Supporting Information

Elucidation of the high CO_2 reduction selectivity by isolated Rh supported on TiO_2: a DFT study

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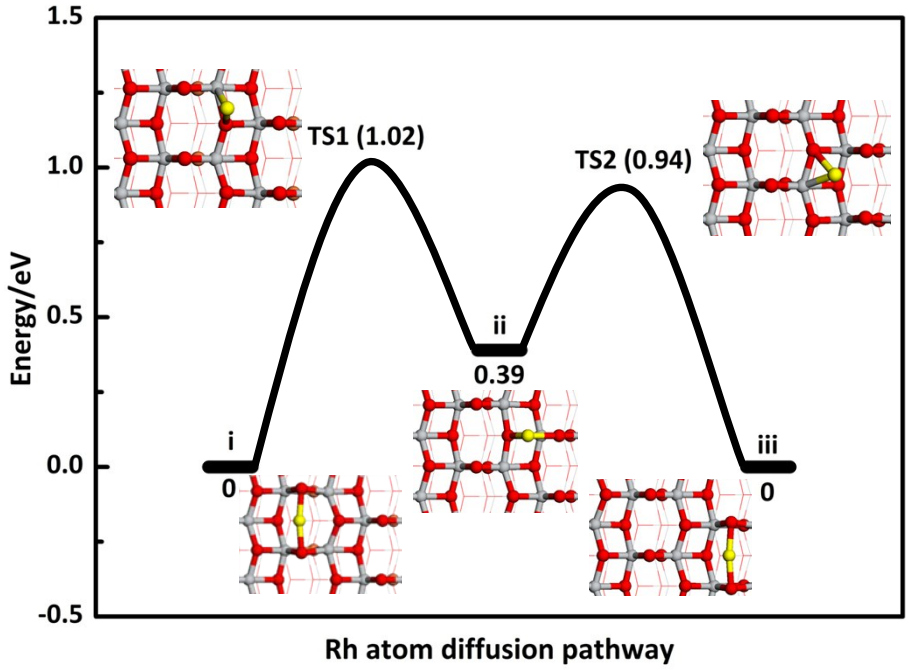

Figure S1 The diffusion pathway of Rh atom from #1 adsorption configuration to #2 adsorption configuration.

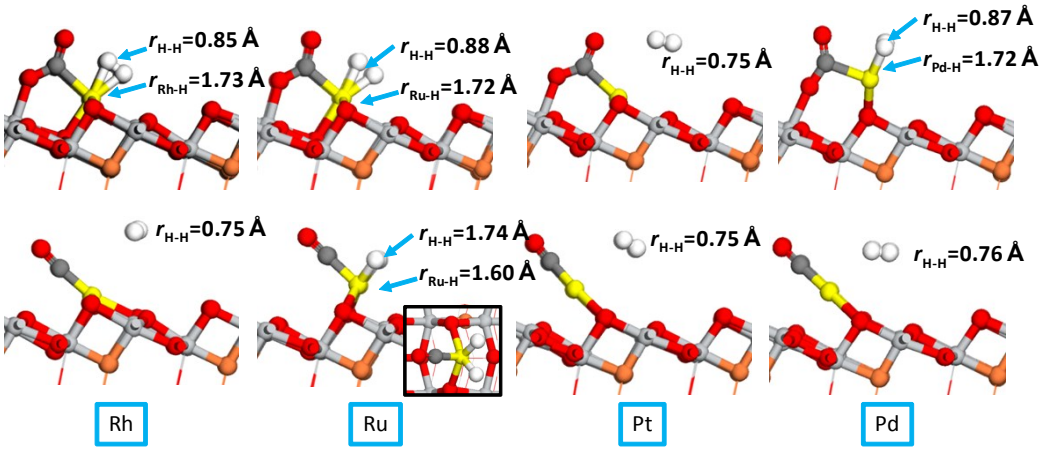

Figure S2 The adsorption structures of CO_2, CO, the co-adsorbed CO-H_2 and CO_2-H_2 on M_1/TiO_2 (M: Rh, Ru, Pd and Pt).

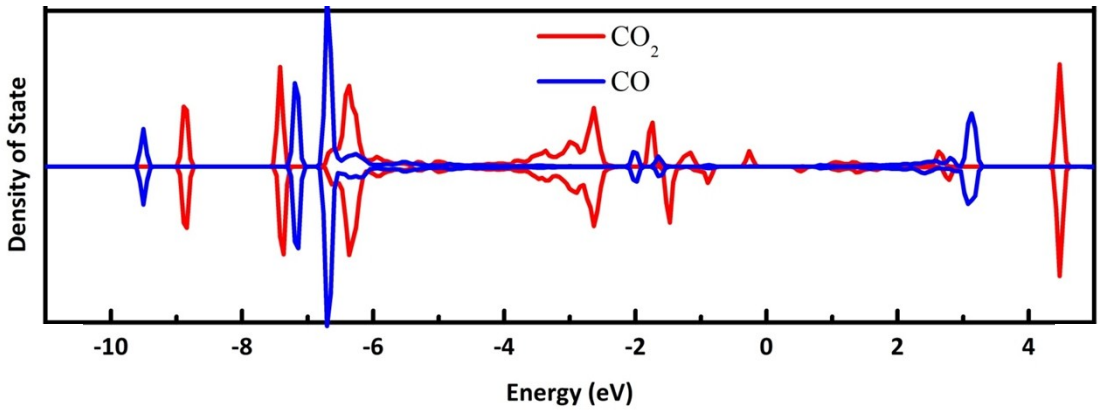

Figure S3 The DOS of CO_2 and CO for CO_2-Rh_1/TiO_2 (red line) and CO-Rh_1/TiO_2 (blue line) system.

Table S1 The activation barriers and reaction energies of elementary steps from the three reaction pathways of RWGS on Rh_1/TiO_2. * and ^ represent the different adsorption sites. O_v represents the surface oxygen vacancy.

	Elementary steps	Reaction barriers/eV	Reaction energies/eV
Pathway 1	$CO_2 + H_2 + 2* \rightarrow *CO_2 + *H_2$	0	-0.77
	$*CO_2 + *H_2 \rightarrow *COOH + *H$	0.24	-0.71
	$*COOH + *H \rightarrow *CO + H_2O + *$	1.92	0.66
	$*CO \rightarrow CO + *$	0	1.48
Pathway 2	$H_2 + * \rightarrow *H_2$	0	-0.58
	$*H_2 + \text{^} \rightarrow *H + \text{^}H$	0.80	-0.22
	$CO_2 + * \rightarrow *CO_2$	0	-0.43
	$*CO_2 + *H \rightarrow *COOH + *$	0.81	0
	$\text{^}H + * \rightarrow *H + \text{^}$	1.10	-0.25
	$*COOH + *H \rightarrow *CO + H_2O + *$	1.92	0.66
	$*CO \rightarrow CO + *$	0	1.48
Pathway 3	$H_2 + * \rightarrow *H_2$	0	-0.58
	$*H_2 + \text{^} \rightarrow *H + \text{^}H$	0.80	-0.22
	$*H + \text{^}H + O_{surf} \rightarrow * + \text{^}H_2O + O_v$	1.83	0.90
	$\text{^}H_2O \rightarrow \text{^} + H_2O$	0	0.64
	$CO_2 + \text{^} \rightarrow \text{^}CO_2$	0	-0.68
	$\text{^}CO_2 + O_v + * \rightarrow *CO + O_{surf} + \text{^}$	0	-0.82
	$*CO \rightarrow CO + *$	0	1.48