Electronic Supplementary Information for

Porous Nanographene Formation on γ-Alumina Nanoparticles via Transition-Metal-Free Methane Activation

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**S1. Materials and Methods**

**S1.1 Sample**
Methane (CH$_4$) was purchased from Sumitomo Seika Chemicals Co., Ltd. with Pure grade (>99.0%) and SEG grade (>99.99%). Deuterated methane (CD$_4$, 99%-d) was purchased from Cambridge Isotope Laboratories, Inc. (DLM-144-PK, Lot: l-23094/E10089963). High purity γ-alumina nanoparticles (ANPs, TH 80/170; γ-Al$_2$O$_3$, particle size: ~10 nm, specific surface area: 158 m$^2$ g$^{-1}$) were donated from Sasol Limited. with Na (equivalent to Na$_2$O) = 20 ppm and Fe (equivalent to Fe$_2$O$_3$) = 50‒100 ppm. All the chemicals were used as received unless otherwise noted.

**S1.2 Reaction Kinetics**
Thermogravimetry was conducted on a thermogravimeter (Netzsch, STA 2500 Regulus) under a steady flow of He with various concentration of CH$_4$ at the total flow rate of 100 mL min$^{-1}$. The standard reactor volume was 50 mL. To suppress air contamination during the analysis, the thermogravimeter was surrounded by a chamber filled with Ar gas supplied at a flow rate of 1 L min$^{-1}$. Typically, 32 mg of γ-ANPs was used for the kinetic analysis of CH$_4$-CVD. The samples were loaded on the reactor of the thermogravimeter, and first heated from room temperature to a specified temperature (1128 – 1173 K) at 10 K min$^{-1}$ under a steady flow of He. This was followed by the constant-temperature heating at the specified temperature for 30 min under a steady flow of He. After the pretreatment, CH$_4$ was introduced to the reactor with a specified partial pressure to initiate CH$_4$-CVD. The rate of CH$_4$-CVD for the kinetic analysis of the first-layer deposition was determined at an inflection point. Formation of nanoporous graphene was confirmed by x-ray diffraction and Raman spectroscopy (Figure S1).

**S1.3 Characterization of γ-Al$_2$O$_3$ Nanoparticles**
High resolution annular dark-field scanning transmission electron microscopy (ADF-STEM) images were captured using JEM-ARM200-F (JEOL Ltd, Japan) at an accelerating voltage of 200kV.

*In situ* infrared (IR) spectra of the Al$_2$O$_3$ nanoparticles (ca. 18.0 mg) at the specified temperature were recorded on a Nicolet 6700 FT-IR spectrometer (ThermoScientific) with a diffuse reflectance infrared Fourier transform (DRIFT) method under a steady flow of Ar at 30 mL min$^{-1}$. The intensity was reported as the Kubelka-Munk function. In the temperature of the sample during the *in-situ* IR measurements was monitored by using an infrared thermometer (Keyence, FT-H40K) to ensure the temperature. We performed 120 scans.

Temperature programmed desorption (TPD) was measured on a gas chromatogram (GC, Varian 490-GC, GL Science). Approximately 1 g of γ-ANP was gently packed in a quartz reactor tube with stacked height of 3~4 cm using quartz wool (4-9 μm, Toso Company, Ltd.). The reactor tube was heated at the rate of 10 K min$^{-1}$ under a steady flow of He (200 mL min$^{-1}$), and the evolved H$_2$O was analyzed by GC. The sampling interval was approximately 2.5 min.
TPD of $\text{H}_2\text{O}$ was immediately followed by TPD of $\text{NH}_3$ with the same configuration of experiment. All the processes are under a steady flow at a total flow rate of 200 mL min$^{-1}$. After cooling to r.t. under He, a mixture of 1.0% of $\text{NH}_3$ and 99% of He was introduced to the quartz reactor tube for 30 min. Then, the reactor tube was subjected to a steady flow of 100% He for 60 min to remove off the gas-phase $\text{NH}_3$. The reactor tube was then heated at the rate of 5 K min$^{-1}$ under a steady flow of He, and the desorbed $\text{NH}_3$ was analyzed by GC.

Magic-angle-spinning (MAS) $^{27}\text{Al}$ nuclear magnetic resonance (NMR) of solid samples were recorded on a JEOL ECA800 (208 MHz) spectrometer. Samples were spun at 25 kHz. The data acquisition employed short radiofrequency pulses (18° flip angle) with relaxation delays of 10 s. The chemical shifts have been reported in $\delta$ ppm units with reference to an external standard of a 1 M aqueous solution of aluminium nitrate ($\text{Al(NO}_3)_3$, 0.00 ppm).

**S1.4 Quantum Chemistry Calculations**

Density functional theory (DFT) calculations on $\gamma\text{-Al}_2\text{O}_3$ surfaces with methane were performed by using the “Vienna ab initio simulation package” (VASP, version 6.1.1).$^{52}$ We performed geometry optimization of local minima (EQs) and transition states (TSs) with the Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA) for the exchange and correlation terms,$^{53}$ together with the Grimme’s-D3 dispersion correction.$^{54}$ A plane-wave basis set was employed within the framework of the projector augmented wave method.$^{55,56}$ The plane-wave cutoff was 450 eV. K-point mesh ware sampled by the (3×3×1) Monkhorst-Pack $k$-point sampling scheme. We used the threshold of self-consistent field energy calculation of $1.0 \times 10^{-6}$ eV atom$^{-1}$.

The surface of $\gamma\text{-Al}_2\text{O}_3$ was modeled using a supercell approach with periodic boundary conditions. To generate the surface models, we first optimized the internal coordinates and cell parameters of the bulk structure of $\gamma\text{-Al}_2\text{O}_3$. As a starting point, we used the coordinates of $\gamma\text{-Al}_2\text{O}_3$ (P2$_1$/m space group).$^{59}$ The optimized lattice parameters of $\gamma\text{-Al}_2\text{O}_3$ were found to be $a = 5.538$ Å, $b = 8.347$ Å, $c = 8.024$ Å, $\beta = 90.60$ deg and $\alpha = \gamma = 90.00$ deg, in good agreement with previous DFT calculations using the dual-range local meta-GGA ML-11 functional and the meta non-separable gradient approximation MN12-L functionals.$^{57}$ Starting from the optimized structure, we constructed a partially hydrated $\gamma\text{-Al}_2\text{O}_3$ (100) surface with an oxygen vacancy as a surface slab containing 96 atoms (corresponding to 4 atomic layers) with a thickness of 12 Å and a vacuum of 15 Å. The initial surface hydration was 7.1 μmol m$^{-2}$. During the structural optimization for $\gamma\text{-Al}_2\text{O}_3$, the all atoms were relaxed. The structure of the triclinic surface unit cell was $a = 8.071$ Å, $b = 8.404$ Å, $c = 26.383$ Å, and $\alpha = \beta = \gamma = 90.00$ deg.

TSs for the elementary reactions were located by using the climbing image nudged elastic band (CI-NEB) method.$^{58,59}$ The convergence of forces for the geometry optimizations of both EQs and TSs were set to be 0.03 eV Å$^{-1}$. All optimized structures are collected in S3 according to the POSCAR format for VASP.

The VASPKIT was used to deal with the charge density and the spin density.$^{510}$ Atomistic models of alumina surfaces were constructed according to the results of ADF-STEM, TPD, and IR analysis of $\gamma$-ANPs. Previous DFT calculations suggest that (100) and (110) surfaces are the most stable surface of $\gamma\text{-Al}_2\text{O}_3$,$^{511}$ and indeed the high-resolution ADF-STEM of $\gamma$-ANPs (Figure 2) shows the presence of {100} surfaces. Significant desorption of water upon heating$^{511,512}$ was confirmed by TPD (Figure 3b), while isolated hydroxyl groups at around 3701 cm$^{-1}$ were confirmed by IR (Figure 3a) to remain even after annealing at 900 ºC for 30
min. Indeed, introduction of hydroxyl groups on surface models gave both thermodynamically and kinetically favored process in CH$_4$ activation on surfaces of $\gamma$-Al$_2$O$_3$.$^{312,13}$

**S2. Supplementary Figures, Tables, and Discussions**  
**S2.1 Characterization of Nano-Porous Graphene (NPG)**

![Figure S1](image)

*Figure S1.* (a) XRD patterns and (b) Raman spectra of nano-porous carbon (NPC) and nano-porous graphene (NPG).

NPG was prepared and characterized by N$_2$ physisorption, XRD, and Raman spectroscopy. The specific surface area of NPC was determined by N$_2$ physisorption and the subsequent BET analysis to be $2.3 \times 10^3$ m$^2$ g$^{-1}$, while NPG gave $1.8 \times 10^3$ m$^2$ g$^{-1}$. These values are well approaching to an ideal value for 2-dimensional graphene (2627 m$^2$ g$^{-1}$). Single-layered deposition by CH$_4$-CVD with a specified reaction time was also confirmed by TEM.$^{314}$ Both XRD and Raman showed single-walled nature of NPG: The suppressed 002 peaks at $2\theta = 22^\circ$ for carbons indicates the fewer stacking of graphene layer, while sharp peaks for 10 at $2\theta = 43^\circ$ indicates the successful growth of hexagons (nanographene) developed in a 2D plane.$^{314}$ Raman spectra of NPG showed an intensifed and red-shifted G’-band, supporting the growth of single-walled graphene structures$^{314-316}$ in NPG after annealing.
S2.2 Reductive treatment of ANP by H₂ before CH₄-CVD

**Figure S2.** Kinetic analysis of CH₄-CVD for porous nanographene with or without pre-treatment of H₂ gas before CH₄-CVD. For the control experiment, He was introduced instead of H₂ for the same period. (a) Weight changes during CH₄-CVD at 900°C as monitored by TG. CH₄ was introduced to the reactor at 0 min. (b) The rate of reaction for CH₄-CVD.
S2.3 Surface Characterization by STEM

**Figure S3.** High resolution STEM-ADF image of γ-ANPs. (a–e) [100] orientation, and (f) [110] orientation.
S2.4 Stability of Surface OH groups toward Surface Activation

In order to analyze the stability of the OH groups on the γ-ANP surface for the surface activation, we performed the in-situ IR experiments under a steady flow of CD$_4$. We find that almost all protons are labile in the presence of CD$_4$ at temperatures higher than 600 °C (Figures S4, S5) while the structure of bulk region remained almost unchanged during the CH$_4$-CVD according to the $^{27}$Al NMR spectra (Figure S9). The D-H exchange between CD$_4$ and isolated OH groups occurred on the γ-ANP surface above 600 °C, and the OH stretching band at $\nu_{OH} = 3701$ cm$^{-1}$ depressed with time constants of 1.2 min and the OD stretching band at $\nu_{OD} = 2730$ cm$^{-1}$ evolved as shown in Figure S4.

This isotope shift can be quantitively rationalized by the change of the reduced mass $\mu$ by the H-D exchange. The vibration frequency $\nu$ of the OH stretching mode is described in eq. (S1) under the harmonic approximation,

$$
\nu = \frac{1}{2\pi} k_f \mu = \frac{1}{2\pi} \left( \frac{k_f}{m_O m_H} \right),
$$

(S1)

where $m_O = 16$ amu, and $m_H = 1$ amu are the masses of oxygen and hydrogen atoms, respectively. The effect of isotope exchange on the vibrational force constant $k_f$ is negligible and the frequency of the deuterated system $\nu_{OD}$ can be written as the rate between reduced mass of OD group $\mu_{OD}$ and that of OH $\mu_{OH}$, and the frequency of the original system $\nu_{OH} = 3701$ cm$^{-1}$,

$$
\nu_{OD} = \sqrt{\frac{m_O m_D}{m_O + m_D}} \nu_{OH},
$$

(S2)

where $m_D = 2$ amu is the mass of deuterium. Resultant $\nu_{OD}$ is calculated to be 2693 cm$^{-1}$, which qualitatively agrees with the experimental value (2730 cm$^{-1}$).
**Figure S4.** Temporal profiles of the OH stretching bands in IR spectra of ANPs at 900 °C (a) in the presence of CH$_4$ (2 mL min$^{-1}$) and (b) in the presence of CD$_4$ (2 mL min$^{-1}$). Depletion at 2350 cm$^{-1}$ is due to CO$_2$.

![Kubelka-Munk Plot](image)

**Figure S5.** Time-course of IR spectra of γ-ANPs in the presence of CD$_4$ at the elevation rate of 16.7 K min$^{-1}$ from 600 °C to 850 °C. Depletion at 2350 cm$^{-1}$ is due to CO$_2$.

**S2.5 Stability of Oxygen Vacancy Sites and Reactivity of CH$_4$ on Them**

**Table S1.** Summary of H$_2$O/NH$_3$ TPD$^a$ and CH$_4$-CVD.

| Conditions for pre-activation$^b$ | Evolved gas | Rate of reactions$^d$ |
|----------------------------------|-------------|----------------------|
|                                  | H$_2$O$^c$  | NH$_3$               |                          |
| 700 °C for 30 min                | 1.1 mmol g$^{-1}$ | 33 μmol g$^{-1}$ | ---                     |
| 900 °C for 30 min                | 1.4 mmol g$^{-1}$ | 19 μmol g$^{-1}$ | 4.8 × 10$^{-9}$ mol s$^{-1}$ |
| 1000 °C for 30 min               | 1.5 mmol g$^{-1}$ | 21 μmol g$^{-1}$ | 3.6 × 10$^{-9}$ mol s$^{-1}$ |

$^a$ The details are shown in the section S1.3; $^b$ under a steady flow of He; $^c$ The amount of water desorbed at the temperatures higher than 300 °C; $^d$ The rate for the first-layer deposition under the standard CH$_4$-CVD condition at 900 °C with a steady flow of CH$_4$ (20 mL min$^{-1}$).
Figure S6. Black line: Energy profile for the formation of a CH$_4$ $\sigma$ complex and the subsequent C–H bond cleavage on a $\gamma$-Al$_2$O$_3$ (100) surface. Red line: Conversion of CH$_4$ to CH$_3$OH on a $\gamma$-Al$_2$O$_3$ (100) surface. The reactive site is a 5-coordinated-Al.
Figure S7. (a) Geometry of a γ-Al$_2$O$_3$ (100) surface with an adsorbed CH$_4$ and (b) the same geometry without CH$_4$ for clarity. Red: oxygen, Blue: aluminum, gray: carbon, and white: hydrogen atoms. The reactive site is tetrahedrally-coordinated (4-coordinated) Al center, and the coordinate is the same for CH$_4^*$ in Figure 4a of the manuscript. The coordinates are shown in Section S3.
**Table S2.** Calculated Bader charges $q$ (in units of $|e|$) of adsorbed CH$_4$* and CH$_3$* species on a γ-Al$_2$O$_3$ (100) surface associated with the CH$_4$ → CH$_3$ + H elementary step. The value in brackets indicates the formal oxidation state corresponding to the Bader charge.

| Property      | Initial State | Transition State (TS1) | Final State |
|---------------|---------------|------------------------|-------------|
| $q$(CH$_4$*)  | $-0.005$      | ---                    | ---         |
| $q$(CH$_3$*)  | ---           | $-0.65$                | $-0.61$     |
| $q$(C)        | $-0.16$       | $-0.77$                | $-0.71$     |
| $q$(H3*des)   | $+0.071$      | $+0.66$                | $+0.66$     |
| $q$(Al7)      | $+2.43 (+3)$  | $+2.35 (+3)$           | $+2.35 (+3)$|
| $q$(O23)      | $-1.58 (-2)$  | $-1.49 (-2)$           | $-1.59 (-2)$|

**Table S3.** Calculated Bader charges $q$ (in units of $|e|$) of adsorbed CH$_3$* and CH$_2$* species on a γ-Al$_2$O$_3$ (100) surface associated with the CH$_3$ → CH$_2$ + H elementary step. The value in brackets indicates the formal oxidation state corresponding to the Bader charge.

| Property      | Initial State | Transition State (TS2) | Final State |
|---------------|---------------|------------------------|-------------|
| $q$(CH$_3$*)  | $-0.61$       | ---                    | ---         |
| $q$(CH$_2$*)  | ---           | $-0.71$                | $-0.71$     |
| $q$(C)        | $-0.71$       | $-0.89$                | $-0.80$     |
| $q$(H5*des)   | $+0.06$       | $+0.64$                | $+0.67$     |
| $q$(Al7)      | $+2.35 (+3)$  | $+2.35 (+3)$           | $+2.38 (+3)$|
| $q$(O45)      | $-1.63 (-2)$  | $-1.50 (-2)$           | $-1.57 (-2)$|
**Figure S8.** Energy profile for the formation of a CH$_4$ $\sigma$ complex and the subsequent C–H bond cleavage on a $\gamma$-Al$_2$O$_3$(100) surface with no oxygen defect. The reactive site is an octahedrally-coordinated (6-coordinated) Al center, and the clouded surface gives radical mechanism rather than the Lewis acid-base mechanism for the bond cleavage reaction.
**Figure S9.** Normalized MAS $^{27}$Al NMR of γ-ANPs before and after CH$_4$-CVD. Relative intensity of the peak for octahedrally coordinated Al-center ($[6]$Al) in the up-field ($\delta = 9$ ppm)$^{517}$ was enhanced as compared with that for tetrahedrally coordinated Al-center ($[4]$Al) in the down-field ($\delta = 68$ ppm)$^{517}$ after CH$_4$-CVD.
Figure S10. XRD of γ-ANPs before (ANP) and after CH₄-CVD (C/ANP).
Curvature reflecting the difference in the rates of CH₄-CVD reactions was recognized at nearly single-layered deposition of carbon (Figs. 1a and 1b), but there was exception at higher partial pressure of CH₄ or at lower temperatures showing the curvature at the number of carbon layers > 1. We also noticed such exceptions for θ-ANP and α-ANP (Fig. S11). This could indicate that a mixture growth on the Al₂O₃ nanoparticles (first layer) and on carbon layer (second layer) was significant under these conditions. Thus, lower partial pressure of CH₄ and higher reaction temperatures as well as the use of γ-ANP would be important for single-layered carbon deposition.

**Figure S11.** Time-course of weight changes during CH₄-CVD on various crystal structures of Al₂O₃ at 900 ºC as monitored by TG.
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Supporting Information
S3. Appendix: Optimized Structures and Energies in Quantum Chemistry Calculations

S3.1 Optimized Structures and Energies for Figure 4

Coordinate for a γ-Al₂O₃ (100) surface with CH₄ σ-complex with a surface proton density of 7.1 μmol m⁻² at a 4-coordinated Al site.

Spin Multiplicity <S²>: 0.006

Absolute Energy: −719.479682 eV.

cell_length_a 8.07075

cell_length_b 8.40443

cell_length_c 26.38316

cell_angle_alpha 90

cell_angle_beta 90

cell_angle_gamma 90

symmetry_space_group_name_H-M 'P 1'
symmetry_Int_Tables_number 1

| Atom | x | y   | z    |   |
|------|---|-----|------|---|
| H    | 1.0 | 0.012525 | 0.411272 | 0.458504 | H |
| H2   | 1.0 | 0.389156 | 0.758581 | 0.967927 | H |
| H3   | 1.0 | 0.698026 | 0.308049 | 0.531916 | H |
| H4   | 1.0 | 0.739746 | 0.514269 | 0.518631 | H |
| H5   | 1.0 | 0.530180 | 0.443189 | 0.520374 | H |
| H6   | 1.0 | 0.646493 | 0.458356 | 0.577451 | H |
| H7   | 1.0 | 0.865656 | 0.323823 | 0.970992 | H |
| H8   | 1.0 | 0.746757 | 0.853057 | 0.493596 | H |
| C1   | 1.0 | 0.654231 | 0.430645 | 0.536903 | C |
| O1   | 1.0 | 0.110810 | 0.590287 | 0.157363 | O |
| O2   | 1.0 | 0.126991 | 0.579497 | 0.367156 | O |
| O3   | 1.0 | 0.616791 | 0.907808 | 0.048522 | O |
| O4   | 1.0 | 0.618926 | 0.917007 | 0.260722 | O |
| O5   | 1.0 | 0.844216 | 0.414243 | 0.993966 | O |
| O6   | 1.0 | 0.863210 | 0.412263 | 0.207681 | O |
| O7   | 1.0 | 0.830444 | 0.416952 | 0.419161 | O |
| O8   | 1.0 | 0.368215 | 0.102009 | 0.097134 | O |
| O9   | 1.0 | 0.363299 | 0.085661 | 0.312928 | O |
| O10  | 1.0 | 0.910452 | 0.097248 | 0.108539 | O |
| O11  | 1.0 | 0.901999 | 0.110408 | 0.320372 | O |
| O12  | 1.0 | 0.418851 | 0.425306 | 0.999761 | O |
| O13  | 1.0 | 0.396402 | 0.420826 | 0.210593 | O |
| O14  | 1.0 | 0.401961 | 0.441531 | 0.423833 | O |
| O15  | 1.0 | 0.159017 | 0.913791 | 0.060543 | O |
| O16  | 1.0 | 0.152386 | 0.907277 | 0.268392 | O |
| O17  | 1.0 | 0.644021 | 0.580040 | 0.158151 | O |
| O18  | 1.0 | 0.638591 | 0.601353 | 0.369087 | O |
| O19  | 1.0 | 0.907293 | 0.404002 | 0.107473 | O |
| O20  | 1.0 | 0.908088 | 0.411988 | 0.322313 | O |
| O21  | 1.0 | 0.421249 | 0.085696 | 0.000782 | O |
| O22  | 1.0 | 0.396766 | 0.084955 | 0.212754 | O |
| O23  | 1.0 | 0.426853 | 0.132654 | 0.444146 | O |
| O24  | 1.0 | 0.156904 | 0.597636 | 0.059375 | O |
| O25  | 1.0 | 0.156913 | 0.596491 | 0.269328 | O |
| O26  | 1.0 | 0.643976 | 0.920901 | 0.159718 | O |
| O27  | 1.0 | 0.646395 | 0.916486 | 0.382605 | O |
| O28  | 1.0 | 0.112524 | 0.911602 | 0.158270 | O |
| O29  | 1.0 | 0.103110 | 0.923428 | 0.366921 | O |
| O30  | 1.0 | 0.617146 | 0.603980 | 0.047211 | O |
| O31  | 1.0 | 0.618472 | 0.589456 | 0.258414 | O |
| O32  | 1.0 | 0.845170 | 0.118494 | 0.998522 | O |
| O33  | 1.0 | 0.863477 | 0.097272 | 0.207279 | O |
| O34  | 1.0 | 0.845781 | 0.093978 | 0.425296 | O |
|   |   |   |   |   | Al   |
|---|---|---|---|---|---|
| O35 | 1.0 | 0.366314 | 0.408812 | 0.095626 | O   |
| O36 | 1.0 | 0.369713 | 0.412090 | 0.310746 | O   |
| O37 | 1.0 | 0.137828 | 0.253004 | 0.157850 | O   |
| O38 | 1.0 | 0.142084 | 0.251362 | 0.371803 | O   |
| O39 | 1.0 | 0.638516 | 0.258524 | 0.057742 | O   |
| O40 | 1.0 | 0.647124 | 0.253117 | 0.260716 | O   |
| O41 | 1.0 | 0.891289 | 0.752840 | 0.109178 | O   |
| O42 | 1.0 | 0.894881 | 0.740346 | 0.320221 | O   |
| O43 | 1.0 | 0.330572 | 0.756593 | 0.000109 | O   |
| O44 | 1.0 | 0.363575 | 0.752308 | 0.213126 | O   |
| O45 | 1.0 | 0.354565 | 0.755493 | 0.425107 | O   |
| O46 | 1.0 | 0.900661 | 0.757970 | 0.999763 | O   |
| O47 | 1.0 | 0.894859 | 0.730620 | 0.104142 | O   |
| O48 | 1.0 | 0.914227 | 0.753497 | 0.010442 | O   |
| O49 | 1.0 | 0.383665 | 0.753497 | 0.010442 | O   |
| O50 | 1.0 | 0.382431 | 0.755530 | 0.315846 | O   |
| O51 | 1.0 | 0.122889 | 0.256524 | 0.053850 | O   |
| O52 | 1.0 | 0.114393 | 0.256781 | 0.266551 | O   |
| O53 | 1.0 | 0.645985 | 0.251255 | 0.163526 | O   |
| O54 | 1.0 | 0.633220 | 0.260363 | 0.366448 | O   |
| O55 | 1.0 | 0.135368 | 0.417876 | 0.462171 | O   |
| O56 | 1.0 | 0.648143 | 0.919690 | 0.495631 | O   |
| Al1 | 1.0 | 0.394203 | 0.925716 | 0.056171 | Al  |
| Al2 | 1.0 | 0.388366 | 0.925054 | 0.268298 | Al  |
| Al3 | 1.0 | 0.137549 | 0.424010 | 0.111684 | Al  |
| Al4 | 1.0 | 0.141246 | 0.417788 | 0.321118 | Al  |
| Al5 | 1.0 | 0.637737 | 0.429274 | 0.013999 | Al  |
| Al6 | 1.0 | 0.622752 | 0.427441 | 0.213397 | Al  |
| Al7 | 1.0 | 0.608664 | 0.430060 | 0.405948 | Al  |
| Al8 | 1.0 | 0.870145 | 0.920810 | 0.162533 | Al  |
| Al9 | 1.0 | 0.887620 | 0.908823 | 0.392393 | Al  |
| Al10 | 1.0 | 0.643600 | 0.080089 | 0.013552 | Al  |
| Al11 | 1.0 | 0.625514 | 0.075905 | 0.214252 | Al  |
| Al12 | 1.0 | 0.616620 | 0.031576 | 0.440742 | Al  |
| Al13 | 1.0 | 0.869725 | 0.582574 | 0.161939 | Al  |
| Al14 | 1.0 | 0.870383 | 0.590931 | 0.376095 | Al  |
| Al15 | 1.0 | 0.392237 | 0.586595 | 0.055100 | Al  |
| Al16 | 1.0 | 0.392264 | 0.581774 | 0.269067 | Al  |
| Al17 | 1.0 | 0.141404 | 0.079642 | 0.113867 | Al  |
| Al18 | 1.0 | 0.132394 | 0.082742 | 0.323974 | Al  |
| Al19 | 1.0 | 0.896764 | 0.243816 | 0.053385 | Al  |
| Al20 | 1.0 | 0.880726 | 0.261485 | 0.272586 | Al  |
| Al21 | 1.0 | 0.506431 | 0.257764 | 0.115979 | Al  |
| Al22 | 1.0 | 0.502352 | 0.244985 | 0.315937 | Al  |
| Al23 | 1.0 | 0.883448 | 0.251325 | 0.161685 | Al  |
| Al24 | 1.0 | 0.864478 | 0.244070 | 0.377086 | Al  |
| Al25 | 1.0 | 0.102397 | 0.758243 | 0.015780 | Al  |
| Al26 | 1.0 | 0.130648 | 0.750868 | 0.221422 | Al  |
| Al27 | 1.0 | 0.233455 | 0.589466 | 0.428129 | Al  |
| Al28 | 1.0 | 0.514930 | 0.750651 | 0.164319 | Al  |
| Al29 | 1.0 | 0.500458 | 0.764329 | 0.377473 | Al  |
| Al30 | 1.0 | 0.139321 | 0.752232 | 0.113593 | Al  |
| Al31 | 1.0 | 0.130852 | 0.757320 | 0.325584 | Al  |
| Al32 | 1.0 | 0.769038 | 0.756627 | 0.052245 | Al  |
| Al33 | 1.0 | 0.753380 | 0.752164 | 0.270819 | Al  |
| Al34 | 1.0 | 0.325129 | 0.255271 | 0.029516 | Al  |
| Al35 | 1.0 | 0.266034 | 0.253710 | 0.218426 | Al  |
| Al36 | 1.0 | 0.275653 | 0.267166 | 0.429342 | Al  |
Coordinate for a calculated transition state of the initial CH₄ activation on a γ-Al₂O₃ (100) surface (TS₁) in Figure 4.

Spin Multiplicity <S²>: 0.023
Absolute Energy: -718.02755056 eV.

cell_length_a 8.07075

cell_length_b 8.40443

cell_length_c 26.38316

cell_angle_alpha 90

cell_angle_beta 90

cell_angle_gamma 90

H1 1.0 0.999497 0.303556 0.474501 H
H2 1.0 0.391601 0.760793 0.967337 H
H3 1.0 0.464363 0.203673 0.481020 H
H4 1.0 0.712861 0.509912 0.506832 H
H5 1.0 0.497569 0.470945 0.516232 H
H6 1.0 0.648007 0.314327 0.518546 H
H7 1.0 0.867957 0.324562 0.970619 H
H8 1.0 0.748970 0.925398 0.510760 H
C1 1.0 0.612045 0.425223 0.498948 C
O1 1.0 0.113042 0.593115 0.156824 O
O2 1.0 0.619910 0.909381 0.048429 O
O3 1.0 0.113042 0.593115 0.156824 O
O4 1.0 0.619910 0.909381 0.048429 O
O5 1.0 0.846619 0.415135 0.993565 O
O6 1.0 0.854767 0.413679 0.207422 O
O7 1.0 0.851724 0.406386 0.417653 O
O8 1.0 0.370901 0.103750 0.097220 O
O9 1.0 0.368545 0.085289 0.314086 O
O10 1.0 0.913061 0.098563 0.108779 O
O11 1.0 0.901088 0.108167 0.319443 O
O12 1.0 0.421397 0.426836 0.999488 O
O13 1.0 0.399752 0.422687 0.209564 O
O14 1.0 0.349359 0.459011 0.423588 O
O15 1.0 0.161162 0.915648 0.060206 O
O16 1.0 0.155682 0.907326 0.267459 O
O17 1.0 0.646804 0.582088 0.158380 O
O18 1.0 0.638885 0.589620 0.379247 O
O19 1.0 0.909879 0.405888 0.107293 O
O20 1.0 0.906185 0.410968 0.319885 O
O21 1.0 0.423676 0.087517 0.000850 O
O22 1.0 0.399038 0.085276 0.213286 O
O23 1.0 0.433242 0.151370 0.448863 O
O24 1.0 0.158967 0.599496 0.058812 O
O25 1.0 0.158247 0.598853 0.266641 O
O26 1.0 0.646398 0.923337 0.159765 O
O27 1.0 0.656598 0.900214 0.386540 O
O28 1.0 0.115218 0.912400 0.158116 O
O29 1.0 0.107945 0.917818 0.364187 O
O30 1.0 0.619791 0.605317 0.047068 O
O31 1.0 0.621889 0.589424 0.259167 O
O32 1.0 0.848004 0.119304 0.998647 O
O33 1.0 0.865736 0.093410 0.207568 O
O34 1.0 0.860184 0.080717 0.423242 O
O35 1.0 0.368541 0.410650 0.095187 O
O36 1.0 0.371357 0.410520 0.309106 O
O37 1.0 0.140856 0.254879 0.157817 O
O38 1.0 0.141113 0.247560 0.369739 O
O39 1.0 0.641399 0.260330 0.057827 O
O40 1.0 0.647898 0.254125 0.262151 O
O41 1.0 0.893263 0.754927 0.109062 O
O42 1.0 0.886538 0.741288 0.323430 O
O43 1.0 0.332227 0.758422 0.999492 O
O44 1.0 0.368685 0.754016 0.212698 O
|   |   |   |   |   |   |
|---|---|---|---|---|---|
|O45| 1.0| 0.349534| 0.776355| 0.424455| O  |
|O46| 1.0| 0.902932| 0.759458| 0.999535| O  |
|O47| 1.0| 0.897402| 0.753153| 0.210552| O  |
|O48| 1.0| 0.964270| 0.713645| 0.425268| O  |
|O49| 1.0| 0.385732| 0.755260| 0.103694| O  |
|O50| 1.0| 0.389613| 0.752501| 0.315629| O  |
|O51| 1.0| 0.125258| 0.257644| 0.053872| O  |
|O52| 1.0| 0.116790| 0.254067| 0.266009| O  |
|O53| 1.0| 0.640533| 0.252371| 0.163919| O  |
|O54| 1.0| 0.624181| 0.254044| 0.374885| O  |
|O55| 1.0| 0.117701| 0.298000| 0.481721| O  |
|O56| 1.0| 0.644366| 0.970071| 0.499747| O  |
|Al1| 1.0| 0.396595| 0.927902| 0.055970| Al |
|Al2| 1.0| 0.393809| 0.925308| 0.269246| Al |
|Al3| 1.0| 0.140103| 0.425627| 0.111445| Al |
|Al4| 1.0| 0.143285| 0.412341| 0.319894| Al |
|Al5| 1.0| 0.640387| 0.430767| 0.013662| Al |
|Al6| 1.0| 0.625883| 0.428248| 0.213944| Al |
|Al7| 1.0| 0.600066| 0.427930| 0.423068| Al |
|Al8| 1.0| 0.871843| 0.923062| 0.162576| Al |
|Al9| 1.0| 0.909049| 0.894152| 0.391853| Al |
|Al10| 1.0| 0.646109| 0.081643| 0.035449| Al |
|Al11| 1.0| 0.626771| 0.077917| 0.214738| Al |
|Al12| 1.0| 0.636791| 0.539557| 0.437749| Al |
|Al13| 1.0| 0.147849| 0.584469| 0.162040| Al |
|Al14| 1.0| 0.871069| 0.572901| 0.376016| Al |
|Al15| 1.0| 0.394550| 0.588439| 0.054525| Al |
|Al16| 1.0| 0.394471| 0.581973| 0.268389| Al |
|Al17| 1.0| 0.144107| 0.081770| 0.113767| Al |
|Al18| 1.0| 0.134109| 0.080999| 0.322633| Al |
|Al19| 1.0| 0.898979| 0.245267| 0.053265| Al |
|Al20| 1.0| 0.81748| 0.258503| 0.271649| Al |
|Al21| 1.0| 0.509082| 0.260270| 0.116128| Al |
|Al22| 1.0| 0.506438| 0.248153| 0.319780| Al |
|Al23| 1.0| 0.886093| 0.253226| 0.161517| Al |
|Al24| 1.0| 0.865835| 0.239222| 0.376911| Al |
|Al25| 1.0| 0.105029| 0.760190| 0.014987| Al |
|Al26| 1.0| 0.136600| 0.753706| 0.218841| Al |
|Al27| 1.0| 0.198504| 0.632965| 0.423595| Al |
|Al28| 1.0| 0.517792| 0.752379| 0.163589| Al |
|Al29| 1.0| 0.501539| 0.754008| 0.379385| Al |
|Al30| 1.0| 0.140113| 0.754763| 0.112582| Al |
|Al31| 1.0| 0.129084| 0.754056| 0.321303| Al |
|Al32| 1.0| 0.771397| 0.758233| 0.051973| Al |
|Al33| 1.0| 0.755889| 0.753181| 0.270756| Al |
|Al34| 1.0| 0.327714| 0.257262| 0.029553| Al |
|Al35| 1.0| 0.270742| 0.255243| 0.218564| Al |
|Al36| 1.0| 0.248800| 0.273813| 0.430931| Al |
Coordinate for a $\gamma$-Al$_2$O$_3$ (100) surface with CH$_3$* and H* in Figure 4.
Spin Multiplicity $<S^2>$: 0.007
Absolute Energy: $-719.813245$ eV.

| cell_length_a       | 8.07075 |
| cell_length_b       | 8.40443 |
| cell_length_c       | 26.38316 |
| cell_angle_alpha    | 90      |
| cell_angle_beta     | 90      |
| cell_angle_gamma    | 90      |

| symmetry_space_group_name_H-M | 'P 1' |
| symmetry_Int_Tables_number   | 1     |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| H1 | 1.0 | -0.004326 | 0.114684 | 0.471138 | H |
| H2 | 1.0 | 0.396313  | 0.760229 | 0.967201 | H |
| H3 | 1.0 | 0.340699  | 0.011573 | 0.438921 | H |
| H4 | 1.0 | 0.678107  | 0.493944 | 0.515064 | H |
| H5 | 1.0 | 0.461261  | 0.470217 | 0.501968 | H |
| H6 | 1.0 | 0.590864  | 0.299604 | 0.511193 | H |
| H7 | 1.0 | 0.875143  | 0.330013 | 0.970016 | H |
| H8 | 1.0 | 0.726134  | 0.985651 | 0.505465 | H |
| C1 | 1.0 | 0.584738  | 0.420596 | 0.495413 | C |
| O1 | 1.0 | 0.116963  | 0.595673 | 0.156889 | O |
| O2 | 1.0 | 0.127031  | 0.583988 | 0.361491 | O |
| O3 | 1.0 | 0.623370  | 0.909859 | 0.047825 | O |
| O4 | 1.0 | 0.625803  | 0.922371 | 0.260012 | O |
| O5 | 1.0 | 0.852515  | 0.415672 | 0.994563 | O |
| O6 | 1.0 | 0.868931  | 0.416026 | 0.207254 | O |
| O7 | 1.0 | 0.872482  | 0.411024 | 0.415214 | O |
| O8 | 1.0 | 0.374490  | 0.104932 | 0.096133 | O |
| O9 | 1.0 | 0.371849  | 0.091680 | 0.312306 | O |
| O10| 1.0 | 0.916527  | 0.101232 | 0.108425 | O |
| O11| 1.0 | 0.904701  | 0.11076 | 0.316610 | O |
| O12| 1.0 | 0.424901  | 0.427211 | 0.999764 | O |
| O13| 1.0 | 0.402877  | 0.426410 | 0.212065 | O |
| O14| 1.0 | 0.229187  | 0.452750 | 0.450958 | O |
| O15| 1.0 | 0.164972  | 0.916449 | 0.059688 | O |
| O16| 1.0 | 0.160988  | 0.910541 | 0.266955 | O |
| O17| 1.0 | 0.650472  | 0.585679 | 0.158917 | O |
| O18| 1.0 | 0.641266  | 0.585017 | 0.379537 | O |
| O19| 1.0 | 0.913705  | 0.408118 | 0.107082 | O |
| O20| 1.0 | 0.907356  | 0.415113 | 0.318240 | O |
| O21| 1.0 | 0.427888  | 0.087161 | 0.999961 | O |
| O22| 1.0 | 0.402894  | 0.088393 | 0.211796 | O |
| O23| 1.0 | 0.391491  | 0.112797 | 0.427314 | O |
| O24| 1.0 | 0.163568  | 0.600402 | 0.058958 | O |
| O25| 1.0 | 0.163165  | 0.601261 | 0.266954 | O |
| O26| 1.0 | 0.650657  | 0.927176 | 0.159254 | O |
| O27| 1.0 | 0.650978  | 0.901542 | 0.382163 | O |
| O28| 1.0 | 0.118821  | 0.915450 | 0.157633 | O |
| O29| 1.0 | 0.108897  | 0.922304 | 0.363544 | O |
| O30| 1.0 | 0.624532  | 0.605315 | 0.047140 | O |
| O31| 1.0 | 0.626151  | 0.930900 | 0.259677 | O |
| O32| 1.0 | 0.853148  | 0.191933 | 0.998216 | O |
| O33| 1.0 | 0.869034  | 0.097899 | 0.207070 | O |
| O34| 1.0 | 0.857302  | 0.083186 | 0.418245 | O |
| O35| 1.0 | 0.373406  | 0.412702 | 0.096046 | O |
| O36| 1.0 | 0.376920  | 0.417662 | 0.313114 | O |
| O37| 1.0 | 0.145244  | 0.257361 | 0.157382 | O |
| O38| 1.0 | 0.132699  | 0.251776 | 0.368848 | O |
| O39| 1.0 | 0.645768  | 0.260115 | 0.057344 | O |
| O40| 1.0 | 0.650207  | 0.258155 | 0.262771 | O |
| O41| 1.0 | 0.897041  | 0.756852 | 0.108850 | O |
| O42| 1.0 | 0.888893  | 0.747190 | 0.322234 | O |
| O43| 1.0 | 0.337813  | 0.758303 | 0.999452 | O |
| O44| 1.0 | 0.372714  | 0.757188 | 0.212478 | O |
|   |   |   |   |   |
|---|---|---|---|---|
| O45 | 1.0 | 0.343279 | 0.758062 | 0.423731 | O |
| O46 | 1.0 | 0.907298 | 0.758639 | 0.999254 | O |
| O47 | 1.0 | 0.901589 | 0.756533 | 0.210252 | O |
| O48 | 1.0 | 0.949849 | 0.721497 | 0.422927 | O |
| O49 | 1.0 | 0.390133 | 0.757377 | 0.103506 | O |
| O50 | 1.0 | 0.391773 | 0.755765 | 0.315568 | O |
| O51 | 1.0 | 0.129501 | 0.259032 | 0.053685 | O |
| O52 | 1.0 | 0.122325 | 0.260175 | 0.265663 | O |
| O53 | 1.0 | 0.650225 | 0.257051 | 0.163843 | O |
| O54 | 1.0 | 0.627870 | 0.252732 | 0.378451 | O |
| O55 | 1.0 | 0.110388 | 0.136214 | 0.481041 | O |
| O56 | 1.0 | 0.622031 | 0.019165 | 0.490685 | O |
| Al1 | 1.0 | 0.400716 | 0.928118 | 0.055188 | Al |
| Al2 | 1.0 | 0.398005 | 0.928747 | 0.268527 | Al |
| Al3 | 1.0 | 0.144332 | 0.428055 | 0.111255 | Al |
| Al4 | 1.0 | 0.147228 | 0.417449 | 0.320148 | Al |
| Al5 | 1.0 | 0.644240 | 0.431057 | 0.013445 | Al |
| Al6 | 1.0 | 0.628937 | 0.432042 | 0.214289 | Al |
| Al7 | 1.0 | 0.653507 | 0.427700 | 0.425303 | Al |
| Al8 | 1.0 | 0.875919 | 0.926438 | 0.162111 | Al |
| Al9 | 1.0 | 0.892324 | 0.897468 | 0.387192 | Al |
| Al10 | 1.0 | 0.650870 | 0.081580 | 0.012481 | Al |
| Al11 | 1.0 | 0.629915 | 0.082712 | 0.214452 | Al |
| Al12 | 1.0 | 0.621760 | 0.665672 | 0.426422 | Al |
| Al13 | 1.0 | 0.875714 | 0.587463 | 0.161850 | Al |
| Al14 | 1.0 | 0.877923 | 0.578601 | 0.371540 | Al |
| Al15 | 1.0 | 0.399266 | 0.588814 | 0.054929 | Al |
| Al16 | 1.0 | 0.398834 | 0.583147 | 0.269081 | Al |
| Al17 | 1.0 | 0.147847 | 0.084120 | 0.113173 | Al |
| Al18 | 1.0 | 0.138861 | 0.084000 | 0.321493 | Al |
| Al19 | 1.0 | 0.903063 | 0.246714 | 0.052460 | Al |
| Al20 | 1.0 | 0.886181 | 0.262611 | 0.269675 | Al |
| Al21 | 1.0 | 0.513448 | 0.259784 | 0.115332 | Al |
| Al22 | 1.0 | 0.509749 | 0.252317 | 0.321821 | Al |
| Al23 | 1.0 | 0.888704 | 0.256622 | 0.160708 | Al |
| Al24 | 1.0 | 0.889578 | 0.242327 | 0.374261 | Al |
| Al25 | 1.0 | 0.109491 | 0.760927 | 0.014665 | Al |
| Al26 | 1.0 | 0.141156 | 0.755348 | 0.218921 | Al |
| Al27 | 1.0 | 0.168364 | 0.636762 | 0.428145 | Al |
| Al28 | 1.0 | 0.521579 | 0.756624 | 0.163369 | Al |
| Al29 | 1.0 | 0.500764 | 0.749241 | 0.380059 | Al |
| Al30 | 1.0 | 0.144067 | 0.756419 | 0.112403 | Al |
| Al31 | 1.0 | 0.140586 | 0.758313 | 0.321915 | Al |
| Al32 | 1.0 | 0.775638 | 0.758745 | 0.051649 | Al |
| Al33 | 1.0 | 0.758913 | 0.758292 | 0.269582 | Al |
| Al34 | 1.0 | 0.331225 | 0.256146 | 0.028750 | Al |
| Al35 | 1.0 | 0.274456 | 0.257429 | 0.217978 | Al |
| Al36 | 1.0 | 0.216650 | 0.253043 | 0.437741 | Al |
Coordinate for a calculated transition state of PT from CH$_3^*$ on a γ-Al$_2$O$_3$ (100) surface (TS2) in Figure 4.

Spin Multiplicity $<S^2>$: 0.9998

Absolute Energy: -718.93307207 eV.

cell_length_a 8.07075

cell_length_b 8.40443

cell_length_c 26.38316

cell_angle_alpha 90

cell_angle_beta 90

cell_angle_gamma 90

| symmetry_space_group_name_H-M | P 1 |
|-------------------------------|-----|
| symmetry_Int_Tables_number    | 1   |

|    |    |    |    |    |
|----|----|----|----|----|
| H1 | 1.0| 0.009663| 0.098484| 0.472939| H  |
| H2 | 1.0| 0.396912| 0.756187| 0.967692| H  |
| H3 | 1.0| 0.355404| 0.042160| 0.458310| H  |
| H4 | 1.0| 0.569990| 0.537756| 0.513039| H  |
| H5 | 1.0| 0.406994| 0.617345| 0.449918| H  |
| H6 | 1.0| 0.485566| 0.339893| 0.503906| H  |
| H7 | 1.0| 0.915912| 0.381922| 0.973496| H  |
| H8 | 1.0| 0.729544| 1.008597| 0.508057| H  |
| C1 | 1.0| 0.547045| 0.441050| 0.486035| C  |
| O1 | 1.0| 0.120565| 0.598794| 0.158752| O  |
| O2 | 1.0| 0.125383| 0.581729| 0.361714| O  |
| O3 | 1.0| 0.628490| 0.910692| 0.405991| O  |
| O4 | 1.0| 0.628314| 0.220444| 0.261775| O  |
| O5 | 1.0| 0.874987| 0.422266| 0.005803| O  |
| O6 | 1.0| 0.876080| 0.413376| 0.209338| O  |
| O7 | 1.0| 0.872812| 0.411366| 0.414755| O  |
| O8 | 1.0| 0.380443| 0.104325| 0.096707| O  |
| O9 | 1.0| 0.375803| 0.086628| 0.314925| O  |
| O10| 1.0| 0.918223| 0.100509| 0.111144| O  |
| O11| 1.0| 0.910629| 0.104167| 0.318073| O  |
| O12| 1.0| 0.406694| 0.425967| 0.003096| O  |
| O13| 1.0| 0.405188| 0.424012| 0.215668| O  |
| O14| 1.0| 0.208745| 0.448376| 0.456177| O  |
| O15| 1.0| 0.168280| 0.915592| 0.600751| O  |
| O16| 1.0| 0.163321| 0.907638| 0.267751| O  |
| O17| 1.0| 0.652457| 0.584320| 0.160713| O  |
| O18| 1.0| 0.648000| 0.582467| 0.376281| O  |
| O19| 1.0| 0.918301| 0.410038| 0.111017| O  |
| O20| 1.0| 0.910240| 0.408566| 0.318695| O  |
| O21| 1.0| 0.424616| 0.080839| 0.999729| O  |
| O22| 1.0| 0.404279| 0.085175| 0.214548| O  |
| O23| 1.0| 0.394740| 0.118196| 0.432529| O  |
| O24| 1.0| 0.165748| 0.600441| 0.060988| O  |
| O25| 1.0| 0.164625| 0.599654| 0.267849| O  |
| O26| 1.0| 0.652603| 0.925691| 0.160927| O  |
| O27| 1.0| 0.646141| 0.899344| 0.384869| O  |
| O28| 1.0| 0.121897| 0.913822| 0.158363| O  |
| O29| 1.0| 0.117397| 0.914956| 0.365218| O  |
| O30| 1.0| 0.625061| 0.598315| 0.042565| O  |
| O31| 1.0| 0.629387| 0.590772| 0.261505| O  |
| O32| 1.0| 0.868657| 0.111268| 0.001625| O  |
| O33| 1.0| 0.870635| 0.097596| 0.209123| O  |
| O34| 1.0| 0.859022| 0.081272| 0.417596| O  |
| O35| 1.0| 0.379013| 0.419829| 0.101983| O  |
| O36| 1.0| 0.379486| 0.418772| 0.315762| O  |
| O37| 1.0| 0.148336| 0.255353| 0.159299| O  |
| O38| 1.0| 0.139503| 0.249948| 0.370361| O  |
| O39| 1.0| 0.651295| 0.261489| 0.056814| O  |
| O40| 1.0| 0.652681| 0.255029| 0.264359| O  |
| O41| 1.0| 0.895484| 0.755261| 0.108235| O  |
| O42| 1.0| 0.889032| 0.749246| 0.321978| O  |
| O43| 1.0| 0.338254| 0.757043| 0.997888| O  |
| O44| 1.0| 0.377545| 0.754988| 0.214036| O  |
|        |     |     |     |     |      |
|--------|-----|-----|-----|-----|------|
| O45    | 1.0 | 0.360350 | 0.706795 | 0.428420 | O    |
| O46    | 1.0 | 0.914182 | 0.756822 | 0.997505 | O    |
| O47    | 1.0 | 0.903685 | 0.755934 | 0.210312 | O    |
| O48    | 1.0 | 0.942266 | 0.720401 | 0.422287 | O    |
| O49    | 1.0 | 0.395821 | 0.757383 | 0.103689 | O    |
| O50    | 1.0 | 0.390590 | 0.753704 | 0.317220 | O    |
| O51    | 1.0 | 0.132650 | 0.255642 | 0.058170 | O    |
| O52    | 1.0 | 0.128094 | 0.255528 | 0.317220 | O    |
| O53    | 1.0 | 0.648411 | 0.255405 | 0.164884 | O    |
| O54    | 1.0 | 0.626325 | 0.250001 | 0.378802 | O    |
| O55    | 1.0 | 0.115258 | 0.122495 | 0.481851 | O    |
| O56    | 1.0 | 0.625826 | 0.038580 | 0.492180 | O    |
| Al1    | 1.0 | 0.407330 | 0.927410 | 0.054332 | Al   |
| Al2    | 1.0 | 0.400547 | 0.928424 | 0.112534 | Al   |
| Al3    | 1.0 | 0.151125 | 0.427717 | 0.112534 | Al   |
| Al4    | 1.0 | 0.150887 | 0.415117 | 0.319086 | Al   |
| Al5    | 1.0 | 0.644007 | 0.422818 | 0.003990 | Al   |
| Al6    | 1.0 | 0.632371 | 0.430670 | 0.214493 | Al   |
| Al7    | 1.0 | 0.654230 | 0.425111 | 0.421487 | Al   |
| Al8    | 1.0 | 0.878422 | 0.926549 | 0.160137 | Al   |
| Al9    | 1.0 | 0.893716 | 0.897774 | 0.384698 | Al   |
| Al10   | 1.0 | 0.656572 | 0.087745 | 0.008909 | Al   |
| Al11   | 1.0 | 0.631617 | 0.080199 | 0.214026 | Al   |
| Al12   | 1.0 | 0.624890 | 0.068868 | 0.426530 | Al   |
| Al13   | 1.0 | 0.878168 | 0.896947 | 0.160145 | Al   |
| Al14   | 1.0 | 0.876298 | 0.575699 | 0.367800 | Al   |
| Al15   | 1.0 | 0.403561 | 0.581084 | 0.055172 | Al   |
| Al16   | 1.0 | 0.401712 | 0.580068 | 0.268545 | Al   |
| Al17   | 1.0 | 0.151911 | 0.085074 | 0.112396 | Al   |
| Al18   | 1.0 | 0.145278 | 0.079746 | 0.322243 | Al   |
| Al19   | 1.0 | 0.902135 | 0.249431 | 0.052301 | Al   |
| Al20   | 1.0 | 0.888997 | 0.253901 | 0.268415 | Al   |
| Al21   | 1.0 | 0.521372 | 0.262485 | 0.112660 | Al   |
| Al22   | 1.0 | 0.511387 | 0.250749 | 0.320644 | Al   |
| Al23   | 1.0 | 0.891545 | 0.255763 | 0.161640 | Al   |
| Al24   | 1.0 | 0.895630 | 0.240816 | 0.373692 | Al   |
| Al25   | 1.0 | 0.113617 | 0.758940 | 0.015237 | Al   |
| Al26   | 1.0 | 0.143116 | 0.753350 | 0.217142 | Al   |
| Al27   | 1.0 | 0.143115 | 0.622432 | 0.428438 | Al   |
| Al28   | 1.0 | 0.522675 | 0.755080 | 0.162397 | Al   |
| Al29   | 1.0 | 0.505705 | 0.743315 | 0.376432 | Al   |
| Al30   | 1.0 | 0.147830 | 0.756266 | 0.112153 | Al   |
| Al31   | 1.0 | 0.141062 | 0.755724 | 0.320408 | Al   |
| Al32   | 1.0 | 0.775371 | 0.753500 | 0.048283 | Al   |
| Al33   | 1.0 | 0.762506 | 0.757479 | 0.267077 | Al   |
| Al34   | 1.0 | 0.324584 | 0.247461 | 0.026250 | Al   |
| Al35   | 1.0 | 0.275808 | 0.254662 | 0.217260 | Al   |
| Al36   | 1.0 | 0.209086 | 0.249486 | 0.438825 | Al   |
Coordinate for a γ-Al₂O₃ (100) surface with CH₂* and 2H* in Figure 4.
Spin Multiplicity \(<S^2>: 1.000
Absolute Energy: −719.36810744 eV.

cell_length_a 8.07075
cell_length_b 8.40443
cell_length_c 26.38316
cell_angle_alpha 90
cell_angle_beta 90
cell_angle_gamma 90
symmetry_space_group_name_H-M 'P 1'
symmetry_Int_Tables_number 1

|     |      |      |      | H     |     |     |     |
|-----|------|------|------|------|-----|-----|-----|
| H1  | 1.0  | 0.079779 | 0.095029 | 0.474032 | H   |
| H2  | 1.0  | 0.397238 | 0.758259 | 0.968677 | H   |
| H3  | 1.0  | 0.357707 | 0.157557 | 0.472574 | H   |
| H4  | 1.0  | 0.603288 | 0.320753 | 0.514956 | H   |
| H5  | 1.0  | 0.427236 | 0.808728 | 0.454746 | H   |
| H6  | 1.0  | 0.419664 | 0.409670 | 0.489593 | H   |
| H7  | 1.0  | 0.916659 | 0.369523 | 0.973787 | H   |
| H8  | 1.0  | 0.684742 | 0.826576 | 0.482903 | H   |
| C1  | 1.0  | 0.531145 | 0.340427 | 0.480117 | C   |
| O1  | 1.0  | 0.121353 | 0.600596 | 0.159491 | O   |
| O2  | 1.0  | 0.123568 | 0.593266 | 0.363603 | O   |
| O3  | 1.0  | 0.626054 | 0.915197 | 0.039483 | O   |
| O4  | 1.0  | 0.627913 | 0.922997 | 0.262659 | O   |
| O5  | 1.0  | 0.880715 | 0.415935 | 0.005880 | O   |
| O6  | 1.0  | 0.870565 | 0.411351 | 0.211296 | O   |
| O7  | 1.0  | 0.879607 | 0.409240 | 0.419945 | O   |
| O8  | 1.0  | 0.384737 | 0.090903 | 0.103519 | O   |
| O9  | 1.0  | 0.376251 | 0.087098 | 0.318723 | O   |
| O10 | 1.0  | 0.920717 | 0.099535 | 0.113344 | O   |
| O11 | 1.0  | 0.910493 | 0.099070 | 0.320589 | O   |
| O12 | 1.0  | 0.395071 | 0.429703 | 0.001965 | O   |
| O13 | 1.0  | 0.404050 | 0.422950 | 0.218525 | O   |
| O14 | 1.0  | 0.178255 | 0.519761 | 0.462814 | O   |
| O15 | 1.0  | 0.166705 | 0.914035 | 0.062202 | O   |
| O16 | 1.0  | 0.163582 | 0.911087 | 0.268103 | O   |
| O17 | 1.0  | 0.653450 | 0.586146 | 0.163009 | O   |
| O18 | 1.0  | 0.646876 | 0.591286 | 0.383010 | O   |
| O19 | 1.0  | 0.920165 | 0.411699 | 0.112884 | O   |
| O20 | 1.0  | 0.903819 | 0.411520 | 0.321816 | O   |
| O21 | 1.0  | 0.402242 | 0.079584 | 0.000606 | O   |
| O22 | 1.0  | 0.403408 | 0.088154 | 0.218131 | O   |
| O23 | 1.0  | 0.476024 | 0.181952 | 0.460761 | O   |
| O24 | 1.0  | 0.165534 | 0.600134 | 0.061994 | O   |
| O25 | 1.0  | 0.162087 | 0.600224 | 0.268844 | O   |
| O26 | 1.0  | 0.653096 | 0.925128 | 0.162403 | O   |
| O27 | 1.0  | 0.648280 | 0.916291 | 0.376687 | O   |
| O28 | 1.0  | 0.122031 | 0.911006 | 0.159463 | O   |
| O29 | 1.0  | 0.118320 | 0.917499 | 0.365632 | O   |
| O30 | 1.0  | 0.625623 | 0.593553 | 0.039312 | O   |
| O31 | 1.0  | 0.629333 | 0.587967 | 0.263685 | O   |
| O32 | 1.0  | 0.879793 | 0.099433 | 0.004726 | O   |
| O33 | 1.0  | 0.870219 | 0.099378 | 0.210961 | O   |
| O34 | 1.0  | 0.859060 | 0.086542 | 0.420877 | O   |
| O35 | 1.0  | 0.383189 | 0.423625 | 0.104382 | O   |
| O36 | 1.0  | 0.377777 | 0.423218 | 0.318619 | O   |
| O37 | 1.0  | 0.147189 | 0.255793 | 0.160798 | O   |
| O38 | 1.0  | 0.124604 | 0.265577 | 0.373730 | O   |
| O39 | 1.0  | 0.658713 | 0.259204 | 0.058293 | O   |
| O40 | 1.0  | 0.653322 | 0.254561 | 0.265591 | O   |
| O41 | 1.0  | 0.889930 | 0.755689 | 0.107561 | O   |
| O42 | 1.0  | 0.886862 | 0.753173 | 0.320384 | O   |
| O43 | 1.0  | 0.336950 | 0.756031 | 1.000531 | O   |
| O44 | 1.0  | 0.378588 | 0.754679 | 0.214870 | O   |
| Atom | X   | Y   | Z   | Element |
|------|-----|-----|-----|---------|
| 045  | 1.0 | 0.360321 | 0.770179 | O       |
| 046  | 1.0 | 0.917166 | 0.751242 | O       |
| 047  | 1.0 | 0.904146 | 0.755899 | O       |
| 048  | 1.0 | 0.929007 | 0.743496 | O       |
| 049  | 1.0 | 0.399276 | 0.756265 | O       |
| 050  | 1.0 | 0.389177 | 0.754057 | O       |
| 051  | 1.0 | 0.135567 | 0.255375 | O       |
| 052  | 1.0 | 0.127168 | 0.256458 | O       |
| 053  | 1.0 | 0.644221 | 0.255980 | O       |
| 054  | 1.0 | 0.637476 | 0.255373 | O       |
| 055  | 1.0 | 0.153410 | 0.185340 | O       |
| 056  | 1.0 | 0.596360 | 0.904684 | O       |
| Al1  | 1.0 | 0.408178 | 0.934694 | Al      |
| Al2  | 1.0 | 0.400732 | 0.930643 | Al      |
| Al3  | 1.0 | 0.155411 | 0.427125 | Al      |
| Al4  | 1.0 | 0.148791 | 0.423542 | Al      |
| Al5  | 1.0 | 0.643209 | 0.409991 | Al      |
| Al6  | 1.0 | 0.632123 | 0.430459 | Al      |
| Al7  | 1.0 | 0.651572 | 0.419574 | Al      |
| Al8  | 1.0 | 0.878671 | 0.925491 | Al      |
| Al9  | 1.0 | 0.887641 | 0.915107 | Al      |
| Al10 | 1.0 | 0.661471 | 0.097459 | Al      |
| Al11 | 1.0 | 0.631218 | 0.080496 | Al      |
| Al12 | 1.0 | 0.639194 | 0.047698 | Al      |
| Al13 | 1.0 | 0.878810 | 0.585425 | Al      |
| Al14 | 1.0 | 0.878338 | 0.588647 | Al      |
| Al15 | 1.0 | 0.405746 | 0.578288 | Al      |
| Al16 | 1.0 | 0.401535 | 0.580929 | Al      |
| Al17 | 1.0 | 0.157388 | 0.084697 | Al      |
| Al18 | 1.0 | 0.149922 | 0.087425 | Al      |
| Al19 | 1.0 | 0.898938 | 0.244944 | Al      |
| Al20 | 1.0 | 0.887232 | 0.253727 | Al      |
| Al21 | 1.0 | 0.519482 | 0.257911 | Al      |
| Al22 | 1.0 | 0.510186 | 0.253916 | Al      |
| Al23 | 1.0 | 0.891926 | 0.256169 | Al      |
| Al24 | 1.0 | 0.878552 | 0.243499 | Al      |
| Al25 | 1.0 | 0.114313 | 0.759396 | Al      |
| Al26 | 1.0 | 0.142446 | 0.755189 | Al      |
| Al27 | 1.0 | 0.147274 | 0.686564 | Al      |
| Al28 | 1.0 | 0.521598 | 0.755444 | Al      |
| Al29 | 1.0 | 0.510662 | 0.755810 | Al      |
| Al30 | 1.0 | 0.152382 | 0.755995 | Al      |
| Al31 | 1.0 | 0.140528 | 0.760338 | Al      |
| Al32 | 1.0 | 0.770914 | 0.755334 | Al      |
| Al33 | 1.0 | 0.760781 | 0.756533 | Al      |
| Al34 | 1.0 | 0.295973 | 0.251953 | Al      |
| Al35 | 1.0 | 0.272525 | 0.255636 | Al      |
| Al36 | 1.0 | 0.098190 | 0.345192 | Al      |
S3.2 Optimized Structures and Energies for Figure S6

**Coordinate** for a γ-Al₂O₃ (100) surface with CH₄ σ-complex at a 5-coordinated Al site.

Absolute Energy: $-731.75658299$ eV.

| Coordinate | Value  | Value  | Value  | Value  |
|------------|--------|--------|--------|--------|
| cell_length_a | 8.070750 | cell_length_b | 8.404430 | cell_length_c | 26.383160 |
| cell_angle_alpha | 90.000000 | cell_angle_beta | 90.000000 | cell_angle_gamma | 90.000000 |
| cell_volume | 1789.571263 |
| space_group_name_H-M_alt | 'P 1' |
| space_group_IT_number | 1 |

| Atom | X | Y | Z | Value  | Value  |
|------|---|---|---|--------|--------|
| H1   | 1.0 | 0.917929 | 0.402544 | 0.444165 | H |
| H2   | 1.0 | 0.430293 | 0.072259 | 0.963119 | H |
| H3   | 1.0 | 0.698900 | 0.423558 | 0.558535 | H |
| H4   | 1.0 | 0.730352 | 0.582663 | 0.514720 | H |
| H5   | 1.0 | 0.525923 | 0.532422 | 0.535311 | H |
| H6   | 1.0 | 0.666923 | 0.627423 | 0.578229 | H |
| H7   | 1.0 | 0.122352 | 0.404754 | 0.500383 | H |
| H8   | 1.0 | 0.381315 | 0.590496 | 0.154556 | H |
| H9   | 1.0 | 0.828333 | 0.320928 | 0.952131 | H |
| H10  | 1.0 | 0.683783 | 0.834203 | 0.495196 | H |
| C1   | 1.0 | 0.655790 | 0.541785 | 0.547048 | C |
| O1   | 1.0 | 0.604802 | 0.267201 | 0.546222 | O |
| O2   | 1.0 | 0.109730 | 0.590496 | 0.154556 | O |
| O3   | 1.0 | 0.118468 | 0.569548 | 0.362387 | O |
| O4   | 1.0 | 0.623466 | 0.914940 | 0.035307 | O |
| O5   | 1.0 | 0.615635 | 0.912945 | 0.257862 | O |
| O6   | 1.0 | 0.768406 | 0.421576 | 0.956204 | O |
| O7   | 1.0 | 0.857361 | 0.407709 | 0.206065 | O |
| O8   | 1.0 | 0.844424 | 0.403586 | 0.414270 | O |
| O9   | 1.0 | 0.374276 | 0.112646 | 0.087387 | O |
| O10  | 1.0 | 0.358715 | 0.080144 | 0.311606 | O |
| O11  | 1.0 | 0.904955 | 0.088489 | 0.108383 | O |
| O12  | 1.0 | 0.896492 | 0.099626 | 0.314347 | O |
| O13  | 1.0 | 0.396195 | 0.414241 | -0.002523 | O |
| O14  | 1.0 | 0.390885 | 0.419355 | 0.208524 | O |
| O15  | 1.0 | 0.372114 | 0.429061 | 0.412812 | O |
| O16  | 1.0 | 0.159240 | 0.915713 | 0.058801 | O |
| O17  | 1.0 | 0.150537 | 0.899657 | 0.266537 | O |
| O18  | 1.0 | 0.639829 | 0.575840 | 0.154991 | O |
| O19  | 1.0 | 0.635591 | 0.585039 | 0.377484 | O |
| O20  | 1.0 | 0.903535 | 0.402527 | 0.108172 | O |
| O21  | 1.0 | 0.899693 | 0.403782 | 0.318544 | O |
| O22  | 1.0 | 0.354199 | 0.072712 | -0.007826 | O |
| O23  | 1.0 | 0.390596 | 0.077464 | 0.210980 | O |
| O24  | 1.0 | 0.394823 | 0.104127 | 0.438144 | O |
| O25  | 1.0 | 0.146444 | 0.602103 | 0.055203 | O |
| O26  | 1.0 | 0.153712 | 0.593946 | 0.266492 | O |
| O27  | 1.0 | 0.639858 | 0.915177 | 0.156130 | O |
| O28  | 1.0 | 0.652038 | 0.905160 | 0.391172 | O |
| O29  | 1.0 | 0.111136 | 0.908170 | 0.155449 | O |
| O30  | 1.0 | 0.095962 | 0.913099 | 0.364212 | O |
| O31  | 1.0 | 0.608673 | 0.597327 | 0.037566 | O |
| O32  | 1.0 | 0.615430 | 0.583986 | 0.256325 | O |
| O33  | 1.0 | 0.882552 | 0.131634 | -0.004844 | O |
| O34  | 1.0 | 0.856913 | 0.086509 | 0.205219 | O |
| O35  | 1.0 | 0.864681 | 0.089454 | 0.423095 | O |
| O36  | 1.0 | 0.361784 | 0.415886 | 0.094312 | O |
| O37  | 1.0 | 0.363630 | 0.403622 | 0.307228 | O |
| O38  | 1.0 | 0.136280 | 0.246876 | 0.156200 | O |
| O39  | 1.0 | 0.125258 | 0.242344 | 0.367612 | O |
|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| O40 | 1.0 | 0.653850 | 0.276956 | 0.052860 | O |
| O41 | 1.0 | 0.639738 | 0.247904 | 0.257526 | O |
| O42 | 1.0 | 0.884933 | 0.748002 | 0.106051 | O |
| O43 | 1.0 | 0.884514 | 0.729793 | 0.317959 | O |
| O44 | 1.0 | 0.322869 | 0.751616 | -0.005031 | O |
| O45 | 1.0 | 0.361172 | 0.748195 | 0.210311 | O |
| O46 | 1.0 | 0.347875 | 0.743636 | 0.426894 | O |
| O47 | 1.0 | 0.890003 | 0.788142 | -0.001557 | O |
| O48 | 1.0 | 0.891849 | 0.746854 | 0.207378 | O |
| O49 | 1.0 | 0.933763 | 0.707033 | 0.423979 | O |
| O50 | 1.0 | 0.387970 | 0.755409 | 0.098207 | O |
| O51 | 1.0 | 0.385257 | 0.748502 | 0.315627 | O |
| O52 | 1.0 | 0.109821 | 0.258259 | 0.056550 | O |
| O53 | 1.0 | 0.109794 | 0.259978 | 0.263153 | O |
| O54 | 1.0 | 0.638194 | 0.246269 | 0.159947 | O |
| O55 | 1.0 | 0.635417 | 0.252517 | 0.363681 | O |
| O56 | 1.0 | 0.123261 | 0.405014 | 0.463552 | O |
| O57 | 1.0 | 0.664476 | 0.945339 | 0.499832 | O |
| A1  | 1.0 | 0.404301 | 0.930189 | 0.048975 | Al |
| A2  | 1.0 | 0.387492 | 0.918819 | 0.267365 | Al |
| A3  | 1.0 | 0.134695 | 0.419214 | 0.110633 | Al |
| A4  | 1.0 | 0.135111 | 0.409157 | 0.316515 | Al |
| A5  | 1.0 | 0.620626 | 0.417023 | 0.002354 | Al |
| A6  | 1.0 | 0.616051 | 0.422591 | 0.210667 | Al |
| A7  | 1.0 | 0.592059 | 0.402196 | 0.412065 | Al |
| A8  | 1.0 | 0.866548 | 0.917168 | 0.159876 | Al |
| A9  | 1.0 | 0.892460 | 0.895831 | 0.397868 | Al |
| A10 | 1.0 | 0.759752 | -0.029019 | -0.019659 | Al |
| A11 | 1.0 | 0.617312 | 0.071677 | 0.210614 | Al |
| A12 | 1.0 | 0.624204 | 0.059495 | 0.443816 | Al |
| A13 | 1.0 | 0.866364 | 0.576373 | 0.159069 | Al |
| A14 | 1.0 | 0.863482 | 0.581133 | 0.371262 | Al |
| A15 | 1.0 | 0.383929 | 0.581840 | 0.049298 | Al |
| A16 | 1.0 | 0.389975 | 0.576565 | 0.267520 | Al |
| A17 | 1.0 | 0.141190 | 0.078655 | 0.110946 | Al |
| A18 | 1.0 | 0.125043 | 0.071328 | 0.319852 | Al |
| A19 | 1.0 | 0.878344 | 0.225629 | 0.054976 | Al |
| A20 | 1.0 | 0.874268 | 0.254232 | 0.268168 | Al |
| A21 | 1.0 | 0.519161 | 0.270225 | 0.107086 | Al |
| A22 | 1.0 | 0.499311 | 0.240240 | 0.314002 | Al |
| A23 | 1.0 | 0.878954 | 0.247401 | 0.160352 | Al |
| A24 | 1.0 | 0.865546 | 0.227228 | 0.370896 | Al |
| A25 | 1.0 | 0.099310 | 0.767719 | 0.013284 | Al |
| A26 | 1.0 | 0.129852 | 0.746273 | 0.217808 | Al |
| A27 | 1.0 | 0.213769 | 0.586978 | 0.423923 | Al |
| A28 | 1.0 | 0.509477 | 0.745884 | 0.160709 | Al |
| A29 | 1.0 | 0.501723 | 0.755516 | 0.381262 | Al |
| A30 | 1.0 | 0.140656 | 0.751019 | 0.110238 | Al |
| A31 | 1.0 | 0.123964 | 0.748670 | 0.322216 | Al |
| A32 | 1.0 | 0.750431 | 0.748250 | 0.052716 | Al |
| A33 | 1.0 | 0.749996 | 0.748173 | 0.267106 | Al |
| A34 | 1.0 | 0.304434 | 0.248574 | 0.027808 | Al |
| A35 | 1.0 | 0.264936 | 0.249360 | 0.215914 | Al |
| A36 | 1.0 | 0.256962 | 0.254941 | 0.423897 | Al |
Coordinate for a calculated transition state of the initial CH$_4$ activation on a γ-Al$_2$O$_3$ (100) surface (TS1) in Figure S6.
Absolute Energy: –731.15875929 eV.

| cell_length_a | 8.070750 |
| cell_length_b | 8.404430 |
| cell_length_c | 26.383160 |
| cell_angle_alpha | 90.000000 |
| cell_angle_beta | 90.000000 |
| cell_angle_gamma | 90.000000 |
| cell_volume | 1789.571263 |
| space_group_name_H-M_alt | 'P 1' |
| space_group_IT_number | 1 |

| H1 | 1.0 | 0.920240 | 0.400297 | 0.445216 | H |
| H2 | 1.0 | 0.446076 | 0.056069 | 0.966456 | H |
| H3 | 1.0 | 0.561919 | 0.045875 | 0.520166 | H |
| H4 | 1.0 | 0.755645 | 0.658765 | 0.491000 | H |
| H5 | 1.0 | 0.521510 | 0.642216 | 0.495072 | H |
| H6 | 1.0 | 0.654002 | 0.584338 | 0.55936 | H |
| H7 | 1.0 | 0.127609 | 0.406266 | 0.501422 | H |
| H8 | 1.0 | 0.392015 | 0.762486 | 0.967252 | H |
| H9 | 1.0 | 0.821895 | 0.302536 | 0.953363 | H |
| H10 | 1.0 | 0.613689 | 0.868908 | 0.504787 | H |
| C1 | 1.0 | 0.643463 | 0.633558 | 0.512911 | C |
| O1 | 1.0 | 0.610577 | 0.276015 | 0.468214 | O |
| O2 | 1.0 | 0.113988 | 0.596167 | 0.158018 | O |
| O3 | 1.0 | 0.118020 | 0.571217 | 0.362424 | O |
| O4 | 1.0 | 0.626232 | 0.911975 | 0.039562 | O |
| O5 | 1.0 | 0.618653 | 0.917782 | 0.260709 | O |
| O6 | 1.0 | 0.772178 | 0.407821 | 0.958558 | O |
| O7 | 1.0 | 0.859057 | 0.408682 | 0.209112 | O |
| O8 | 1.0 | 0.846876 | 0.404233 | 0.415123 | O |
| O9 | 1.0 | 0.373672 | 0.114030 | 0.088357 | O |
| O10 | 1.0 | 0.361968 | 0.081373 | 0.314132 | O |
| O11 | 1.0 | 0.907286 | 0.090389 | 0.110455 | O |
| O12 | 1.0 | 0.899208 | 0.102416 | 0.314982 | O |
| O13 | 1.0 | 0.398394 | 0.408191 | 0.001087 | O |
| O14 | 1.0 | 0.393592 | 0.423396 | 0.212612 | O |
| O15 | 1.0 | 0.370005 | 0.441124 | 0.416136 | O |
| O16 | 1.0 | 0.159311 | 0.915029 | 0.061107 | O |
| O17 | 1.0 | 0.152807 | 0.901854 | 0.267916 | O |
| O18 | 1.0 | 0.642895 | 0.580726 | 0.159124 | O |
| O19 | 1.0 | 0.638874 | 0.587873 | 0.380216 | O |
| O20 | 1.0 | 0.907042 | 0.411381 | 0.112283 | O |
| O21 | 1.0 | 0.898203 | 0.404932 | 0.319865 | O |
| O22 | 1.0 | 0.355829 | 0.063164 | 0.992858 | O |
| O23 | 1.0 | 0.392555 | 0.080863 | 0.213547 | O |
| O24 | 1.0 | 0.391845 | 0.111184 | 0.438487 | O |
| O25 | 1.0 | 0.149614 | 0.601396 | 0.058658 | O |
| O26 | 1.0 | 0.154973 | 0.595946 | 0.268258 | O |
| O27 | 1.0 | 0.641762 | 0.919997 | 0.159435 | O |
| O28 | 1.0 | 0.650073 | 0.900787 | 0.395952 | O |
| O29 | 1.0 | 0.114311 | 0.910955 | 0.157936 | O |
| O30 | 1.0 | 0.100048 | 0.915917 | 0.364996 | O |
| O31 | 1.0 | 0.612412 | 0.592096 | 0.040479 | O |
| O32 | 1.0 | 0.619561 | 0.585933 | 0.260068 | O |
| O33 | 1.0 | 0.884407 | 0.109602 | 0.994427 | O |
| O34 | 1.0 | 0.859028 | 0.093033 | 0.206950 | O |
| O35 | 1.0 | 0.862193 | 0.087925 | 0.421755 | O |
| O36 | 1.0 | 0.365508 | 0.419917 | 0.098834 | O |
| O37 | 1.0 | 0.367960 | 0.407995 | 0.310923 | O |
| O38 | 1.0 | 0.139875 | 0.249967 | 0.157440 | O |
| O39 | 1.0 | 0.125166 | 0.246149 | 0.368439 | O |
| O40 | 1.0 | 0.661563 | 0.272238 | 0.054814 | O |
| O41 | 1.0 | 0.641205 | 0.250435 | 0.260303 | O |
| O42 | 1.0 | 0.885766 | 0.751125 | 0.108905 | O |
|  |  |   |   |   |
|---|---|---|---|---|
| O43 | 1.0 | 0.882053 | 0.738707 | 0.321977 | O |
| O44 | 1.0 | 0.327203 | 0.746235 | 0.998405 | O |
| O45 | 1.0 | 0.367114 | 0.751074 | 0.213673 | O |
| O46 | 1.0 | 0.344930 | 0.747810 | 0.429936 | O |
| O47 | 1.0 | 0.893103 | 0.774880 | 0.999668 | O |
| O48 | 1.0 | 0.894479 | 0.751045 | 0.210349 | O |
| O49 | 1.0 | 0.949767 | 0.706879 | 0.425416 | O |
| O50 | 1.0 | 0.389301 | 0.756959 | 0.101557 | O |
| O51 | 1.0 | 0.385043 | 0.750348 | 0.318190 | O |
| O52 | 1.0 | 0.107422 | 0.258430 | 0.057218 | O |
| O53 | 1.0 | 0.114563 | 0.253782 | 0.264832 | O |
| O54 | 1.0 | 0.636685 | 0.251026 | 0.161815 | O |
| O55 | 1.0 | 0.630414 | 0.243521 | 0.369417 | O |
| O56 | 1.0 | 0.117073 | 0.407649 | 0.464748 | O |
| O57 | 1.0 | 0.640459 | 0.983044 | 0.500351 | O |
| Al1  | 1.0 | 0.408163 | 0.927698 | 0.050890 | Al |
| Al2  | 1.0 | 0.390853 | 0.921653 | 0.268445 | Al |
| Al3  | 1.0 | 0.136249 | 0.423987 | 0.111240 | Al |
| Al4  | 1.0 | 0.138404 | 0.412362 | 0.316438 | Al |
| Al5  | 1.0 | 0.623802 | 0.412822 | 0.004500 | Al |
| Al6  | 1.0 | 0.119066 | 0.426970 | 0.212547 | Al |
| Al7  | 1.0 | 0.589616 | 0.410655 | 0.415413 | Al |
| Al8  | 1.0 | 0.868619 | 0.920402 | 0.161249 | Al |
| Al9  | 1.0 | 0.894893 | 0.893784 | 0.395571 | Al |
| Al10 | 1.0 | 0.742888 | 0.961881 | 0.975011 | Al |
| Al11 | 1.0 | 0.619449 | 0.075289 | 0.212131 | Al |
| Al12 | 1.0 | 0.622716 | 0.084181 | 0.432368 | Al |
| Al13 | 1.0 | 0.869795 | 0.579683 | 0.160712 | Al |
| Al14 | 1.0 | 0.866937 | 0.579032 | 0.371240 | Al |
| Al15 | 1.0 | 0.387853 | 0.579404 | 0.051866 | Al |
| Al16 | 1.0 | 0.393587 | 0.577947 | 0.268850 | Al |
| Al17 | 1.0 | 0.144303 | 0.080666 | 0.112388 | Al |
| Al18 | 1.0 | 0.128708 | 0.073601 | 0.319764 | Al |
| Al19 | 1.0 | 0.878989 | 0.205986 | 0.052359 | Al |
| Al20 | 1.0 | 0.876852 | 0.255260 | 0.267273 | Al |
| Al21 | 1.0 | 0.520766 | 0.269963 | 0.107407 | Al |
| Al22 | 1.0 | 0.501603 | 0.242285 | 0.315711 | Al |
| Al23 | 1.0 | 0.878590 | 0.253156 | 0.160588 | Al |
| Al24 | 1.0 | 0.873496 | 0.231605 | 0.370736 | Al |
| Al25 | 1.0 | 0.101318 | 0.765943 | 0.014800 | Al |
| Al26 | 1.0 | 0.133436 | 0.748095 | 0.217851 | Al |
| Al27 | 1.0 | 0.193733 | 0.603274 | 0.425551 | Al |
| Al28 | 1.0 | 0.511702 | 0.749897 | 0.162104 | Al |
| Al29 | 1.0 | 0.496121 | 0.753721 | 0.382436 | Al |
| Al30 | 1.0 | 0.142457 | 0.753596 | 0.111988 | Al |
| Al31 | 1.0 | 0.128607 | 0.751714 | 0.322341 | Al |
| Al32 | 1.0 | 0.755689 | 0.746584 | 0.053224 | Al |
| Al33 | 1.0 | 0.752683 | 0.752398 | 0.268505 | Al |
| Al34 | 1.0 | 0.298903 | 0.238997 | 0.025993 | Al |
| Al35 | 1.0 | 0.266690 | 0.252792 | 0.216001 | Al |
| Al36 | 1.0 | 0.257031 | 0.265115 | 0.423848 | Al |
Coordinate for a γ-Al₂O₃ (100) surface with CH₃* and H* in Figure S6. Absolute Energy: −735.4894316 eV.

cell_length_a 8.070750

cell_length_b 8.404430

cell_length_c 26.383160

cell_angle_alpha 90.000000

cell_angle_beta 90.000000

cell_angle_gamma 90.000000

cell_volume 1789.571263

| mol | x     | y     | z     | Coordination |
|-----|-------|-------|-------|--------------|
| H1  | 1.0   | 0.920806 | 0.416708 | 0.445179 | H |
| H2  | 1.0   | 0.454286 | 0.063327 | 0.966430 | H |
| H3  | 1.0   | 0.319484 | 0.002360 | 0.433871 | H |
| H4  | 1.0   | 0.610200 | 0.432055 | 0.533295 | H |
| H5  | 1.0   | 0.429203 | 0.317138 | 0.519836 | H |
| H6  | 1.0   | 0.607844 | 0.220170 | 0.544821 | H |
| H7  | 1.0   | 0.131170 | 0.431022 | 0.968250 | H |
| H8  | 1.0   | 0.823690 | 0.312047 | 0.51249 | H |
| H9  | 1.0   | 0.568567 | 0.880729 | 0.50626 | H |
| C1  | 1.0   | 0.566060 | 0.315602 | 0.519540 | C |
| O1  | 1.0   | 0.629214 | 0.287386 | 0.469707 | O |
| O2  | 1.0   | 0.129358 | 0.609141 | 0.158642 | O |
| O3  | 1.0   | 0.123781 | 0.583731 | 0.362801 | O |
| O4  | 1.0   | 0.635554 | 0.921791 | 0.040463 | O |
| O5  | 1.0   | 0.624030 | 0.930817 | 0.261153 | O |
| O6  | 1.0   | 0.775984 | 0.417061 | 0.958030 | O |
| O7  | 1.0   | 0.864648 | 0.420422 | 0.209722 | O |
| O8  | 1.0   | 0.850064 | 0.417351 | 0.414479 | O |
| O9  | 1.0   | 0.379645 | 0.125096 | 0.088326 | O |
| O10 | 1.0   | 0.365763 | 0.093327 | 0.314335 | O |
| O11 | 1.0   | 0.913268 | 0.102080 | 0.110653 | O |
| O12 | 1.0   | 0.902982 | 0.114064 | 0.315228 | O |
| O13 | 1.0   | 0.404731 | 0.417364 | 0.001913 | O |
| O14 | 1.0   | 0.398809 | 0.435425 | 0.215792 | O |
| O15 | 1.0   | 0.383596 | 0.446087 | 0.420575 | O |
| O16 | 1.0   | 0.165675 | 0.925754 | 0.061224 | O |
| O17 | 1.0   | 0.157698 | 0.913849 | 0.268013 | O |
| O18 | 1.0   | 0.648939 | 0.593536 | 0.160096 | O |
| O19 | 1.0   | 0.642544 | 0.599670 | 0.380230 | O |
| O20 | 1.0   | 0.913921 | 0.425834 | 0.113374 | O |
| O21 | 1.0   | 0.901764 | 0.417868 | 0.319645 | O |
| O22 | 1.0   | 0.363145 | 0.072478 | 0.993842 | O |
| O23 | 1.0   | 0.397786 | 0.092710 | 0.213814 | O |
| O24 | 1.0   | 0.367099 | 0.110529 | 0.437763 | O |
| O25 | 1.0   | 0.156671 | 0.612322 | 0.059022 | O |
| O26 | 1.0   | 0.159789 | 0.608008 | 0.268807 | O |
| O27 | 1.0   | 0.647699 | 0.932317 | 0.160068 | O |
| O28 | 1.0   | 0.652105 | 0.914421 | 0.392026 | O |
| O29 | 1.0   | 0.120046 | 0.923033 | 0.158196 | O |
| O30 | 1.0   | 0.105374 | 0.928505 | 0.364923 | O |
| O31 | 1.0   | 0.619621 | 0.601400 | 0.040918 | O |
| O32 | 1.0   | 0.625433 | 0.598184 | 0.260976 | O |
| O33 | 1.0   | 0.890484 | 0.114251 | 0.993335 | O |
| O34 | 1.0   | 0.864824 | 0.106006 | 0.207138 | O |
| O35 | 1.0   | 0.868617 | 0.097643 | 0.422011 | O |
| O36 | 1.0   | 0.372015 | 0.431685 | 0.099719 | O |
| O37 | 1.0   | 0.372490 | 0.420273 | 0.312229 | O |
| O38 | 1.0   | 0.146178 | 0.261689 | 0.157514 | O |
| O39 | 1.0   | 0.126302 | 0.260623 | 0.368269 | O |
| O40 | 1.0   | 0.670228 | 0.281948 | 0.054988 | O |
| O41 | 1.0   | 0.645782 | 0.262523 | 0.260853 | O |
| O42 | 1.0   | 0.891963 | 0.762955 | 0.109344 | O |

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| Element | x  | y  | z  | Charge |
|---------|----|----|----|--------|
| O43     | 1.0| 0.885777| 0.753487| 0.322731|
| O44     | 1.0| 0.335771| 0.756578| 0.998919|
| O45     | 1.0| 0.373262| 0.763733| 0.214218|
| O46     | 1.0| 0.341864| 0.767765| 0.428459|
| O47     | 1.0| 0.901048| 0.781583|-0.000281|
| O48     | 1.0| 0.900288| 0.763616| 0.210822|
| O49     | 1.0| 0.954323| 0.721193| 0.424718|
| O50     | 1.0| 0.390533| 0.768540| 0.102068|
| O51     | 1.0| 0.389108| 0.762855| 0.318387|
| O52     | 1.0| 0.111845| 0.268335| 0.057096|
| O53     | 1.0| 0.119944| 0.265090| 0.265232|
| O54     | 1.0| 0.641680| 0.263530| 0.162095|
| O55     | 1.0| 0.633988| 0.255726| 0.370235|
| O56     | 1.0| 0.115711| 0.433238| 0.464435|
| O57     | 1.0| 0.638776| 0.972081| 0.499111|
| Al1     | 1.0| 0.415591| 0.938032| 0.051018|
| Al2     | 1.0| 0.396086| 0.934220| 0.268303|
| Al3     | 1.0| 0.142218| 0.436055| 0.111207|
| Al4     | 1.0| 0.142748| 0.425175| 0.316518|
| Al5     | 1.0| 0.630292| 0.439721| 0.212925|
| Al6     | 1.0| 0.598674| 0.419666| 0.414565|
| Al7     | 1.0| 0.874628| 0.932628| 0.161255|
| Al8     | 1.0| 0.894226| 0.905432| 0.392905|
| Al9     | 1.0| 0.744590| 0.970201| 0.973157|
| Al10    | 1.0| 0.624848| 0.087798| 0.212247|
| Al11    | 1.0| 0.640832| 0.075552| 0.444140|
| Al12    | 1.0| 0.876165| 0.592058| 0.160951|
| Al13    | 1.0| 0.869910| 0.589373| 0.369804|
| Al14    | 1.0| 0.395006| 0.590083| 0.502282|
| Al15    | 1.0| 0.399207| 0.589429| 0.269270|
| Al16    | 1.0| 0.150830| 0.092438| 0.112353|
| Al17    | 1.0| 0.132979| 0.086488| 0.319347|
| Al18    | 1.0| 0.884415| 0.209426| 0.051011|
| Al19    | 1.0| 0.881350| 0.266949| 0.266954|
| Al20    | 1.0| 0.526935| 0.280774| 0.107071|
| Al21    | 1.0| 0.505964| 0.253918| 0.316323|
| Al22    | 1.0| 0.883750| 0.265950| 0.160372|
| Al23    | 1.0| 0.873677| 0.241921| 0.370820|
| Al24    | 1.0| 0.109101| 0.776530| 0.014627|
| Al25    | 1.0| 0.139485| 0.759947| 0.217543|
| Al26    | 1.0| 0.175511| 0.635521| 0.426826|
| Al27    | 1.0| 0.517217| 0.762452| 0.162268|
| Al28    | 1.0| 0.500324| 0.764139| 0.382083|
| Al29    | 1.0| 0.148203| 0.765356| 0.112013|
| Al30    | 1.0| 0.136194| 0.764030| 0.322135|
| Al31    | 1.0| 0.763408| 0.756533| 0.052927|
| Al32    | 1.0| 0.758065| 0.765458| 0.268358|
| Al33    | 1.0| 0.303104| 0.247893| 0.025366|
| Al34    | 1.0| 0.271816| 0.264537| 0.215925|
| Al35    | 1.0| 0.252243| 0.284856| 0.423719|
Supporting Information

Coordinate for a calculated transition state from CH$_3$* on a γ-Al$_2$O$_3$ (100) surface (TS3) in Figure S6.
Absolute Energy: –734.90592846 eV.

|                     |     |     |     |     |
|---------------------|-----|-----|-----|-----|
| cell_length_a       | 8.070750 |
| cell_length_b       | 8.404430 |
| cell_length_c       | 26.383160 |
| cell_angle_alpha    | 90.000000 |
| cell_angle_beta     | 90.000000 |
| cell_angle_gamma    | 90.000000 |
| cell_volume         | 1789.571263 |
| space_group_name_H-M_alt | 'P 1' |
| space_group_IT_number | 1 |

|   |     |     |     |     |     |
|---|-----|-----|-----|-----|
| H1 | 1.0 | 0.878798 | 0.413373 | 0.449579 | H |
| H2 | 1.0 | 0.452120 | 0.055973 | 0.966720 | H |
| H3 | 1.0 | 0.316144 | 0.998889 | 0.431882 | H |
| H4 | 1.0 | 0.535542 | 0.543100 | 0.533514 | H |
| H5 | 1.0 | 0.479016 | 0.335993 | 0.529587 | H |
| H6 | 1.0 | 0.667816 | 0.392185 | 0.559001 | H |
| H7 | 1.0 | 0.174586 | 0.444668 | 0.498809 | H |
| H8 | 1.0 | 0.399931 | 0.766877 | 0.968159 | H |
| H9 | 1.0 | 0.824437 | 0.303567 | 0.952502 | H |
| H10 | 1.0 | 0.529432 | 1.014650 | 0.509586 | H |
| C1 | 1.0 | 0.583355 | 0.421278 | 0.527514 | C |
| O1 | 1.0 | 0.696856 | 0.409237 | 0.481470 | O |
| O2 | 1.0 | 0.118922 | 0.901528 | 0.158589 | O |
| O3 | 1.0 | 0.122411 | 0.578516 | 0.362271 | O |
| O4 | 1.0 | 0.631296 | 0.914454 | 0.040661 | O |
| O5 | 1.0 | 0.622810 | 0.923657 | 0.261260 | O |
| O6 | 1.0 | 0.777559 | 0.409065 | 0.959267 | O |
| O7 | 1.0 | 0.862922 | 0.412872 | 0.210034 | O |
| O8 | 1.0 | 0.860943 | 0.410207 | 0.412601 | O |
| O9 | 1.0 | 0.377788 | 0.117161 | 0.088756 | O |
| O10 | 1.0 | 0.367387 | 0.086839 | 0.314780 | O |
| O11 | 1.0 | 0.911337 | 0.094688 | 0.111065 | O |
| O12 | 1.0 | 0.902623 | 0.106943 | 0.315619 | O |
| O13 | 1.0 | 0.403408 | 0.409843 | 0.001996 | O |
| O14 | 1.0 | 0.398040 | 0.428328 | 0.215399 | O |
| O15 | 1.0 | 0.391747 | 0.433740 | 0.417281 | O |
| O16 | 1.0 | 0.163287 | 0.918036 | 0.061343 | O |
| O17 | 1.0 | 0.157471 | 0.908251 | 0.267418 | O |
| O18 | 1.0 | 0.647402 | 0.585604 | 0.160008 | O |
| O19 | 1.0 | 0.644326 | 0.592268 | 0.376634 | O |
| O20 | 1.0 | 0.912119 | 0.417707 | 0.113552 | O |
| O21 | 1.0 | 0.900452 | 0.410379 | 0.319534 | O |
| O22 | 1.0 | 0.360912 | 0.064984 | 0.993171 | O |
| O23 | 1.0 | 0.396753 | 0.085903 | 0.214060 | O |
| O24 | 1.0 | 0.365080 | 0.106808 | 0.435061 | O |
| O25 | 1.0 | 0.154560 | 0.604239 | 0.059083 | O |
| O26 | 1.0 | 0.158087 | 0.600886 | 0.267971 | O |
| O27 | 1.0 | 0.645607 | 0.925268 | 0.160234 | O |
| O28 | 1.0 | 0.647451 | 0.901646 | 0.387172 | O |
| O29 | 1.0 | 0.118332 | 0.915209 | 0.158248 | O |
| O30 | 1.0 | 0.107641 | 0.921699 | 0.364073 | O |
| O31 | 1.0 | 0.617721 | 0.593891 | 0.041129 | O |
| O32 | 1.0 | 0.624239 | 0.591678 | 0.260658 | O |
| O33 | 1.0 | 0.888785 | 0.106496 | 0.993923 | O |
| O34 | 1.0 | 0.862968 | 0.098772 | 0.207624 | O |
| O35 | 1.0 | 0.865528 | 0.085909 | 0.419529 | O |
| O36 | 1.0 | 0.370056 | 0.423646 | 0.099749 | O |
| O37 | 1.0 | 0.372204 | 0.414393 | 0.311614 | O |
| O38 | 1.0 | 0.144365 | 0.254120 | 0.157895 | O |
| O39 | 1.0 | 0.126692 | 0.254223 | 0.367873 | O |
| O40 | 1.0 | 0.667962 | 0.274343 | 0.055555 | O |
| O41 | 1.0 | 0.644325 | 0.255806 | 0.262739 | O |
| O42 | 1.0 | 0.889977 | 0.755460 | 0.109315 | O |
| Atom | X Position | Y Position | Z Position | Element |
|------|------------|------------|------------|----------|
| O43  | 0.887045   | 0.749362   | 0.321828   | O        |
| O44  | 0.333178   | 0.748619   | 0.998977   | O        |
| O45  | 0.371977   | 0.756203   | 0.213879   | O        |
| O46  | 0.338046   | 0.758886   | 0.426954   | O        |
| O47  | 0.898593   | 0.773749   | 0.999710   | O        |
| O48  | 0.898611   | 0.756461   | 0.210598   | O        |
| O49  | 0.947432   | 0.718360   | 0.422907   | O        |
| O50  | 0.393158   | 0.760583   | 0.102026   | O        |
| O51  | 0.386234   | 0.754234   | 0.317219   | O        |
| O52  | 0.110337   | 0.266407   | 0.057483   | O        |
| O53  | 0.119167   | 0.258005   | 0.265454   | O        |
| O54  | 0.639892   | 0.256083   | 0.162776   | O        |
| O55  | 0.629883   | 0.242264   | 0.376539   | O        |
| O56  | 0.127497   | 0.439986   | 0.464820   | O        |
| O57  | 0.635859   | 0.035232   | 0.494013   | O        |
| Al1  | 0.413379   | 0.930428   | 0.051153   | Al       |
| Al2  | 0.395453   | 0.928106   | 0.268203   | Al       |
| Al3  | 0.140422   | 0.428367   | 0.111402   | Al       |
| Al4  | 0.142912   | 0.419303   | 0.316301   | Al       |
| Al5  | 0.629038   | 0.414635   | 0.005042   | Al       |
| Al6  | 0.623784   | 0.431925   | 0.213308   | Al       |
| Al7  | 0.605383   | 0.429000   | 0.418312   | Al       |
| Al8  | 0.872275   | 0.925268   | 0.161205   | Al       |
| Al9  | 0.892563   | 0.898062   | 0.388390   | Al       |
| Al10 | 0.742245   | 0.963489   | 0.973322   | Al       |
| Al11 | 0.623494   | 0.080991   | 0.212624   | Al       |
| Al12 | 0.630999   | 0.069319   | 0.429184   | Al       |
| Al13 | 0.874292   | 0.584561   | 0.160929   | Al       |
| Al14 | 0.870586   | 0.582597   | 0.368560   | Al       |
| Al15 | 0.393106   | 0.582370   | 0.052360   | Al       |
| Al16 | 0.397648   | 0.582274   | 0.268294   | Al       |
| Al17 | 0.149073   | 0.084927   | 0.112575   | Al       |
| Al18 | 0.134687   | 0.080473   | 0.318993   | Al       |
| Al19 | 0.882531   | 0.202754   | 0.051482   | Al       |
| Al20 | 0.879885   | 0.259388   | 0.267254   | Al       |
| Al21 | 0.525055   | 0.272929   | 0.107670   | Al       |
| Al22 | 0.505789   | 0.249104   | 0.319478   | Al       |
| Al23 | 0.882676   | 0.258400   | 0.160787   | Al       |
| Al24 | 0.882262   | 0.236028   | 0.371443   | Al       |
| Al25 | 0.106593   | 0.768630   | 0.014641   | Al       |
| Al26 | 0.138258   | 0.753806   | 0.217100   | Al       |
| Al27 | 0.163192   | 0.636842   | 0.426819   | Al       |
| Al28 | 0.515900   | 0.754681   | 0.162062   | Al       |
| Al29 | 0.495151   | 0.750105   | 0.380452   | Al       |
| Al30 | 0.146080   | 0.757648   | 0.111915   | Al       |
| Al31 | 0.137664   | 0.757421   | 0.321260   | Al       |
| Al32 | 0.761280   | 0.749215   | 0.052937   | Al       |
| Al33 | 0.756599   | 0.758637   | 0.267966   | Al       |
| Al34 | 0.301726   | 0.240482   | 0.025774   | Al       |
| Al35 | 0.271195   | 0.257790   | 0.216217   | Al       |
| Al36 | 0.251512   | 0.285227   | 0.423495   | Al       |
Coordinate for a γ-Al₂O₃ (100) surface with CH₃OH* in Figure S6.

Absolute Energy: –735.56165834eV.

| Coordinate | x     | y     | z     | H      |
|------------|-------|-------|-------|--------|
| H1         | 1.0   | 0.878798 | 0.413373 | 0.449579 |
| H2         | 1.0   | 0.452120 | 0.055973 | 0.966720 |
| H3         | 1.0   | 0.316144 | 0.998889 | 0.431882 |
| H4         | 1.0   | 0.535542 | 0.543100 | 0.533514 |
| H5         | 1.0   | 0.479016 | 0.335993 | 0.529587 |
| H6         | 1.0   | 0.667816 | 0.392185 | 0.559001 |
| H7         | 1.0   | 0.174586 | 0.444668 | 0.498809 |
| H8         | 1.0   | 0.399931 | 0.766877 | 0.968159 |
| H9         | 1.0   | 0.824437 | 0.303567 | 0.952502 |
| H10        | 1.0   | 0.529432 | 1.014650 | 0.509586 |
| C1         | 1.0   | 0.583555 | 0.421278 | 0.527514 |
| C2         | 1.0   | 0.699836 | 0.409237 | 0.481470 |
| C3         | 1.0   | 0.118922 | 0.601528 | 0.158589 |
| O1         | 1.0   | 0.631296 | 0.578516 | 0.362271 |
| O2         | 1.0   | 0.122411 | 0.914454 | 0.406611 |
| O3         | 1.0   | 0.622810 | 0.923657 | 0.261260 |
| O4         | 1.0   | 0.777559 | 0.409065 | 0.959267 |
| O5         | 1.0   | 0.862922 | 0.412872 | 0.210034 |
| O6         | 1.0   | 0.860943 | 0.410207 | 0.412601 |
| O7         | 1.0   | 0.377788 | 0.111761 | 0.088756 |
| O8         | 1.0   | 0.367387 | 0.086839 | 0.314780 |
| O9         | 1.0   | 0.911337 | 0.094688 | 0.111065 |
| O10        | 1.0   | 0.902623 | 0.106943 | 0.315619 |
| O11        | 1.0   | 0.403408 | 0.409843 | 0.001996 |
| O12        | 1.0   | 0.398040 | 0.428328 | 0.213399 |
| O13        | 1.0   | 0.391747 | 0.433740 | 0.417281 |
| O14        | 1.0   | 0.163287 | 0.918036 | 0.061343 |
| O15        | 1.0   | 0.157471 | 0.908251 | 0.267418 |
| O16        | 1.0   | 0.647402 | 0.585604 | 0.160008 |
| O17        | 1.0   | 0.644326 | 0.592268 | 0.376634 |
| O18        | 1.0   | 0.912119 | 0.417707 | 0.113552 |
| O19        | 1.0   | 0.900452 | 0.410379 | 0.319534 |
| O20        | 1.0   | 0.916012 | 0.104984 | 0.993171 |
| O21        | 1.0   | 0.396753 | 0.085903 | 0.214060 |
| O22        | 1.0   | 0.365080 | 0.106808 | 0.435061 |
| O23        | 1.0   | 0.154560 | 0.604239 | 0.059083 |
| O24        | 1.0   | 0.158087 | 0.600886 | 0.267971 |
| O25        | 1.0   | 0.645607 | 0.925268 | 0.160234 |
| O26        | 1.0   | 0.647451 | 0.901646 | 0.387172 |
| O27        | 1.0   | 0.118332 | 0.915209 | 0.158248 |
| O28        | 1.0   | 0.107641 | 0.921669 | 0.364073 |
| O29        | 1.0   | 0.617721 | 0.593891 | 0.041129 |
| O30        | 1.0   | 0.624239 | 0.591678 | 0.260658 |
| O31        | 1.0   | 0.888785 | 0.106469 | 0.993923 |
| O32        | 1.0   | 0.862968 | 0.098772 | 0.207624 |
| O33        | 1.0   | 0.865528 | 0.085909 | 0.419529 |
| O34        | 1.0   | 0.370056 | 0.423646 | 0.099749 |
| O35        | 1.0   | 0.372204 | 0.414393 | 0.311614 |
| O36        | 1.0   | 0.144365 | 0.254120 | 0.157895 |
| O37        | 1.0   | 0.126692 | 0.254223 | 0.367873 |
| O38        | 1.0   | 0.667962 | 0.274343 | 0.055555 |
| O39        | 1.0   | 0.644325 | 0.255806 | 0.262739 |
| O40        | 1.0   | 0.889777 | 0.755460 | 0.109315 |

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| 043 | 1.0 | 0.887045 | 0.749362 | 0.321828 | O  
| 044 | 1.0 | 0.333178 | 0.748619 | 0.999710 | O  
| 045 | 1.0 | 0.371977 | 0.756203 | 0.122776 | O  
| 046 | 1.0 | 0.338046 | 0.758886 | 0.426954 | O  
| 047 | 1.0 | 0.898593 | 0.773749 | 0.999710 | O  
| 048 | 1.0 | 0.898611 | 0.756461 | 0.210598 | O  
| 049 | 1.0 | 0.947432 | 0.718360 | 0.422907 | O  
| 050 | 1.0 | 0.393158 | 0.760583 | 0.102026 | O  
| 051 | 1.0 | 0.362346 | 0.754234 | 0.317219 | O  
| 052 | 1.0 | 0.110337 | 0.260407 | 0.057483 | O  
| 053 | 1.0 | 0.119167 | 0.258005 | 0.265454 | O  
| 054 | 1.0 | 0.639892 | 0.256083 | 0.162776 | O  
| 055 | 1.0 | 0.629883 | 0.242264 | 0.376539 | O  
| 056 | 1.0 | 0.127497 | 0.439986 | 0.464820 | O  
| 057 | 1.0 | 0.635859 | 0.035232 | 0.494013 | O  
| Al1 | 1.0 | 0.413379 | 0.930428 | 0.051153 | Al  
| Al2 | 1.0 | 0.395453 | 0.928106 | 0.268203 | Al  
| Al3 | 1.0 | 0.140422 | 0.428367 | 0.111402 | Al  
| Al4 | 1.0 | 0.142912 | 0.419303 | 0.316301 | Al  
| Al5 | 1.0 | 0.629038 | 0.414635 | 0.050542 | Al  
| Al6 | 1.0 | 0.623784 | 0.431925 | 0.213308 | Al  
| Al7 | 1.0 | 0.605383 | 0.429000 | 0.418312 | Al  
| Al8 | 1.0 | 0.872275 | 0.925268 | 0.161205 | Al  
| Al9 | 1.0 | 0.895263 | 0.898062 | 0.388390 | Al  
| Al10 | 1.0 | 0.742245 | 0.963489 | 0.973322 | Al  
| Al11 | 1.0 | 0.623494 | 0.080991 | 0.212824 | Al  
| Al12 | 1.0 | 0.633099 | 0.069319 | 0.429184 | Al  
| Al13 | 1.0 | 0.874292 | 0.584561 | 0.169029 | Al  
| Al14 | 1.0 | 0.870586 | 0.582597 | 0.368560 | Al  
| Al15 | 1.0 | 0.393106 | 0.582370 | 0.052360 | Al  
| Al16 | 1.0 | 0.397648 | 0.582274 | 0.268294 | Al  
| Al17 | 1.0 | 0.149073 | 0.084927 | 0.112575 | Al  
| Al18 | 1.0 | 0.134687 | 0.080473 | 0.318993 | Al  
| Al19 | 1.0 | 0.882531 | 0.202754 | 0.051482 | Al  
| Al20 | 1.0 | 0.879885 | 0.259388 | 0.267254 | Al  
| Al21 | 1.0 | 0.525055 | 0.272929 | 0.107670 | Al  
| Al22 | 1.0 | 0.505789 | 0.249104 | 0.319478 | Al  
| Al23 | 1.0 | 0.882676 | 0.258400 | 0.160787 | Al  
| Al24 | 1.0 | 0.882262 | 0.236028 | 0.371443 | Al  
| Al25 | 1.0 | 0.106593 | 0.768630 | 0.014641 | Al  
| Al26 | 1.0 | 0.138258 | 0.753806 | 0.217100 | Al  
| Al27 | 1.0 | 0.163192 | 0.636842 | 0.426819 | Al  
| Al28 | 1.0 | 0.515900 | 0.754681 | 0.162062 | Al  
| Al29 | 1.0 | 0.495151 | 0.750105 | 0.380452 | Al  
| Al30 | 1.0 | 0.146080 | 0.757648 | 0.111915 | Al  
| Al31 | 1.0 | 0.137664 | 0.757421 | 0.321260 | Al  
| Al32 | 1.0 | 0.761280 | 0.749215 | 0.052937 | Al  
| Al33 | 1.0 | 0.756599 | 0.758637 | 0.267966 | Al  
| Al34 | 1.0 | 0.301726 | 0.240482 | 0.025774 | Al  
| Al35 | 1.0 | 0.271195 | 0.257790 | 0.216217 | Al  
| Al36 | 1.0 | 0.251512 | 0.285227 | 0.423495 | Al  

Supporting Information
Optimized Structures and Energies for Figure S8

Coordinate for a $\gamma$-Al$_2$O$_3$ (100) surface with CH$_4$ $\sigma$-complex at a 6-coordinated Al site.

Absolute Energy: $-751.20248905$ eV.

cell_length_a = 8.070750

cell_length_b = 8.404430

cell_length_c = 26.383160

cell_angle_alpha = 90.000000

cell_angle_beta = 90.000000

cell_angle_gamma = 90.000000

cell_volume = 1789.571263

space_group_name_H-M_alt = 'P 1'

| Atom | x      | y      | z      | Element |
|------|--------|--------|--------|---------|
| H    | 0.000647 | 0.431891 | 0.446116 | H       |
| H    | 0.397608 | 0.758756 | 0.963031 | H       |
| H    | 0.870488 | 0.312798 | 0.966527 | H       |
| H    | 0.573832 | 0.796423 | 0.505100 | H       |
| H    | 0.272796 | 0.835634 | 0.398556 | H       |
| H    | 0.271406 | 0.002458 | 0.462014 | H       |
| H    | 0.843184 | 0.145696 | 0.447270 | H       |
| H    | 0.848942 | 0.716110 | 0.448037 | H       |
| H    | 0.658037 | 0.556409 | 0.550341 | H       |
| H    | 0.575993 | 0.516356 | 0.612460 | H       |
| C    | 0.454986 | 0.477515 | 0.556797 | H       |
| H    | 0.630540 | 0.355652 | 0.570290 | H       |
| C    | 0.658774 | 0.227307 | 0.468866 | O       |
| O    | 0.620666 | 0.599222 | 0.455137 | O       |
| O    | 0.118417 | 0.581923 | 0.150846 | O       |
| O    | 0.127608 | 0.583215 | 0.361494 | O       |
| O    | 0.624612 | 0.903348 | 0.044615 | O       |
| O    | 0.621451 | 0.918417 | 0.263303 | O       |
| O    | 0.849375 | 0.407438 | -0.012199 | O     |
| O    | 0.868542 | 0.407173 | 0.203658 | O       |
| O    | 0.858931 | 0.430101 | 0.411832 | O       |
| O    | 0.376508 | 0.097723 | 0.095119 | O       |
| O    | 0.373472 | 0.092954 | 0.312919 | O       |
| O    | 0.914556 | 0.91267 | 0.105388 | O       |
| O    | 0.905570 | 0.102053 | 0.320048 | O       |
| O    | 0.426961 | 0.420271 | 0.994823 | O       |
| O    | 0.399640 | 0.417798 | 0.205912 | O       |
| O    | 0.397411 | 0.404877 | 0.415910 | O       |
| O    | 0.166605 | 0.901026 | 0.055735 | O       |
| O    | 0.155206 | 0.917205 | 0.264850 | O       |
| O    | 0.651776 | 0.575618 | 0.154193 | O       |
| O    | 0.657389 | 0.643572 | 0.354562 | O       |
| O    | 0.912459 | 0.395732 | 0.102188 | O       |
| O    | 0.909678 | 0.413748 | 0.31437 | O       |
| O    | 0.429336 | 0.081886 | 0.996628 | O       |
| O    | 0.402379 | 0.081175 | 0.211801 | O       |
| O    | 0.336166 | 0.092580 | 0.448538 | O       |
| O    | 0.164857 | 0.592937 | 0.053537 | O       |
| O    | 0.150858 | 0.599089 | 0.263520 | O       |
| O    | 0.649046 | 0.917548 | 0.159010 | O       |
| O    | 0.660241 | 0.932165 | 0.405259 | O       |
| O    | 0.124011 | 0.910491 | 0.153193 | O       |
| O    | 0.128808 | 0.921816 | 0.364706 | O       |
| O    | 0.625024 | 0.599693 | 0.042269 | O       |
| O    | 0.616713 | 0.587665 | 0.253960 | O       |
| O    | 0.852600 | 0.112314 | 0.994526 | O       |
| O    | 0.868774 | 0.091329 | 0.205271 | O       |
| O    | 0.929182 | 0.113219 | 0.421156 | O       |
| O    | 0.372846 | 0.402912 | 0.090047 | O       |
|  |  |  |  |  |
|---|---|---|---|---|
| O38 | 1.0 | 0.369439 | 0.417061 | 0.305235 | O |
| O39 | 1.0 | 0.144400 | 0.248091 | 0.258874 | O |
| O40 | 1.0 | 0.137443 | 0.259692 | 0.362830 | O |
| O41 | 1.0 | 0.140521 | 0.251663 | 0.153272 | O |
| O42 | 1.0 | 0.902398 | 0.765765 | 0.320709 | O |
| O43 | 1.0 | 0.396669 | 0.735357 | 0.995096 | O |
| O44 | 1.0 | 0.137443 | 0.259692 | 0.362830 | O |
| O45 | 1.0 | 0.646442 | 0.254074 | 0.053410 | O |
| O46 | 1.0 | 0.651521 | 0.251663 | 0.258874 | O |
| O47 | 1.0 | 0.899196 | 0.750876 | 0.103411 | O |
| O48 | 1.0 | 0.336669 | 0.735357 | 0.995096 | O |
| O49 | 1.0 | 0.902398 | 0.765765 | 0.320709 | O |
| O50 | 1.0 | 0.925551 | 0.747324 | 0.420244 | O |
| O51 | 1.0 | 0.396669 | 0.735357 | 0.995096 | O |
| O52 | 1.0 | 0.378565 | 0.751382 | 0.307377 | O |
| O53 | 1.0 | 0.129561 | 0.248455 | 0.049615 | O |
| O54 | 1.0 | 0.117719 | 0.250326 | 0.262123 | O |
| O55 | 1.0 | 0.648983 | 0.246209 | 0.160587 | O |
| Al1 | 1.0 | 0.403861 | 0.921285 | 0.052225 | Al |
| Al2 | 1.0 | 0.393965 | 0.930145 | 0.267270 | Al |
| Al3 | 1.0 | 0.142309 | 0.419890 | 0.106183 | Al |
| Al4 | 1.0 | 0.143593 | 0.422999 | 0.311547 | Al |
| Al5 | 1.0 | 0.645422 | 0.424806 | 0.009250 | Al |
| Al6 | 1.0 | 0.627990 | 0.425741 | 0.209596 | Al |
| Al7 | 1.0 | 0.628495 | 0.398498 | 0.430223 | Al |
| Al8 | 1.0 | 0.875979 | 0.916140 | 0.159125 | Al |
| Al9 | 1.0 | 0.897715 | 0.929024 | 0.382263 | Al |
| Al10 | 1.0 | 0.650718 | 0.075065 | 0.009500 | Al |
| Al11 | 1.0 | 0.630716 | 0.068353 | 0.213099 | Al |
| Al12 | 1.0 | 0.567775 | 0.045835 | 0.458439 | Al |
| Al13 | 1.0 | 0.878867 | 0.583495 | 0.160017 | Al |
| Al14 | 1.0 | 0.880217 | 0.590776 | 0.366740 | Al |
| Al15 | 1.0 | 0.399561 | 0.582899 | 0.050109 | Al |
| Al16 | 1.0 | 0.389785 | 0.583874 | 0.261335 | Al |
| Al17 | 1.0 | 0.147760 | 0.075825 | 0.108720 | Al |
| Al18 | 1.0 | 0.144175 | 0.084508 | 0.317994 | Al |
| Al19 | 1.0 | 0.902547 | 0.227668 | 0.049149 | Al |
| Al20 | 1.0 | 0.883356 | 0.249930 | 0.265298 | Al |
| Al21 | 1.0 | 0.514640 | 0.254474 | 0.111582 | Al |
| Al22 | 1.0 | 0.510793 | 0.259101 | 0.316501 | Al |
| Al23 | 1.0 | 0.886213 | 0.248304 | 0.156924 | Al |
| Al24 | 1.0 | 0.874555 | 0.261556 | 0.368724 | Al |
| Al25 | 1.0 | 0.110109 | 0.754742 | 0.010838 | Al |
| Al26 | 1.0 | 0.132613 | 0.761471 | 0.215760 | Al |
| Al27 | 1.0 | 0.251242 | 0.563824 | 0.418507 | Al |
| Al28 | 1.0 | 0.521506 | 0.745543 | 0.160587 | Al |
| Al29 | 1.0 | 0.571231 | 0.737221 | 0.408888 | Al |
| Al30 | 1.0 | 0.144454 | 0.747515 | 0.108852 | Al |
| Al31 | 1.0 | 0.142493 | 0.759536 | 0.317597 | Al |
| Al32 | 1.0 | 0.777551 | 0.751864 | 0.046971 | Al |
| Al33 | 1.0 | 0.694025 | 0.749097 | 0.293842 | Al |
| Al34 | 1.0 | 0.333444 | 0.251690 | 0.025708 | Al |
| Al35 | 1.0 | 0.271245 | 0.249691 | 0.213155 | Al |
| Al36 | 1.0 | 0.233931 | 0.263123 | 0.423719 | Al |
Coordinate for a calculated transition state of the CH$_4$ activation on a γ-Al$_2$O$_3$ (100) surface (TS1) in Figure S8.

Absolute Energy: –748.39713689 eV.

cell_length_a 8.070750
cell_length_b 8.404430
cell_length_c 26.383160
cell_angle_alpha 90.000000
cell_angle_beta 90.000000
cell_angle_gamma 90.000000
cell_volume 1789.571263

space_group_name_H-M_alt 'P 1'
space_group_IT_number 1

H1         1.0     0.026189     0.433421     0.450212    H
H2         1.0     0.398855     0.757379     0.963082    H
H3         1.0     0.894729     0.344723     0.967341    H
H4         1.0     0.598421     0.89456    0.534915    H
H5         1.0     0.257766     0.897019     0.417964    H
H6         1.0     0.274648     0.065829     0.486932    H
H7         1.0     0.954007     0.082717     0.447181    H
H8         1.0     0.812876     0.702044     0.439219    H
H9         1.0     0.633206     0.523465     0.544152    H
H10        1.0     0.623490     0.492217     0.611751    H
H11        1.0     0.441411     0.471270     0.573039    H
H12        1.0     0.603044     0.327710     0.568296    H
C1         1.0     0.576010     0.453975     0.574674    C
O1         1.0     0.482589     0.319493     0.456514    O
O2         1.0     0.471270     0.082717     0.544152    O
O3         1.0     0.471270     0.082717     0.544152    O
O4         1.0     0.471270     0.082717     0.544152    O
O5         1.0     0.471270     0.082717     0.544152    O
O6         1.0     0.471270     0.082717     0.544152    O
O7         1.0     0.471270     0.082717     0.544152    O
O8         1.0     0.471270     0.082717     0.544152    O
O9         1.0     0.471270     0.082717     0.544152    O
O10        1.0     0.471270     0.082717     0.544152    O
O11        1.0     0.471270     0.082717     0.544152    O
O12        1.0     0.471270     0.082717     0.544152    O
O13        1.0     0.471270     0.082717     0.544152    O
O14        1.0     0.471270     0.082717     0.544152    O
O15        1.0     0.471270     0.082717     0.544152    O
O16        1.0     0.471270     0.082717     0.544152    O
O17        1.0     0.471270     0.082717     0.544152    O
O18        1.0     0.471270     0.082717     0.544152    O
O19        1.0     0.471270     0.082717     0.544152    O
O20        1.0     0.471270     0.082717     0.544152    O
O21        1.0     0.471270     0.082717     0.544152    O
O22        1.0     0.471270     0.082717     0.544152    O
O23        1.0     0.471270     0.082717     0.544152    O
O24        1.0     0.471270     0.082717     0.544152    O
O25        1.0     0.471270     0.082717     0.544152    O
O26        1.0     0.471270     0.082717     0.544152    O
O27        1.0     0.471270     0.082717     0.544152    O
O28        1.0     0.471270     0.082717     0.544152    O
O29        1.0     0.471270     0.082717     0.544152    O
O30        1.0     0.471270     0.082717     0.544152    O
O31        1.0     0.471270     0.082717     0.544152    O
O32        1.0     0.471270     0.082717     0.544152    O
O33        1.0     0.471270     0.082717     0.544152    O
O34        1.0     0.471270     0.082717     0.544152    O
O35        1.0     0.471270     0.082717     0.544152    O
O36        1.0     0.471270     0.082717     0.544152    O
O37        1.0     0.471270     0.082717     0.544152    O
O38        1.0     0.471270     0.082717     0.544152    O
O39        1.0     0.471270     0.082717     0.544152    O
O40        1.0     0.471270     0.082717     0.544152    O

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| O41  | 1.0 | 0.647871 | 0.257377 | 0.054727 | O  |
| O42  | 1.0 | 0.657716 | 0.249536 | 0.258774 | O  |
| O43  | 1.0 | 0.899771 | 0.750965 | 0.104078 | O  |
| O44  | 1.0 | 0.897721 | 0.761458 | 0.315313 | O  |
| O45  | 1.0 | 0.340002 | 0.753625 | 0.995223 | O  |
| O46  | 1.0 | 0.372257 | 0.747469 | 0.207205 | O  |
| O47  | 1.0 | 0.326936 | 0.804970 | 0.430118 | O  |
| O48  | 1.0 | 0.911185 | 0.757333 | 0.994372 | O  |
| O49  | 1.0 | 0.901561 | 0.748720 | 0.205271 | O  |
| O50  | 1.0 | 0.913932 | 0.733431 | 0.416469 | O  |
| O51  | 1.0 | 0.392965 | 0.756038 | 0.099307 | O  |
| O52  | 1.0 | 0.386940 | 0.747519 | 0.309279 | O  |
| O53  | 1.0 | 0.132347 | 0.250659 | 0.160507 | O  |
| O54  | 1.0 | 0.120649 | 0.242758 | 0.265068 | O  |
| O55  | 1.0 | 0.656409 | 0.844749 | 0.160507 | O  |
| O56  | 1.0 | 0.630428 | 0.265979 | 0.368422 | O  |
| O57  | 1.0 | 0.149447 | 0.453056 | 0.457008 | O  |
| O58  | 1.0 | 0.558335 | 0.954826 | 0.506033 | O  |
| Al1  | 1.0 | 0.404599 | 0.294666 | 0.052731 | Al |
| Al2  | 1.0 | 0.396702 | 0.296194 | 0.265061 | Al |
| Al3  | 1.0 | 0.147967 | 0.421061 | 0.108533 | Al |
| Al4  | 1.0 | 0.154435 | 0.415781 | 0.317333 | Al |
| Al5  | 1.0 | 0.647586 | 0.424493 | 0.009532 | Al |
| Al6  | 1.0 | 0.634694 | 0.411106 | 0.208904 | Al |
| Al7  | 1.0 | 0.605399 | 0.453066 | 0.420077 | Al |
| Al8  | 1.0 | 0.877685 | 0.919518 | 0.157900 | Al |
| Al9  | 1.0 | 0.873802 | 0.906942 | 0.375199 | Al |
| Al10 | 1.0 | 0.653503 | 0.078451 | 0.009998 | Al |
| Al11 | 1.0 | 0.633036 | 0.072738 | 0.211124 | Al |
| Al12 | 1.0 | 0.555080 | 0.841396 | 0.451699 | Al |
| Al13 | 1.0 | 0.877749 | 0.578853 | 0.156624 | Al |
| Al14 | 1.0 | 0.882200 | 0.572409 | 0.365846 | Al |
| Al15 | 1.0 | 0.400930 | 0.584638 | 0.490606 | Al |
| Al16 | 1.0 | 0.395624 | 0.579225 | 0.259007 | Al |
| Al17 | 1.0 | 0.151252 | 0.078551 | 0.110227 | Al |
| Al18 | 1.0 | 0.154581 | 0.091275 | 0.327359 | Al |
| Al19 | 1.0 | 0.905042 | 0.242535 | 0.050306 | Al |
| Al20 | 1.0 | 0.889378 | 0.242958 | 0.270702 | Al |
| Al21 | 1.0 | 0.515320 | 0.259253 | 0.113241 | Al |
| Al22 | 1.0 | 0.511511 | 0.250713 | 0.315791 | Al |
| Al23 | 1.0 | 0.895419 | 0.248722 | 0.158261 | Al |
| Al24 | 1.0 | 0.846512 | 0.247320 | 0.376547 | Al |
| Al25 | 1.0 | 0.112690 | 0.757479 | 0.010751 | Al |
| Al26 | 1.0 | 0.139759 | 0.751755 | 0.213823 | Al |
| Al27 | 1.0 | 0.222814 | 0.615121 | 0.419530 | Al |
| Al28 | 1.0 | 0.524952 | 0.744980 | 0.158844 | Al |
| Al29 | 1.0 | 0.514195 | 0.707386 | 0.364928 | Al |
| Al30 | 1.0 | 0.146484 | 0.750076 | 0.108068 | Al |
| Al31 | 1.0 | 0.135328 | 0.760623 | 0.315297 | Al |
| Al32 | 1.0 | 0.778756 | 0.753624 | 0.046702 | Al |
| Al33 | 1.0 | 0.758950 | 0.747739 | 0.264493 | Al |
| Al34 | 1.0 | 0.334732 | 0.252989 | 0.026774 | Al |
| Al35 | 1.0 | 0.275441 | 0.250879 | 0.216883 | Al |
| Al36 | 1.0 | 0.284089 | 0.282759 | 0.434177 | Al |
**Coordinate** for a $\gamma$-Al$_2$O$_3$ (100) surface with CH$_3^*$ and H* in Figure S8.

Absolute Energy: $-750.95318799$ eV.

| cell_length_a       | 8.070750 |
| cell_length_b       | 8.404430 |
| cell_length_c       | 26.383160 |
| cell_angle_alpha    | 90.000000 |
| cell_angle_beta     | 90.000000 |
| cell_angle_gamma    | 90.000000 |
| cell_volume         | 1789.571263 |
| space_group_name_H-M_alt | 'P 1' |
| space_group_IT_number | 1 |

H1  | 1.0 | 0.018659 | 0.441341 | 0.456484 | H |
H2  | 1.0 | 0.396617 | 0.756631 | 0.965021 | H |
H3  | 1.0 | 0.913047 | 0.373586 | 0.970718 | H |
H4  | 1.0 | 0.610094 | 0.807523 | 0.487339 | H |
H5  | 1.0 | 0.259443 | 0.851052 | 0.403042 | H |
H6  | 1.0 | 0.172607 | 0.028528 | 0.477112 | H |
H7  | 1.0 | 0.699976 | 0.494704 | 0.509246 | H |
H8  | 1.0 | 0.826800 | 0.782912 | 0.444653 | H |
H9  | 1.0 | 0.609816 | 0.494704 | 0.509246 | H |
H10 | 1.0 | 0.668849 | 0.429763 | 0.598238 | H |
H11 | 1.0 | 0.441206 | 0.447640 | 0.583623 | H |
H12 | 1.0 | 0.557311 | 0.382484 | 0.580671 | C |
O1  | 1.0 | 0.439885 | 0.135680 | 0.443514 | O |
O2  | 1.0 | 0.608765 | 0.547465 | 0.476415 | O |
O3  | 1.0 | 0.119572 | 0.599833 | 0.155885 | O |
O4  | 1.0 | 0.121768 | 0.592975 | 0.363410 | O |
O5  | 1.0 | 0.627135 | 0.911220 | 0.041974 | O |
O6  | 1.0 | 0.627002 | 0.923190 | 0.258495 | O |
O7  | 1.0 | 0.874551 | 0.425052 | 0.002429 | O |
O8  | 1.0 | 0.870043 | 0.416423 | 0.206732 | O |
O9  | 1.0 | 0.858386 | 0.431637 | 0.415948 | O |
O10 | 1.0 | 0.379939 | 0.103152 | 0.095185 | O |
O11 | 1.0 | 0.376632 | 0.093406 | 0.312637 | O |
O12 | 1.0 | 0.917596 | 0.107170 | 0.108880 | O |
O13 | 1.0 | 0.908708 | 0.106270 | 0.320023 | O |
O14 | 1.0 | 0.406429 | 0.427847 | 0.999530 | O |
O15 | 1.0 | 0.409256 | 0.427771 | 0.210723 | O |
O16 | 1.0 | 0.393644 | 0.430909 | 0.411054 | O |
O17 | 1.0 | 0.167517 | 0.916115 | 0.058191 | O |
O18 | 1.0 | 0.160761 | 0.914427 | 0.265007 | O |
O19 | 1.0 | 0.651847 | 0.586313 | 0.157272 | O |
O20 | 1.0 | 0.644632 | 0.606122 | 0.370795 | O |
O21 | 1.0 | 0.917723 | 0.410806 | 0.108311 | O |
O22 | 1.0 | 0.912397 | 0.415169 | 0.317811 | O |
O23 | 1.0 | 0.422548 | 0.083041 | 0.997688 | O |
O24 | 1.0 | 0.403253 | 0.089844 | 0.212260 | O |
O25 | 1.0 | 0.118965 | 0.128333 | 0.468248 | O |
O26 | 1.0 | 0.165103 | 0.609099 | 0.058219 | O |
O27 | 1.0 | 0.159273 | 0.605512 | 0.265935 | O |
O28 | 1.0 | 0.650616 | 0.928006 | 0.157993 | O |
O29 | 1.0 | 0.644553 | 0.933446 | 0.372563 | O |
O30 | 1.0 | 0.120761 | 0.914754 | 0.155706 | O |
O31 | 1.0 | 0.121626 | 0.925044 | 0.363199 | O |
O32 | 1.0 | 0.625053 | 0.598836 | 0.039273 | O |
O33 | 1.0 | 0.626933 | 0.593122 | 0.257710 | O |
O34 | 1.0 | 0.866154 | 0.110763 | 0.999445 | O |
O35 | 1.0 | 0.869907 | 0.098680 | 0.207084 | O |
O36 | 1.0 | 0.856272 | 0.096967 | 0.419399 | O |
O37 | 1.0 | 0.378054 | 0.418458 | 0.098018 | O |
O38 | 1.0 | 0.372528 | 0.421724 | 0.308622 | O |
O39 | 1.0 | 0.146801 | 0.256840 | 0.157136 | O |
O40 | 1.0 | 0.138420 | 0.258409 | 0.369361 | O |
| Atom | X | Y | Z | Element |
|------|---|---|---|---------|
| O41  | 1.0 | 0.650324 | 0.261917 | O      |
| O42  | 1.0 | 0.652586 | 0.257939 | O      |
| O43  | 1.0 | 0.894606 | 0.756826 | O      |
| O44  | 1.0 | 0.894002 | 0.759586 | O      |
| O45  | 1.0 | 0.337574 | 0.757889 | O      |
| O46  | 1.0 | 0.374127 | 0.757712 | O      |
| O47  | 1.0 | 0.345146 | 0.770613 | O      |
| O48  | 1.0 | 0.913754 | 0.756619 | O      |
| O49  | 1.0 | 0.902060 | 0.757962 | O      |
| O50  | 1.0 | 0.906601 | 0.763497 | O      |
| O51  | 1.0 | 0.395535 | 0.757413 | O      |
| O52  | 1.0 | 0.387564 | 0.760003 | O      |
| O53  | 1.0 | 0.131864 | 0.255772 | O      |
| O54  | 1.0 | 0.122257 | 0.256447 | O      |
| O55  | 1.0 | 0.648912 | 0.256938 | O      |
| O56  | 1.0 | 0.645380 | 0.275047 | O      |
| O57  | 1.0 | 0.141894 | 0.446816 | O      |
| O58  | 1.0 | 0.680925 | 0.897137 | O      |
| Al1  | 1.0 | 0.406235 | 0.928963 | Al     |
| Al2  | 1.0 | 0.398017 | 0.934822 | Al     |
| Al3  | 1.0 | 0.150562 | 0.428572 | Al     |
| Al4  | 1.0 | 0.146215 | 0.423928 | Al     |
| Al5  | 1.0 | 0.643734 | 0.422636 | Al     |
| Al6  | 1.0 | 0.631146 | 0.432472 | Al     |
| Al7  | 1.0 | 0.618220 | 0.446998 | Al     |
| Al8  | 1.0 | 0.876516 | 0.928446 | Al     |
| Al9  | 1.0 | 0.881298 | 0.932924 | Al     |
| Al10 | 1.0 | 0.655377 | 0.088956 | Al     |
| Al11 | 1.0 | 0.631458 | 0.082842 | Al     |
| Al12 | 1.0 | 0.629114 | 0.042928 | Al     |
| Al13 | 1.0 | 0.877531 | 0.585657 | Al     |
| Al14 | 1.0 | 0.873272 | 0.595735 | Al     |
| Al15 | 1.0 | 0.403281 | 0.582318 | Al     |
| Al16 | 1.0 | 0.398286 | 0.584928 | Al     |
| Al17 | 1.0 | 0.151614 | 0.086111 | Al     |
| Al18 | 1.0 | 0.149257 | 0.092855 | Al     |
| Al19 | 1.0 | 0.901074 | 0.249687 | Al     |
| Al20 | 1.0 | 0.885393 | 0.257991 | Al     |
| Al21 | 1.0 | 0.520553 | 0.262018 | Al     |
| Al22 | 1.0 | 0.512509 | 0.268087 | Al     |
| Al23 | 1.0 | 0.892419 | 0.257243 | Al     |
| Al24 | 1.0 | 0.877104 | 0.263165 | Al     |
| Al25 | 1.0 | 0.112918 | 0.759456 | Al     |
| Al26 | 1.0 | 0.140009 | 0.759069 | Al     |
| Al27 | 1.0 | 0.245611 | 0.577827 | Al     |
| Al28 | 1.0 | 0.521713 | 0.756699 | Al     |
| Al29 | 1.0 | 0.514481 | 0.769730 | Al     |
| Al30 | 1.0 | 0.147397 | 0.756941 | Al     |
| Al31 | 1.0 | 0.138547 | 0.762609 | Al     |
| Al32 | 1.0 | 0.775033 | 0.754565 | Al     |
| Al33 | 1.0 | 0.761861 | 0.757790 | Al     |
| Al34 | 1.0 | 0.323506 | 0.259056 | Al     |
| Al35 | 1.0 | 0.273407 | 0.258909 | Al     |
| Al36 | 1.0 | 0.268238 | 0.268468 | Al     |