Supplementary Materials for

Conversion of Methane with Oxygen to Produce Hydrogen
Catalyzed by Triatomic Rh₃⁻ Cluster Anion

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1. Method.

Experimental Method. The negatively charged rhodium clusters (Rh\textsuperscript{−}) were generated by laser ablation of a rotating and translating Rh disk in the presence of a 6 atm He carrier gas. The reactivity experiments were carried out in a double ion trap system, which includes two quadrupole mass filters (QMF) and two linear ion traps (LIT). Among many generated Rh\textsuperscript{−} clusters, the triatomic Rh\textsubscript{3}\textsuperscript{−} ions of interest were mass-selected by using the first QMF\textsuperscript{1} and entered into the first LIT reactor,\textsuperscript{2} where they were confined and thermalized by collisions with a pulse of buffer gas He and then reacted with \textsuperscript{12}CH\textsubscript{4} or CD\textsubscript{4}. The second QMF mass-selected the product ions (e.g., Rh\textsubscript{3}CH\textsubscript{2}\textsuperscript{−}) resulting from the first LIT to inject into the second LIT for further reaction with \textsuperscript{16}O\textsubscript{2} or \textsuperscript{18}O\textsubscript{2} molecule. The Rh\textsubscript{3}O\textsuperscript{−} cluster was also generated by laser ablation of Rh disk in the presence of 0.02% \textsuperscript{16}O\textsubscript{2}/He for reaction with reductant molecules of CO and H\textsubscript{2}. The prepared Rh\textsubscript{3}O\textsuperscript{−} anions were mass-selected by a QMF, thermalized by collisions with buffer gas He, and then interacted with CO or H\textsubscript{2} in a LIT. A reflection time-of-flight mass spectrometer\textsuperscript{3} (TOF-MS) was used to detect the cluster ions ejected from the LIT reactor.

The rate constants of the reactions between cluster ions and small molecules (e.g., CH\textsubscript{4}, O\textsubscript{2}, CO or H\textsubscript{2}) were determined by using the following equations:

\[ I_R = \exp(-k_1 \times \rho \times t_R) \quad (S1a) \]
\[ I_p = 1 - \exp (k_1 \times \rho \times t_R) \quad (S1b) \]

in which \(I_R\) and \(I_p\) are the relative intensities of the reactant and product cluster ions, respectively; \(k_1\) is the pseudo-first-order rate coefficient, \(\rho\) is the molecular density of small molecules in the ion trap reactor, and \(t_R\) is the reaction time.

The photoelectron imaging spectroscopy (PEIS) experiments of reaction intermediates Rh\textsubscript{3}CH\textsubscript{2}\textsuperscript{−} and Rh\textsubscript{3}O\textsuperscript{−} were conducted with a separate apparatus of tandem TOF-MS equipped with a laser ablation cluster source, a LIT reactor, and a photoelectron imaging spectrometer. The Rh\textsubscript{3}CH\textsubscript{2}\textsuperscript{−} was generated from the reaction of pre-formed Rh\textsubscript{3}\textsuperscript{−} cluster with CH\textsubscript{4} in the LIT reactor, whereas Rh\textsubscript{3}O\textsuperscript{−} was produced by laser ablation of Rh disk in the presence of 1% \textsuperscript{16}O\textsubscript{2}/He in the cluster source. The generated ions were selected by a mass gate and crossed with a 500 nm laser beam. The electrons from photo-detachment were energy-analyzed by the photoelectron imaging spectrometer.\textsuperscript{4} The PEIS spectrum was calibrated using the spectrum of Au\textsuperscript{−} taken at the similar conditions. The resolution of the photoelectron imaging spectrometer was approximately 30 meV at electron kinetic energy of 1 eV.

Theoretical Method. The density functional theory (DFT) calculations using Gaussian 09 program\textsuperscript{5} were carried out to investigate the structures of reaction intermediates Rh\textsubscript{3}X\textsuperscript{−} (X= CH\textsubscript{2}, CO, O) as well as the reaction pathways of Rh\textsubscript{3}− + CH\textsubscript{4}, Rh\textsubscript{3}CH\textsubscript{2}− + O\textsubscript{2}, and Rh\textsubscript{3}O\textsuperscript{−} + CO. The PBE functional\textsuperscript{6} has been proved to perform well for bare rhodium clusters\textsuperscript{7} so the results by PBE method are given throughout this work. The TZVP basis sets\textsuperscript{8} for C, H and O atoms and the D95V basis set combined with the Stuttgart/Dresden relativistic effective core potentials (denoted as SDD in Gaussian software)\textsuperscript{9} for Rh atom were used. The reaction pathway calculations involved geometry optimization of reaction intermediates (IMs) and transition states (TSs) through which the IMs transfer to each other. The initial guess structures of the TS species were obtained through relaxed potential energy surface scans using single or multiple internal coordinates.\textsuperscript{10} Vibrational frequency calculations were performed to check that the IMs or TSs have zero and only one imaginary frequency, respectively. Intrinsic reaction coordinate calculations were performed so that a transition state connects two
appropriate local minima. The zero-point vibration corrected energies \(|\Delta H_0|\) in unit of eV are reported in this work.

The Rice–Ramsperger–Kassel–Marcus (RRKM) theory\(^{11}\) and RRKM-based variational transition state theory (VTST)\(^{11}\) were used to calculate (i) the rate \((k_d)\) for desorption of neutral product (e.g., CO) from the reaction intermediate \(\text{Rh}_3\text{CO}_2^-\) \((3I19)\) and (ii) the rate \((k_{IC})\) for internal conversion of \(\text{Rh}_3\text{CO}_2^-\) \((3I19)\) in the reaction pathway of \(\text{3Rh}_3\text{CH}_2^- + \text{O}_2\). For these calculations, the energy \((E)\) of the reaction intermediate and the energy barrier \((E^\ddagger)\) for each step were needed. The reaction intermediate \(\text{Rh}_3\text{CO}_2^-\) \((3I19)\) possesses the vibrational energies \((E_{\text{vib}})\) of \(\text{Rh}_3\text{CH}_2^-\) and \(\text{O}_2\), the center of mass kinetic energy \((E_k)\), and the binding energy \((E_b)\) between the separated reactants according to the distribution of degree of freedom. The \(k\) value was calculated by the Equation S2:

\[
k(E) = gN^\ddagger(E-E^\ddagger)/\rho(E)/h
\]

in which \(g\) is the symmetry factor (\(g\) is taken as 1), \(\rho(E)\) denotes the density of states of the reaction intermediates at the energy \(E\), \(N^\ddagger(E-E^\ddagger)\) is the total number of the states of the transition state with a barrier \(E^\ddagger\) \((E^\ddagger\) was zero-point-vibration corrected energy), and \(h\) is the Planck constant. The \(\rho(E)\) and \(N^\ddagger(E-E^\ddagger)\) were obtained by the direct count method\(^{12}\) with the DFT-calculated vibrational frequencies under the approximation of harmonic vibrations. The \(E_{\text{vib}}, E_b,\) and \(E^\ddagger\) were all from DFT calculations and \(E_k = \mu v^2/2\), in which \(\mu\) is the reduced mass and \(v\) is the velocity. Because no distinct transition state exists on the potential energy surfaces for desorption of CO from \(\text{Rh}_3\text{CO}_2^-\) \((3I19)\), the VTST calculations were performed through partial geometry optimizations of \(\text{Rh}_3\text{CO}_2^-\) \((3I19)\) by fixing the distance between Rh atom and C atom at variable values. The \(k(E)\) value of each step was estimated and the minimum rate was considered as the \(k_d\) value.
2. Additional experimental results for cluster reactions.

Figure S1. TOF mass spectra for the reactions of mass-selected Rh₃O₅⁻ (γ = 0 or 1) with He (a), CH₄ (b), CD₄ (c), ¹⁶O₂ (d) or H₂ (e) at room temperature. The pressures of reactant gases are shown. The reaction times are 3.6 ms for (b and c), 3.3 ms for (d1 and d2), 3.6 ms for (d3 and d4), 2.2 ms for (e), respectively. The peak marked with an asterisk in panel (d2) can be assigned to Rh₂O₃⁻ originating from the oxidation of Rh₃O⁻ that was generated from the reaction of Rh₃⁻ with residual water in the gas handling system.
Figure S2. Variations of relative ion intensities with respect to the CH₄, CD₄, ¹⁶O₂, CO or H₂ pressures in the reaction of Rh₃O⁻ (y = 0 or 1) cluster with CH₄, CD₄, ¹⁶O₂, CO or H₂. The solid lines are fitted to the experimental data points by using the equations derived with the approximation of the pseudo-first-order reaction mechanism for the reactive species.
3. Additional theoretical results for structures of reaction intermediates and reaction pathways.

Figure S3. (a) DFT calculated isomeric structures of reaction intermediate Rh$_3$CH$_2^-$. The relative energies are given in eV. The symmetry and electronic states are also shown. (b) Comparison between the experimental photoelectron spectrum and the simulated density of states (DOS) spectra for the low-lying energy isomers of Rh$_3$CH$_2^-$ with different electronic states. The DOS spectra were conducted by fitting the distribution of the transition lines with unit-area Gaussian functions of 0.40 eV full width at half maximum (FWHM).
Figure S4. (a) DFT calculated isomeric structures of reaction intermediate Rh₃O⁻. The relative energies are given in eV. The symmetry and electronic states are also shown. (b) Comparison between the experimental photoelectron spectrum and the simulated density of states (DOS) spectra for the low-lying energy isomers of Rh₃O⁻ with different electronic states. The DOS spectra were conducted by fitting the distribution of the transition lines with unit-area Gaussian functions of 0.20 eV full width at half maximum (FWHM).
Figure S5. DFT calculated potential energy profile for the reaction of $^5$Rh$_3^-$ + CH$_4$ (R1). The relative energies ($\Delta H_0$, eV) of reaction intermediates, transition states, and products with respect to the separated reactants are given. The superscript denotes the spin multiplicity.

DFT calculations about the path of $^3$Rh$_3$CH$_2^-$ $\rightarrow$ $^3$Rh$_3$C$^-$ + H$_2$ demonstrate that an overall positive barrier (+0.18 eV, $^{3}$TS8") is encountered for activation of the C−H bond in $^3$Rh$_3$CH$_2^-$. Note that the activation of the fourth C−H bond in I8 is kinetically favorable, however, the reaction of $^3$Rh$_3^-$ + CH$_4$ $\rightarrow$ $^3$Rh$_3$C$^-$ + 2H$_2$ is endothermic by 0.72 eV, in consistent with the absence of product ion Rh$_3$C$^-$ in experiments (Figure 1b in main text). By contrast, the dissociative adsorption of an O$_2$ molecule by Rh$_3$CH$_2^-$ ion significantly lowers the energy level of potential energy surfaces and renders desorption of the second H$_2$ molecule (I18 $\rightarrow$ I19) thermodynamically and kinetically favorable (Figure S7).
Figure S6. DFT calculated potential energy curves (PECs) for the interconversion of $^5\text{I}_4 \rightarrow ^3\text{TS}_4$ in the reaction of $^5\text{Rh}_3^- + \text{CH}_4$ (Figure S5). The curve for the triplet state was obtained from the intrinsic reaction coordinate (IRC) calculation. The energies of the quintet states were calculated at the IRC determined geometries of triplet states. The relative energies with respect to the separated reactants ($^5\text{Rh}_3^- + \text{CH}_4$) are shown without zero-point vibration correction. The relative energy of the crossing point (CP1) with zero-point vibration correction is $-0.42$ eV.
**Figure S7.** DFT calculated potential energy profile for the reaction of $^3\text{Rh}_3\text{CH}_2^-$ ($^1\text{TS3}$) with O$_2$. The relative energies ($\Delta H_0$, eV) of reaction intermediates, transition states, and products with respect to the separated reactants ($^1\text{Rh}_3\text{CH}_2^- + \text{O}_2$) are given. The superscript denotes the spin multiplicity.
Figure S8. DFT calculated potential energy curves (PECs) for the interconversion of $^{3}\text{TS19} \rightarrow {5}\text{I22}$ in the reaction of $^{3}\text{RhCH}_2^- + \text{O}_2 \rightarrow {5}\text{Rh}^- + \text{H}_2 + \text{CO}_2$ (Figure S7). The curve for the triplet state was obtained from the intrinsic reaction coordinate (IRC) calculation. The energies of the quintet states were calculated at the IRC determined geometries of triplet states. The relative energies with respect to the separated reactants ($^{3}\text{RhCH}_2^- + \text{O}_2$) are shown without zero-point vibration correction. The relative energy of the crossing point (CP2) with zero-point vibration correction is $-3.66$ eV.
Figure S9. DFT calculated potential energy profile for the reaction of $^3\text{Rh}_3\text{CH}_2^-$ ($^3\text{IS3}$) + O$_2$ → $^3\text{Rh}_3\text{O}^-$ + CH$_2$O. The relative energies ($\Delta H_0$, eV) of reaction intermediates, transition states, and products with respect to the separated reactants ($^3\text{Rh}_3\text{CH}_2^- + \text{O}_2$) are given. The superscript denotes the spin multiplicity.
Table S1. The virtual frequency values of all of the transition states shown in Figures 4 (main text), S5, S7, and S9.

| TSs  | Frequency (cm⁻¹) | TSs  | Frequency (cm⁻¹) |
|------|------------------|------|------------------|
| ⁵TS1 | −741.06          | ³TS13| −116.40          |
| ⁵TS2 | −82.37           | ³TS14| −325.10          |
| ⁵TS3 | −62.16           | ³TS15| −174.39          |
| ³TS4 | −762.54          | ³TS16| −577.41          |
| ³TS5 | −838.54          | ³TS17| −215.27          |
| ³TS6 | −226.54          | ³TS18| −89.26           |
| ³TS7 | −327.76          | ³TS19| −366.75          |
| ³TS8' | −781.49         | ⁵TS20| −20.86           |
| ³TS8''| −793.88         | ³TS21| −163.22          |
| ³TS8 | −432.77          | ³TS22| −166.76          |
| ³TS9 | −148.31          | ³TS23| −184.18          |
| ³TS10| −131.31          | ³TS24| −283.03          |
| ³TS11| −402.65          | ³TS25| −764.14          |
| ³TS12| −188.29          | ³TS26| −105.59          |
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