

Supporting Information

for

Mechanistic Insights into Heterogeneous Methane Activation

Allegra A. Latimer,¹ Hassan Aljama,¹ Arvin Kakekhani,¹ Jong Suk Yoo,¹ Ambarish Kulkarni,¹ Charlie Tsai,¹
Max Garcia-Melchor,¹ Frank Abild-Pedersen,^{1,2} Jens K. Nørskov^{1,2,*}

¹ SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford
University, 450 Serra Mall Stanford, California 94305, USA

² SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill
Road, Menlo Park, California 94025, United States

* corresponding author: norskov@stanford.edu

Table 1. A complete list of energies used in all figures and calculations. Values are referenced to CH₄, H₂O and O₂.

Class	Catalyst	EH	EFS	Radical TS	Surface-Stabilized TS
110 Rutile Oxide (O ^b) ^a	IrO ₂	-0.27	-1.56	0.94	0.17
110 Rutile Oxide (O ^b)	RuO ₂	0.03	-0.30	n.c.	0.71
110 Rutile Oxide (O ^b)	TiO ₂	0.83	0.53	n.c.	1.37
110 Rutile Oxide (O ^b)	RhO ₂	-0.74	-1.33	n.c.	0.41
110 Rutile Oxide (O ^c) ^b	IrO ₂	-0.79	0.56	0.33	n.c.
110 Rutile Oxide (O ^c)	RuO ₂	-0.09	1.03	0.95	n.c.
110 Rutile Oxide (O ^c)	RhO ₂	-1.05	0.17	0.14	n.c.
110 Rutile Oxide (O ^c)	MoO ₂	0.98	2.19	1.83	n.c.
111 Clean Metal	Ag	1.69	2.08	2.76	2.55
111 Clean Metal	Cu	1.27	1.40	2.27	1.88
111 Clean Metal	Pd	0.79	0.32	1.85	0.95
111 Clean Metal	Pt	0.95	0.25	2.14	0.99
111 Clean Metal	Rh	0.88	0.38	1.95	0.88
111 Clean Metal	Au	1.72	1.79	2.53	2.27
111 O-Promoted Metal	Ag	-0.41	-0.02	0.95	n.s.
111 O-Promoted Metal	Cu	0.37	0.46	1.52	1.45
111 O-Promoted Metal	Pd	0.56	0.14	1.50	1.50
111 O-Promoted Metal	Pt	0.60	-0.05	1.52	1.41
111 O-Promoted Metal	Rh	0.86	0.41	1.80	1.44
111 O-Promoted Metal	Au	-0.19	-0.08	1.15	n.s.
111 O-Promoted Metal	Ir	0.87	0.23	2.04	1.61
111 O-Promoted Metal	Re	1.49	1.21	2.43	1.42
111 O-Promoted Metal	Ru	1.12	0.68	2.05	1.39
111 OH-Promoted Metal	Ag	0.62	1.01	n.c.	1.39
111 OH-Promoted Metal	Cu	1.03	1.15	n.c.	1.63
111 OH-Promoted Metal	Pd	0.57	0.10	n.c.	1.16
111 OH-Promoted Metal	Pt	0.24	-0.46	n.c.	0.89
111 OH-Promoted Metal	Rh	0.92	0.43	n.c.	1.25

^a Hydrogen abstraction takes place at a bridging oxygen

^b Hydrogen abstraction takes places at a cus oxygen

111 OH-Promoted Metal	Au	-0.01	0.06	n.c.	1.18
MgO (110)	Li-Doped ^c	-0.97	-0.05	0.54	n.c.
MgO (110)	Na-Doped	-0.63	0.63	0.67	n.c.
MgO (110)	K-Doped	-0.77	0.72	0.77	n.c.
MgO (110)	Undoped	1.46	-0.09	n.c.	0.53
MgO (321)	Undoped	0.06	-1.67	n.c.	-0.18
MgO (111)	Undoped	1.29	0.96	n.c.	1.65
CaO(110)	Undoped	0.83	-0.21	n.c.	0.45
PdO on Pd	-	0.33	-0.12	n.c.	1.20
O@Ca@O@MoS ₂	-	-1.01	-0.31	0.83	1.10
Doped MoS ₂ ^d	Fe-Doped	-1.01	0.10	0.83	1.10
Doped MoS ₂	Rh-Doped	-0.51	0.58	0.65	n.c.
Doped MoS ₂	Co-Doped	-0.06	0.99	1.24	n.c.
Doped MoS ₂	Ru-Doped	-0.64	0.52	0.72	n.c.
Doped MoS ₂	Ir-Doped	0.39	1.44	1.66	n.c.
Doped MoS ₂	Cr-Doped	0.28	1.38	1.54	n.c.
Doped MoS ₂	Cu-Doped	0.32	1.43	1.47	n.c.
Doped MoS ₂	Au-Doped	1.35	0.92	n.c.	1.17
Doped MoS ₂	Rh-Doped	1.25	0.84	n.c.	1.19
Doped MoS ₂	Pt-Doped	1.65	0.99	n.c.	1.13

n.c.	not calculated
n.s.	not stable

Discussion of Scaling between E_O and E_H on O-Promoted Metals

For oxygen-promoted metals, E_H is defined as

$$E_H = E_{OH} - E_O \quad (1)$$

To understand how E_H scaled with E_C , we assume that E_O approximately scales with $1/2E_C$ by bond order conservation, since oxygen has only two electrons available for bonding while carbon has four.

^c Doped MgO systems consisted of an alkali metal substituted for a surface Mg. Hydrogen abstraction takes place at the oxygen adjacent to the dopant.

^d In doped MoS₂ systems

$$E_O \approx \frac{1}{2}E_C + b \quad (2)$$

We also know that EOH scales with 1/2 EO as follows:

$$E_{OH} = \frac{1}{2}E_O + b \quad (3)$$

Plugging in expressions for EOH and EO in the definition for EH gives the following relationship, clearly showing we expect EH to scale as -1/4EC.

$$E_H = -\frac{1}{4}E_C + b \quad (4)$$

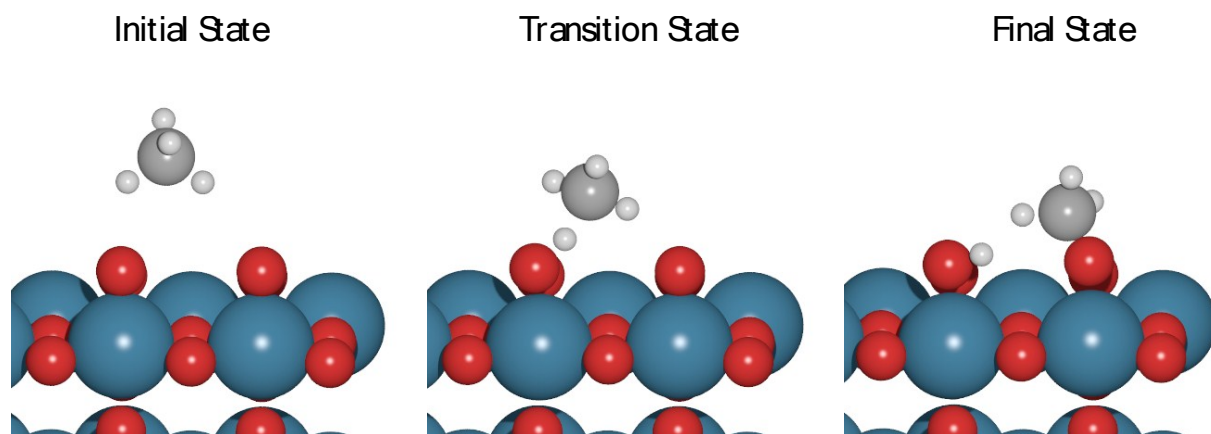


Figure S1. IS, TS and FS of methane activation on IrO₂(110). The active sites are two coordinatively unsaturated (cus) oxygen atoms. A strictly energetic analysis would predict the methyl group to be surface-stabilized ($E_H=-0.8$, $E_{CH_3}=-2.0$), but the TS is clearly radical-like.

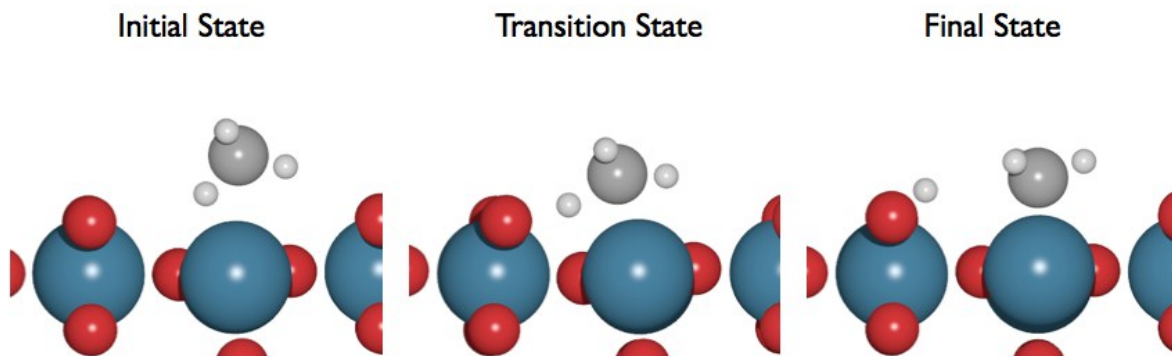


Figure S2. IS, TS and FS of methane activation on IrO₂(110). The active sites are a bridging oxygen and a metal cus site. Here, the distance is comparable to the 2O^c site shown in Fig. S1, but the TS is surface-stabilized. The notable difference is that the active site here is made up of an acid-base pair.

