

Electronic Supplementary Information (ESI)

S1: Gas phase equilibria

Gas phase equilibria above the metal crucible or graphene surface in the CVD reactor, where (g) or (s) in parentheses indicates whether the phase is in its gaseous or solid state. Gibbs free energy at 298 K has been calculated using data from the NIST-JANAF thermochemical tables (<http://kinetics.nist.gov/janaf/>)

Equilibrium	ΔG (kJmol ⁻¹)
Above Mo or W surface	
$\text{MoO}_3(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow \text{Mo}(\text{s}) + 3\text{H}_2\text{O}(\text{g})$	-241 (5a)
$\text{WO}_3(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow \text{W}(\text{s}) + 3\text{H}_2\text{O}(\text{g})$	-295 (5b)
$\text{MoO}_3(\text{g}) + \text{CH}_4(\text{g}) \leftrightarrow \text{Mo}(\text{s}) + \text{CO}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	-369 (5c)
$\text{WO}_3(\text{g}) + \text{CH}_4(\text{g}) \leftrightarrow \text{W}(\text{s}) + \text{CO}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	-423 (5d)
Above graphene surface	
$6\text{MoO}_3(\text{g}) + 3\text{CH}_4(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 3\text{Mo}_2\text{C}(\text{s}) + 18\text{H}_2\text{O}(\text{g})$	-310 (6a)
$3\text{WO}_3(\text{g}) + 3\text{CH}_4(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 3\text{WC}(\text{s}) + 9\text{H}_2\text{O}(\text{g})$	-397 (6b)
$6\text{MoO}_3(\text{g}) + 7\text{CH}_4(\text{g}) \leftrightarrow 3\text{Mo}_2\text{C}(\text{s}) + 4\text{CO}(\text{g}) + 14\text{H}_2\text{O}(\text{g})$	-378 (6c)
$3\text{WO}_3(\text{g}) + 4\text{CH}_4(\text{g}) \leftrightarrow 3\text{WC}(\text{s}) + 4\text{CO}(\text{g}) + 8\text{H}_2\text{O}(\text{g})$	-300 (6d)