Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Methanol Decomposition Reactions over Boron-Doped Graphene Supported Ru-Pt Catalyst

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Supporting Information

Table S1. The geometric parameters of metal clusters adsorbed on boron doped graphene surface.

	C– C (Å)	**C– B (Å)**	**M– M (Å)**
Ref 60 (Pt_2Ru_4/B-C)	1.41– 1.47	1.50 – 1.53	2.20 – 3.53
This work (Pt_2Ru_2/B-C)	1.41 – 1.47	1.51 – 1.55	2.50 – 3.03

Table S2. Calculated adsorption energies of metal cluster, per Ru-Pt atom, for 2Ru and 2Pt atoms deposited on pristine graphene and boron-doped graphene surface.

Surface	E_{ads}, eV
RuPt/Graphene	-0.68
RuPt/B-doped graphene	-1.98

Table S3. Calculated adsorption energies (E_{ads}, in eV) and bond distance (bond length, in Å) of methanol molecule adsorbed on Ru–Pt/graphene surface at different sites, top Ru_2, top Ru_1 and top Pt_2.

Species	Sites	E_{ads}	d(O–Ru)	d(O–Pt)	d(C–H)	d(O–H)
CH_3OH	Ru2	-0.52	2.19	3.32	1.10	0.98
	Ru1	-0.61	2.19	3.88	1.10	0.98
	Pt2	-0.55	3.47	2.23	1.10	1.00

Table S4. The Pt adsorption energies on boron-doped graphene surface in different cutoff energy and K-points setting.

Cutoff energy	E_{ads}[a]	Cpu time (sec)	Kpoints[b]	E_{ads}	Cpu time (sec)
325	-3.17	1317	441	-3.17	1343
350	-3.17	1343	551	-3.17	816
375	-3.18	1568	661	-3.18	3217
400	-3.17	1583	771	-3.18	2332

[a] the Pt adsorption energy is calculated with a 5 x 5 x 1 Monkhorst-Pack k-point

[b] the Pt adsorption energy is calculated with a plane wave energy cutoff of 350 eV

Table S5. Calculated adsorption energies (E_{ads}, in eV) and bond distance (bond length, in Å) of methanol molecule adsorbed on Ru–Pt/boron doped graphene surface at different sites, A (Ru_2–Pt_1), B & F (top Ru_1), C (top Ru_2), D (Ru_1–Ru_2), E (Ru_1–Pt_2), and G (top Pt_1)).

Species	Sites	E_{ads}	d(O–Ru)	d(O–Pt)	d(C–H)	d(O–H)
CH_3OH	(A)	-0.84	2.22	3.13	1.10	1.02
	(B)[1a]	-0.80	2.21	3.16	1.10	1.00
	(C)	-0.95	2.18	3.99	1.10	0.98
	(D)	-0.60	2.22	3.57	1.10	0.98
	(E)	-0.65	2.21	3.35	1.10	0.98
	(F)[2a]	-0.74	2.20	3.34	1.10	0.98
	(G)	-0.48	-	3.21	1.10	1.01

[a]1 means OH bond points to Pt, and 2 means C-H bond points to Pt

Table S6. Activation energy (‡E) and zero-point energy corrected activation energies ($^{‡}E_{ZPE)}$ of potential energy surface on Ru-Pt/boron doped graphene surface. ('*' indicates the species is adsorbed on the catalyst surface)

Reaction pathways	$^{‡}E$ (eV)	$^{‡}E_{ZPE}$(eV)
Pathway A		
$CH_3OH^*_{(A)} \rightarrow [CH_3O^* + H^*]$	0.67	0.61
$CH_3O^* \rightarrow [CH_2O^* + 2H^*]$	0.70	0.48
$CH_2O^* \rightarrow [CHO^* + 3H^*]$	0.36	0.18
$CHO^* \rightarrow [CO^* + 4H^*]$	2.47	2.39
$CHO^* \rightarrow CHO^*$	0.91	0.89
$CHO^* \rightarrow [CO^* + 4H^*]$	0.15	0.08
Pathway B		
$CH_3OH^*_{(C)} \rightarrow CH_3OH^*_{(B)}$	0.42	0.41
$CH_3OH^*_{(B)} \rightarrow [CH_3O^* + H^*]$	0.43	0.24
$CH_3O^* \rightarrow [CH_2O^* + 2H^*]$	0.55	0.38
$CH_2O^* \rightarrow [CHO^* + H^*]$	0.94	0.76
$CH_2O^* \rightarrow CH_2O^*$	1.06	1.03
$CHO^* \rightarrow [CO^* + 4H^*]$	0.15	0.08

Table S7. Desorption energy (E_{des}), barriers ($^{‡}E$) and reaction energies (ΔE) of the rate determining steps of CH_3OH decomposition on different surfaces.

Surfaces	E_{des} (eV)	‡E (eV)	ΔE (eV)
Ru–Pt/boron doped graphene	0.84 (Site A), 0.80 (site B), 0.95 (site C)	0.94	-0.08
PtRu (111) [1]	0.70	1.01	-0.18
Pd (100) [2]	0.42	1.79	-0.07
Ru (0001) [3]	0.28	0.63	-0.02
Ir (111) [4]	0.34	0.51	-0.15
$PtPd_3$ (111) [5]	0.12	0.95	0.74
Au (111) [6]	0.17	2.00	1.29

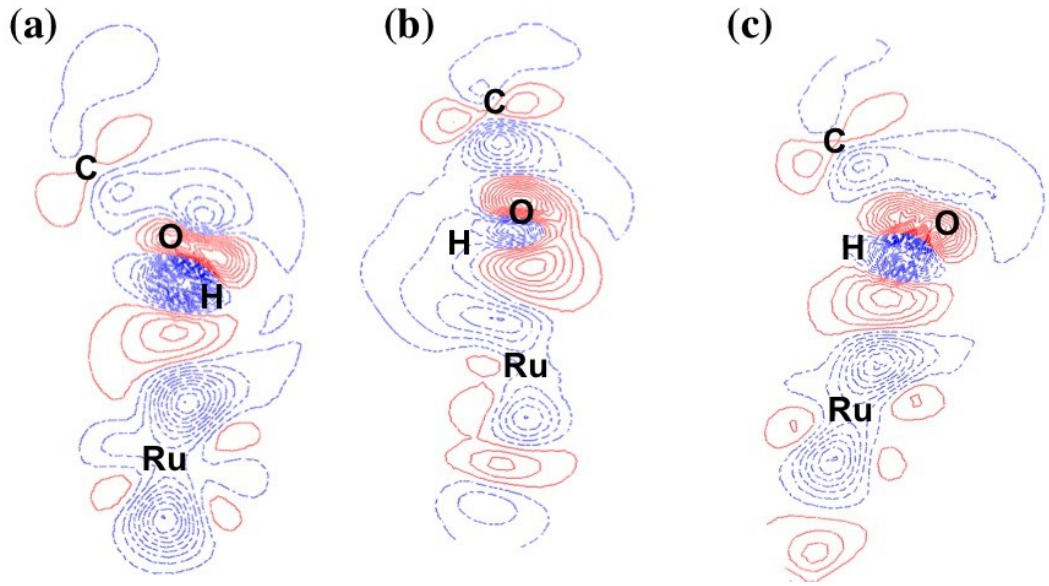

Figure S1. Electron density difference plot (e/Bohr^3) for the different methanol adsorption configuration on Ru–Pt/boron doped graphene surface. The blue dash-lines represents the loss of electron and the red solid-lines show electron accumulation. (a) site A, (b) site B, and (c) site C.

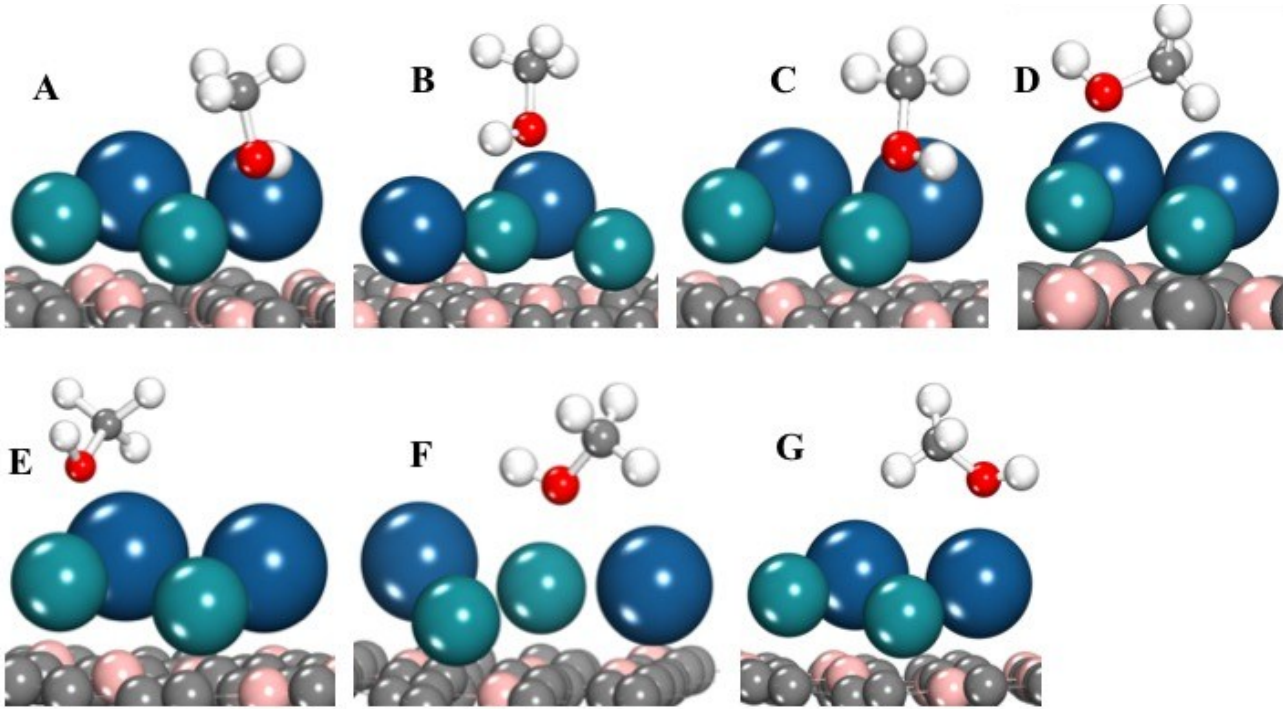

Figure S2. Different possible adsorption sites of methanol on Ru–Pt/boron-doped graphene surface, A (Ru_2–Pt_1), B & F (top Ru_1), C (top Ru_2), D (Ru_1–Ru_2), E (Ru_1–Pt_2), and G (top Pt_1)). Atomic spheres: Blue, Pt; green, Ru; gray, C; orange, O; pale yellow B.

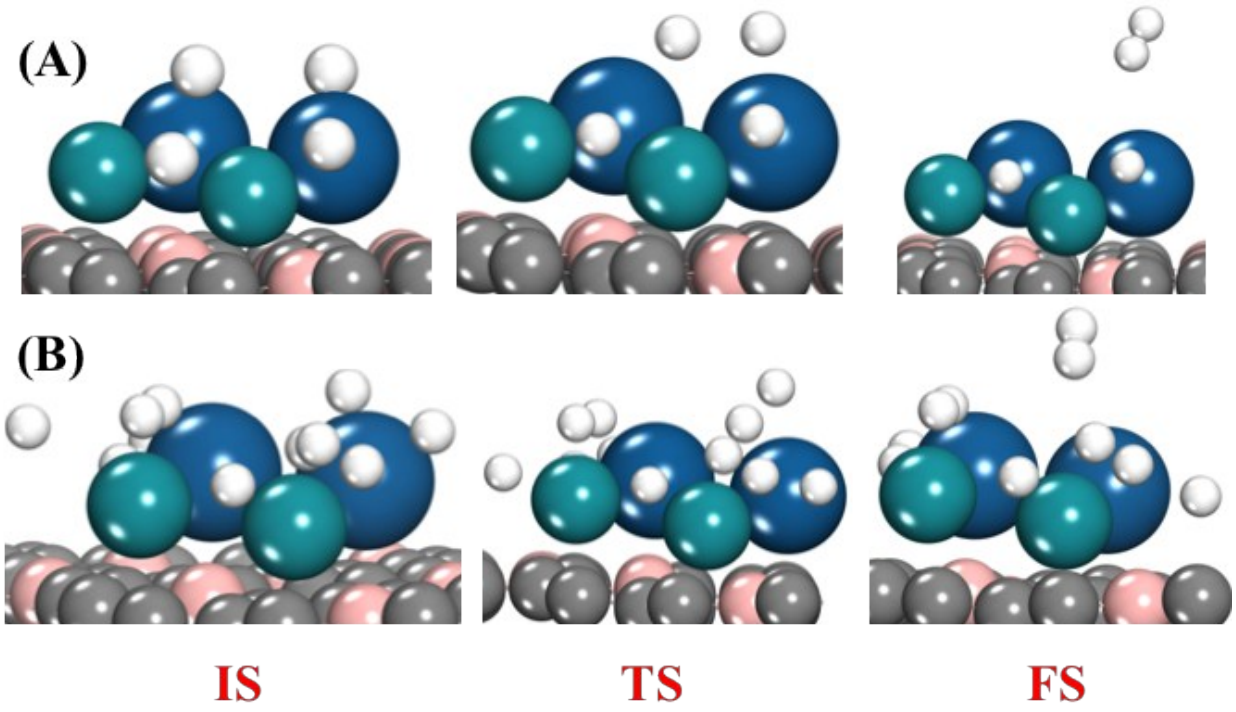

Figure S3. Schematic representation of the Initial state (IS), Transition state (TS) and Final state (FS) of the hydrogen recombination reaction (H + H→H_2) at different coverage (A) 4H (B) coverage 12H on Ru-Pt/boron-doped graphene surface.

References

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