Supporting Information for

DFT+U Calculations on Substitutionally Doped (Ni, Cu, Zn) Mg-vanadate Surfaces for the Oxidative Dehydrogenation of Alkanes

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S1. Optimizations of Ni, Cu, and Zn-doped Mg-vanadate Surfaces

Table S1. Number of atoms present in each surface and the *k*-point selection for surface optimization calculations

Bulk	Surface	K-grid mesh	Total # of atoms
V_2O_5	010	3×3×1	133
	110	5×4×1	133
MgV_2O_6	001	3×3×1	115
	10-1	3×4×1	115
	111	4×5×1	61
t-$Mg_2V_2O_7$	001	3×3×1	95
	100 Mg-rich	3×3×1	95
	100 V-rich	3×3×1	95
	210	3×3×1	95
m-$Mg_2V_2O_7$	001	4×6×1	95
	010	6×4×1	95
	011	3×3×1	95
$Mg_3V_2O_8$	010	6×4×1	111
	110	5×3×1	111

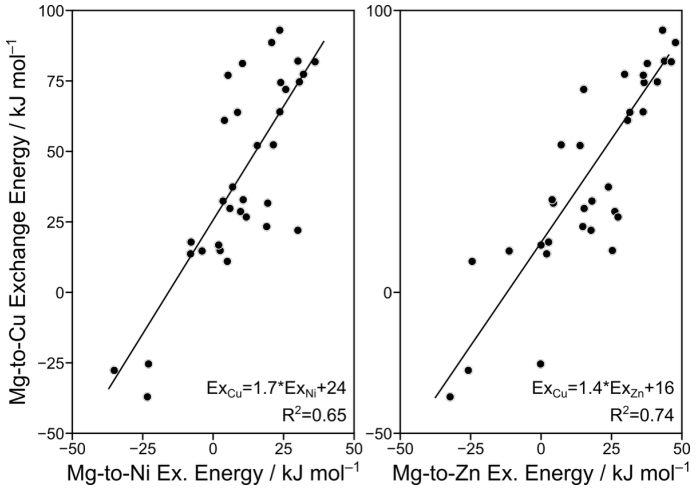

Figure S1. Correlations between Cu exchange energies (kJ mol^{-1}) as a function of a) Ni and b) Zn exchange energies. Linear regressions along their R-square values are also provided.

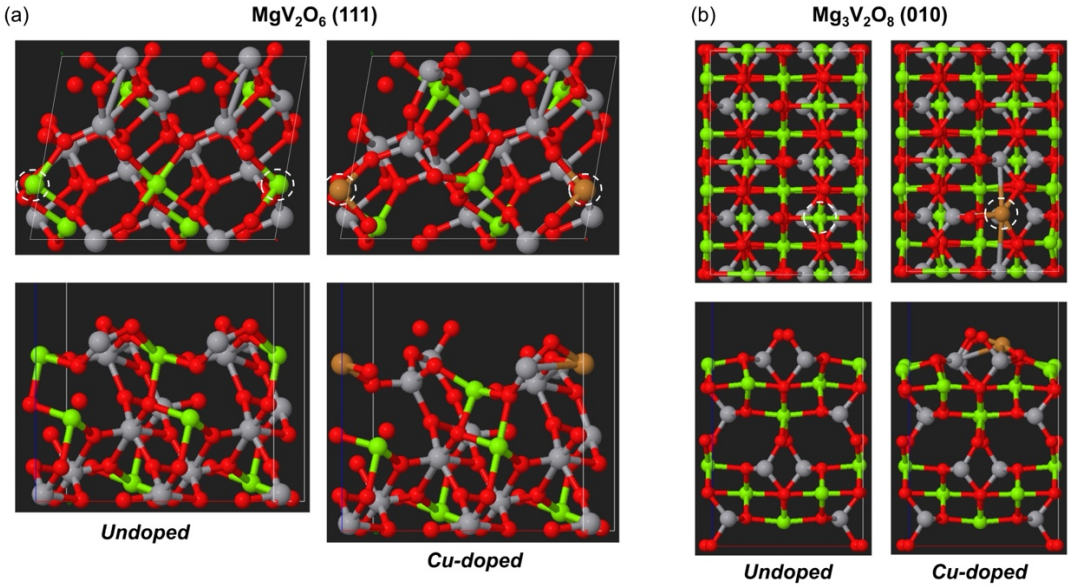

Figure S2. Top (above) and side (below) geometries of the slab-structure models of Cu atom doped (a) MgV_2O_6 (111) and (b) $Mg_3V_2O_8$ (010) surfaces in comparison with their corresponding undoped state. After the incorporation of the Cu dopant, both these surfaces undergo restructuring. The gray, red, light green, dark gray, and brown colored atoms denote the V, O, Mg, C, and Cu, respectively.

S2. Methyl-addition energies across Ni, Cu, and Zn-doped Mg-vanadate Surfaces

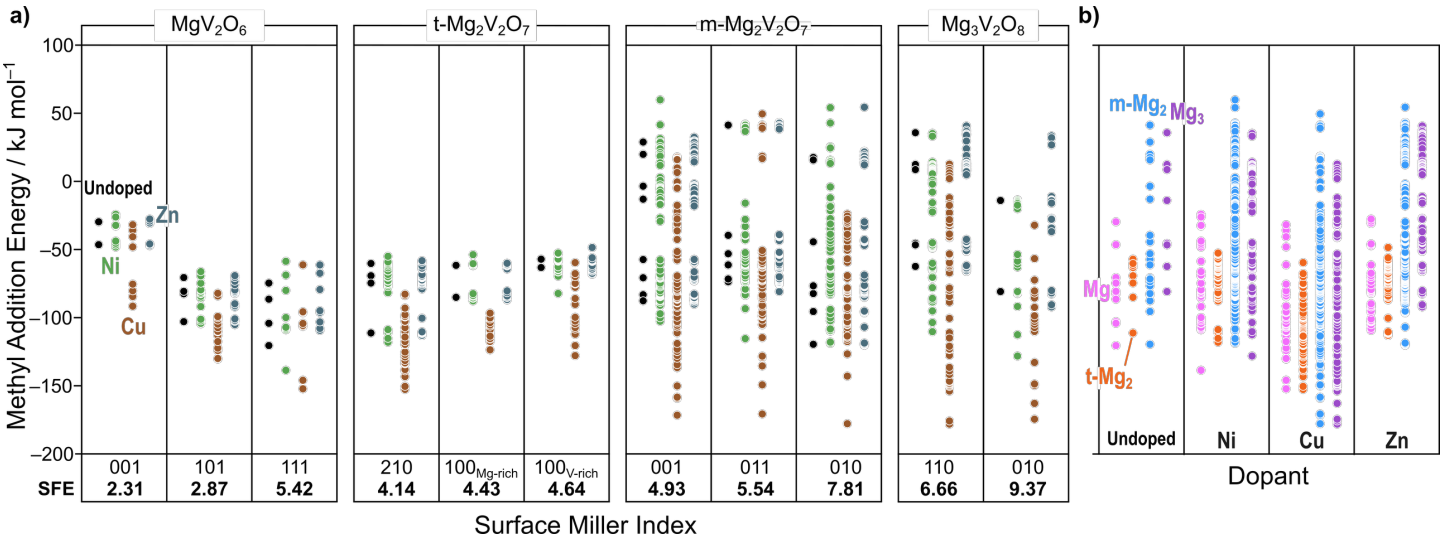

Figure S3. Methyl addition energies on Mg-vanadate surfaces: (a) MAE on undoped (black), Ni-doped (green), Cu-doped (brown), and Zn-doped (grey blue) MgV_2O_6, t-MgV_2O_7, m-$Mg_2V_2O_7$, and $Mg_3V_2O_8$ surfaces. The Miller index for each surface is provided along with the surface formation energy (SFE) of the undoped surface. (b) MAE values on undoped, Ni-doped, Cu-doped, and Zn-doped surfaces from MgV_2O_6 (Mg, pink), $Mg_2V_2O_7$ triclinic (t-Mg_2, orange) and monoclinic (m-Mg_2, blue), and $Mg_3V_2O_6$ (Mg_3, purple) bulk materials.

S3. HAE and MAE across Ni, Cu, and Zn-doped Mg-vanadate Surfaces as a Function of Surface Features

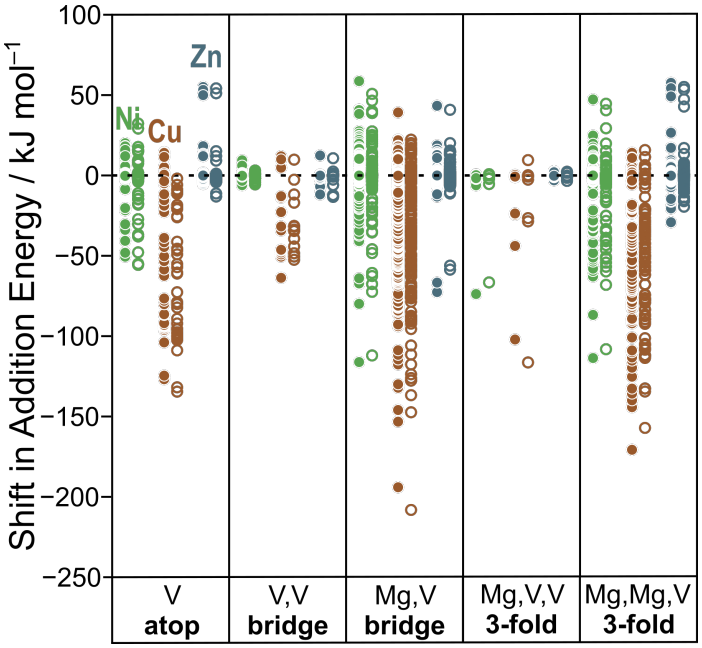

Figure S4. Shift in hydrogen and methyl addition energies on Mg-vanadate surfaces as a function of O-atom coordination: HAE_{shift} (filled) and MAE_{shift} (hollow) on Ni-doped (green), Cu-doped (brown), and Zn-doped (grey blue) MgV_2O_6, t-MgV_2O_7, m-$Mg_2V_2O_7$, and $Mg_3V_2O_8$ surfaces.

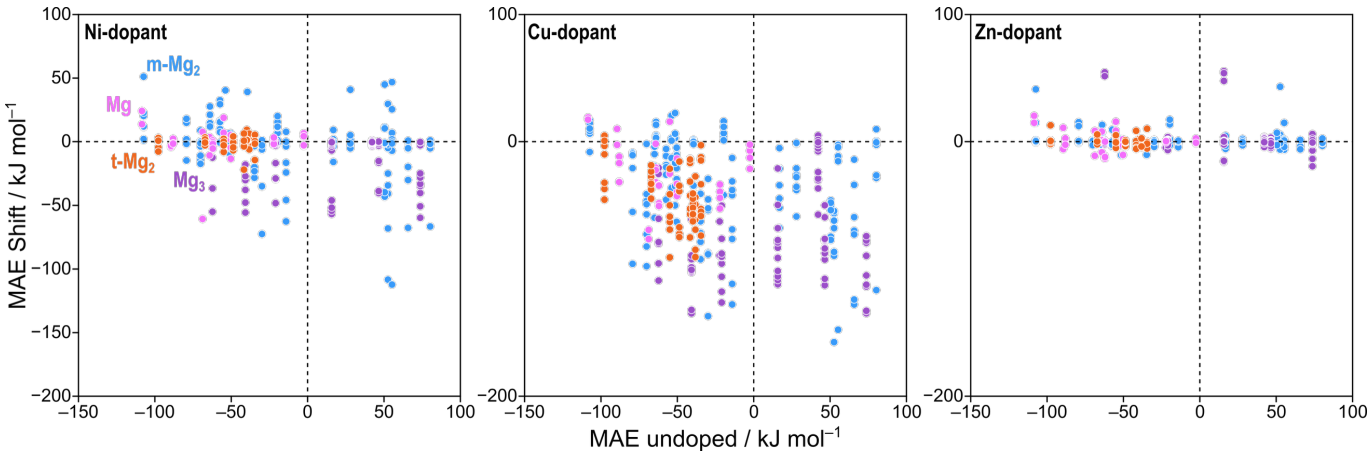

Figure S5. Shift in MAE values upon doping as a function of the MAE of undoped surfaces for a) Ni-, b) Cu- and c) Zn-doped MgV_2O_6 (pink), t-$Mg_2V_2O_7$ (orange), m-$Mg_2V_2O_7$ (blue), and $Mg_3V_2O_8$ (purple).

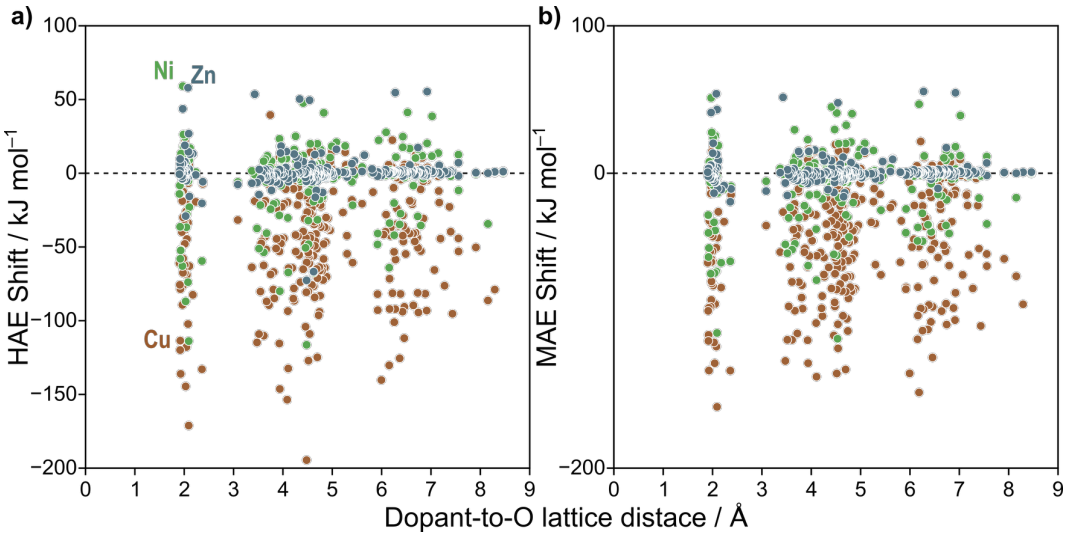

Figure S6. Shifts in (a) hydrogen addition and (b) methyl addition energies (kJ mol^{-1}) as a function of dopant (Ni, green; Cu, brown; Zn, blue) to O atom lattice distance (Angstroms / Å). Lattice distances are taken from the optimized undoped structures, defined as the distance between the Mg-atom to be exchanged and the surface O-atom with H* (HAE) or CH_3* (MAE).

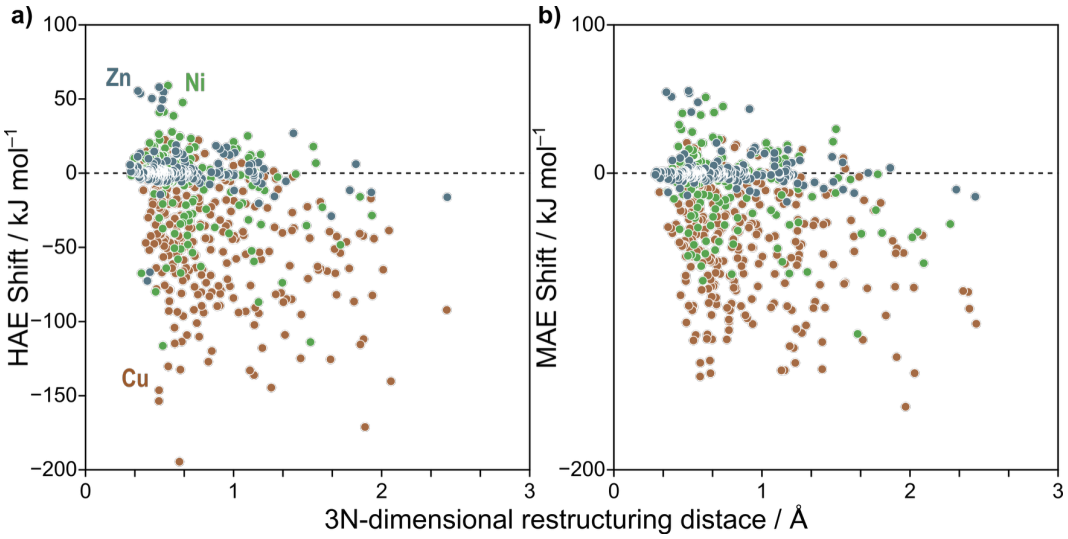

Figure S7. Shifts in (a) hydrogen addition and (b) methyl addition energies (kJ mol^{-1}) as a function restructuring distance (Angstroms / Å) for Ni- (green), Cu- (brown), and Zn-doped (blue) Mg-vanadate surfaces. Restructuring distances (3-N dimensional) are measured between the optimized undoped surface and the optimized doped surfaces upon relaxation with H* or CH_3*.