Supporting information for

The synergetic effect of Pd, In and Zr on the mechanism of Pd/In_2O_3-ZrO_2 for CO_2 hydrogenation to methanol

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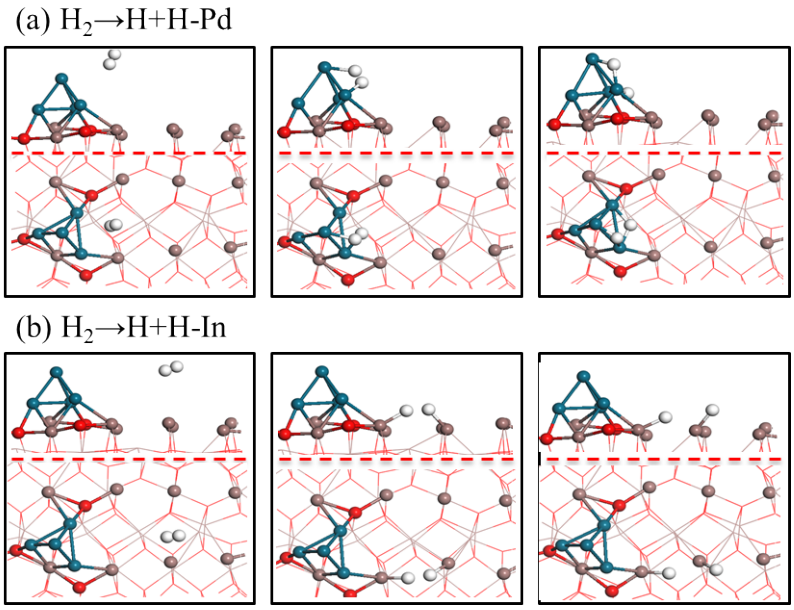

Fig. S1. The initial, transition and final states of H_2 dissociation on (a) Pd_4 cluster and (b) In site of $Pd_4/In_2O_3(110)$-3O model

Table S1 Calculated reaction energies, E_r (eV), and activation barriers, E_a (eV), of H_2 dissociations

Reaction site	E_a	E_r
(a) Pd site on $Pd_4/In_2O_3(110)$-3O	0.16	-0.75
(b) In site on $Pd_4/In_2O_3(110)$-3O	0.69	0.46
(c) In site on $In_2O_3(110)$-In	0.96	0.71

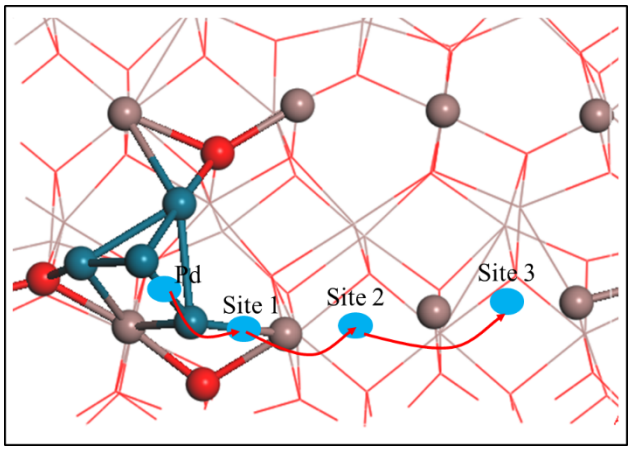

Fig. S2. The transfer pathway of H on $Pd_4/In_2O_3(110)$-3O surface

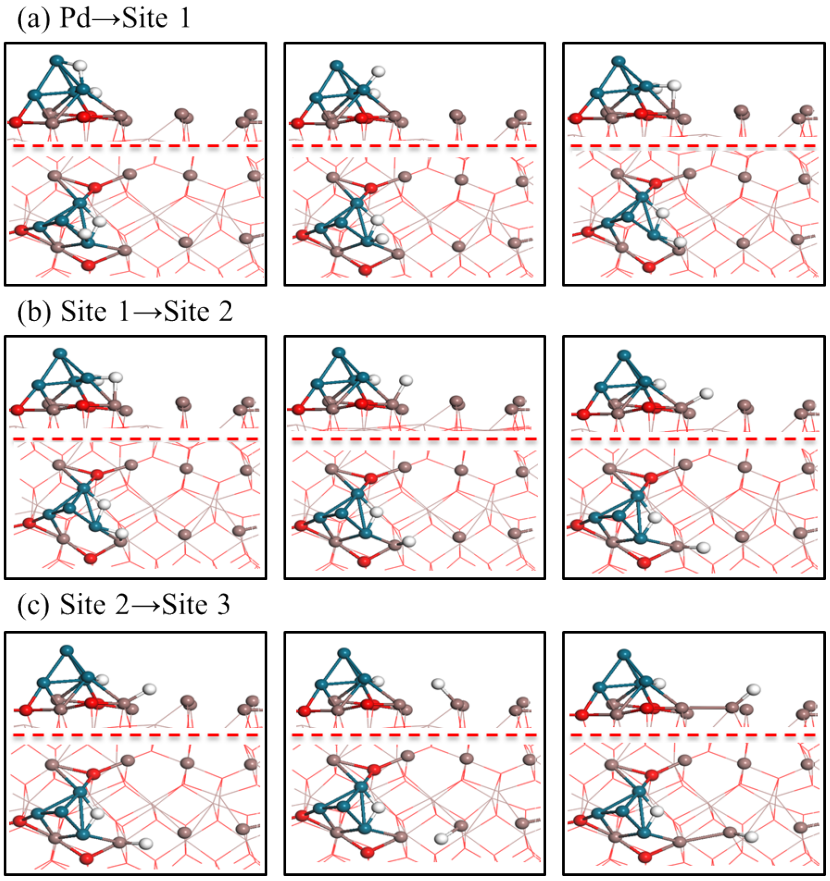

Fig. S3. The initial, transitional and final states of the H transfer on Pd_4/In_2O_3(110)-3O surface

Table S2 Calculated reaction energies, E_r (eV), and activation barriers, E_a (eV), of H transfers

Diffusion site	E_a	E_r
(a) Pd site → Site 1	0.63	0.34
(b) Site 1 → Site 2	0.55	0.24
(c) Site 2 → Site 3	0.66	0.03

Table S3 Calculated reaction energies, E_r (eV), and activation barriers, E_a (eV), of elementary reaction steps in CO_2 conversion on In_2O_3(110)-In surface

Elementary reaction step	E_a	E_r
(a) CO_2 + H → HCOO	0.76	-0.87
(b) CO_2 + H → COOH	0.99	0.01

Table S4 The adsorption energies of intermediates, E_{ab} (eV), on $Pd_4/In_2O_3(110)$-4O/Zr model

Species	E_{ab}
b-CO_2	-0.78
p-CO_2	-0.62
CO	-1.26
HCOO	-2.99
H_2COO	-5.42
H_2COOH	-3.04
H_2CO	-1.21
H_3CO	-2.93
H_3COH	-0.51
COOH	-2.06
HCOOH	-0.71
HCO	-2.13