Electronic Supplementary Material (ESI) for Nanoscale.

Electronic supplementary information

What are the Active Carbon Species during Graphene Chemical Vapor Deposition Growth?

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Table S1. Comparison of binding energies E_b of various C precursors on Cu(111), Ni(111), Ir(111) and Rh(111) surfaces by using DFT-D2 and GGA-PBE methods. C-I and C-II represent the carbon monomer on metal surface and subsurface, respectively. The character T, F, and H denote the top, fcc, and hcp adsorption sites on metal surfaces, and O denotes the octahedral adsorption sites on metal subsurface, respectively. Here N/A represents that CH_4 molecule is not sensitive to the adsorption sites of metal surfaces.

Metal Surface	**CH_i species**	**Stable adsorption site**	**E_b**	
			DFT-D2	**GGA-PBE**
Cu(111)	C-I	F	3.39	4.90
	C-II	O	3.89	5.39
	CH	F	5.25	4.96
	CH_2	F	3.40	3.05
	CH_3	F	1.79	1.14
	CH_4	N/A	0.21	0.05
Ni(111)	C-I	H	5.29	6.76
	C-II	O	5.84	7.27
	CH	F	6.71	6.42
	CH_2	F	4.44	4.06
	CH_3	F	2.40	1.98
	CH_4	N/A	0.21	0.06
Ir(111)	C-I	H	5.68	7.08
	C-II	O	3.99	5.51
	CH	H (or F)	7.24	6.78
	CH_2	F	4.69	4.10
	CH_3	T	2.55	1.87
	CH_4	N/A	0.39	0.04
Rh(111)	C-I	H	5.71	7.21
	C-II	O	5.45	6.90
	CH	H	7.04	6.72
	CH_2	F	4.09	4.16
	CH_3	F	2.27	1.83
	CH_4	N/A	0.25	0.03

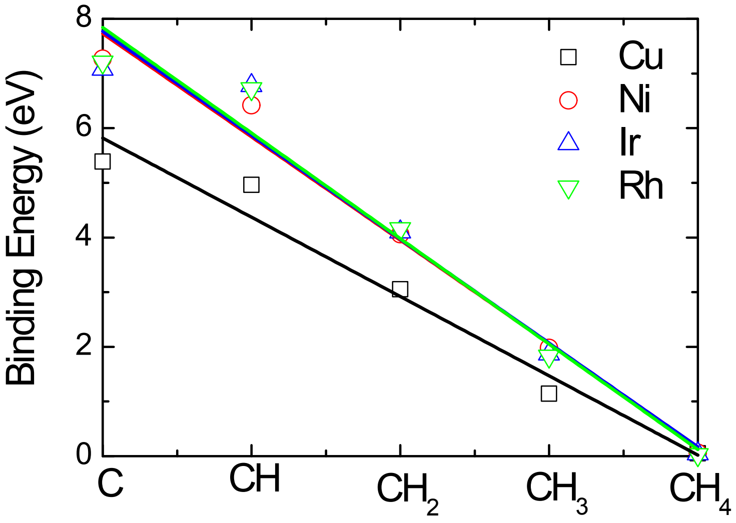

Fig. S1 The binding energies of CH_i (i =0, 1, 2, 3, 4) species on Cu, Ni, Ir, and Rh surfaces as a function of the number of H in the CH_i species.

Computational details for relative Gibbs free energy

The relative Gibbs free energy (ΔG_f) of CH_i species (i = 0, 1, 2, and 3) on metal surfaces is defined as,[1-3]

$$\Delta G_f = E_T - E_M + \Delta F_{vib} - n_C\mu_C - n_H\mu_H \qquad (1)$$

where E_T and E_M are total energies of metal surface with and without adsorbed CHi, respectively, $n_C = 1$ and $n_H = i$ are the number of C and H atoms in CH_i, respectively. ΔF_{vib} is the change of vibrational contributions of CH_i species on metal surfaces to system free energy. F_{vib} is defined as[3]

$$F_{vib}(\omega, T) = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) - kT\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega})\right] \qquad (2)$$

where $\beta = 1/kT$ and ω is the vibrational frequency of CH_i species on metal surfaces. F_{vib} is equal to the zero-point energy (ZPE) at the temperature $T = 0$ K. Table S2 lists zero-point energies (ZPE), vibrational entropies multiplied by temperature (T = 1200 K), and total vibrational contributions to the free energy of various CH_i species (i=0, 1, 2, and 3) on Cu(111), Ni(111), Ir(111) and Rh(111) surfaces. μ_H is the hydrogen chemical potential, that is a function of temperature and H_2 partial pressure. The μ_H can be written as,[1,2]

$$2\mu_H(T, p) = E_{H_2} - kT\ln\left(\frac{kT}{p} \times g \times \zeta_{trans} \times \zeta_{rot} \times \zeta_{vib}\right) \qquad (3)$$

where E_{H2} is DFT calculated energy of a hydrogen molecule (-6.760 eV), k is Boltzmann constant, p is partial pressure of H_2, and g is the degree of degeneracy of the electron energy level. ζ_{trans}, ζ_{rot}, and ζ_{vib} are the partition functions for translational, rotational, and vibration motions, respectively. Taking one-half of the energy of a H_2 molecule (E_{H2}) as a reference, the dependence of μ_H on temperature T and H_2 partial pressure p is shown in Fig. S2. μ_C is carbon chemical potential and it depends on growth temperature T and the partial pressure ratio of CH_4 and H_2 during the growth,[4]

$$\mu_C\left(T, \frac{p_{CH4}}{p_{H2}}\right) = \Delta E - 2\mu_H^* + kT\ln\frac{p_{CH4}}{p_{H2}} \qquad (4)$$

where ΔE is the DFT energy difference of CH_4 and H_2 molecules ($\Delta E = E_{CH4} - 2E_{H2}$ = -10.507 eV), and μ_H^* is related to the term of T and H_2 pressure of Eq.(3).

Table S2. Zero-point energies (ZPE), vibrational entropies multiplied by temperature (T = 1200 K), and vibrational contributions to the free energy of various CH_i species (i=0, 1, 2, and 3) on Cu(111), Ni(111), Ir(111) and Rh(111) surfaces. C-I and C-II represent the carbon monomer on metal surface and subsurface, respectively.

Surface	**CH_i**	**ZPE (eV)**	**TS (eV)**	**F_{vib} (eV)**
Cu(111)	C-I	0.09	0.30	-0.21
	C-II	0.10	0.30	-0.20
	CH	0.34	0.52	-0.18
	CH_2	0.58	0.78	-0.20
	CH_3	0.91	0.95	-0.04
Ni(111)	C-I	0.11	0.29	-0.18
	C-II	0.11	0.29	-0.18
	CH	0.35	0.51	-0.16
	CH_2	0.57	0.78	-0.21
	CH_3	0.89	0.94	-0.05
Ir(111)	C-I	0.10	0.30	-0.20
	C-II	0.10	0.30	-0.20
	CH	0.38	0.50	-0.12
	CH_2	0.59	0.74	-0.15
	CH_3	0.95	1.11	-0.16
Rh(111)	C-I	0.10	0.30	-0.20
	C-II	0.10	0.30	-0.20
	CH	0.36	0.51	-0.15
	CH_2	0.59	0.74	-0.15
	CH_3	0.88	0.95	-0.07

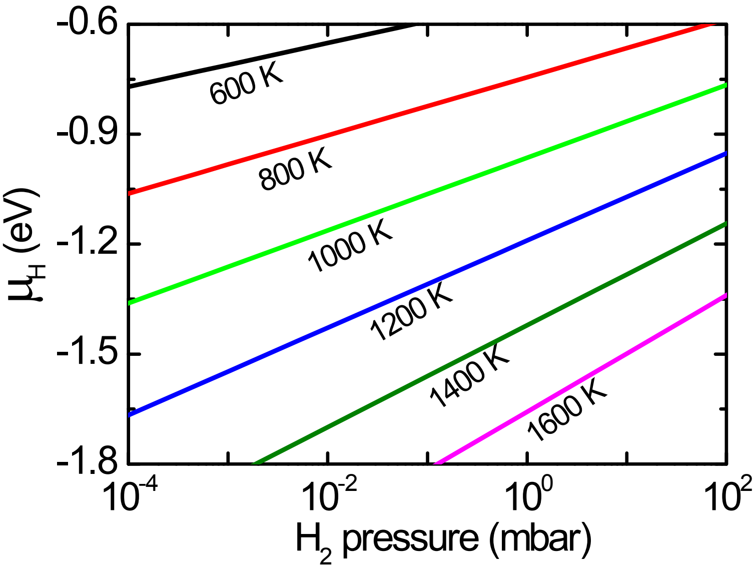

Fig. S2 The dependence of H chemical potential μ_H (eV) on temperature T and H_2 pressure p. Here one-half of the energy of a H_2 molecule is taken as a reference.

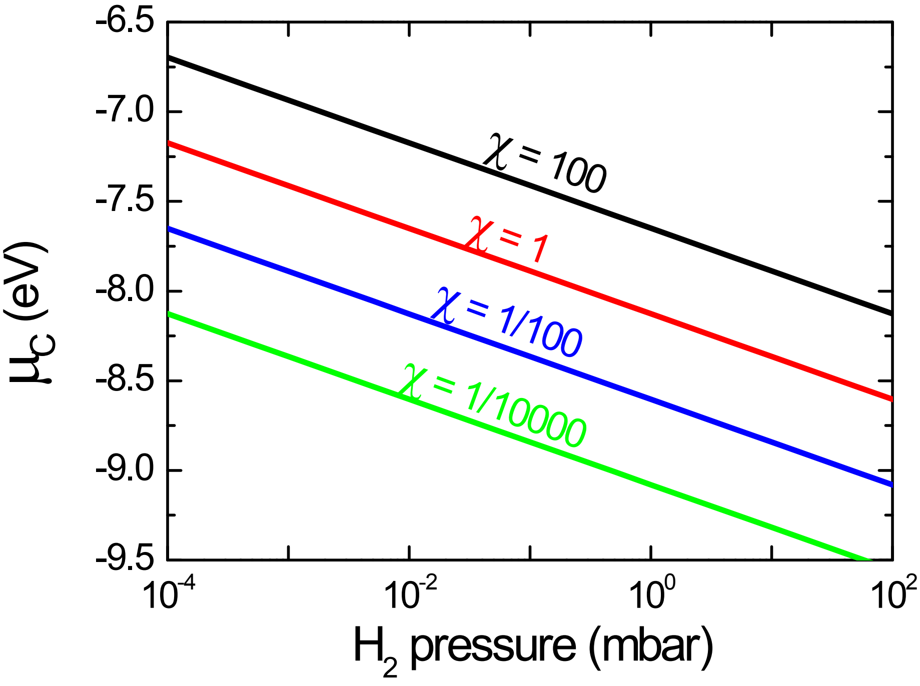

Fig. S3 The carbon chemical potential μ_C (eV) as a function of H_2 pressure (P_{H2}) for the ratio of partial pressures between CH_4 and H_2 ($\chi = P_{CH4} / P_{H2}$) at 100, 1, 1/100, and 1/1000.

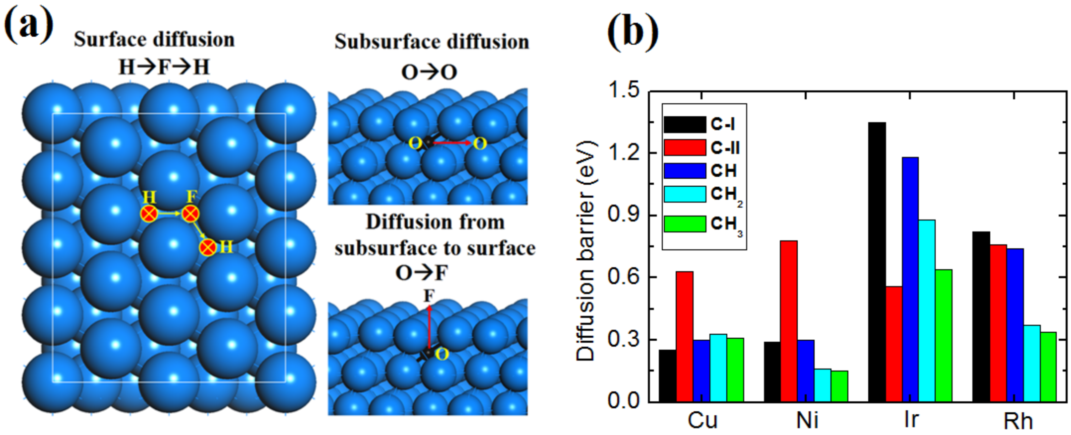

Fig. S4 (a) Diffusion pathways and (b) diffusion barriers of various CH_i species (i = 0,1 ,2, 3) on Cu(111), Ni(111), Ir(111), and Rh(111) surfaces. The surface diffusion pathway is H→F→H, the diffusion pathway of C atom in metal subsurface is O→O, and the diffusion pathway of C atom from subsurface to surface is O→F. C-I and C-II represent the carbon atom on metal surface and subsurface, respectively.

Notes and references

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