Supporting information

For

C-H bond activation by aluminum oxide cluster anions, an experimental and theoretical study

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1. Schematic diagram of reflectron TOF-MS and cluster source
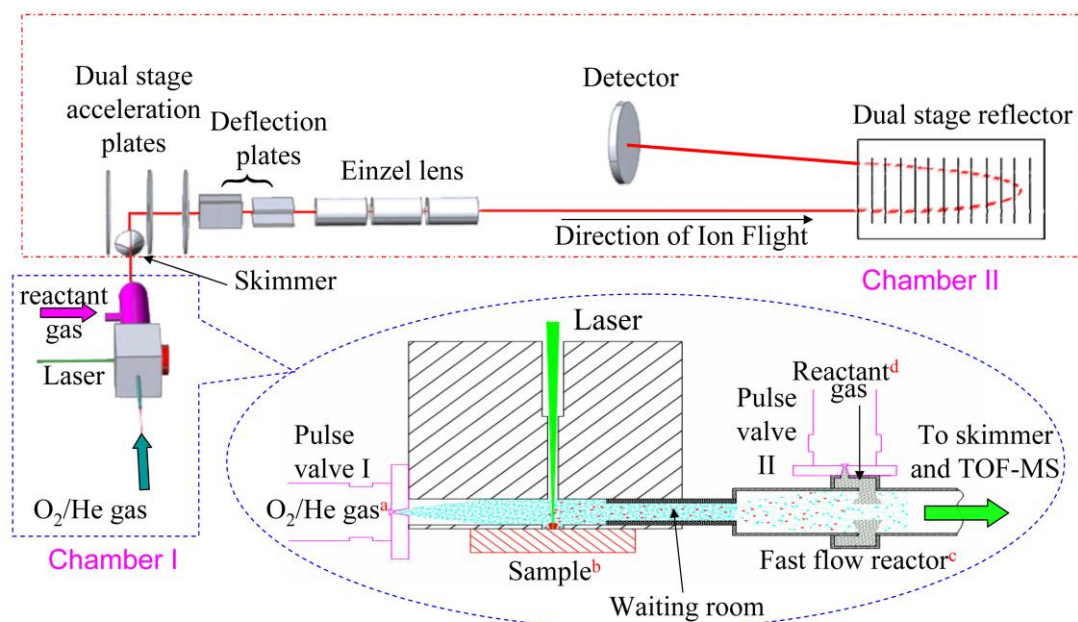

Fig. S1 A schematic diagram of the reflectron TOF-MS (Chamber II) coupled with a cluster source (Chamber I). a: carrier gas, 0.25% O_2/He with a backing pressure of 6 atm; b: aluminum metal disk (99.99% purity); c: 220 Pa at T = 300 K; d: 5% n-C_4H_{10}/He or 5% n-C_4D_{10}/He.

2. Additional theoretical results

All the provided structures are calculated at density functional theory (B3LYP) level firstly, and the structures with lower energies are re-optimized at MP2 level. Because at B3LYP level, the calculated spin density of $Al_2O_4^-$ is nearly evenly localized on the two terminally bonded oxygen atoms in its lowest-lying structure, and the calculated potential energy profile for reaction $Al_2O_4^-$ + n-C_4H_{10} is slightly dynamics unfavorable (Fig. S8, Page 10). This is not consistent with the observed hydrogen atom abstraction experimental results (Fig. 1). In Figs. S2‐S6, only the structures below or slightly higher than 2.0 eV with respect to the lowest-lying structures are given, and the structures higher than 2.5 eV are omitted. The results calculated at B3LYP level are also given in the parentheses.
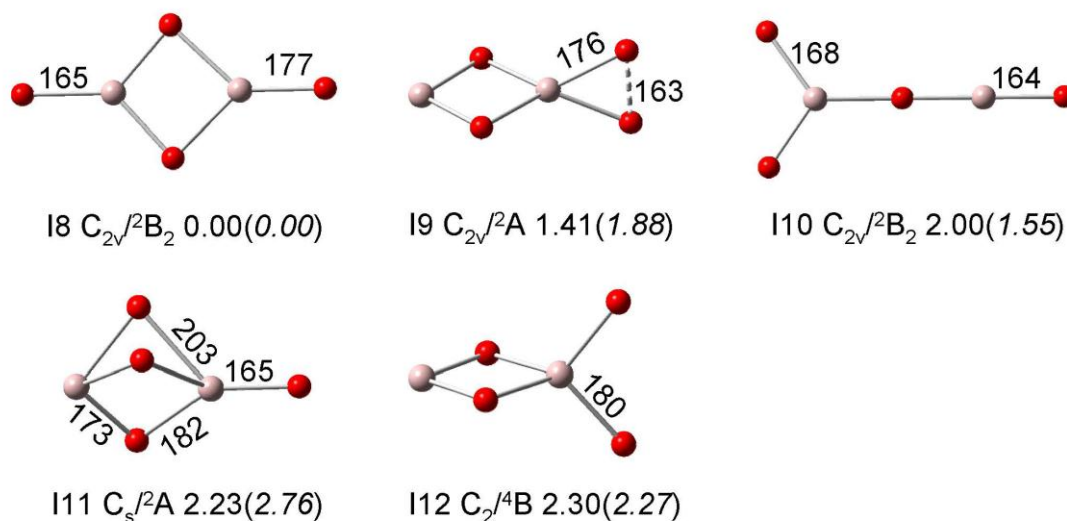
I8 C$_{2v}$/^{2}B$_2$ 0.00(*0.00*)   I9 C$_{2v}$/^{2}A 1.41(*1.88*)   I10 C$_{2v}$/^{2}B$_2$ 2.00(*1.55*)

I11 C$_s$/^{2}A 2.23(*2.76*)   I12 C$_2$/^{4}B 2.30(*2.27*)

Fig. S2 MP2/TZVP calculated lower-lying isomeric structures of **Al$_2$O$_4$**$^-$ cluster. The relative energy below each structure is zero-point vibrational energy corrected and in unit of eV. Some bond lengths are given in pm. The energies calculated at B3LYP/TZVP level are also given in the parentheses.
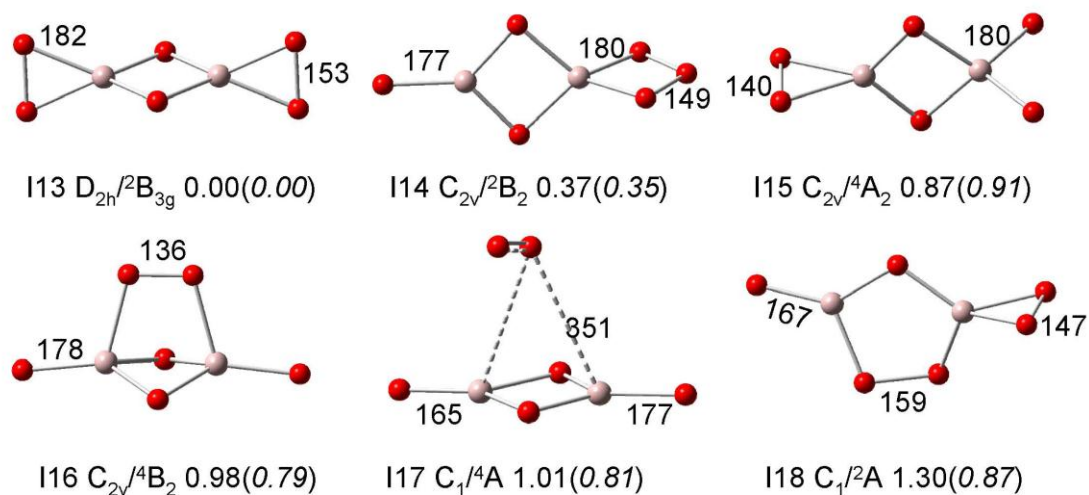
Fig. S3 MP2/TZVP calculated lower-lying isomeric structures of **Al$_2$O$_6$**$^-$ cluster. The relative energy below each structure is zero-point vibrational energy corrected and in unit of eV. Some bond lengths are given in pm. The energies calculated at B3LYP/TZVP level are also given in the parentheses.
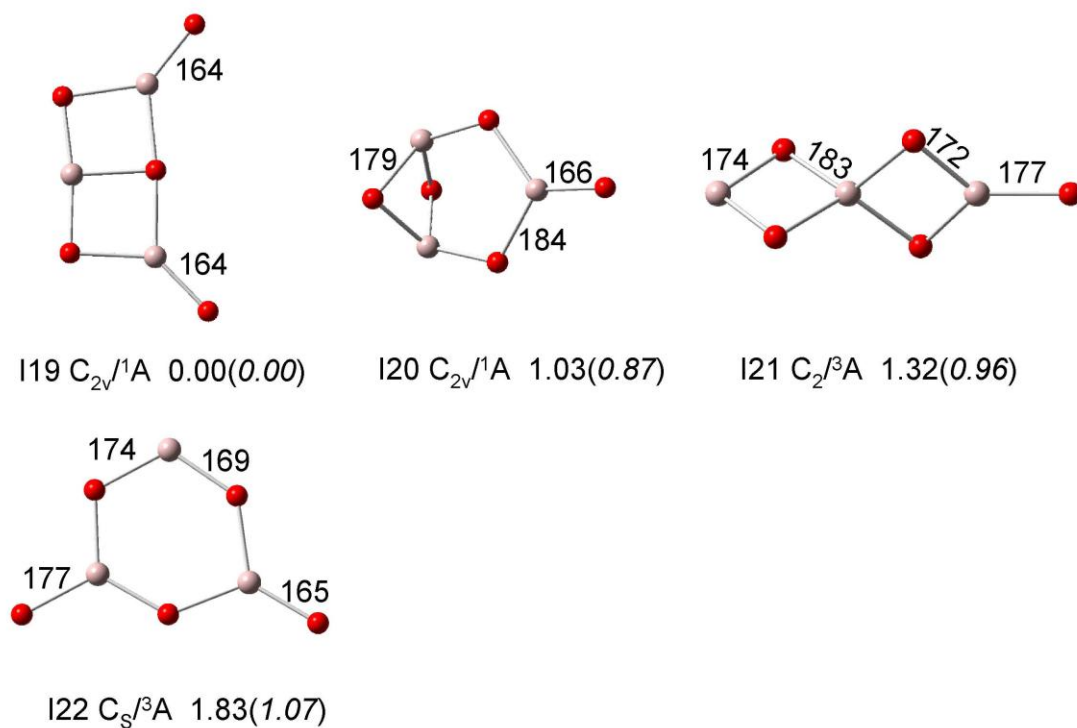
I19 C$_{2v}$/^{1}A 0.00(*0.00*)   I20 C$_{2v}$/^{1}A 1.03(*0.87*)   I21 C$_2$/^{3}A 1.32(*0.96*)

I22 C$_S$/^{3}A 1.83(*1.07*)

Fig. S4 MP2/TZVP calculated lower-lying isomeric structures of **Al$_3$O$_5^-$** cluster. The relative energy below each structure is zero-point vibrational energy corrected and in unit of eV. Some bond lengths are given in pm. The energies calculated at B3LYP/TZVP level are also given in the parentheses.
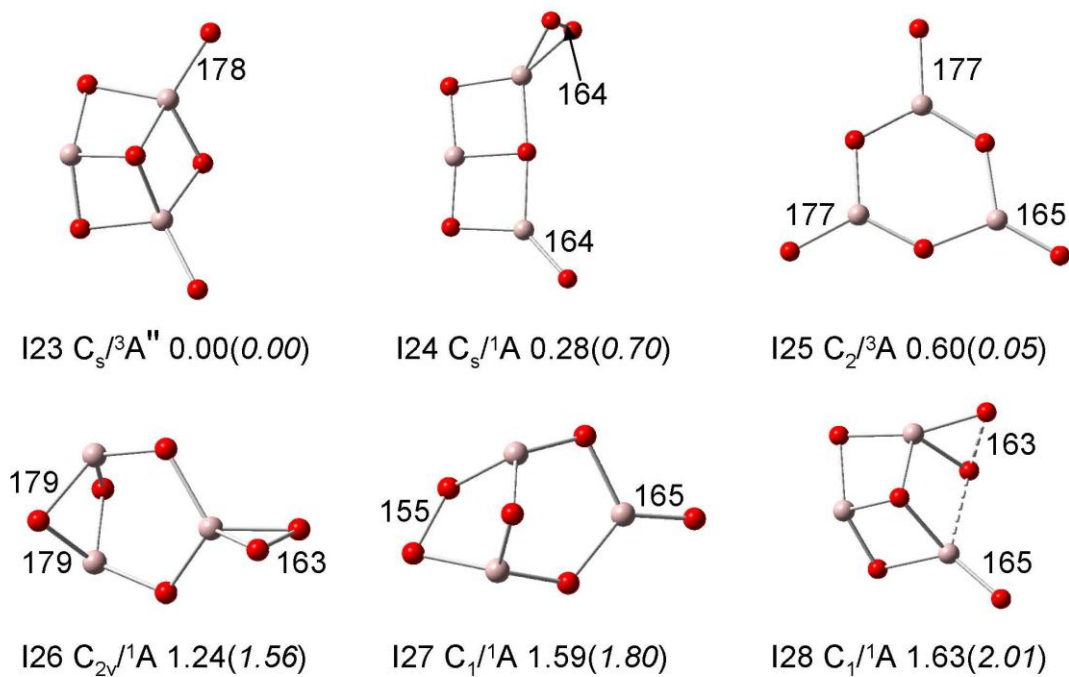
I23 C$_s$/^{3}A" 0.00(*0.00*) I24 C$_s$/^{1}A 0.28(*0.70*) I25 C$_2$/^{3}A 0.60(*0.05*)

I26 C$_{2v}$/^{1}A 1.24(*1.56*) I27 C$_1$/^{1}A 1.59(*1.80*) I28 C$_1$/^{1}A 1.63(*2.01*)

Fig. S5 MP2/TZVP calculated lower-lying isomeric structures of **Al$_3$O$_6^-$** cluster. The relative energy below each structure is zero-point vibrational energy corrected and in unit of eV. Some bond lengths are given in pm. The energies calculated at B3LYP/TZVP level are also given in the parentheses.
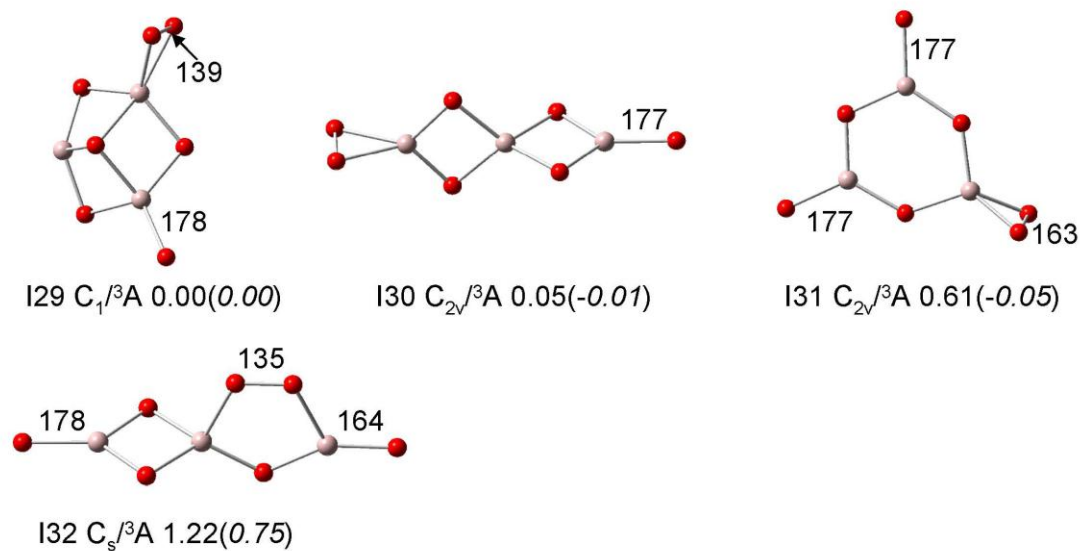
Fig. S6 MP2/TZVP calculated lower-lying isomeric structures of **Al₃O₇⁻** cluster. The relative energy below each structure is zero-point vibrational energy corrected and in unit of eV. Some bond lengths are given in pm. The energies calculated at B3LYP/TZVP level are also given in the parentheses.
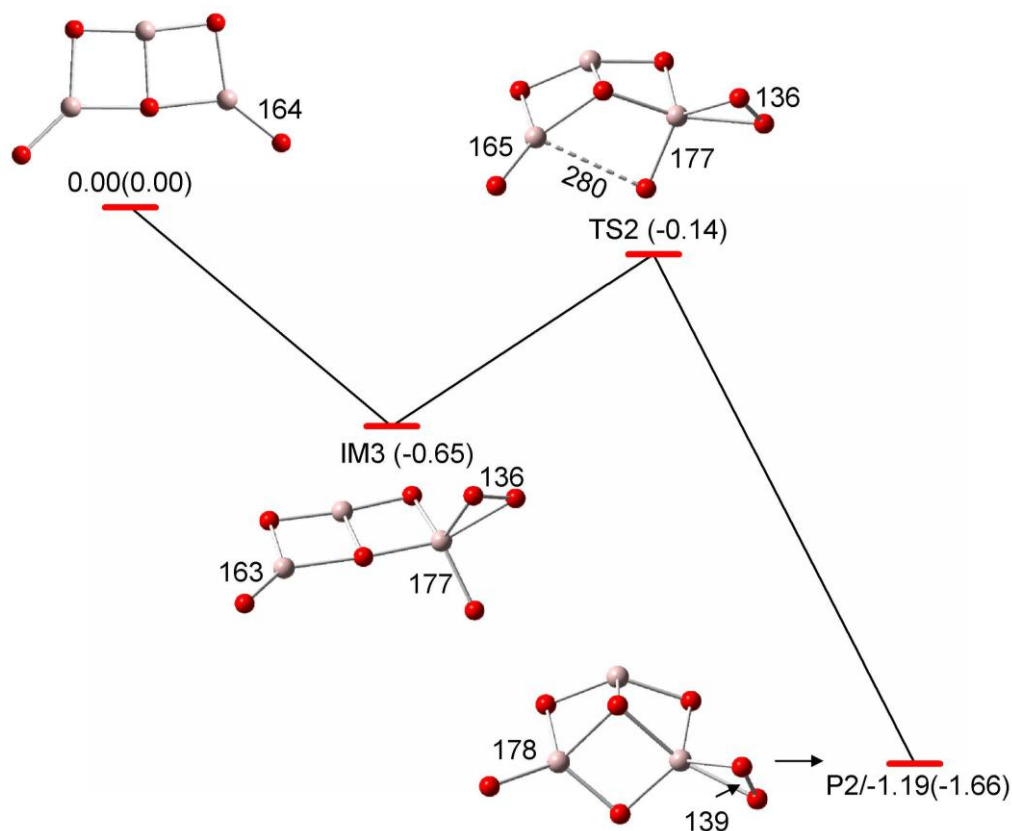
Fig. S7 The calculated potential energy profile for reaction $Al_3O_5^- + O_2 \rightarrow Al_3O_7^-$. The relative ΔH_{0K} values in eV and bond lengths in pm are given. The B3LYP-calculated values are given in the parentheses. For IM3 and TS2, only the energies calculated at B3LYP level are listed. The calculation is performed on the triplet state, because the corresponding singlet structures are much higher in energy.
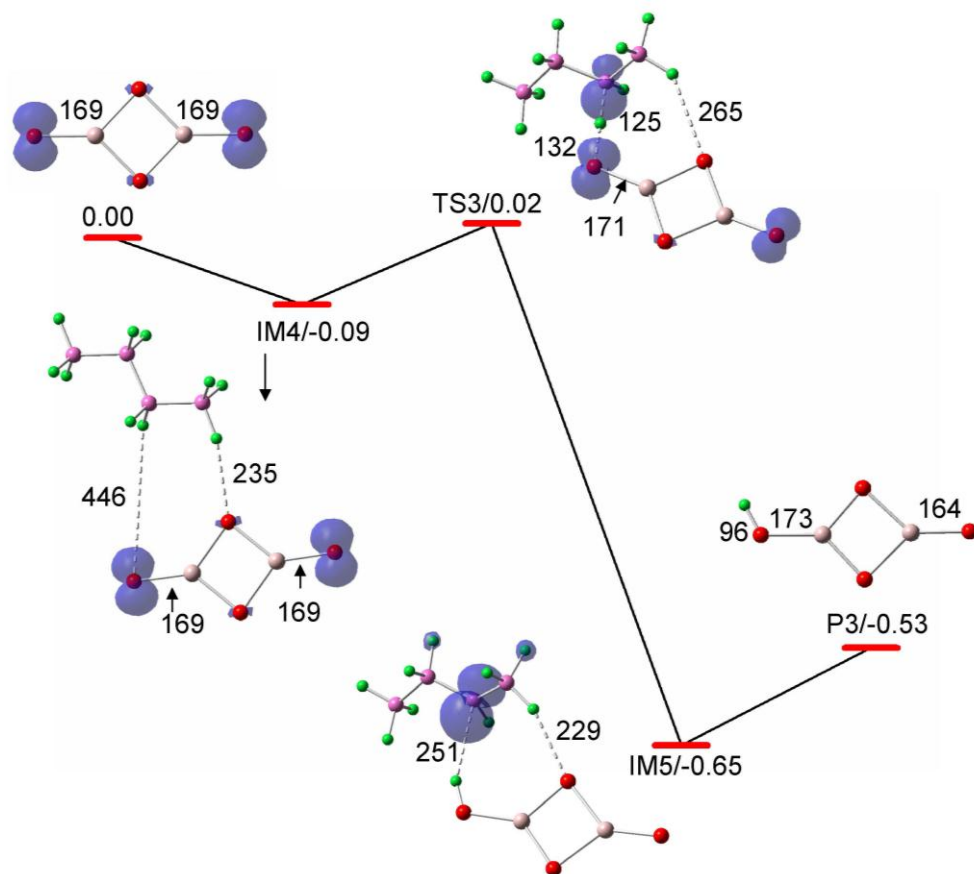
Fig. S8 B3LYP/TZVP calculated potential energy profile for reaction $Al_2O_4^- + n\text{-}C_4H_{10} \rightarrow Al_2O_4H^-$ $+ 2\text{-}C_4H_9$. The relative ΔH_{0K} values in eV and bond lengths in pm are given.