Supporting Information, 2nd Revision to *the Journal of Physical Chemistry C*

Adsorbed CO_2-Mediated CO_2 Photoconversion Cycle into Solar Fuel at the O Vacancy Site of Zirconium Oxide

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1. Results and Discussion

Chart S1. The density of states during the CO_2 adsorption (Scheme 3) using (a, b) ZrO_2 and (c, d) Ni–ZrO_2. (a)–(d) correspond to panels A-a, A-b, B-a′, and B-b′, respectively, in Scheme 3.

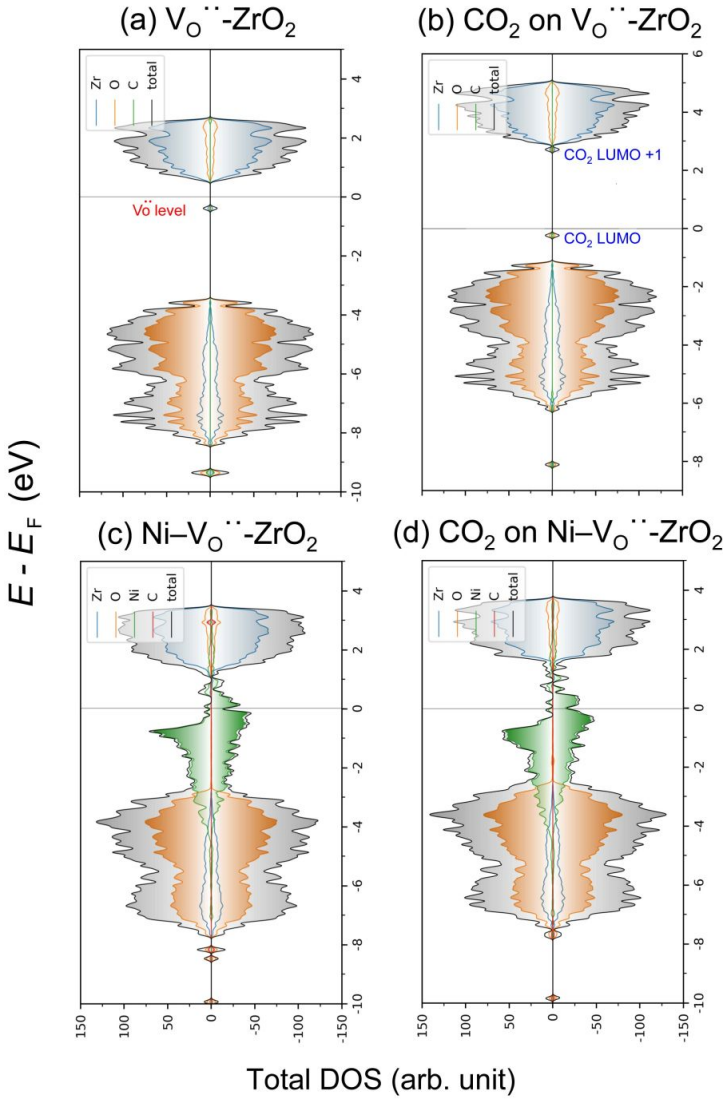


Chart S2. (A) Monoclinic ZrO_2 (1 1 1) faces with parameters of a = 1.35 nm, b = 1.464 nm, c = 1.488 nm, α = 114.68°, β = 61.79°, γ = 116.44° and 192 atoms comprising 64 ZrO_2 units comprising a $V_O^{\bullet\bullet}$ site by removal of O atom bound to two Zr atoms combined with a Ni cluster comprising 19 atoms with a 2.0-nm vacuum layer introduced in the direction of the x-axis. Green, Zr atom; red, O atom; silver, Ni atom. (B) The orientation of the a $V_O^{\bullet\bullet}$ site and Ni cluster over ZrO_2 (1 1 1) surface depicted using VESTA version 3.5.7.[S1].

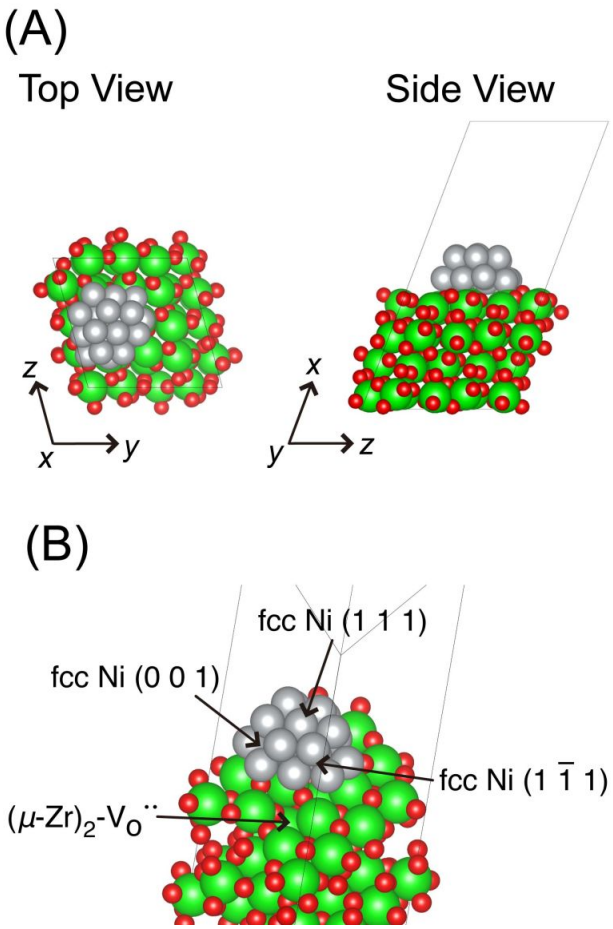


Chart S3. Three-dimensional illustration of surface species (Scheme 4A) during CO_2 photoreduction to methane over the ZrO_2 (1 1 1) surface neighboring to Ni nanoparticle depicted using OVITO version 3.7.8.[S2] The panels (a′)–(x) correspond to species a′–x, respectively, in Scheme 4A except for the panel (TS from d′ to s) corresponding to the transition state (TS) between d′ and s.

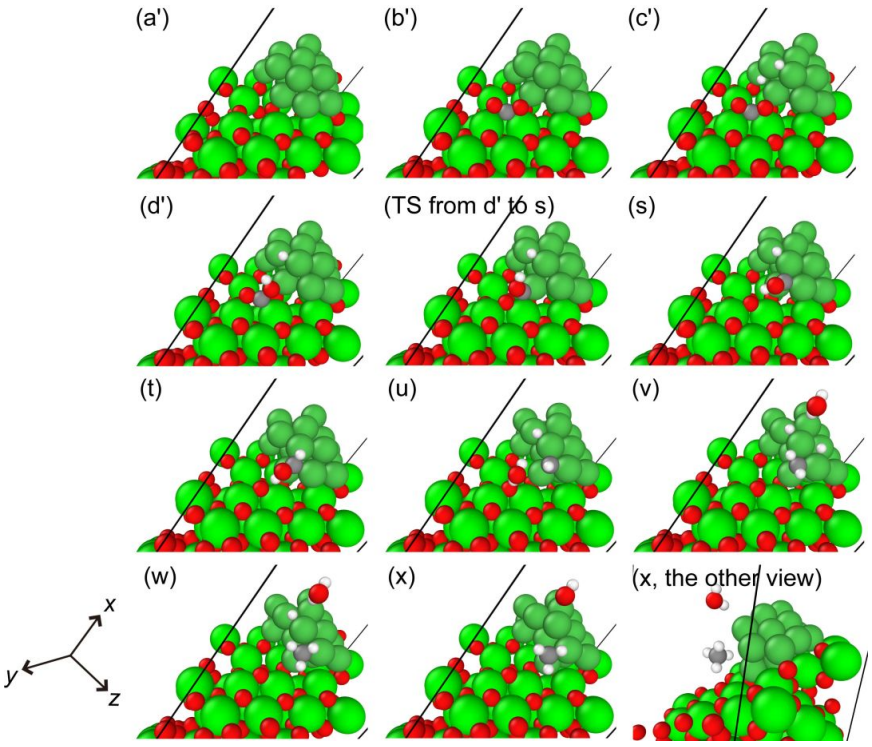
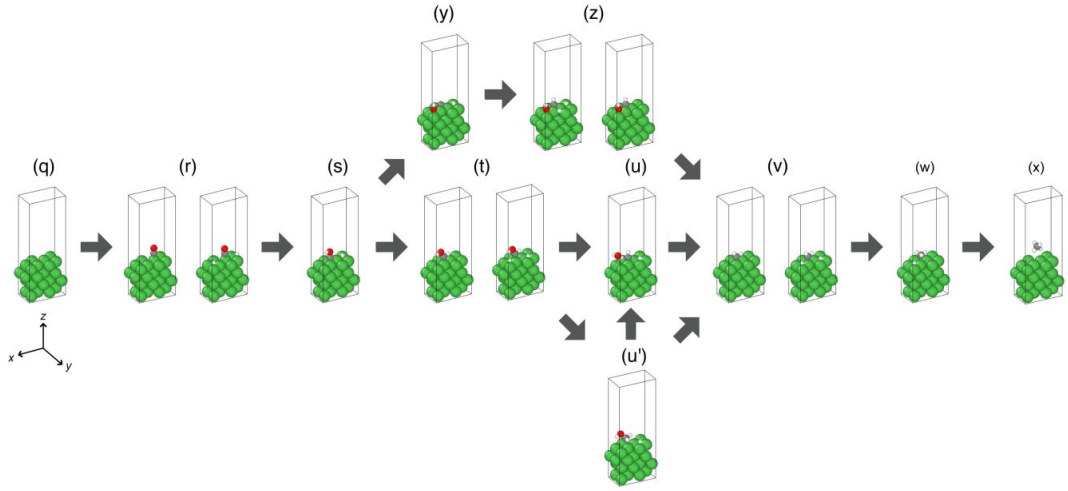


Chart S4. Three-dimensional illustration of surface species (Scheme 5A) during CO_2 photoreduction to methane over the Ni (1 1 1) surface depicted using OVITO version 3.7.8.[S2] The panels (q)–(u), (u′), and (v)–(z) correspond to species q–u, u′, and v–z, respectively, in Scheme 5A.



REFERENCES

(S1) Momma, K.; Izumi, F. *VESTA 3* for Three-Dimensional Visualization of Crystal, Volumetric and Morphology data. *J. Appl. Cryst.* **2011**, *44*, 1272–1276.

(S2) A. Stukowski, A. Visualization and Analysis of Atomistic Simulation Data with OVITO–the Open Visualization Tool. *Modelling Simul. Mater. Sci. Eng.* **2010**, *18*(1), 015012.