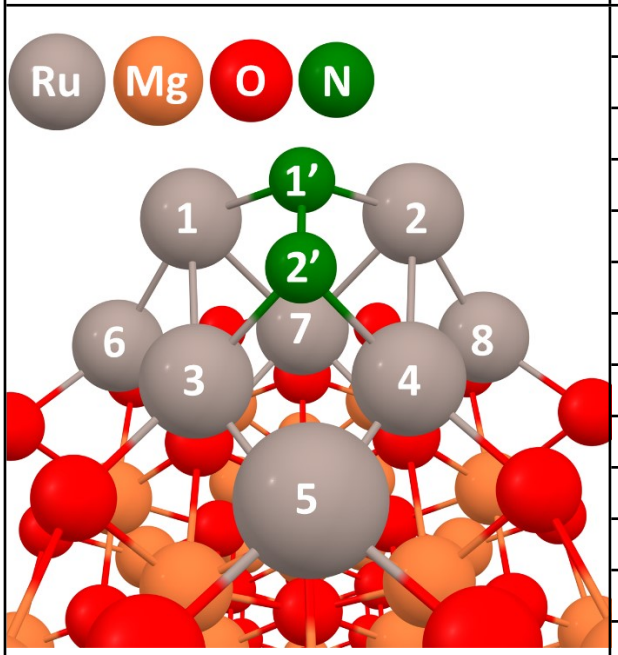
Supplementary Information

Mechanistic understanding of N_2 activation: A comparison of unsupported and supported Ru catalysts

Yves Ira A. Reyes,[a] Kai-Shiang Yang[a], Ho Viet Thang[b], Carmine Coluccini[c], Shih-Yuan Chen[d], Hsin-Yi Tiffany Chen[a,e,f] *

[a]*Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan*
[b]*The University of Danang, University of Science and Technology, 54 Nguyen Luong Bang, Danang 550000, Vietnamc*
[c]*Institute of New Drug Development, China Medical University, No. 91 Hsueh-Shih Road, Taichung 40402, Taiwan*
[d]*National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8559, Japan.*
[e]*College of Semiconductor Research, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu 300044, Taiwan*
[f]*Department of Material Science and Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu 300044, Taiwan*

Table S1. The Bader charges (in |e|) of the Ru atoms and the MgO substrate of the Ru_8(B5-like)/MgO(111) model catalyst before and after the adsorption of N_2 in the side-on configuration.

Structure	Atom No.	Bare	Side-on N_2*	Charge Difference
	Ru1	-0.05	0.20	0.25
	Ru2	-0.06	0.21	0.27
	Ru3	0.64	0.87	0.23
	Ru4	0.58	0.85	0.28
	Ru5	1.04	1.21	0.17
	Ru6	1.13	1.05	-0.08
	Ru7	0.71	0.69	-0.02
	Ru8	1.15	1.05	-0.10
	Ru Total	**5.13**	**6.12**	**0.99**
	N1'	-	-0.48	-0.48
	N2'	-	-0.55	-0.55
	N_2 Total	**-**	**-1.03**	**-1.03**
	MgO	-5.13	-5.10	0.04

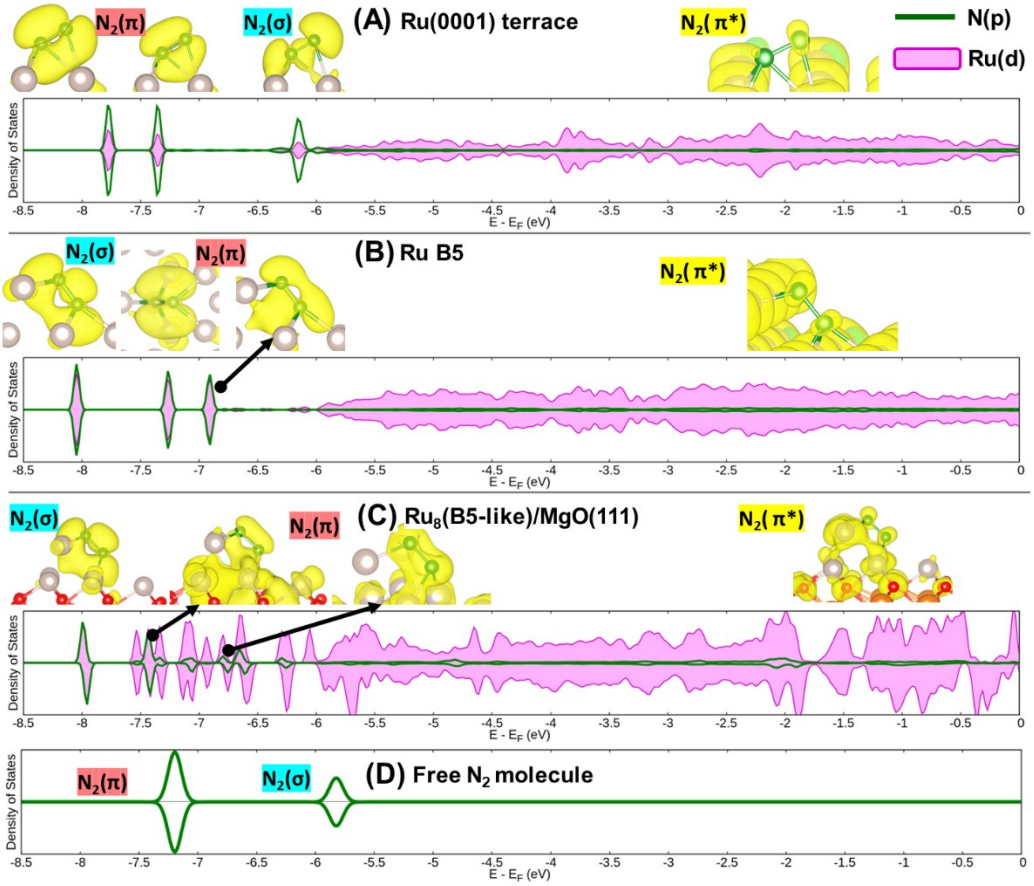


Figure S1. Plots depicting the partial density of states (PDOS), below Fermi energy, projected onto the p orbitals of the side-on N_2* molecule, and the d orbitals of the Ru atoms bonded to N_2, on the (A) Ru (0001) terrace, (B) Ru B5, and (C) Ru_8(B5-like)/MgO(111) models. The plots of the partial charge density depict the electron density distribution corresponding to orbitals at different energy regions. The partial charge density are labelled as $N_2(\sigma)$, $N_2(\pi)$ or $N_2(\pi^*)$ according to the shape of the N_2 orbital that corresponds to that of the partial density plots.

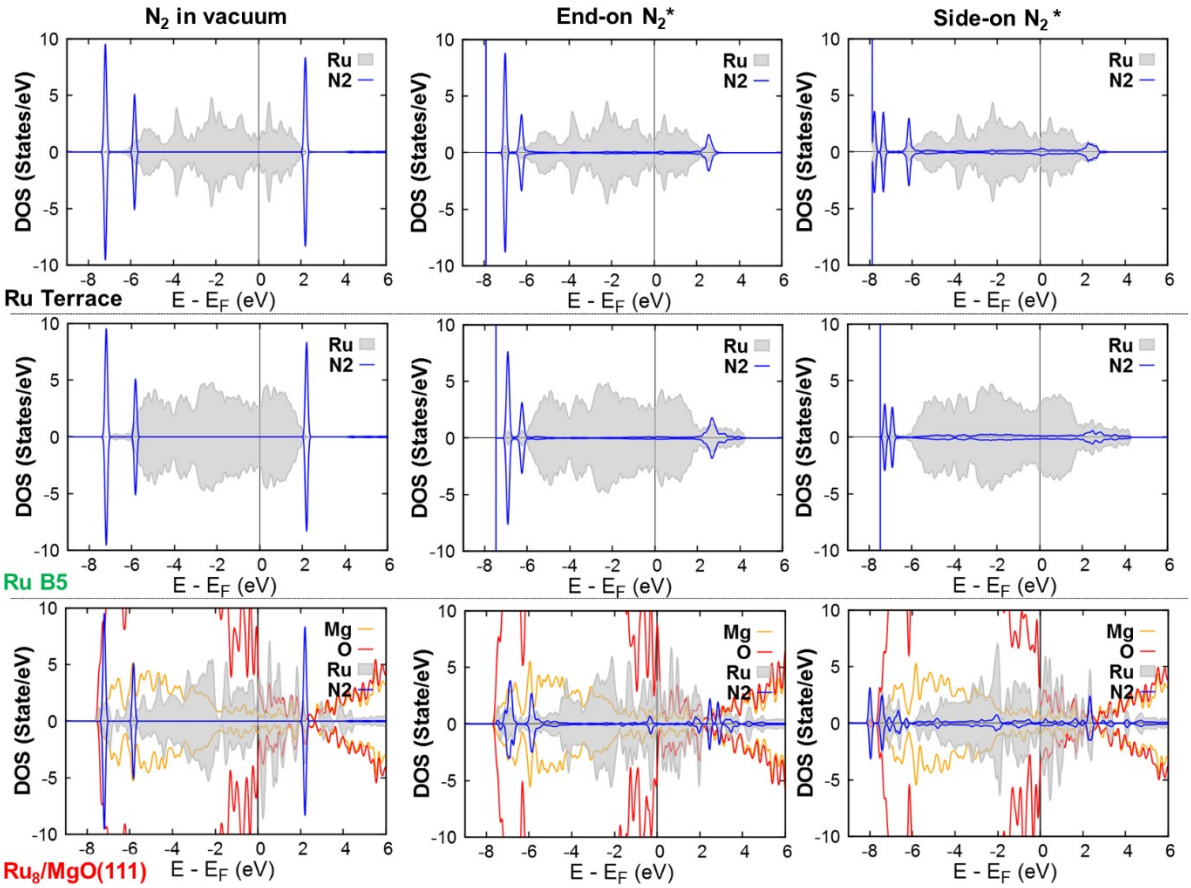


Figure S2. Partial density of states (PDOS) projected on Mg, O, Ru, and N (represented as the orange, red, grey, and blue lines, respectively). From left to right: free N_2, end-on N_2* adsorption, and side-on N_2 adsorption. From top to bottom: the Ru (0001) terrace, Ru B5, and Ru_8(B5-like)/MgO(111) models. Compared to side-on N_2* adsorption, end-on N_2* adsorption exhibits insignificant Ru-N coupling in the -4 to 0 eV region relative to the fermi energy for all three systems.

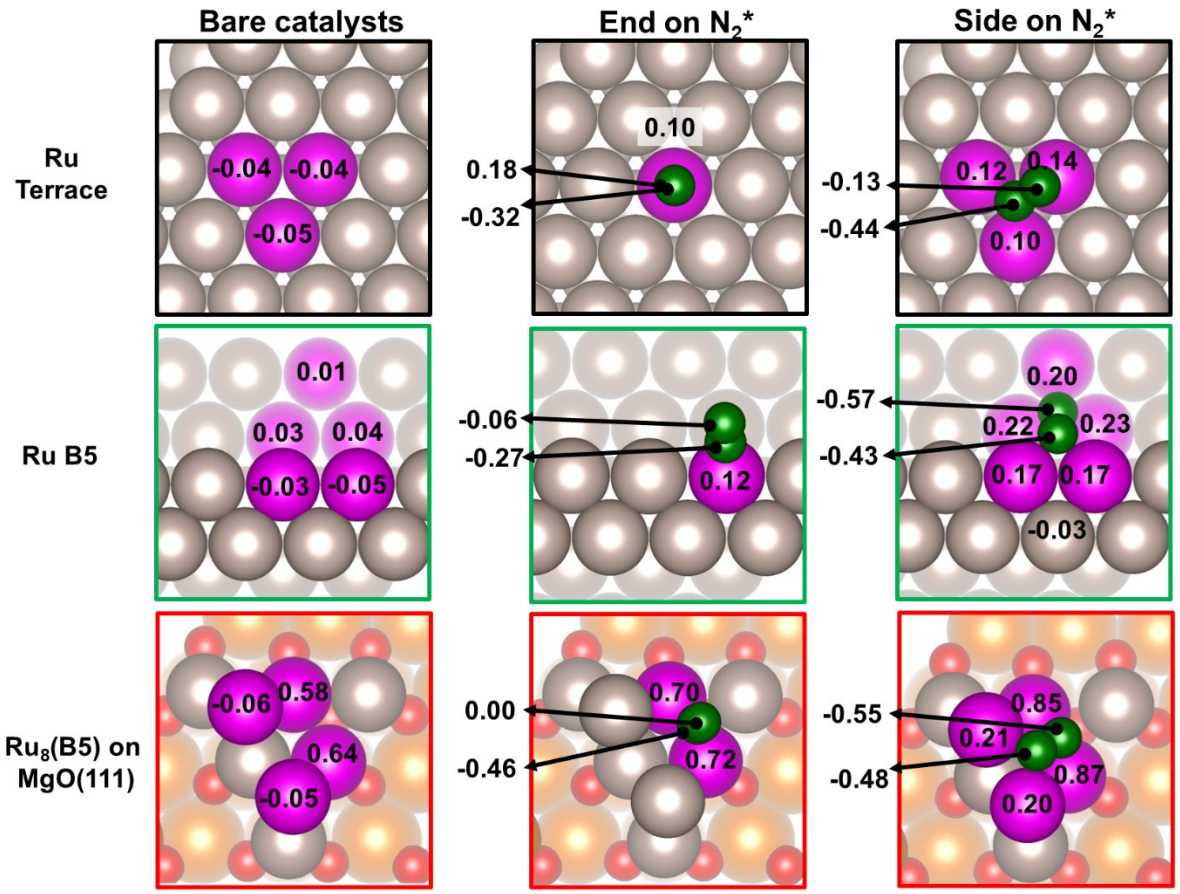


Figure S3. Optimised structures of the Ru(0001) terrace, Ru B5, and Ru_8(B5 like)/MgO(111) models in their bare form and with N_2* adsorbed in both the end-on and side-on configurations. Green, magenta, grey, orange, and red spheres represent the N, Ru in contact with N, Ru not in contact with N, Mg, and O atoms, respectively. The black values refer to the corresponding Bader charges of the N atoms and the Ru atoms before and after N_2 adsorption. The Bader charges of the N atoms are more negative in the side-on N_2* configurations than in the end-on N_2* configurations for all three systems; the most negative overall Bader charges of N_2 are observed in the Ru_8(B5-like)/MgO(111) system.