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ARTICLE

Modification of catalytic properties of the Au_4 nanocluster for the conversion of methane-to-methanol: Synergic effects of metallic adatoms and defective graphene support

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Table S1. ZPE-corrected relative energies of the system along the steps of the catalytic cycle for the partial oxidation of methane by N_2O over the graphene-deposited Au_5 catalyst. The energy of the isolated subsystems in their lowest-energy spin state is taken as zero.

Steps	Relative Energy (kcal·mol^{-1})	
	Doublet spin-state	Quartet spin-state
Isolated systems	0.0	18.8
N_2O adsorption	-4.5	14.1
N_2O decomposition transition state (TS1)	11.6	21.7
N_2 adsorption on Au_5O	-9.2	-2.1
N_2 desorption	-5.9	1.4
CH_4 adsorption	-9.4	2.0
C-H bond activation transition state (TS2)	5.9	16.8
Intermediate of C-H bond activation	-32.8	-25.0
Two-centered recombination		
C-O formation transition state (TS3)	7.2	10.6
One-centered recombination		
CH_3 Shift transition state ($TS3_{B1}$)	-17.3	-10.1
IV_B intermediate	-20.1	-34.5
C-O formation transition state ($TS3_{B2}$)	5.9	18.5
CH_3OH adsorption	-39.4	-20.6
CH_3OH desorption	-28.9	-10.1

Table S2. . ZPE-corrected relative energies of the system along the steps of the catalytic cycle for the partial oxidation of methane by N_2O over the graphene-deposited Au_4Pd catalyst. The energy of the isolated subsystems in their lowest-energy spin state is taken as zero.

Steps	**Relative Energy (kcal·mol^{-1})**	
	Singlet spin-state	**Triplet spin-state**
Isolated systems	0.0	0.8
N_2O adsorption	-4.6	-3.6
N_2O decomposition transition state (TS1)	9.2	11.1
N_2 adsorption on Au_4OPd	-8.6	-9.6
N_2 desorption	-5.2	-6.0
CH_4 adsorption	-8.8	-10.0
C-H bond activation transition state (TS2)	9.2	5.7
Intermediate of C-H bond activation	-36.7	-33.9
Two-centered recombination		
C-O formation transition state (TS3)	5.7	0.6
One-centered recombination		
CH_3 Shift transition state ($TS3_{B1}$)	-17.4	-18.4
IV_B intermediate	-18.8	-19.3
C-O formation transition state ($TS3_{B2}$)	6.5	5.6
CH_3OH adsorption	-41.1	-39.0
CH_3OH desorption	-28.9	-28.1

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Table S3. ZPE-corrected relative energies of the system along the steps of the catalytic cycle for the partial oxidation of methane by N_2O over the graphene-deposited Au_4Pt catalyst. The energy of the isolated subsystems in their lowest-energy spin state is taken as zero.

Steps	**Relative Energy (kcal·mol^{-1})**	
	Singlet spin-state	**Triplet spin-state**
Isolated systems	0.0	3.5
N_2O adsorption	-4.6	-1.0
N_2O decomposition transition state (TS1)	7.2	12.4
N_2 adsorption on Au_4OPt	-11.3	-6.0
N_2 desorption	-8.1	-2.6
CH_4 adsorption	-10.5	-4.9
C-H bond activation transition state (TS2)	7.2	7.9
Intermediate of C-H bond activation	-35.2	-30.2
Two-centered recombination		
C-O formation transition state (TS3)	6.5	3.3
One-centered recombination		
CH_3 Shift transition state ($TS3_{B1}$)	-19.6	-15.5
IV_B intermediate	-21.6	-16.6
C-O formation transition state ($TS3_{B2}$)	6.6	7.5
CH_3OH adsorption	-41.2	-36.1
CH_3OH desorption	-28.9	-25.4

Table S4. Optimized geometries of complexes along the steps of the catalytic cycle for the N_2O decomposition over the Au_5/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps			
	Isolated systems	N_2O adsorption	TS1	N_2 adsorption on OAu_5
N-N	1.13	1.14 (1.14)	1.16 (1.16)	1.11 (1.11)
N-O	1.18	1.19 (1.19)	1.74 (1.61)	
Au1-Au4	2.86 (2.86)	2.87 (2.86)	3.05 (2.92)	2.82 (2.85)
Au1-O		3.23 (3.22)	2.02 (2.07)	2.07 (2.15)
Au4-O				2.07 (2.15)

Table S5. Optimized geometries of complexes along the steps of the catalytic cycle for the partial oxidation of methane over the Au_5O/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps					
	Isolated systems	CH_4 adsorption	TS2	Intermediate IV	TS3	Methanol adsorption
C-H (methane)	1.09	1.09 (1.09)	1.29 (1.32)			
H-O		2.45 (2.96)	1.39 (1.25)	0.96 (0.97)	0.97 (0.97)	0.96 (0.96)
Au1-Au4	2.82 (2.85)	2.82 (2.88)	3.02 (2.90)	3.06 (2.90)	2.95 (2.94)	2.88 (2.86)
Au1-O	2.07 (2.15)	2.06 (2.15)	1.97 (2.05)	2.06 (2.05)	2.24 (2.17)	2.54 (2.52)
Au4-O	2.07 (2.15)	2.07 (2.14)				
Au4-C			2.40 (2.44)	2.08 (2.07)	2.52 (2.85)	
C-O					2.06 (2.13)	1.43 (1.43)

Table S6. Optimized geometries of complexes along the steps of the catalytic cycle for the formation of methanol through the one-centered recombination transition state over the Au_5O/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps		
	$TS3_{B1}$	IV_B intermediate	$TS3_{B2}$
H-O	0.96 (0.97)	0.97 (0.96)	0.97 (0.97)
Au1-Au4	2.66 (2.69)	2.66 (2.84)	2.70 (2.68)
Au1-O	2.11 (2.11)	2.10 (2.24)	2.22 (2.23)
Au1-C	2.11 (2.12)	2.09 (2.05)	2.42 (2.53)
Au4-C	3.14 (3.16)		
C-O			2.00 (2.05)

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Table S7. Optimized geometries of complexes along the steps of the catalytic cycle for the N_2O decomposition over the Au_4Pd/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps			
	Isolated systems	**N_2O adsorption**	**TS1**	**N_2 adsorption on OAu_4Pd**
N-N	1.13	1.14 (1.14)	1.16 (1.16)	1.11 (1.11)
N-O	1.18	1.19 (1.19)	1.68 (1.63)	
Au1-Au4	2.85 (2.81)	2.85 (2.81)	3.04 (3.11)	2.91 (2.99)
Au1-O		2.97 (3.22)	2.04 (2.07)	2.05 (2.05)
Au4-O				2.09 (2.12)

Table S8. Optimized geometries of complexes along the steps of the catalytic cycle for the partial oxidation of methane over the Au_4OPd/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps					
	Isolated systems	**CH_4 adsorption**	**TS2**	**Intermediate IV**	**TS3**	**Methanol adsorption**
C-H (methane)	1.09	1.09 (1.09)	1.30 (1.33)			
H-O		2.50 (2.54)	1.35 (1.25)	0.96 (0.97)	0.97 (0.97)	0.96 (0.97)
Au1-Au4	2.91 (2.99)	2.91 (3.00)	3.00 (2.98)	2.91 (2.95)	2.98 (2.95)	2.86 (2.73)
Au1-O	2.04 (2.04)	2.04 (2.04)	1.99 (2.04)	2.06 (2.04)	2.25 (2.17)	2.46 (2.65)
Au4-O	2.09 (2.13)	2.11 (2.17)				
Au4-C			2.43 (2.43)	2.08 (2.08)	2.52 (2.79)	
C-O					2.04 (2.16)	1.43 (1.42)

Table S9. Optimized geometries of complexes along the steps of the catalytic cycle for the formation of methanol through the one-centered recombination transition state over the Au_4OPd/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps		
	$TS3_{B1}$	**IV_B intermediate**	**$TS3_{B2}$**
H-O	0.96 (0.97)	0.97 (0.97)	0.97 (0.97)
Au1-Au4	2.67 (2.68)	2.67 (2.66)	2.67 (2.66)
Au1-O	2.11 (2.14)	2.11 (2.09)	2.20 (2.20)
Au1-C	2.12 (2.09)	2.10 (2.10)	2.42 (2.42)
Au4-C	3.17 (3.43)		
C-O			2.02 (2.02)

Table S10. Optimized geometries of complexes along the steps of the catalytic cycle for the N_2O decomposition over the Au_4Pt/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps			
	Isolated systems	N_2O adsorption	TS1	N_2 adsorption on OAu_4Pt
N-N	1.13	1.14 (1.14)	1.16 (1.16)	1.11 1.11
N-O	1.18	1.19 (1.19)	1.71 (1.64)	
Au1-Au4	2.87 (2.83)	2.88 (2.83)	3.03 (2.97)	2.80 (2.98)
Au1-O		2.99 (3.16)	2.03 (2.05)	2.07 (2.04)
Au4-O				2.11 (2.12)

Table S11. Optimized geometries of complexes along the steps of the catalytic cycle for the partial oxidation of methane over the Au_4OPt/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps					
	Isolated systems	CH_4 adsorption	TS2	Intermediate IV	TS3	Methanol adsorption
C-H (methane)	1.09	1.09 (1.09)	1.29 (1.32)			
H-O		2.19 (2.26)	1.37 (1.27)	0.97 (0.97)	0.97 (0.97)	0.96 (0.96)
Au1-Au4	2.79 (2.97)	2.80 (2.98)	3.03 (2.99)	3.32 (3.02)	2.96 (2.90)	2.88 (2.82)
Au1-O	2.07 (2.04)	2.07 (2.05)	1.98 (2.03)	2.04 (2.03)	2.27 (2.21)	2.50 (2.58)
Au4-O	2.11 (2.12)	2.11 (2.12)				
Au4-C			2.41 (2.42)	2.08 (2.09)	2.52 (2.66)	
C-O					2.03 (2.06)	1.43 (1.43)

Table S12. Optimized geometries of complexes along the steps of the catalytic cycle for the formation of methanol through the one-centered recombination transition state over the Au_4OPt/graphene. The values in parenthesis are for the high-spin state. *(*Distances are in Angstroms*)*

Parameters	Steps		
	$TS3_{B1}$	IV_B intermediate	$TS3_{B2}$
H-O	0.96 (0.97)	0.97 (0.97)	0.97 (0.97)
Au1-Au4	2.65 (2.67)	2.65 (2.66)	2.66 (2.66)
Au1-O	2.13 (2.14)	2.12 (2.09)	2.22 (2.19)
Au1-C	2.11 (2.12)	2.09 (2.10)	2.44 (2.42)
Au4-C	3.18 (3.28)		
C-O			2.01 (2.03)

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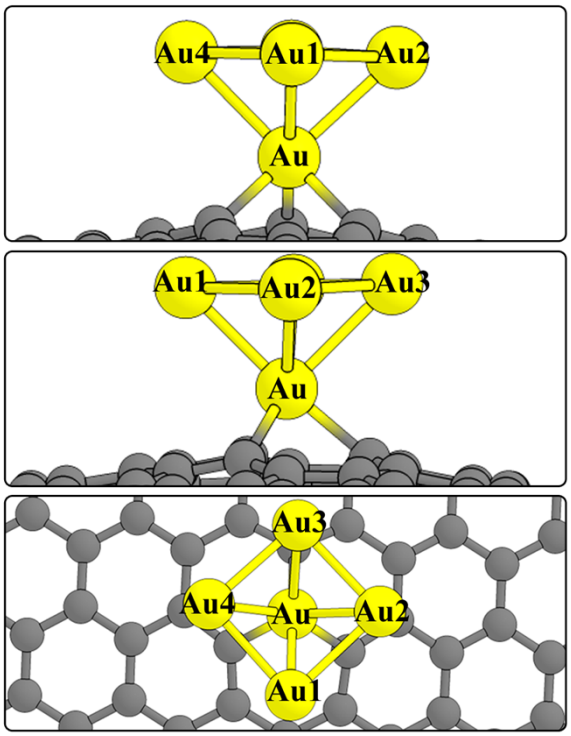
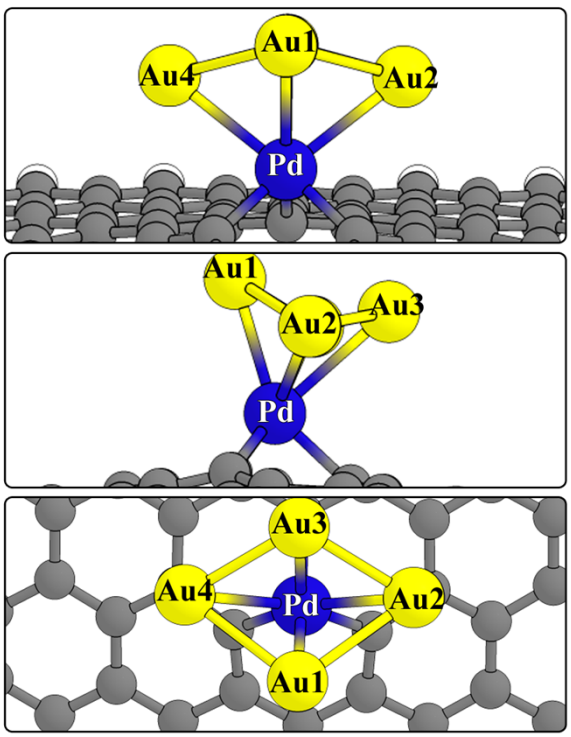


Front view of Au_5/graphene model

Side view of Au_5/graphene model

Top view of Au_5/graphene model

Fig. S1. Different views of the ground-state structure of Au_5/graphene.



Front view of Au_4Pd/graphene model

Side view of Au_4Pd/graphene model

Top view of Au_4Pd/graphene model

Fig. S2. Different views of the ground-state structure of the Au_4Pd/graphene.

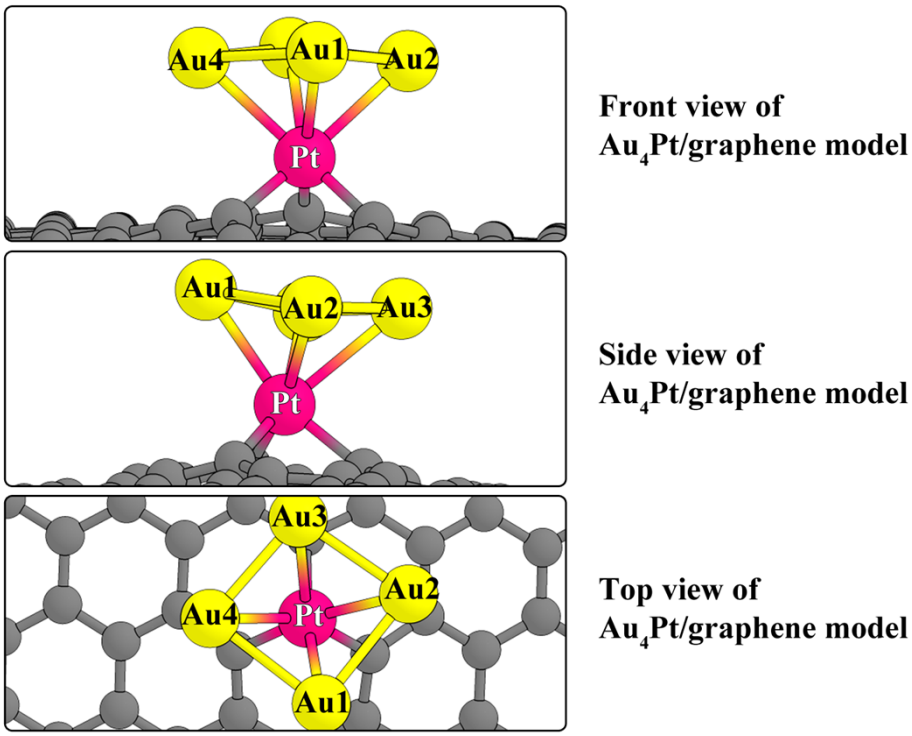


Fig. S3. Different views of the ground-state structure of the Au_4Pt/graphene.

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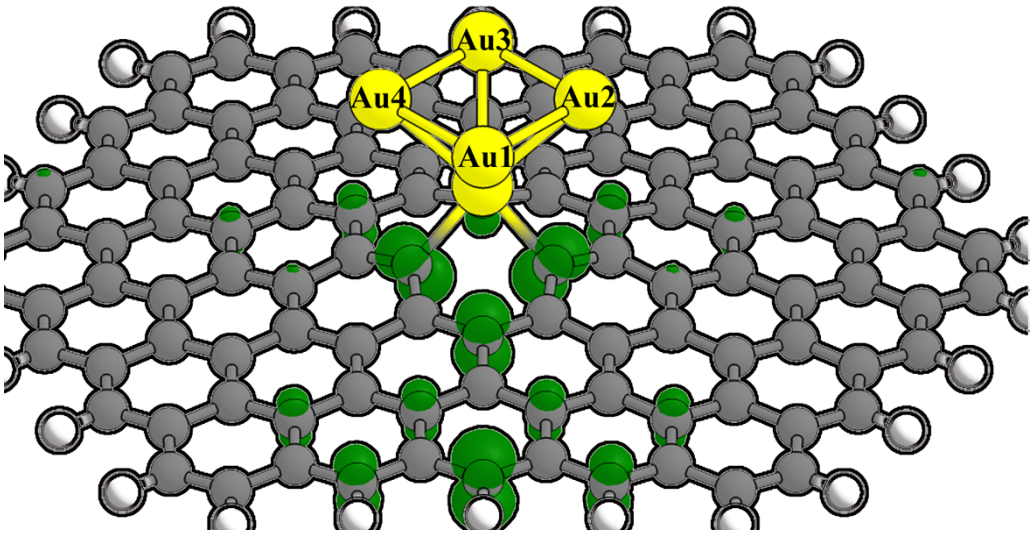


Fig. S4. Au_5 on graphene. Areas where spin polarization is larger than 0.005 $e \cdot au^{-3}$ are shown in green.

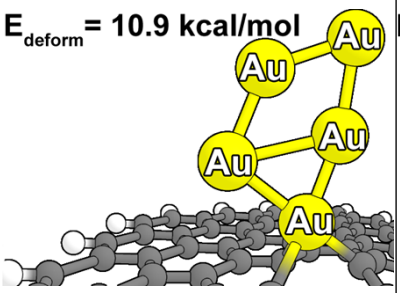
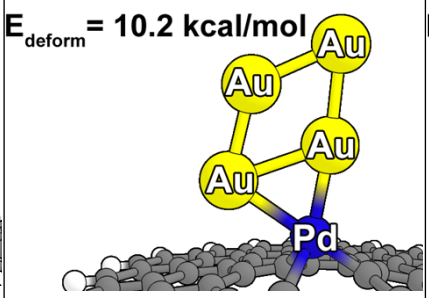
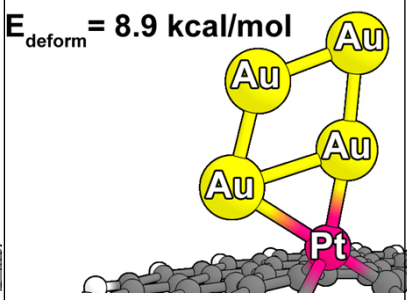
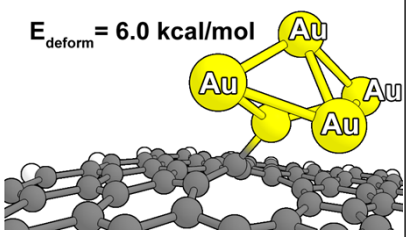
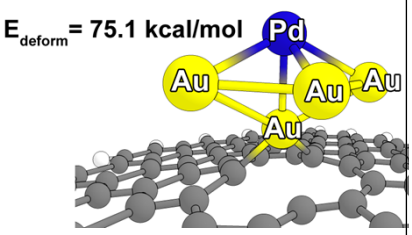
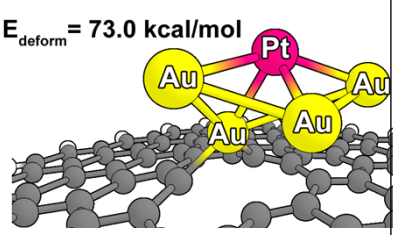
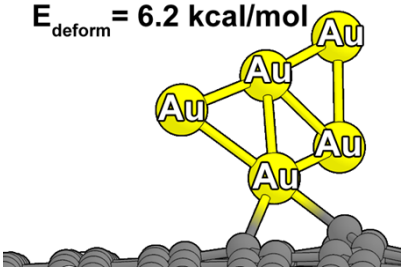
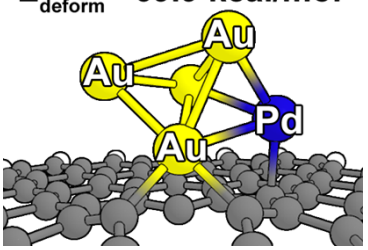
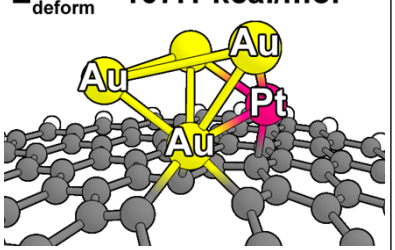
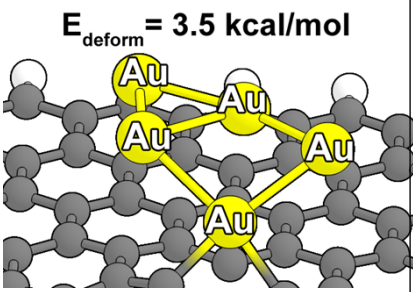
Complexes	Systems		
	Au_5/graphene	Au_4Pd/graphene	Au_4Pt/graphene
A1			
A2			
A3			
A4			

Fig. S5. Different configurations of the ground-state structure of the Au_5/graphene, Au_4Pd/graphene, and Au_4Pt/graphene, respectively. The deformation energies (E_{deform}) as differences of their energies and the energy of their relating system in Fig. 1. The positive values indicate the instability of the complex as compared with the structure in Fig. 1.

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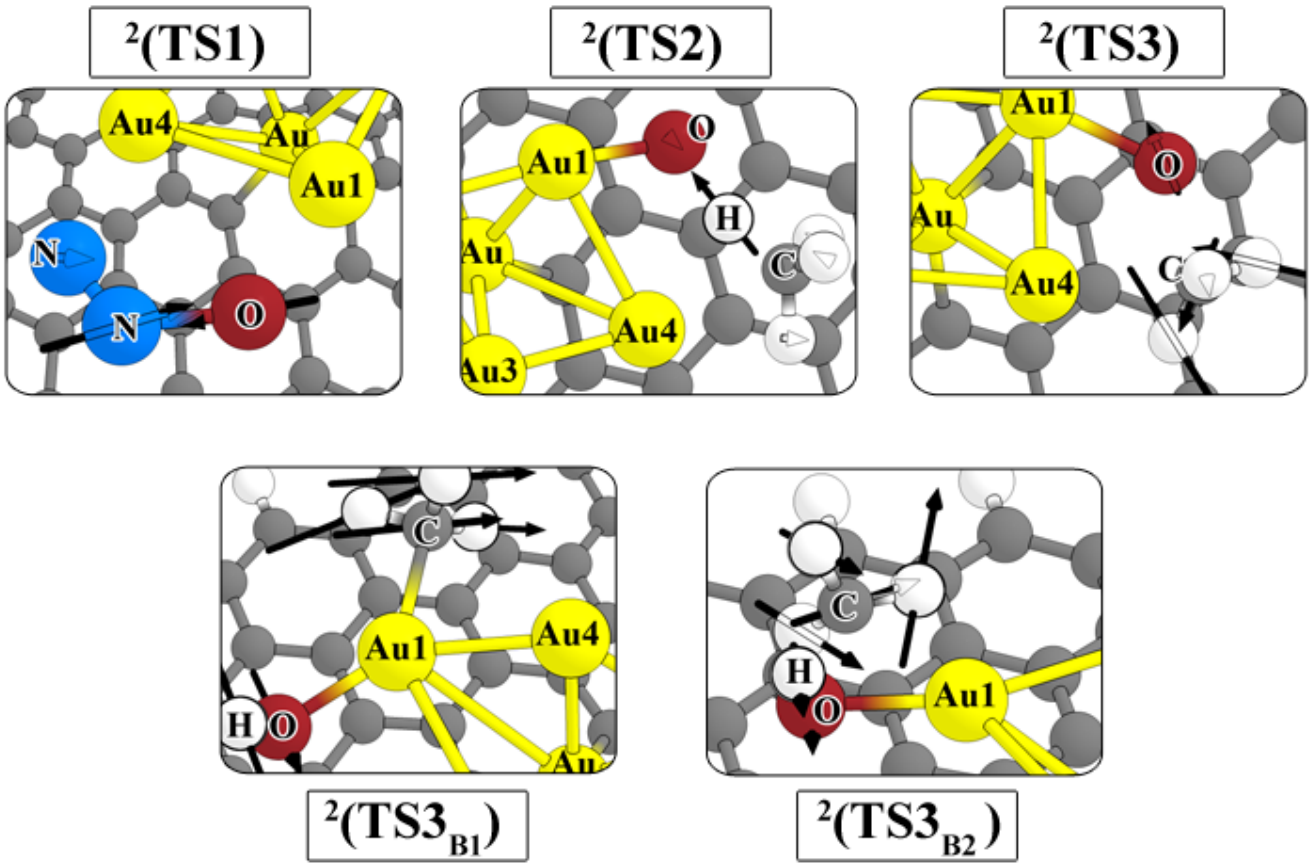

Fig. S6. Vibrational modes corresponding to the imaginary frequency at the transition states for partial oxidation of methane by N_2O as oxidant over the Au_5/graphene material. The superscript indicates the ground state of the transition state complexes.

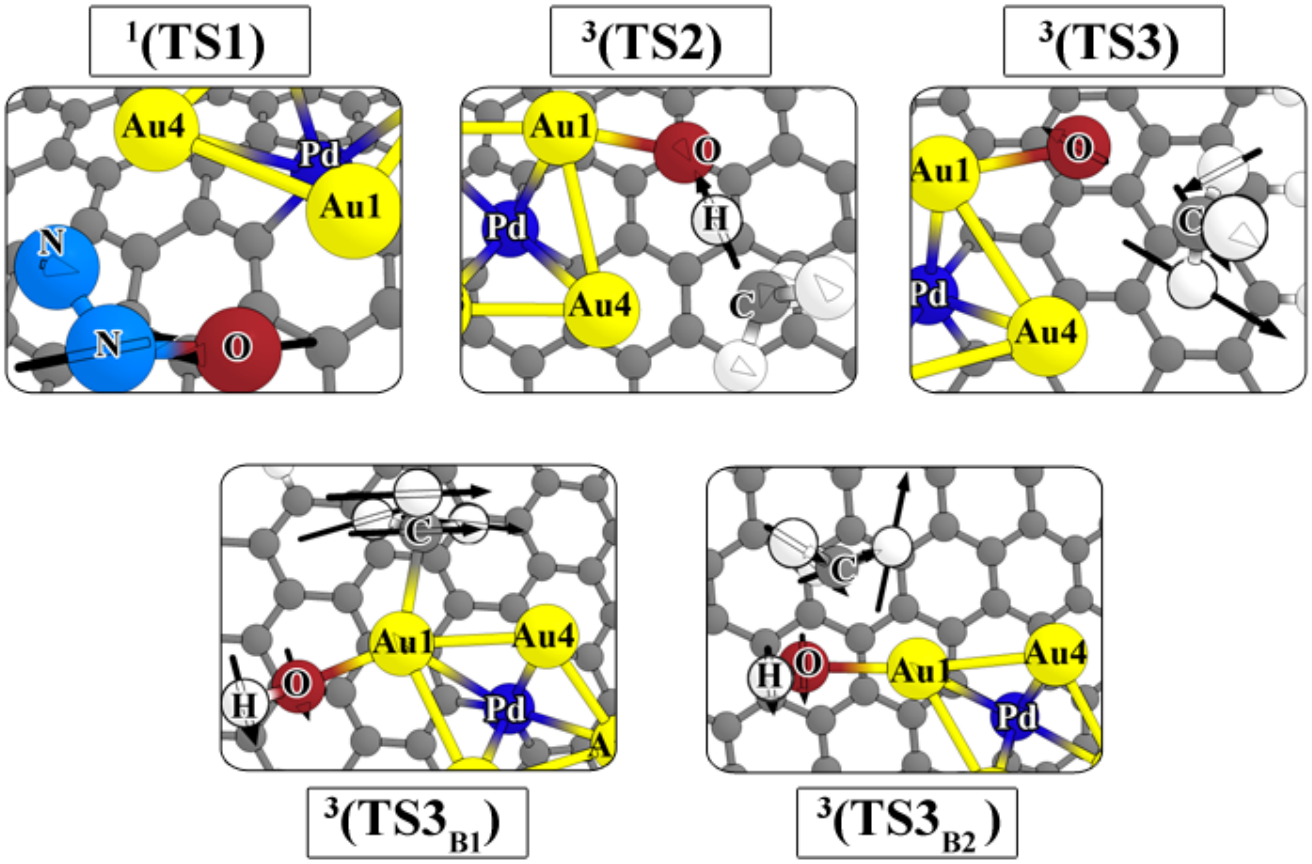

Fig. S7. Vibrational modes corresponding to the imaginary frequency at the transition states for partial oxidation of methane by N_2O as oxidant over the Au_4Pd/graphene material. The superscript indicates the ground state of the transition state complexes.

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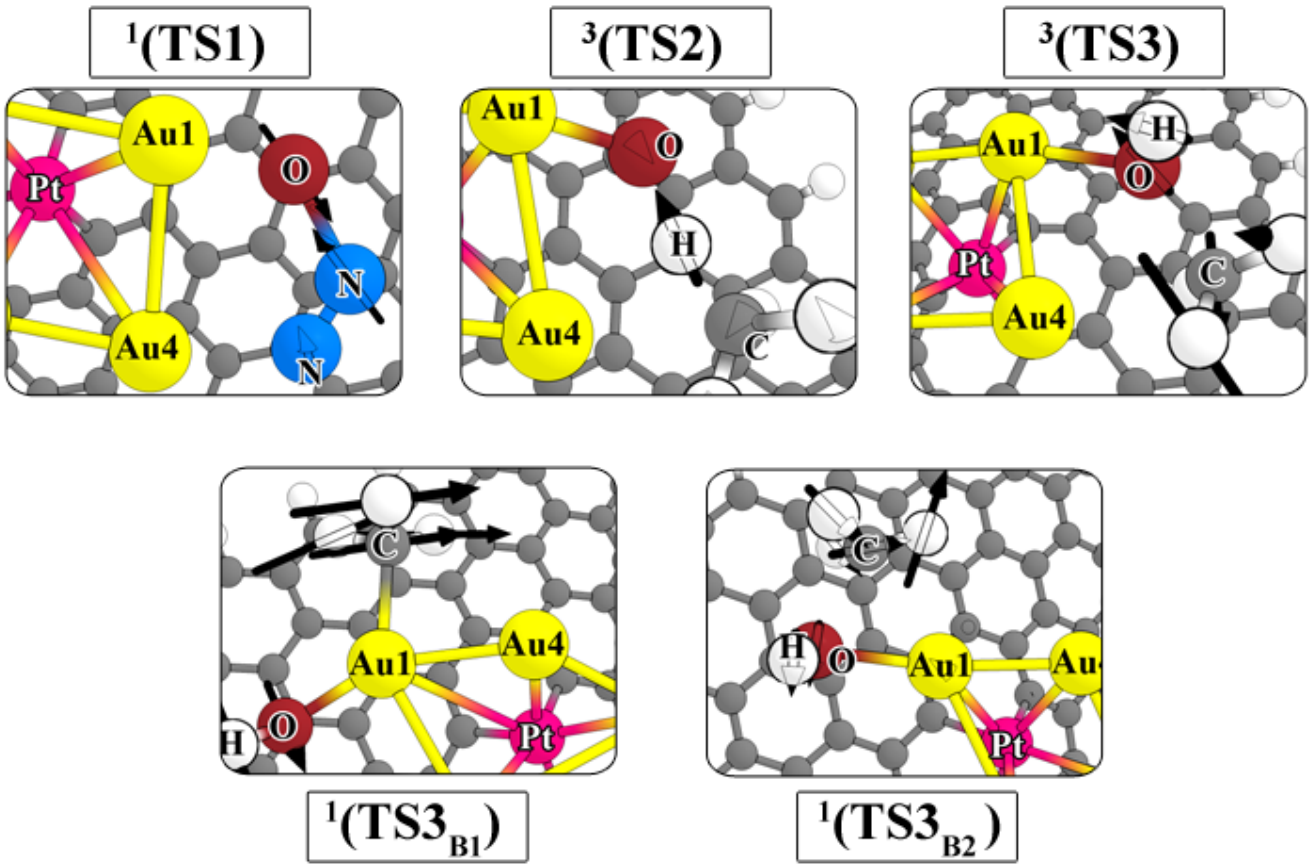


Fig. S8. Vibrational modes corresponding to the imaginary frequency at the transition states for partial oxidation of methane by N_2O as oxidant over the Au_4Pt/graphene material. The superscript indicates the ground state of the transition state complexes.

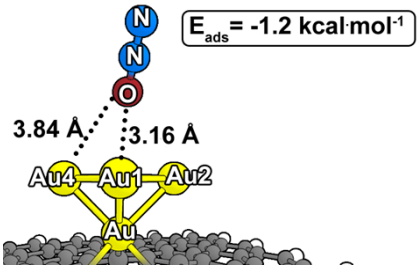
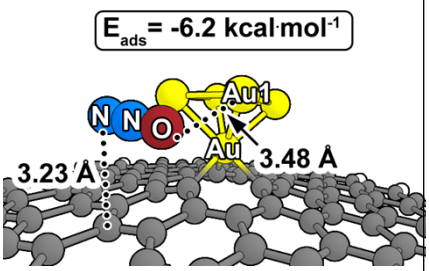
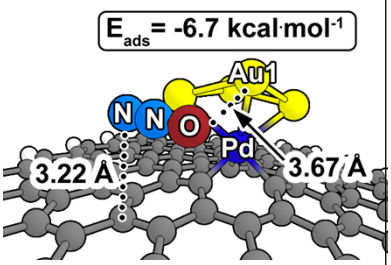
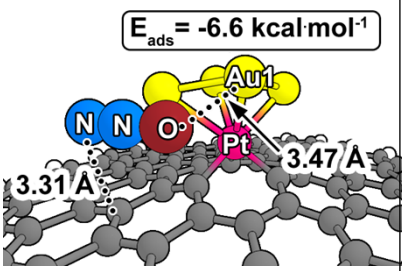
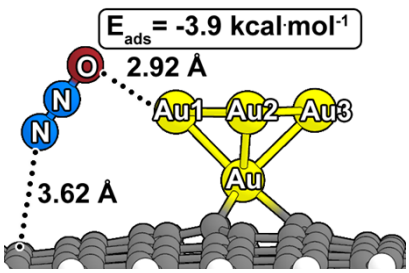
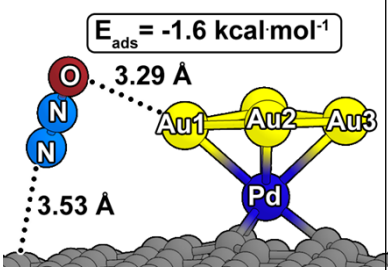
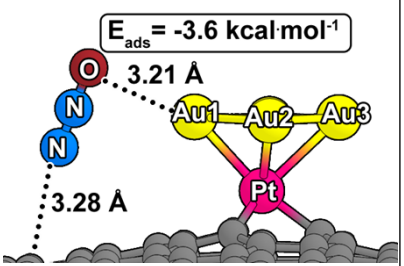
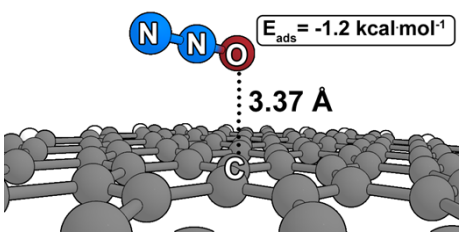
Modes of adsorption	Systems		
	Au_5/graphene	Au_4Pd/graphene	Au_4Pt/graphene
$N_2O\perp Au_4$ plane		-	-
$N_2O \parallel$ Au1-Au4 direction			
Between Au1 and graphene			
(a)			
N_2O-- graphene			
(b)			

Fig. S9. Different configurations of N_2O adsorption: (a) on the Au_5/graphene, Au_4Pd/graphene, and Au_4Pt/graphene, respectively and (b) on the graphene. Energies are the adsorption energy of the complexes.

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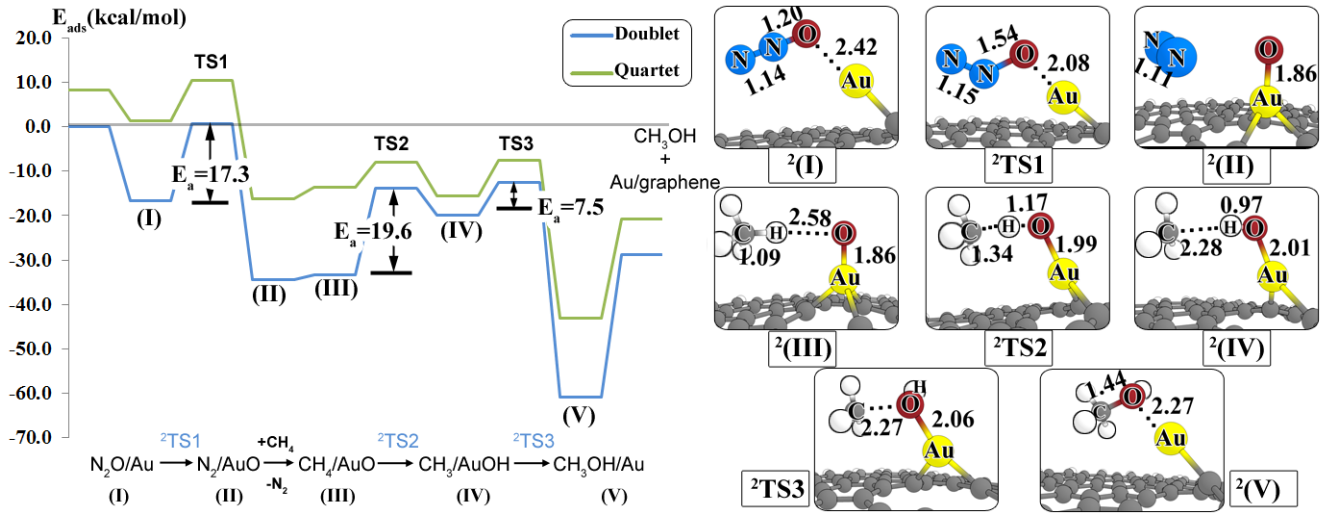

Fig. S10. Complete energetic profiles (kcal·mol^{-1}) along the low-spin state (blue solid line) and the high-spin state (green solid line) of the Au-doped graphene catalyst for the partial oxidation of methane and the corresponding geometries.

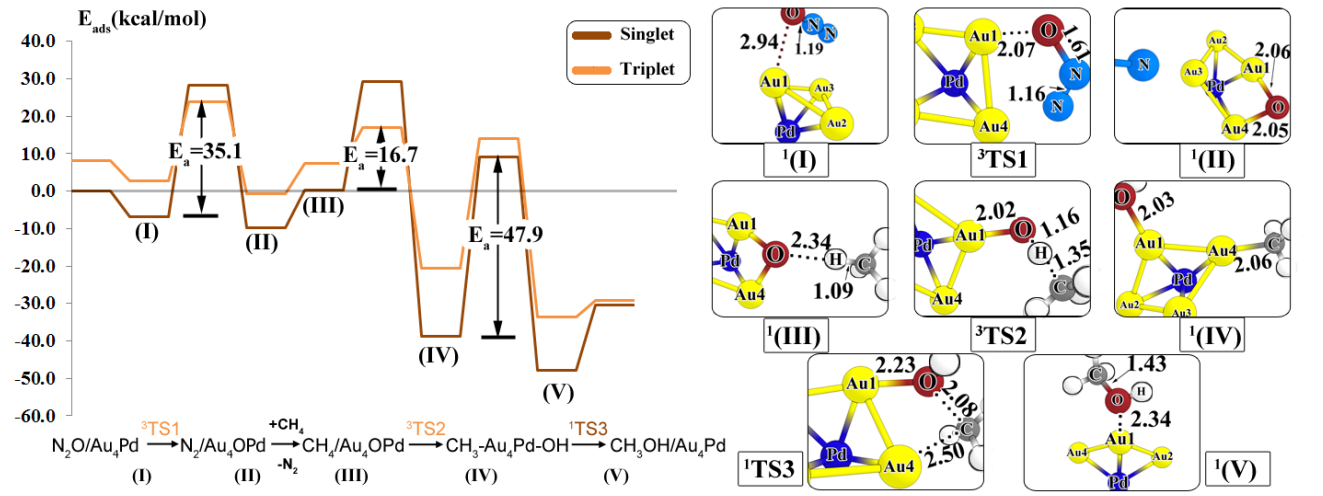

Fig. S11. Complete energetic profiles (kcal·mol^{-1}) along the low-spin state (brown solid line) and the high-spin state (orange solid line) of the unsupported Au_4Pd cluster for the partial oxidation of methane and the corresponding geometries.

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