

Table S1. Total energies (eV) of the investigated structures.

Nomenclature	Composition	Energy (eV)
V^{bcc}	V	-8.9219
$\frac{1}{2} \text{O}_2$	O	-4.8883
SiO ₂ film	Si ₈ O ₂₀ Mo ₅₆	-806.7240
(SiO ₂) _{α} -quartz	SiO ₂	-23.9280
VO ₂ (gas)	VO ₂	-21.1232
V ₂ O ₃ (gas)	V ₂ O ₃	-37.5722
V ₂ O ₄ (gas)	V ₂ O ₄	-46.9420
V ₂ O ₅ (gas)	V ₂ O ₅	-54.6081
V ₄ O ₈ (gas)	V ₄ O ₈	-98.7471
V ₄ O ₁₀ (gas)	V ₄ O ₁₀	-115.7926
V ₆ O ₁₂ (gas)	V ₆ O ₁₂	-149.1093
V ₆ O ₁₅ (gas)	V ₆ O ₁₅	-174.8520
monomer/Si ₇ O ₂₀ /Mo(112)	VSi ₇ O ₂₁ Mo ₅₆	-815.8486
red-monomer/Si ₇ O ₂₀ /Mo(112)	VSi ₇ O ₂₀ Mo ₅₆	-808.4223
dimer/Si ₆ O ₂₀ /Mo(112)	V ₂ Si ₆ O ₂₂ Mo ₅₆	-824.8572
red-dimer-1/Si ₆ O ₂₀ /Mo(112)	V ₂ Si ₆ O ₂₁ Mo ₅₆	-817.5929
red-dimer-2/Si ₆ O ₂₀ /Mo(112)	V ₂ Si ₆ O ₂₀ Mo ₅₆	-810.3973
VO ₂ /Si ₈ O ₂₀ /Mo(112)	VSi ₈ O ₂₂ Mo ₅₆	-828.7839
VO/Si ₈ O ₂₀ /Mo(112)	VSi ₈ O ₂₁ Mo ₅₆	-819.6901
V ₂ O ₄ /Si ₈ O ₂₀ /Mo(112)	V ₂ Si ₈ O ₂₄ Mo ₅₆	-854.7461
V ₂ O ₃ /Si ₈ O ₂₀ /Mo(112)	V ₂ Si ₈ O ₂₃ Mo ₅₆	-845.3669
V ₂ O ₅ /Si ₈ O ₂₀ /Mo(112)	V ₂ Si ₈ O ₂₅ Mo ₅₆	-863.2694
V ₂ O ₄ /Si ₈ O ₂₀ /Mo(112)	V ₂ Si ₈ O ₂₄ Mo ₅₆	-854.2941
V ₄ O ₈ /Si ₈ O ₂₀ /Mo(112) – Fig. 3A	V ₄ Si ₈ O ₂₈ Mo ₅₆	-903.6918
V ₄ O ₇ /Si ₈ O ₂₀ /Mo(112)	V ₄ Si ₈ O ₂₇ Mo ₅₆	-894.9278
V ₄ O ₈ /Si ₈ O ₂₀ /Mo(112) – Fig. 4A	V ₄ Si ₈ O ₂₈ Mo ₅₆	-906.1464
V ₄ O ₈ /Si ₈ O ₂₀ /Mo(112) – Fig. 4B	V ₄ Si ₈ O ₂₈ Mo ₅₆	-906.3562
V ₄ O ₁₀ /Si ₈ O ₂₀ /Mo(112)	V ₄ Si ₈ O ₃₀ Mo ₅₆	-923.4142

$V_4O_9/Si_8O_{20}/Mo(112)$	$V_4Si_8O_{29}Mo_{56}$	-914.5433
$V_4O_8/Si_8O_{20}/Mo(112)$	$V_4Si_8O_{28}Mo_{56}$	-906.3566
$V_6O_{12}/Si_8O_{20}/Mo(112)$	$V_6Si_8O_{32}Mo_{56}$	-955.9158
$V_6O_{15}/Si_8O_{20}/Mo(112)$	$V_6Si_8O_{35}Mo_{56}$	-982.2309
