Supporting Information
Tuning Selectivity in the Direct Conversion of Methane to Methanol: Bimetallic Synergistic Effects on the Cleavage of C–H and O–H Bonds over NiCu/CeO₂ Catalysts

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Theoretical Models and Computational Methods

All electronic structure calculations were carried out using the spin-polarized DFT approach, as implemented in the Vienna ab initio simulation package (VASP) (vasp site, http://www.vasp.at; version vasp.5.3.5).1,2 Ce (4f, 5s, 5p, 5d, 6s), O (2s, 2p), Ni (3p, 3d, 4s) and Cu (3p, 3d, 4s) electrons were explicitly treated as valence states within the projector
augmented wave (PAW)\textsuperscript{3} method with a plane-wave cutoff energy of 415 eV, whereas the remaining electrons were considered as part of the atomic cores. Total energies and forces were calculated with a precision of $10^{-6}$ eV and $10^{-2}$ eV/Å for electronic and force convergence, respectively, within the DFT+U approach by Dudarev et al.\textsuperscript{4} ($U_{\text{eff}} = U - J = 4.5$ eV for the Ce 4f electrons) with the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE),\textsuperscript{5} including long-range dispersion corrections, employing the so-called DFT-D3 approach.\textsuperscript{6,7}

The Ni$_{4-x}$Cu$_x$.CeO$_2$(111) ($x = 1,..,4$) model catalysts consist of a flat four-atom bimetallic cluster on the CeO$_2$(111) surface. They were modelled employing surface unit cells with 3 × 3 periodicity, with the calculated ceria bulk equilibrium lattice constant (CeO$_2$: 5.485 Å), and a two CeO$_2$-tri-layer slab. In all surface models, consecutive slabs were separated by at least a 12 Å-thick vacuum layer to avoid interaction between the slabs and their periodic images. Monkhorst-Pack grids with a 2 × 2 × 1 k-point sampling were used. All metal/ceria models used in this work are shown in Figure 1 in the main text. All atoms in the bottom O–Ce–O tri-layer were kept fixed at their optimized bulk-truncated positions during geometry optimization, whereas the rest of the atoms were allowed to fully relax.

The adsorption energies of methane and water were calculated according to the following equation for the example of the dissociative adsorption of methane:

\[
E_{\text{ads}} = E[(\text{CH}_3 + \text{H})/\text{Ni}_{4-x}\text{Cu}_x.\text{CeO}_2(111)] - E[\text{Ni}_{4-x}\text{Cu}_x.\text{CeO}_2(111)] - E[\text{CH}_4_{\text{gas}}] \quad (1)
\]

where $E[(\text{CH}_3+\text{H})/\text{Ni}_{4-x}\text{Cu}_x.\text{CeO}_2(111)]$ is the total energy of the methyl and hydrogen species co-adsorbed on the surface, $E[\text{Ni}_{4-x}\text{Cu}_x.\text{CeO}_2(111)]$ is the total energy of the surface without the adsorbate, $E[\text{CH}_4_{\text{gas}}]$ is the energy of the methane molecule in the gas phase. No ZPE corrections have been considered.

To locate transition state (TS) structures, we employed the climbing image nudged elastic band method (CI-NEB)\textsuperscript{8,9} with nine images for each reaction pathway. For all the TS
reported in this work, we have found only one imaginary frequency, and the full geometry optimizations starting from its back and forward nearest configurations (along the reaction path) ended in a non-dissociated and dissociated state, respectively.

In the calculated potential energy profiles, the energy barrier, $E_{\text{Barrier}} = E_{TS} - E_{IS}$, equals the difference between the energy of the transition state, $E_{TS}$, and the initial (molecularly chemisorbed) state, $E_{IS}$, whereas the effective or apparent energy barrier is given by the energy of the transition state, $E_{TS}$, referenced to gas-phase CH$_4$ and the clean surface.

**Models Stability**

The results in Figure S1 indicate that as the size of the clusters increases, the stability per atom increases, in line with previous work.$^{10}$ The supported flat Ni$_4$, Cu$_4$ and Ni$_3$Cu$_1$ clusters are slightly less stable than the corresponding pyramidal ones, for which only the atoms in direct contact with the support are oxidized. In addition, the formation energies of the flat Ni$_4$ (Ni$_4$.flat), pyramidal (Ni$_4$.pyr), as well as the flat and pyramidal Ni$_3$Cu$_1$ clusters (Ni$_3$Cu$_1$.flat and Ni$_3$Cu$_1$.pyr) were calculated with respect to the (flat) Ni$_3$ cluster and an adsorbed isolated Ni$_1$/Cu$_1$ atom, according to the following equations:

$E(Ni_4.\text{flat}) + E(\text{CeO}_2) - E(Ni_3) - E(Ni_1) = -0.27 \text{ eV}$

$E(Ni_4.\text{pyr}) + E(\text{CeO}_2) - E(Ni_3) - E(Ni_1) = -0.39 \text{ eV}$

$E(Ni_3Cu_1.\text{flat}) + E(\text{CeO}_2) - E(Ni_3) - E(Cu_1) = -0.45 \text{ eV}$

$E(Ni_3Cu_1.\text{pyr}) + E(\text{CeO}_2) - E(Ni_3) - E(Cu_1) = -0.73 \text{ eV}$

In all cases, the formation energy is negative, which indicates that the formation of these structures are energetically favored. Although this information is relevant, it would be incomplete without the calculation of diffusion barriers of adsorbed Cu$_1$ species to attach to Ni$_3$ clusters, forming Ni$_3$Cu$_1$ flat clusters, followed by the pathway for the formation of Ni$_3$Cu$_1$.pyr from Ni$_3$Cu$_1$.flat (see Figure S1). The results in Figure S1 reveal that the diffusion of an isolated Cu$_1$ species and attachment to the Ni$_3$ cluster to form the Ni$_3$Cu$_1$.flat cluster is likely to occur since the barrier is as low as 0.33 eV, however, the formation of a pyramidal
Ni₃Cu₁.pyr structure (Ni₃Cu₁.pyr.1) from the Ni₃Cu₁.flat has a barrier of 0.85 eV, which is 2.57 times higher. In short, kinetic considerations also support the choice of the model systems in this study.

Figure S1: Adsorbed Ni₄₋ₓCuₓ (x = 0 to 4) on CeO₂(111). The average adsorption energy of Ni₄₋ₓCuₓ species is listed below each structure in eV per metallic atom. The pathway for the formation of the Ni₃Cu₁.flat cluster from the adsorbed Ni₃ cluster and the diffusion of Cu₁ species, followed by the pathway for the formation of a Ni₃Cu₁.pyr from the Ni₃Cu₁.flat is shown. Ni and Cu atoms are depicted in blue and brown, respectively, while surface/subsurface oxygen atoms are in red/green, Ce⁴⁺ in white, and Ce³⁺ in gray.
Table S1: Bader charges, computed as differences with respect to the nominal charges of the corresponding isolated atoms. (a) Supported clusters Ni$_{4-x}$Cu$_x$.CeO$_2$. (b) Bimetallic nanoparticle in the gas phase (Ni$_{4-x}$Cu$_x$.gas), i.e., the free-standing Ni$_{4-x}$Cu$_x$ clusters, which result from the removal of the CeO$_2$(111) support from the Ni$_{4-x}$Cu$_x$.CeO$_2$ systems, without further optimization of the geometry. Each atom is labeled following the numbering in Figure 1 in the main text. Numbers in blue (brown) refer to the Ni (Cu) species.

| (a) $\Delta q$ Ni$_{4-x}$Cu$_x$.CeO$_2$ | Catalyst          | at. 1  | at. 2  | at. 3  | at. 4  | Total  |
|---------------------------------------|-------------------|--------|--------|--------|--------|--------|
| Ni$_4$.CeO$_2$                        | -0.360            | -0.217 | -0.281 | -0.232 | -1.090 |
| Ni$_3$Cu$_1$.CeO$_2$                  | -0.332            | -0.237 | -0.263 | -0.242 | -1.075 |
| Ni$_2$Cu$_2$.CeO$_2$                  | -0.290            | -0.264 | -0.260 | -0.251 | -1.066 |
| Ni$_1$Cu$_3$.CeO$_2$                  | -0.323            | -0.237 | -0.263 | -0.261 | -1.083 |
| Cu$_4$.CeO$_2$                        | -0.343            | -0.233 | -0.280 | -0.224 | -1.080 |

| (b) $\Delta q$ Ni$_{1-x}$Cu$_x$.gas | Catalyst          | at. 1  | at. 2  | at. 3  | at. 4  | Total  |
|-------------------------------------|-------------------|--------|--------|--------|--------|--------|
| Ni$_4$.CeO$_2$                      | 0.117             | -0.116 | 0.112  | -0.113 | 0.000  |
| Ni$_3$Cu$_1$.CeO$_2$                | 0.087             | -0.150 | 0.125  | -0.150 | -0.088 |
| Ni$_2$Cu$_2$.CeO$_2$                | 0.134             | -0.184 | 0.134  | -0.172 | -0.088 |
| Ni$_1$Cu$_3$.CeO$_2$                | 0.106             | -0.140 | 0.100  | -0.152 | -0.087 |
| Cu$_4$.CeO$_2$                      | 0.119             | -0.163 | 0.115  | -0.158 | -0.086 |
Table S2: Occupation percentage of the $d$ and the $d_{z^2}$ bands for the indicated atom position of each Ni$_{4-x}$Cu$_x$.CeO$_2$ model catalyst and free standing Ni$_{4-x}$Cu$_x$.gas clusters. $d$-band center values of Ni$_{4-x}$Cu$_x$.CeO$_2$ are also indicated.

|                         | Ni$_{4-x}$Cu$_x$.CeO$_2$ | Ni$_{4-x}$Cu$_x$.gas |
|-------------------------|---------------------------|----------------------|
| **(a) $d$ band Occupation (%)** |                            |                      |
| Catalyst                | at. 1 | at. 2 | at. 3 | at. 4 | at. 1 | at. 2 | at. 3 | at. 4 |
| Ni$_4$.CeO$_2$           | 71.75 | 72.74 | 73.07 | 72.72 | 76.10 | 76.00 | 76.06 | 76.012 |
| Ni$_3$Cu$_1$.CeO$_2$     | 89.83 | 90.61 | 98.53 | 90.32 | 87.47 | 88.41 | 97.61 | 88.38 |
| Ni$_2$Cu$_2$.CeO$_2$     | 98.60 | 91.04 | 98.64 | 91.03 | 97.30 | 88.49 | 97.31 | 88.46 |
| Ni$_1$Cu$_3$.CeO$_2$     | 98.63 | 98.63 | 98.45 | 91.08 | 97.77 | 98.20 | 97.76 | 88.53 |
| Cu$_4$.CeO$_2$           | 98.68 | 98.81 | 98.17 | 98.47 | 97.86 | 98.22 | 97.83 | 98.17 |
| **(b) $d_{z^2}$ band Occupation (%)** |                            |                      |
| Catalyst                | at. 1 | at. 2 | at. 3 | at. 4 | at. 1 | at. 2 | at. 3 | at. 4 |
| Ni$_4$.CeO$_2$           | 71.28 | 70.36 | 68.54 | 66.76 | 85.10 | 84.02 | 85.29 | 83.97 |
| Ni$_3$Cu$_1$.CeO$_2$     | 88.75 | 81.72 | 99.13 | 79.42 | 95.75 | 98.13 | 99.43 | 97.91 |
| Ni$_2$Cu$_2$.CeO$_2$     | 99.03 | 74.56 | 99.01 | 74.43 | 99.44 | 95.93 | 99.46 | 95.87 |
| Ni$_1$Cu$_3$.CeO$_2$     | 99.26 | 99.38 | 99.07 | 71.04 | 99.13 | 99.19 | 99.17 | 90.55 |
| Cu$_4$.CeO$_2$           | 99.40 | 99.28 | 98.59 | 99.15 | 99.38 | 99.29 | 99.40 | 99.29 |
| **(c) $d$ band Center (eV)** |                |                      |
| Catalyst                | at. 1 | at. 2 | at. 3 | at. 4 | at. 1 | at. 2 | at. 3 | at. 4 |
| Ni$_4$.CeO$_2$           | −1.25 | −1.41 | −1.27 | −1.46 | −1.53 | −1.75 | −2.04 | −1.78 |
| Ni$_3$Cu$_1$.CeO$_2$     | −1.89 | −1.59 | −1.99 | −1.56 | −1.89 | −2.09 | −2.03 | −1.55 |
| Ni$_2$Cu$_2$.CeO$_2$     | −1.89 | −2.09 | −2.03 | −1.55 | −1.95 | −2.22 | −2.14 | −2.21 |
| Ni$_1$Cu$_3$.CeO$_2$     | −1.89 | −2.09 | −2.03 | −1.55 | −1.95 | −2.22 | −2.14 | −2.21 |
| Cu$_4$.CeO$_2$           | 97.86 | 98.22 | 97.83 | 98.17 | 97.86 | 98.22 | 97.83 | 98.17 |
Table S3: Calculated energies (in eV) for the initial, \( E_{IS} \), final, \( E_{FS} \), and transition state structures, \( E_{TS} \), for the \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \) reaction over the \( \text{Ni}_{1-x}\text{Cu}_x\text{CeO}_2(111) \) as well as the \( \text{Ni}(111) \) and \( \text{Cu}(111) \) surfaces. All energies are relative to \( \text{CH}_4 \) in the gas phase and the corresponding clean surfaces. The predicted \( E_{TS} \) values correspond to the values obtained using the \( E_{TS} = (0.67 \ E_{FS} +1.04) \) linear scaling relation for the actual calculated final state, \( E_{FS} \). The predicted \( E_{\text{Barrier}} \) values correspond to the activation energy barrier calculated as the energy difference between the predicted energy of the transition state and the calculated energy of the initial state. The model catalysts whose \( E_{TS} \) energy is less than zero is related to the fact that on them \( \text{CH}_4 \) binds relatively strongly, so that if the barrier for the first \( \text{H} \) abstraction from the chemisorbed \( \text{CH}_4 \) molecule is sufficiently low, \( E_{TS} \) will be negative when referenced to gas-phase \( \text{CH}_4 \) and the clean surface.

| Catalyst         | Reaction Channel | \( E_{IS} \) | \( E_{FS} \) | \( E_{\text{React}} \) | \( E_{TS} \) | \( E_{\text{Barrier}} \) | \( \Delta E_{TS} = \Delta E_{\text{Barrier}} \) |
|------------------|------------------|--------------|--------------|----------------|-------------|----------------|------------------------------|
| \( \text{Ni}(111) \) | Ni               | -0.26        | -0.35        | -0.09          | 0.81        | 0.64           | 1.07               | 0.90                        | -0.17                      |
| \( \text{Ni}_4 \)  | Ni               | -0.24        | -1.04        | -0.80          | 0.34        | -0.10          | 0.58               | 0.14                        | -0.44                      |
| \( \text{Ni}_3\text{Cu}_1 \) | Ni            | -0.10        | -1.24        | -1.07          | 0.26        | 0.17           | 0.36               | 0.27                        | -0.09                      |
|                   | Cu               | -0.26        | -1.19        | -0.93          | 0.24        | 0.81           | 0.50               | 1.07                        | +0.57                      |
| \( \text{Ni}_2\text{Cu}_2 \) | Ni            | -0.28        | -0.82        | -0.54          | 0.49        | -0.17          | 0.77               | 0.11                        | -0.66                      |
|                   | Cu               | -0.23        | -0.97        | -0.74          | 0.39        | 0.50           | 0.62               | 0.73                        | +0.11                      |
| \( \text{Ni}_1\text{Cu}_3 \) | Ni            | -0.22        | -1.02        | -0.80          | 0.36        | 0.00           | 0.58               | 0.22                        | -0.36                      |
|                   | Cu               | -0.32        | -1.00        | -0.68          | 0.37        | 0.98           | 0.69               | 1.30                        | +0.54                      |
| \( \text{Cu}_4 \)  | Cu               | -0.24        | -1.29        | -1.05          | 0.18        | 0.84           | 0.42               | 1.08                        | +0.66                      |
| \( \text{Cu}(111) \) | Cu               | -0.26        | +0.38        | +0.64          | 1.29        | 1.16           | 1.55               | 1.42                        | -0.13                      |

Figure S2: Reaction pathways for a) \( \text{CH}_4 \) and b) \( \text{H}_2\text{O} \) activation on \( \text{Ni}(111) \) and \( \text{Cu}(111) \).
Figure S3: Initial, transition and final state structures for the first dehydrogenation of CH$_4$ and H$_2$O on the Ni(111) and Cu(111) surfaces. Selected distances are indicated in pm.
Figure S4: Energy barriers for the dissociation of CH₄ (upper panel) and H₂O (lower panel) for each Ni₄₋ₓCuₓ.CeO₂ model catalyst. The thick arrows indicate the activation sites of the CH₄ → CH₃ + H reaction pathways. For pathways where a Ni or Cu site in the Ni₄₋ₓCuₓ cluster and a surface O site work cooperatively, that is, in the final state, OH species are bound to the metal particle whereas H species form OH species with surface oxygen atoms, the thin arrows indicate the location of the H atom.
Table S4: Energy (in eV) and geometrical parameters for the molecular initial state (IS) structure of the adsorption of CH$_4$ on Ni$_{4-x}$Cu$_x$.CeO$_2$. Distances between the carbon atom and the bimetallic particle (C–B), as well as between the carbon atom and the hydrogen atoms (C–H), are indicated (in pm). The charge gained by the C atom upon adsorption of CH$_4$ with respect to molecule in the gas phase is also indicated. All energies are relative to CH$_4$ in the gas phase and the corresponding clean surfaces.

| State | Activation Site | $E_{IS}$ (eV) | $d$(C–B) (pm) | $d$(C–H) (pm) | $q - q_{CH_4gas}$ (C) |
|-------|----------------|--------------|---------------|---------------|------------------------|
| IS.1  | Ni (at. 4)     | -0.24        | 212           | 119; 110 ($\times$3) | 0.16                   |
| IS.2  | Ni (at. 3)     | -0.38        | 221           | 114; 112; 110 ($\times$2) | 0.11                   |
|       | CH$_4$/Ni$_{3}$Cu$_1$.CeO$_2$ |          |               |               |                        |
| IS.1  | Ni (at. 4)     | -0.10        | 270           | 111; 110 ($\times$3) | 0.08                   |
| IS.2  | NiCu (at. 2 and 3) | -0.23      | 365; 373      | 110 ($\times$4)  | 0.05                   |
| IS.3  | Cu (at. 3)     | -0.26        | 308           | 110 ($\times$4)  | 0.00                   |
|       | CH$_4$/Ni$_2$Cu$_2$.CeO$_2$ |          |               |               |                        |
| IS.1  | Ni (at. 4)     | -0.28        | 260           | 112; 110 ($\times$3) | 0.05                   |
| IS.2  | Cu (at. 3)     | -0.23        | 310           | 110 ($\times$4)  | 0.01                   |
|       | CH$_4$/Ni$_1$Cu$_3$.CeO$_2$ |          |               |               |                        |
| IS.1  | Ni (at. 4)     | -0.22        | 245           | 110; 113; 110 ($\times$3) | 0.02                   |
| IS.2  | Cu (at. 2)     | -0.32        | 304           | 110 ($\times$4)  | 0.04                   |
|       | CH$_4$/Cu$_4$.CeO$_2$ |          |               |               |                        |
| IS.1  | Cu (at. 3)     | -0.24        | 261           | 110 ($\times$2); 111 ($\times$2) | 0.06                   |
| IS.2  | Cu (at. 4)     | -0.16        | 319           | 110 ($\times$4)  | 0.02                   |

Figure S5: Initial, transition and final state structures for the non-cooperative first dehydrogenation of CH$_4$ on Ni$_4$.CeO$_2$ (cf. Figure S11). Representative distances are indicated in pm. Ni atoms are depicted in blue, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.
Figure S6: Initial, transition and final state structures for the non-cooperative first dehydrogenation of CH\textsubscript{4} on Cu\textsubscript{4}.CeO\textsubscript{2} (cf. Figure S12). Representative distances are indicated in pm. Cu atoms are depicted in brown, while surface/subsurface oxygen atoms are in red/green, Ce\textsuperscript{4+} in white, and Ce\textsuperscript{3+} in gray.
Figure S7: Total density of states (DOS) of the bimetallic particle and $dz^2$-projected density of states for each metallic atom in the particle.
Figure S8: Initial, transition and final state structures for the non-cooperative first dehydrogenation of CH$_4$ on Ni$_3$Cu$_1$.CeO$_2$ (cf. Figure S13). Representative distances are indicated in pm. Ni and Cu atoms are depicted in blue and brown, respectively, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.

Figure S9: Initial, transition and final state structures for the non-cooperative first dehydrogenation of CH$_4$ on Ni$_2$Cu$_2$.CeO$_2$ (cf. Figure S14). Representative distances are indicated in pm. Ni and Cu atoms are depicted in blue and brown, respectively, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.
Figure S10: Initial, transition and final state structures for the non-cooperative first dehydrogenation of CH$_4$ on Ni$_1$Cu$_3$.CeO$_2$ (cf. Figure S15). Representative distances are indicated in pm. Ni and Cu atoms are depicted in blue and brown, respectively, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.

Figure S11: Non-cooperative reaction pathways for CH$_4$ activation on Ni$_4$.CeO$_2$. 
Figure S12: Non-cooperative reaction pathways for CH$_4$ activation on Cu$_4$.CeO$_2$.

Figure S13: Non-cooperative reaction pathways for CH$_4$ activation on Ni$_3$.Cu$_1$.CeO$_2$. 
Figure S14: Non-cooperative reaction pathways for CH$_4$ activation on Ni$_2$Cu$_2$.CeO$_2$.

Figure S15: Non-cooperative reaction pathways for CH$_4$ activation on Ni$_1$Cu$_3$.CeO$_2$. 
Table S5: Binding of the H atom to the supported clusters (in eV, with respect to 1/2 H$_2$), calculated by removing the CH$_3$ species from the TS structures, with and without further optimization.

| Catalyst               | Hydrogen Adsorption Energy (eV) | Full relax | TS single point |
|------------------------|---------------------------------|------------|-----------------|
| Ni$_4$.CeO$_2$         | -1.22                           | –          | -0.92           |
| Ni$_3$Cu$_1$.CeO$_2$   | -1.03                           | -0.55      | -0.34           |
| Ni$_2$Cu$_2$.CeO$_2$   | -1.19                           | -0.72      | -0.74           |
| Ni$_1$Cu$_3$.CeO$_2$   | -1.03                           | -0.50      | -0.50           |
| Cu$_4$.CeO$_2$         | -0.60                           | -0.31      | –               |

Figure S16: Energy barrier as a function of the H atom binding energy (with respect to 1/2 H$_2$), calculated by removing the CH$_3$ species from the TS structures without further optimization, for a) Ni active site and b) Cu active site.

Figure S17: Hydrogen adsorption on the Ni$_{1-x}$Cu$_x$.CeO$_2$ surfaces, the binding energies were calculated respect to 1/2 H$_2$. 
Table S6: Energy (in eV) and geometrical parameters for the transition state (TS) structure of the \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \) reaction over the Ni\(_{4-x}\)Cu\(_x\).CeO\(_2\) surfaces. Distances between the carbon atom and the bimetallic particle (C–B), as well as between the carbon atom and the hydrogen atoms (C–H), and between the Ni/Cu atoms and the hydrogen atoms (Ni/Cu–H), are indicated (in pm). All energies are relative to CH\(_4\) in the gas phase and the corresponding clean surfaces.

| State     | Activation Site | \( E_{TS} \) (eV) | \( d(\text{C–B}) \) (pm) | \( d(\text{C–H}) \) (pm) | \( d(\text{Ni–H}) \) (pm) | \( d(\text{Cu–H}) \) (pm) |
|-----------|----------------|-------------------|---------------------------|--------------------------|--------------------------|--------------------------|
| \( \text{TS(\text{CH}_4 \rightarrow \text{CH}_3 + \text{H})/Ni_{4-x}\text{Cu}_x\text{.CeO}_2} \) | \( \text{TS.1 } \) Ni (at. 4) | -0.10 | 198 | 153 | 110 (x3) | 152; 194 | 210; 292 | - |
|           | \( \text{TS.2 } \) Ni (at. 3) | -0.05 | 196 | 160; 111 | 110 (x2) | 151; 198 | 220; 353 | - |
| \( \text{TS(\text{CH}_4 \rightarrow \text{CH}_3 + \text{H})/Ni_x\text{Cu}_1\text{.CeO}_2} \) | \( \text{TS.1 } \) Ni (at. 4) | +0.17 | 237 | 114 | 110 (x3) | 173; 246 | 304 | 258 |
|           | \( \text{TS.2 } \) NiCu (at. 2 and 3) | +0.56 | 216; 219 | 139 | 110 (x3) | 153; 230 | 311 | 216 |
|           | \( \text{TS.3 } \) Cu (at. 3) | +0.82 | 246; 293 | 107 | 110 (x3) | 190; 290 | 368 | 186 |
| \( \text{TS(\text{CH}_4 \rightarrow \text{CH}_3 + \text{H})/Ni_x\text{Cu}_2\text{.CeO}_2} \) | \( \text{TS.1 } \) Ni (at. 4) | -0.17 | 197 | 151 | 110 (x3) | 152; 197 | 213; 295 |
|           | \( \text{TS.2 } \) Cu (at. 3) | +0.50 | 203 | 158 | 110 (x3) | 187; 194 | 160; 338 |
| \( \text{TS(\text{CH}_4 \rightarrow \text{CH}_3 + \text{H})/Ni_x\text{Cu}_3\text{.CeO}_2} \) | \( \text{TS.1 } \) Ni (at. 4) | 0.00 | 196 | 158 | 110 (x3) | 150 | 199; 223 | 291 |
|           | \( \text{TS.2 } \) Cu (at. 2) | +0.98 | 207 | 172 | 110 (x3) | 213 | 149; 265 | 268 |
| \( \text{TS(\text{CH}_4 \rightarrow \text{CH}_3 + \text{H})/Cu_4\text{.CeO}_2} \) | \( \text{TS.1 } \) Cu (at. 4) | +1.09 | 211 | 154 | 110 (x3) | - | 153; 201 | - |
|           | \( \text{TS.2 } \) Cu (at. 3) | +0.84 | 209 | 155 | 110 (x3) | - | 158; 200 | - | 222; 281 |
Table S7: Energy (in eV) and geometrical parameters for the final state (FS) structure of the CH$_4$ → CH$_3$ + H reaction over the Ni$_{4-x}$Cu$_x$CeO$_2$ surfaces. Distances between the carbon atom and the bimetallic particle (C–B), as well as between the carbon atom and the hydrogen atoms (C–H), and between the Ni/Cu atoms and the hydrogen atoms (Ni/Cu–H), are indicated (in pm). All energies are relative to CH$_4$ in the gas phase and the corresponding clean surfaces.

| State | Activation Site | E$_{FS}$ (eV) | d(C–B) (pm) | d(C–H) (pm) | d(Ni–H) (pm) | d(Cu–H) (pm) |
|-------|----------------|--------------|-------------|-------------|--------------|--------------|
|       |                |              | (CH$_3$ + H)/Ni$_4$.CeO$_2$ |              |              |              |
| FS.1  | Ni (at. 4)     | -1.04        | 204; 207    | 293; 114    | 157; 170     | -            |
|       | Ni (at. 3)     | -1.00        | 197; 215    | 318; 113    | 171; 175 (×2)| -            |
|       | (CH$_3$ + H)/Ni$_3$Cu$_1$.CeO$_2$ |              |              |              |              |              |
| FS.1  | Ni (at. 4)     | -1.24        | 206 (×2)    | 285; 113    | 171; 305     | 155          |
|       | NiCu (at. 2 and 3) | -1.19       | 196; 218    | 313; 112    | 170; 173     | 356          |
|       | Cu (at. 3)     | -1.19        | 196; 218    | 313; 112    | 170; 173     | 356          |
|       | (CH$_3$ + H)/Ni$_2$Cu$_2$.CeO$_2$ |              |              |              |              |              |
| FS.1  | Ni (at. 4)     | -0.82        | 203; 207    | 269; 113    | 166          | 158          |
|       | Cu (at. 3)     | -0.97        | 197; 210    | 320; 112    | 163          | 162          |
|       | (CH$_3$ + H)/Ni$_1$Cu$_3$.CeO$_2$ |              |              |              |              |              |
| FS.1  | Ni (at. 4)     | -1.02        | 198; 203    | 311; 115    | 284          | 160; 164     |
|       | Cu (at. 2)     | -1.00        | 204; 206    | 292; 112    | 166          | 157; 315     |
|       | (CH$_3$ + H)/Cu$_4$.CeO$_2$ |              |              |              |              |              |
| FS.1  | Cu (at. 4)     | -1.15        | 199; 208    | 309; 113    | -            | 160; 164     |
|       | Cu (at. 3)     | -1.29        | 199; 206    | 337; 113    | -            | 161; 163     |

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Figure S18: Intermediate states for the CH$_4$ dehydrogenation to CH + 3 H over the Ni$_{4-x}$Cu$_x$.CeO$_2$ surfaces, as reported in Figure 3 in the main text.

Figure S19: Non-cooperative reaction pathways for H$_2$O activation on Ni$_4$.CeO$_2$. 

Figure S20: Non-cooperative reaction pathways for H$_2$O activation on Ni$_3$Cu$_1$.CeO$_2$. 

Figure S21: Non-cooperative reaction pathways for H$_2$O activation on Ni$_2$Cu$_2$.CeO$_2$. 

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Figure S22: Non-cooperative reaction pathways for H₂O activation on Ni₁Cu₃. CeO₂.

Figure S23: Non-cooperative reaction pathway for H₂O activation on Cu₄. CeO₂.
Figure S24: Initial, transition and final state structures for the non-cooperative first dehydrogenation of H$_2$O on Ni$_4$.CeO$_2$ (cf. Figure S19). Selected distances are indicated in pm. Ni atoms are depicted in blue, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.

Figure S25: Initial, transition and final state structures for the non-cooperative first dehydrogenation of H$_2$O on Ni$_3$.Cu$_1$.CeO$_2$ (cf. Figure S20). Selected distances are indicated in pm. Ni and Cu atoms are depicted in blue and brown, respectively, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.
Figure S26: Initial, transition and final state structures for the non-cooperative first dehydrogenation of H$_2$O on Ni$_2$Cu$_2$.CeO$_2$ (cf. Figure S21). Selected distances are indicated in pm. Ni and Cu atoms are depicted in blue and brown, respectively, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.

Figure S27: Initial, transition and final state structures for the non-cooperative first dehydrogenation of H$_2$O on Ni$_1$.Cu$_3$.CeO$_2$ (cf. Figure S22). Selected distances are indicated in pm. Ni and Cu atoms are depicted in blue and brown, respectively, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.
Figure S28: Initial, transition and final state structures for the non-cooperative first dehydrogenation of H$_2$O on Cu$_4$.CeO$_2$ (cf. Figure S23). Selected distances are indicated in pm. Cu atoms are depicted in brown, while surface/subsurface oxygen atoms are in red/green, Ce$^{4+}$ in white, and Ce$^{3+}$ in gray.

Table S8: Energy (in eV) and geometrical parameters for the molecular initial state (IS) structure of the adsorption of H$_2$O on Ni$_{1-x}$Cu$_x$.CeO$_2$. Distances between the oxygen atom in water and the bimetallic particle (O–A), as well as between the oxygen atom and the hydrogen atoms (O–H), are indicated (in pm). The charge gained by the O atom upon adsorption of H$_2$O with respect to molecule in the gas phase is also indicated. All energies are relative to H$_2$O in the gas phase and the corresponding clean surfaces.

| State   | $E_{IS}$ (eV) | $d$(O–A) (pm) | $d$(O–H) (pm) | $q - q_{H_2O_{gas}}$(O) |
|---------|---------------|---------------|---------------|------------------------|
| H$_2$O/Ni$_{1,2}$CeO$_2$ |
| IS.1    | −0.66         | 210           | 98 (×2)       | −0.014                 |
| IS.2    | −0.93         | 201           | 98; 99        | −0.001                 |
| H$_2$O/Ni$_{3,4}$Cu$_{1,2}$CeO$_2$ |
| IS.1    | −0.62         | 209           | 98 (×2)       | −0.006                 |
| IS.2    | −0.84         | 193; 373      | 99; 103       | 0.05                   |
| IS.3    | −0.67         | 200           | 98; 100       | 0.00                   |
| H$_2$O/Ni$_{2,3}$Cu$_{2,4}$CeO$_2$ |
| IS.1    | −0.66         | 210           | 98 (×2)       | −0.020                 |
| IS.2    | −0.61         | 203           | 98; 99        | −0.017                 |
| H$_2$O/Ni$_{3,4}$Cu$_{3,4}$CeO$_2$ |
| IS.1    | −0.71         | 206           | 98 (×2)       | −0.015                 |
| IS.2    | −0.73         | 196           | 98; 100       | +0.009                 |
| H$_2$O/Cu$_{4,5}$CeO$_2$ |
| IS.1    | −0.88         | 194           | 98; 101       | +0.022                 |
Table S9: Energy (in eV) and geometrical parameters for the transition state (TS) structure of the H₂O → OH + H reaction over the Ni₄₋ₓCuₓCeO₂ surfaces. Distances between the oxygen atom and the bimetallic particle (O–B), as well as between the oxygen atom and the hydrogen atoms (O–H), and between the Ni/Cu atoms and the hydrogen atoms (Ni/Cu–H), are indicated (in pm). All energies are relative to H₂O in the gas phase and the corresponding clean surfaces.

| State | E_{TS} (eV) | d(O–B) (pm) | d(O–H) (pm) | d(Ni–H) (pm) | d(Cu–H) (pm) |
|-------|-------------|-------------|-------------|--------------|--------------|
|       |             |             |             |              |              |
| TS(H₂O → OH + H)/Ni₄.CeO₂ |             |             |             |              |              |
| TS.1  | −0.20       | 186         | 98; 141     | 173; 179; 229; 270 | −            |
| TS.2  | −0.52       | 190         | 98; 139     | 185 (×2); 211; 396 | −            |
|       |             |             |             |              |              |
| TS(H₂O → OH + H)/Ni₃Cu₁.CeO₂ |             |             |             |              |              |
| TS.1  | −0.29       | 186         | 98; 137     | 183 (×2); 197 | 329          |
| TS.2  | −0.63       | 187         | 98; 134     | 182; 190; 301 | 238          |
| TS.3  | −0.41       | 190         | 98; 135     | 185; 186; 213 | 300          |
|       |             |             |             |              |              |
| TS(H₂O → OH + H)/Ni₂Cu₂.CeO₂ |             |             |             |              |              |
| TS.1  | −0.37       | 186         | 98; 136     | 180; 182 | 200; 304 |
| TS.2  | −0.27       | 188         | 98; 135     | 189; 190 | 225; 318 |
|       |             |             |             |              |              |
| TS(H₂O → OH + H)/Ni₁Cu₃.CeO₂ |             |             |             |              |              |
| TS.1  | −0.05       | 192         | 98; 139     | 176 | 188; 203; 308 |
| TS.2  | −0.43       | 187         | 98; 138     | 179 | 178; 229; 307 |
|       |             |             |             |              |              |
| TS(H₂O → OH + H)/Cu₄.CeO₂ |             |             |             |              |              |
| TS.1  | −0.61       | 186; 277    | 98; 139     | − | 180; 182; 241; 302 |
Table S10: Energy (in eV) and geometrical parameters for the final state (FS) structure of the \( \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \) reaction over the \( \text{Ni}_{1-x}\text{Cu}_x\text{CeO}_2 \) surfaces. Distances between the oxygen atom and the bimetallic particle (O–B), as well as between the oxygen atom and the hydrogen atoms (O–H), and between the Ni/Cu atoms and the hydrogen atoms (Ni/Cu–H), are indicated (in pm). All energies are relative to \( \text{H}_2\text{O} \) in the gas phase and the corresponding clean surfaces.

| State       | \( E_{FS} \) (eV) | \( d(\text{O–B}) \) (pm) | \( d(\text{O–H}) \) (pm) | \( d(\text{Ni–H}) \) (pm) | \( d(\text{Cu–H}) \) (pm) |
|-------------|-------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| (OH + H)/Ni\(_{1-x}\)Cu\(_x\)CeO\(_2\) |                  |                          |                          |                          |                          |
| FS.1        | -1.99             | 182; 194                 | 98; 283                  | 167; 168; 192; 374        | -                        |
| FS.2        | -1.66             | 175                      | 98; 304                  | 171 (×2); 175; 346        | -                        |
| (OH + H)/Ni\(_{1-x}\)Cu\(_1\)CeO\(_2\) |                  |                          |                          |                          |                          |
| FS.1/FS.2   | -2.01             | 186; 197                 | 97; 282                  | 166; 167; 198             | 379                      |
| FS.3        | -1.34             | 175                      | 98; 306                  | 167; 183; 338             | 173                      |
| (OH + H)/Ni\(_1\)Cu\(_2\)CeO\(_2\) |                  |                          |                          |                          |                          |
| FS.1        | -1.82             | 186; 195                 | 97; 286                  | 169; 185                  | 167; 372                 |
| FS.2        | -1.97             | 186; 194                 | 97; 292                  | 169; 180                  | 170; 378                 |
| (OH + H)/Ni\(_{1-x}\)Cu\(_3\)CeO\(_2\) |                  |                          |                          |                          |                          |
| FS.1/FS.2   | -1.97             | 186; 195                 | 97; 274                  | 177                      | 168; 170; 363            |
| (OH + H)/Cu\(_4\)CeO\(_2\) |                  |                          |                          |                          |                          |
| FS.1        | -2.08             | 188; 190                 | 98; 335                  | -                        | 161 (×2)                 |

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