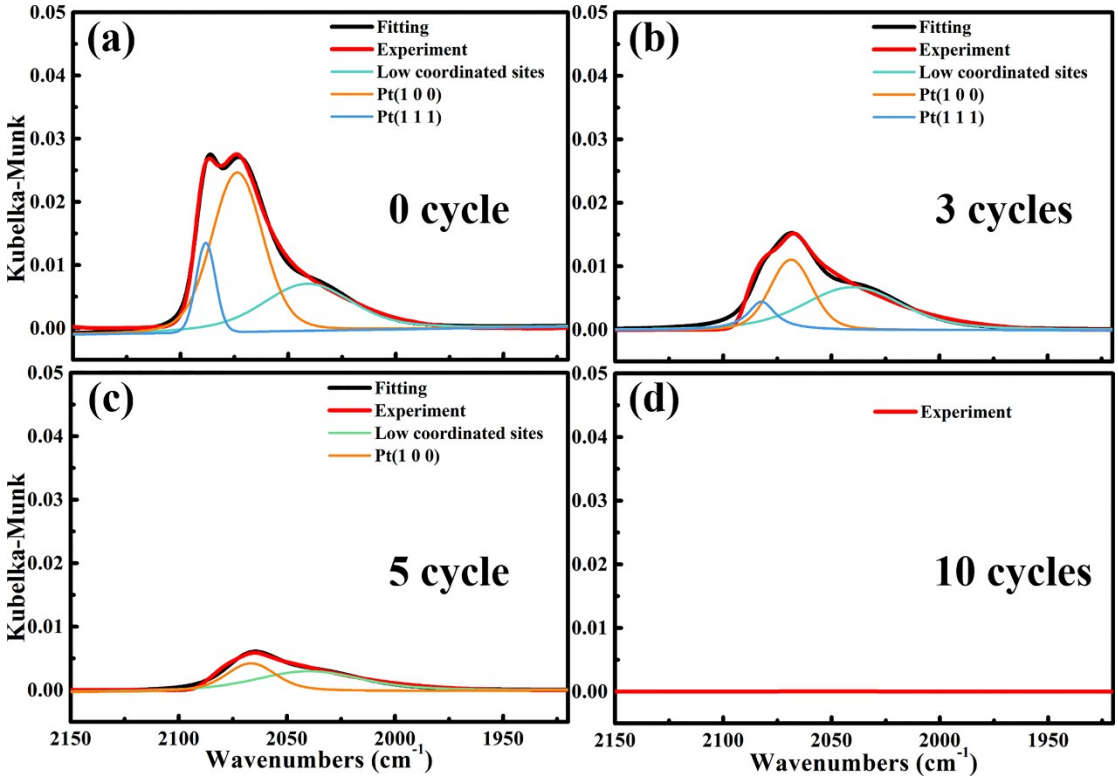

Figure S13. Fitting curves of linear CO adsorption spectra on AlOx coated Pt nanoparticles after (a) 0, (b) 3, (c) 5 and (d) 10 ALD cycles.

Figure S13 shows the fitting curves of linear CO adsorption spectra on three sites with different ALD cycles (0, 3, 5 and 10 cycles). Actually, there is already an apparent trend that with the ALD cycles increasing, the peak intensity of CO adsorption spectra towards Pt (111), (100) and edge sites gradually decrease and after 5 cycles, the signal of CO adsorption almost disappears. Hence, the phenomenon that CO adsorption signal

on three sites nearly simultaneously disappears, indicates no selectivity of AlO_x deposition on Pt nanoparticles with TMA as Al-containing precursor.