Supporting Information

Gas-Phase Mechanism of $O^+/Ni^{2+}$-Mediated Methane Conversion to Formaldehyde

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1. Experimental methods

The infrared photodissociation (IRPD) experiments are performed on a cryogenic ion trap tandem mass spectrometer using the widely tunable, intense IR radiation from the Fritz–Haber–Institute Free–Electron Laser (FHI FEL). In brief, NiAl₂O₄⁺ ions are produced in a pulsed laser vaporization source by focusing a frequency–doubled Nd:YAG laser (50 Hz, 5–10 mJ) onto a rotating NiAl (50/50 at %) metal rod. The resulting plasma is quenched with a gas pulse of 1% O₂ seeded in He. Cluster ions are formed during expansion through a clustering channel downstream from the rod and pass through a 4 mm diameter skimmer and are collimated in a radio frequency (RF) decapole ion guide. The desired cations are mass–selected using a quadrupole mass filter, deflected 90° in an electrostatic quadrupole deflector, and focused into a cryogenic RF ring–electrode ion trap. The trap is continuously filled with pure He gas or a reactant gas/buffer gas mix of 0.01 % CH₄ in He gas at an ion–trap temperature of 10 K or 100K and 300K, respectively. Many collisions of the trapped ions with the mixture gas provide gentle cooling of the internal degrees of freedom close to the ambient temperature. Under these conditions, the He–tagged NiAl₂O₄⁺He¹⁻₂ or the reactions between NiAl₂O₄⁺ and CH₄ are formed.

For the IRPD experiments of the NiAl₂O₄⁺-He complex we used the He atoms as a messenger tag at 10 K (Figure S1). For the IPRD experiments of NiAl₂O₄H⁺·CH₄ and NiAl₂O₃H₂⁺·CH₄, we used the CH₄ molecule as a messenger tag at 100K (Figure S2). All ions are extracted from the ion trap at 5 Hz and focused both temporally and spatially into the center of the extraction region of an orthogonally mounted reflection time–of–flight (TOF) tandem photofragmentation mass–spectrometer. Here, the ions are irradiated with a counter–propagating IR laser pulse produced by the FHI FEL (within 500–1250 cm⁻¹, bandwidth: ~0.5 % fwhm, pulse energy: 1–25 mJ). All parent and photofragment ions are then accelerated toward an MCP detector and monitored simultaneously. IRPD scans are recorded by averaging about 100 TOF mass spectra per wavelength step (4 cm⁻¹ or 5 cm⁻¹) and scanning the wavelength. Typically, at least three scans are summed to obtain the final IRPD spectrum. The photodissociation cross section σ_IRPD is determined as described previously.

The conversion of the TOF mass spectrum from time–of–flight (μs) to mass–to–charge ratio (u) units is achieved by fitting a second order polynomial function to at least three calibration points obtained with only He in the trap.

Note that the mass spectrometric study requires the use of very low concentration CH₄ in He mixtures (~0.01%) in order to minimize formation of larger complexes with methane under our experimental conditions. These mixtures are obtained by successive dilution, which is not a very accurate method. The absolute error of the CH₄ concentrations used was
estimated to be around ±300%. Here we are predominantly interested in a qualitative analysis of the mass spectra (peak positions of dominant peaks) in order to identify the mass-to-charge ratio of the main product ions formed. The isotopic reaction with CD$_4$ was mainly performed to confirm the assignment of the mass peaks P1 and P2 based on the observed isotope-dependent mass shift. This does not require exactly the same number densities.

**Figure S1.** Time–of–flight (TOF) mass spectrum obtained after storing mass-selected NiAl$_2$O$_4^+$ ions for 200 ms in the ion trap filled with He and held at 10 K.

**Figure S2.** Time–of–flight (TOF) mass spectrum obtained after storing mass-selected NiAl$_2$O$_4^+$ ions for 200 ms in the ion trap filled with CH$_4$/He and held at 100 K.
2. Theoretical methods

Density functional theory (DFT) calculations using Gaussian 16\(^4\) were carried out to investigate the structures of NiAl\(_2\)O\(_4^+\) and the mechanisms of reaction with CH\(_4\). The B3P86\(^5\) functional and the TZVP basis sets\(^6\) were used throughout.

The reaction mechanism calculations involved geometry optimization of reaction intermediates (IMs) and transition states (TSs). The initial guess structures of the TS species were obtained through relaxed potential energy surface scans using single or multiple internal coordinates.\(^7\) Vibrational frequency calculations were performed to check that the IMs or TSs have zero and only one imaginary frequency, respectively. The intrinsic reaction coordinate calculations\(^8\) were carried out to make sure that a TS connects two appropriate minima. The obtained reaction energies were corrected with zero-point vibrational energies to give reaction enthalpies at zero Kelvin (\(\Delta H_0\)). The NBO analysis was performed with NBO 3.1.\(^9\) CCSD(T)\(^10\) single-point energies at the B3P86 optimized structures \(^2\)R and \(^4\)R were also calculated.

To obtain a quantitative measure for the agreement of experimental and theoretical spectra, the cosine similarity score is used.\(^11\) The score \(S\) expresses the similarity between two spectra, where the intensity of the experimental and predicted absorptions is represented by vectors \(A\) and \(B\) in eq. 1. The score can vary from zero to unity, with a value closer to 1 indicating greater similarity.

\[
S = \cos(\theta) = \frac{A \cdot B}{||A|| ||B||} = \frac{\sum_{i=1}^{n} A_i B_i}{\sqrt{\sum_{i=1}^{n} A_i^2} \sqrt{\sum_{i=1}^{n} B_i^2}}
\]  

(1)

The Rice–Ramsperger–Kassel–Marcus (RRKM) theory\(^12\) and RRKM-based variational transition state theory (VTST)\(^12\) were used to calculate the rate constants of \((k_c)\) transition state \(^2\)1/\(^2\)2 conversion and \((k_d)\) CH\(_3^*\) radical desorption from intermediates \(^2\)1, respectively. The values are shown in Table S4 in Section 4.5.
3. Additional experimental results

3.1 Experimental results for the IRPD spectroscopy of R·He, P1·CH₄ and P2·CH₄

Table S1 Experimental band positions (in cm⁻¹, see Figs. 1 and 4), harmonic vibrational wavenumbers (in cm⁻¹, Figs. 1 and 4), IR intensities (in parentheses, in km mol⁻¹) of NiAl₂O₄⁺·He, NiAl₂O₄H⁺·CH₄ and NiAl₂O₃H₂⁺·CH₄, and band assignments.

| Band | Exp. | B3P86/TZVP | Assignment[^c] |
|------|------|------------|----------------|
| R·He |      |            |                |
| a    | 982  | 984(209)   | ν^as (O₉–Al–O₉) |
| b    | 946  | 948(318)   | ν (Al–O₉)       |
| c    | 773  | 780(161)   | ν^as (Ni–O₉–Al) |
| d    | 733  | 721(50)    | δ (O₉–Al₂) and δ (Ni–O₉–Al) |
| e    | 697  | 686(75)    | δ (O–Al)        |
| P1·CH₄ |    |            |                |
| a    | 1023 | 1023(157)  | ν (Al–OH)       |
| b    | 981  | 986(423)   | ν (O–Al–O)      |
| c    | 769  | 771(176)   | ν (Al–O–Ni)     |
| d    | 740  | 733(108)   | δ (Al–O–Al)     |
| e    | 706  | 697(147)   | δ (Al–O–Al)     |
| f    | 596/618 | 607(65)/620(37) | δ (Al–O–Al/Ni) |
| P2·CH₄ |    |            |                |
| a    | 1029 | 1031(218)  | ν (Al–OH)       |
| b    | 834  | 838(190)   | ν (Ni–OAl₂)     |
| c    | 814  | 811(415)   | δ (O–Al–O)      |
| d    | 763  | 756(121)   | δ (Al–O–Al)     |
| e    | 596  | 599(53)    | δ (H–Al–O)      |
| F    | 529  | 510(210)   | δ (Al–H and O–H) |

[^c] Stretching (ν), bending (δ), symmetric (s), antisymmetric (as). terminal oxygen atom (O₉), bridge oxygen atom (O₉).
3.2 Time–of–flight mass spectra for reaction between $\text{Al}_3\text{O}_4^+$ and $\text{CH}_4$

Figure S3. TOF mass spectra for the reactions of mass selected $\text{Al}_3\text{O}_4^+$ with a) He, b) 1900 mPa 0.04% $\text{CH}_4$/He at 100K, c) He and d) 1900 mPa 0.04% $\text{CH}_4$/He at 300K for 200 ms.
4. Additional DFT results

4.1 Structures

Figure S4. DFT calculated isomers of NiAl₂O₄⁺. The symmetries, electronic states, zero-point vibration corrected energies (kJ mol⁻¹) with respect to the most stable isomer, and bond lengths (pm) are given. Note that the spin distributions are different in IS01 and IS03: IS01 features a local d⁸ high spin configuration at Ni and an antiferromagnetically coupled radical electron at the terminal O, while in IS03 Ni(d⁸) is diamagnetic (local low spin). IS07 has ferromagnetic coupling between high spin Ni(d⁸) and the terminal O centered radical electron. In IS13 Ni is formally in an excited d⁷s¹ quintet configuration.
Figure S5. Experimental IRPD spectra (dark red) of R·He at 10 K and the harmonic B3P86/TZVP IR spectra (green, Gaussian line function convolution FWHM=15 cm\(^{-1}\)) of low-energy doublet and quartet structures of NiAl\(_2\)O\(_4\)^+ (R) (relative energies given in kJ mol\(^{-1}\)). The assignment for peaks a-e is shown in Table S1. The cosine similarity score S is given in parentheses. Figure S5b shows the best S value obtained with a scaling factor of 0.998 for Figure S5c.

We compare calculated harmonic wave numbers with observed (anharmonic) fundamentals. Scaling accounts for both neglected anharmonicities and systematic errors of the calculated harmonic force constants. Depending on the method employed, these may partially compensate each other.

In the present case the effect of using a scaling factor is negligible. The S value for R is 0.91 without a scaling, while the maximum S value (0.93) is obtained for a scaling factor of 0.998, which is very close to unity.
Figure S6. DFT calculated isomers of product ions (P1) NiAl₂O₄H⁺ and (P2) NiAl₂O₃H₂⁺. The symmetries, electronic states, zero-point vibration corrected energies (kJ mol⁻¹) with respect to the most stable isomer, and bond lengths (pm) are given. The assignment for peaks a-e are shown in Table S1.
Figure S7. Experimental IRPD spectra (dark red) of methane tagged P1·CH₄ ions at 100 K and the harmonic B3P86/TZVP IR spectra (green, Gaussian line function convolution FWHM=15 cm⁻¹) of ³P1-Ni-CH₄ and the isomers shown in Figure S6 (blue, Ni; pink, Al; red, O; grey, C; white, H). The energies relative to the reactants (in kJ mol⁻¹) are shown in brackets. The assignment for peaks a-e is shown in Table S1.
Figure S8. Experimental IRPD spectra (dark red) of a) methane tagged P1·CH₄ ions at 100 K and the harmonic B3P86/TZVP IR spectra (green, Gaussian line function convolution FWHM=15 cm⁻¹) of isomers b) ³P₁-Ni·CH₄, c) ³P₁-Al(O₃)-CH₄, and d) ³P₁-Al(O₂-OH)-CH₄ with different methane adsorption sites (blue, Ni; pink, Al; red, O; grey, C; white, H). The energies relative to the reactants (in kJ mol⁻¹) are shown in brackets.
Figure S9. Experimental IRPD spectra (dark red) of methane tagged P2-CH₄ ions at 100 K and the harmonic B3P86/TZVP IR spectra (green, Gaussian line function convolution FWHM=15 cm⁻¹) of P2-Ni-CH₄ and the isomers shown in Figure S6 (blue, Ni; pink, Al; red, O; grey, C; white, H). The energies relative to the reactants (in kJ mol⁻¹) are shown in brackets.
Figure S10. Experimental IRPD spectra (dark red) of a) methane tagged P2·CH4 ions at 100 K and the harmonic B3P86/TZVP IR spectra (green, Gaussian line function convolution FWHM=15 cm⁻¹) of isomers b) ²P2-Ni-CH4, c) ²P2-Al(OH)-CH4, and d) ²P2-Al(H)-CH4 with different methane adsorption sites (blue, Ni; pink, Al; red, O; grey, C; white, H). The energies relative to the reactants are shown in the bracket.
4.2 Reaction mechanisms

Figure S11: The most favorable doublet potential energy surface (PES) for the reaction of NiAl₂O₄⁺(R) with CH₄ calculated at the B3P86/TZVP level (blue, Ni; pink, Al; red, O; gray, C; white, H). The relative zero-point vibration corrected energies ΔH₀K are given in kJ·mol⁻¹ and bond lengths are given in pm. All the structures including transition states are shown here.
Figure S12: The most favorable quartet potential energy surface (PES, red trace) for the reaction of NiAl₂O₄⁺ with CH₄ calculated at the B3P86/TZVP level. The most favorable doublet PES (gray trace) is shown for comparison. The relative zero-point vibration corrected energies $\Delta H_{0K}$ are given in kJ·mol⁻¹ and bond lengths are given in pm. From ²⁴ and ⁴⁴ on, Ni⁺ is in different electron configurations, d⁹ and d⁹s¹, respectively. This means that starting from ⁴ the system is in an electronically excited state which explains the much higher energy.
Figure S13: Additional DFT doublet PES for methane adsorption and initial activation. The zero-point vibration corrected energies with respect to the separated reactants are given in kJ mol\(^{-1}\). Bond lengths are given in pm. Note that the methyl radical is located above the NiAl\(_2\)O\(_4\)H\(^+\) surface in \(2^2c\), while the methyl radical is located below the NiAl\(_2\)O\(_4\)H\(^+\) surface in \(2^2\).
Figure S14: DFT calculated doublet PES for methane initial activation on the Ni site. The zero-point vibration corrected energies with respect to the separated reactants are given in kJ mol\(^{-1}\). Bond lengths are given in pm.
Figure S15: DFT calculated doublet PES for formation of the free CO + H₂ (syngas) molecules from intermediate ß5. The zero-point vibration corrected energies with respect to the separated reactants are given in kJ mol⁻¹. Bond lengths are given in pm. The reaction to produce free CO + H₂ (syngas) is less exothermic than that to produce formaldehyde.
4.3 Ni oxidation state in structures $^23$ and $^24$

Both $^23$ and $^24$ have the same CH$_4$-NiAl$_2$O$_4^+$ composition, and in both $^23$ and $^24$ the 4 O and 2 Al atoms are in their usual oxidation states -2 and +3, see Table S2. In both species one H atom forms an OH bond and, hence, is in the +1 oxidation state. In $^23$, the CH$_3$ species is a methyl radical (see spin density in Figure 5 of the main manuscript) which is weakly attached to Al (bond distance of 221 pm) and, hence, has a total oxidation state of 0. As the total charge is +1 this leaves a +2 oxidation state for Ni in $^23$.

In contrast, in $^24$, there is no spin-density on the CH$_3$ species. It has formed a bond with an O atom (distance 144 pm) resulting in a methoxy species with oxidation states of -2 and +1 for O and CH$_3$, respectively.

**Table S2.** Oxidation states for $^23$ and $^24$.

|   | O$_4$  | 4(-2) | -8  | Al$_2$ | 2(+3) | +6  | H   | +1  | CH$_3$ | 0   | Ni | +2  | O$_4$  | 4(-2) | -8  |
|---|--------|-------|-----|--------|-------|-----|-----|-----|--------|-----|----|-----|--------|-------|-----|
| $^23$ |        |   |     |        |       |     |     |     |        |     |    |     | $^24$  |        |     |
|     |        |   |     |        |       |     |     |     |        |     |    |     |        |       |     |

Figure S16 shows the NPA charges obtained with the NBO analysis$^9$ for the different structures along the reactions path. The sudden change when passing from $^23$ to $^24$ also reflects the change of the Ni oxidation state from +2 to +1.

![Figure S16](image-url)

**Figure S16:** DFT calculated NPA charges of the Ni atom for the structures on the path to $^2P2$. 

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4.4 Reaction enthalpies and free energies

Table S3. ΔH and ΔG values (kJ mol⁻¹) for different temperatures T at 1 atm pressure of key structures ³P1 + CH₃• and ²1/²2 relative to ²R + CH₄.

| Value         | ΔH₀K  | ΔH₁₀₀K | ΔH₂₉₈K | ΔG₁₀₀K | ΔG₂₉₈K |
|---------------|-------|--------|--------|--------|--------|
| ³P1 + CH₃•    | -102  | -102   | -100   | -103   | -107   |
| ²1/²2         | -110  | -111   | -109   | -101   | -82    |

4.5 RRKM rate constants

Table S4. Calculated rate constants for the dissociations of ²1 into products ³P1 and the conversion of ²1 into ²1/²2.

| ΔH₀K (kJ/mol) | Rate constant (s⁻¹) | k_dis(²1→³P1) | k_c(²1→²1/²2) |
|---------------|---------------------|---------------|---------------|
| ²1            | ³P1                 | ²1/²2         |               |
| -116.0        | -101.9              | -109.9        | 1.9×10¹¹      | 5.9×10¹⁰ |

For these calculations, the energy (E) of intermediate ²1 and the energy barrier (E*) for ²1 → ²1/²2 and ²1 → ³P1 were needed. The reaction intermediate ²1 possesses the vibrational energies (E_vib) of NiAl₂O₄⁺ and CH₄, the center of mass kinetic energy (E_k), and the binding energy (E_b) which is the energy difference between the separated reactants (NiAl₂O₄⁺ + CH₄) and the reaction complex ²1. The values of E_vib and E_b were taken from the DFT calculations and E_k = μv²/2, in which μ is the reduced mass of ²1 and v is the velocity (~660 m/s).

\[
E(²1) = E_{vib}(NiAl₂O₄⁺) + E_{vib}(CH₄) + E_k + E_b
\]  

(2)

The rate constant (k) value was calculated by the eq. 3:

\[
k(E) = \frac{g N°(E-E*)}{\hbar \rho(E)}
\]

(3)

in which \( g \) is the symmetry factor (\( g \) is taken as 1), \( \rho(E) \) denotes the density of states of the reaction intermediates at the energy \( E \), \( N°(E-E*) \) is the total number of the states of the transition state with a barrier \( E^\ddagger(E^\ddagger \text{ was zero-point-vibration corrected energy}) \), and \( \hbar \) is the Planck constant. The \( \rho(E) \) and \( N°(E-E*) \) were obtained by the direct count method[13] with the DFT calculated vibrational frequencies under the approximation of harmonic vibrations.

For desorption of neutral products CH₃• from ²1, the VTST calculations were performed through partial geometry optimizations of NiAl₂O₄HCH₃• by fixing the distance between
NiAl$_2$O$_4$H and CH$_3$ moiety at variable values. The $k(E)$ value of each step was estimated and the minimum rate was considered as the $k_d$ value.

5. References

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