Supporting information

Cuboctahedral Platinum (Pt_{79}) Nanocluster Enclosed by Well Defined Facets Favours the Di-sigma Adsorption and Improves the Reaction Kinetics for Methanol Fuel Cell

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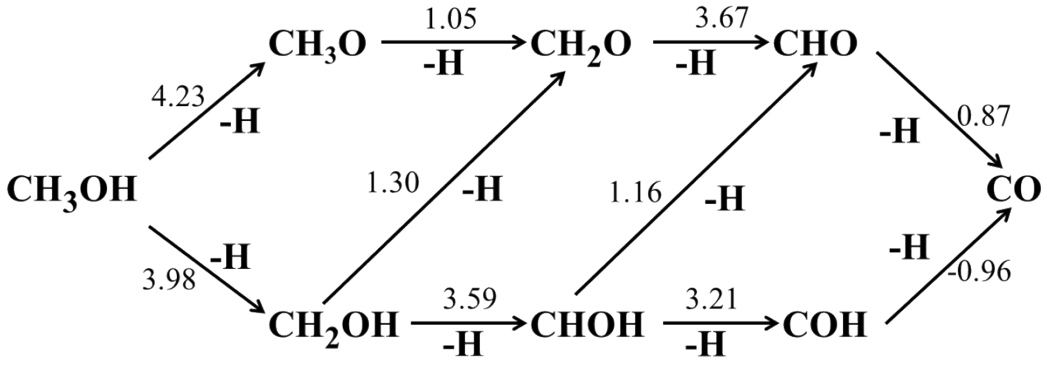
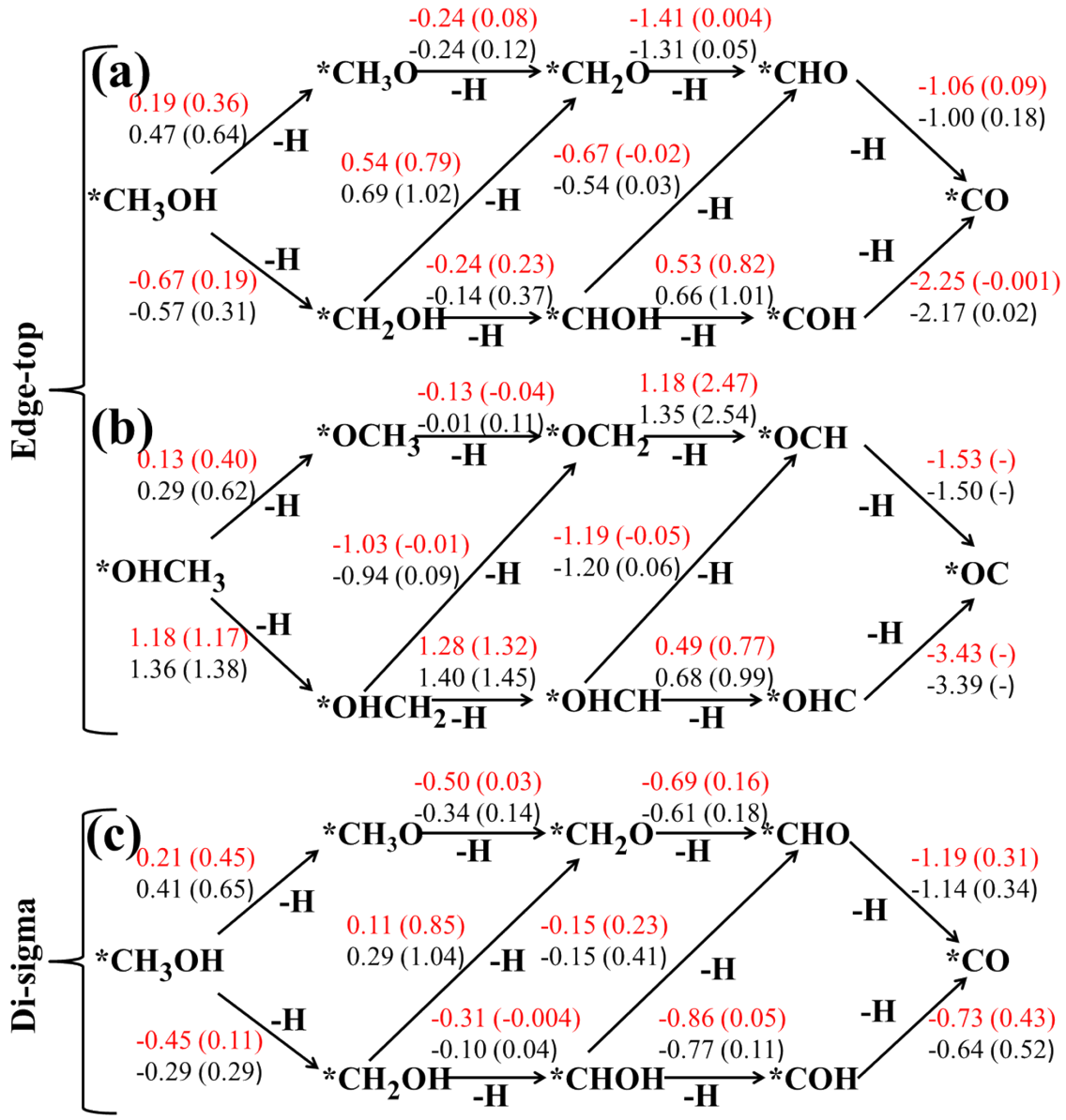
Table S1: Adsorption energy (eV), adsorption behaviour, relative energy (eV) and key bond lengths (Å) of the possible intermediates. Here (t), (b), and (h) represents the intermediates adsorbed at the top, bridge and three-fold hollow site respectively.

Species	Adsorption Energy			Relative Energy			Bond length		
	Edge		Bridge	Edge		Bridge	Edge		Bridge
	*C-	*O-		*C-	*O-		Pt-C	Pt-O	
CH_3OH	-0.24 (t)	-0.38 (t)	-0.19 (d)	0.19	0.00	0.18	3.24	2.52	Pt-H(C) 2.83 Pt-H(O) 2.71 Pt-C 3.32 Pt-O 3.59
CH_3O	-3.61 (t)	-2.47 (t)	-2.25 (d)	0.44	0.00	0.13	3.59	1.97	Pt-H 2.09 Pt-O 2.01
CH_2OH	-2.76 (t)	-1.07 (b)	-2.78 (t)	0.00	1.56	0.03	2.08	3.10, 3.70	Pt-H 2.41 Pt-H 2.43 Pt-C 2.08
CHOH	-3.67 (t)	-0.25 (t)	-4.86 (d)	0.15	3.18	0.00	1.89	2.73	Pt-C 2.03 Pt-O 2.72
CH_2O	-0.17 (t)	-0.55 (t)	-1.94 (d)	0.37	0.10	0.00	2.67	2.18	Pt-C 2.11 Pt-O 2.05
CHO	-3.03 (t)	-0.60 (t)	-3.47 (d)	0.00	2.38	0.08	1.96	2.25	Pt-C 2.07 Pt-O 2.15
COH	-3.94 (t)	-0.64 (t)	-5.67 (h)	1.58	4.68	0.00	1.78	2.75	Pt-C 2.02
CO	-2.22 (t)	0.04 (t)	-2.29 (h)	0.14	2.04	0.00	1.94	2.51	Pt-C 2.11

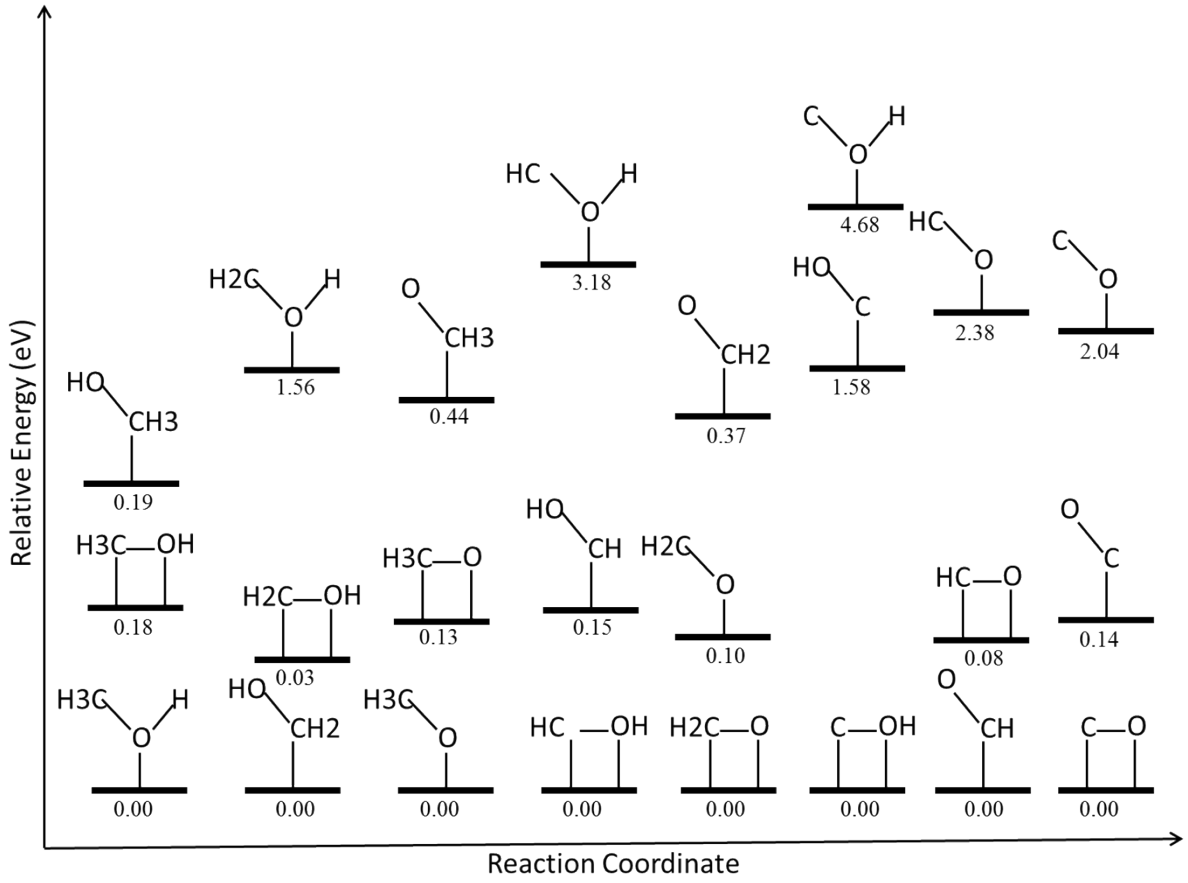
Scheme S1: Gas phase energetic (energy in eV) for the complete methanol dehydrogenation pathway to show the effect of the catalyst.



Scheme S2: The reaction energies (eV) and activation barriers (eV, values in parenthesis) for the successive methanol dehydrogenation at different binding sites (a) adsorbed through C-atom and (b) O-atom at top edge position and (c) bridge position.[Values in the black colour are without ZPE and entropy correction whereas red colour are including ZPE and entropy correction]



Scheme S3: Relative energetic (eV) for all the reaction intermediates.



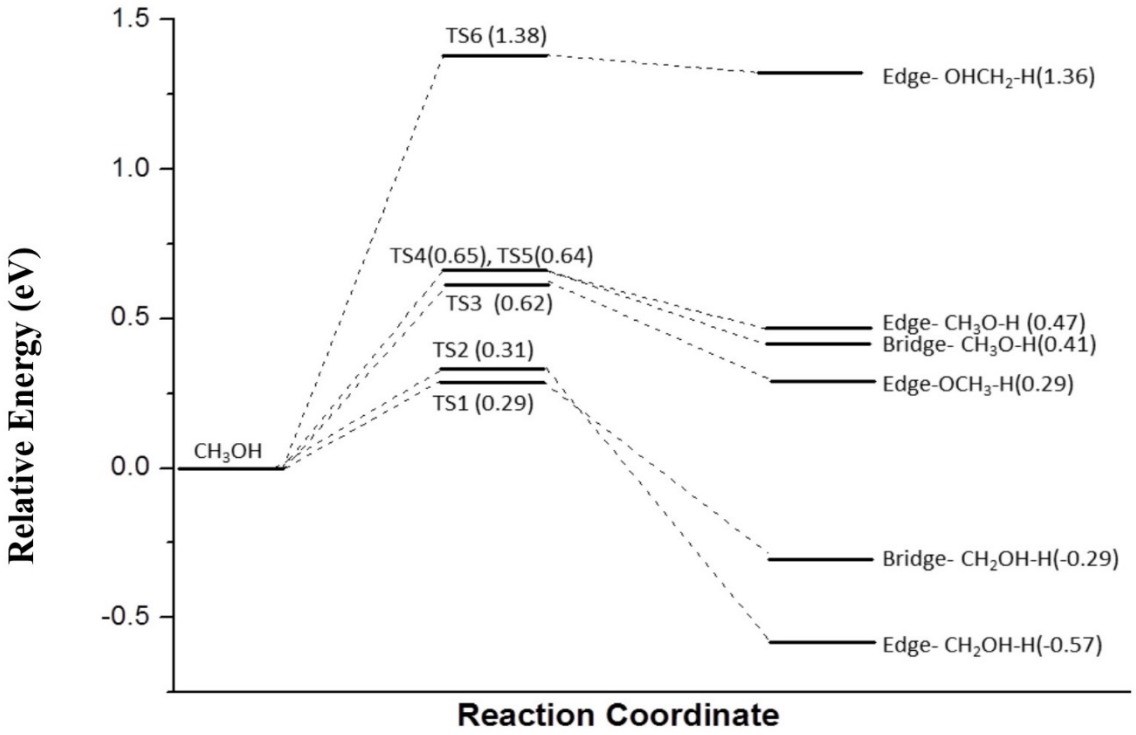
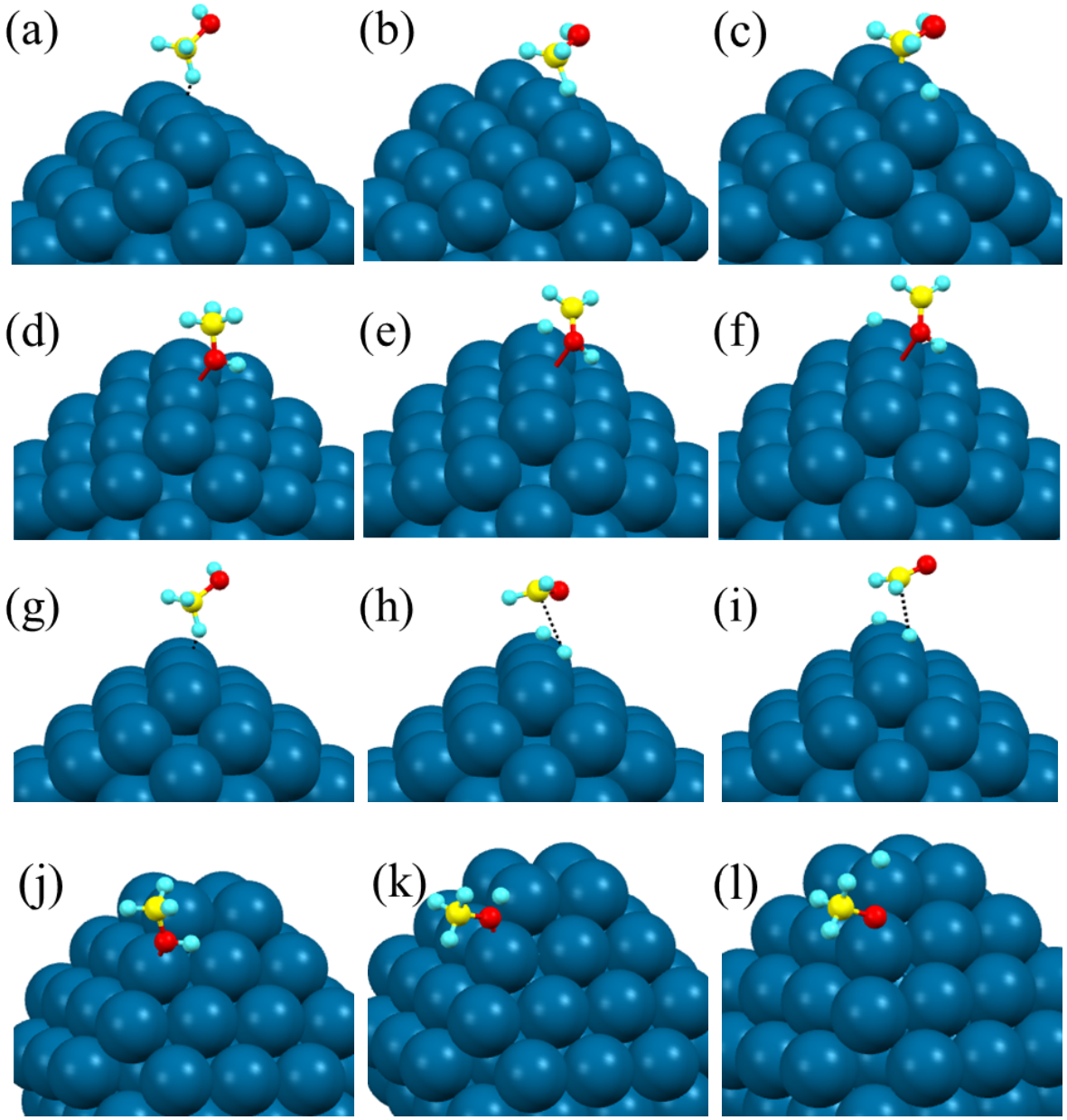


Figure S1: Reaction energy profile for the first C-H/O-H bond dissociation of methanol at the different active sites (Edge and bridge) of the nanocluster surface. Here TS means transition state.


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)

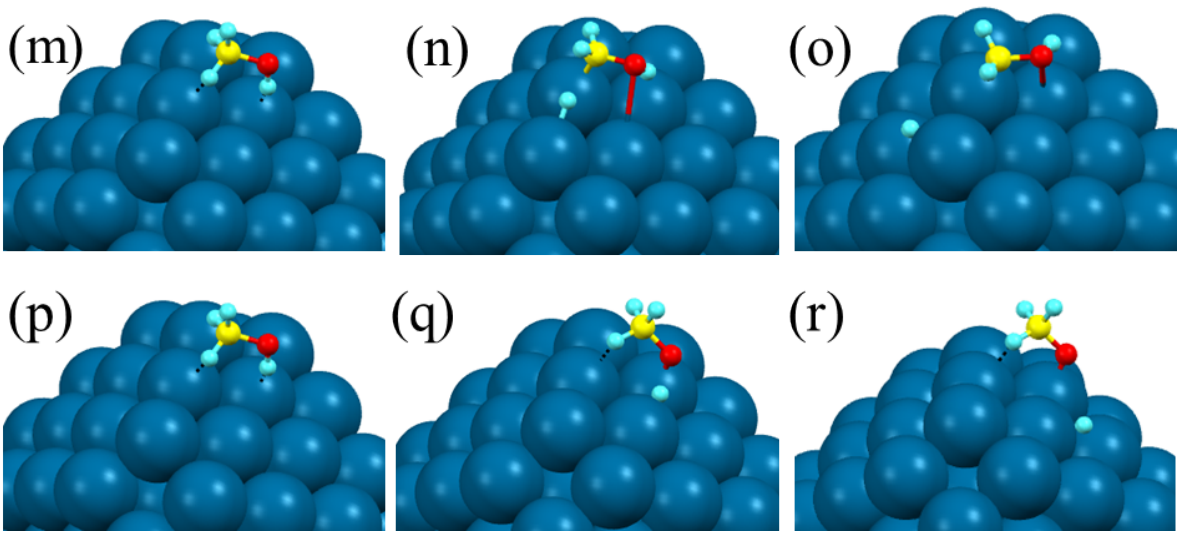


Figure S2: First to third columns are the structures of the initial state, transition state and final state. At the edge position, [(a)-(c)] $CH_3OH \rightarrow CH_2OH\text{-}H$; [(d)-(f)] $OHCH_3 \rightarrow OHCH_2\text{-}H$; [(g)-(i)] $CH_3OH \rightarrow CH_3O\text{-}H$; [(j)-(l)] $OHCH_3 \rightarrow OCH_3\text{-}H$, and at the bridge position [(m)-(o)] $CH_3OH \rightarrow CH_2OH\text{-}H$; [(p)-(r)] $CH_3OH \rightarrow CH_3O\text{-}H$.

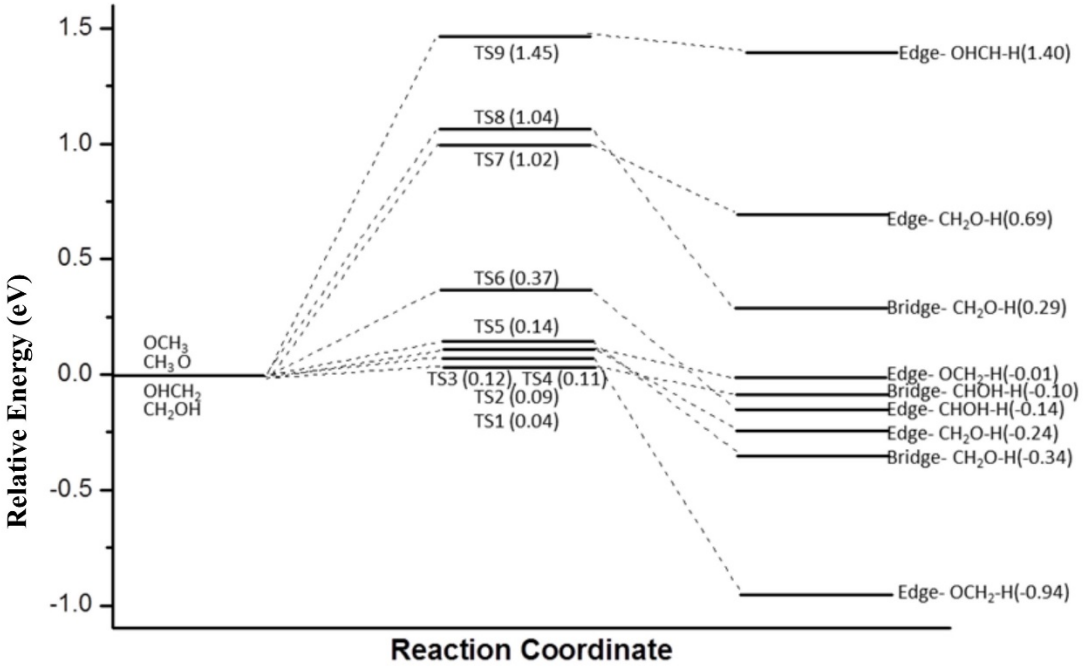
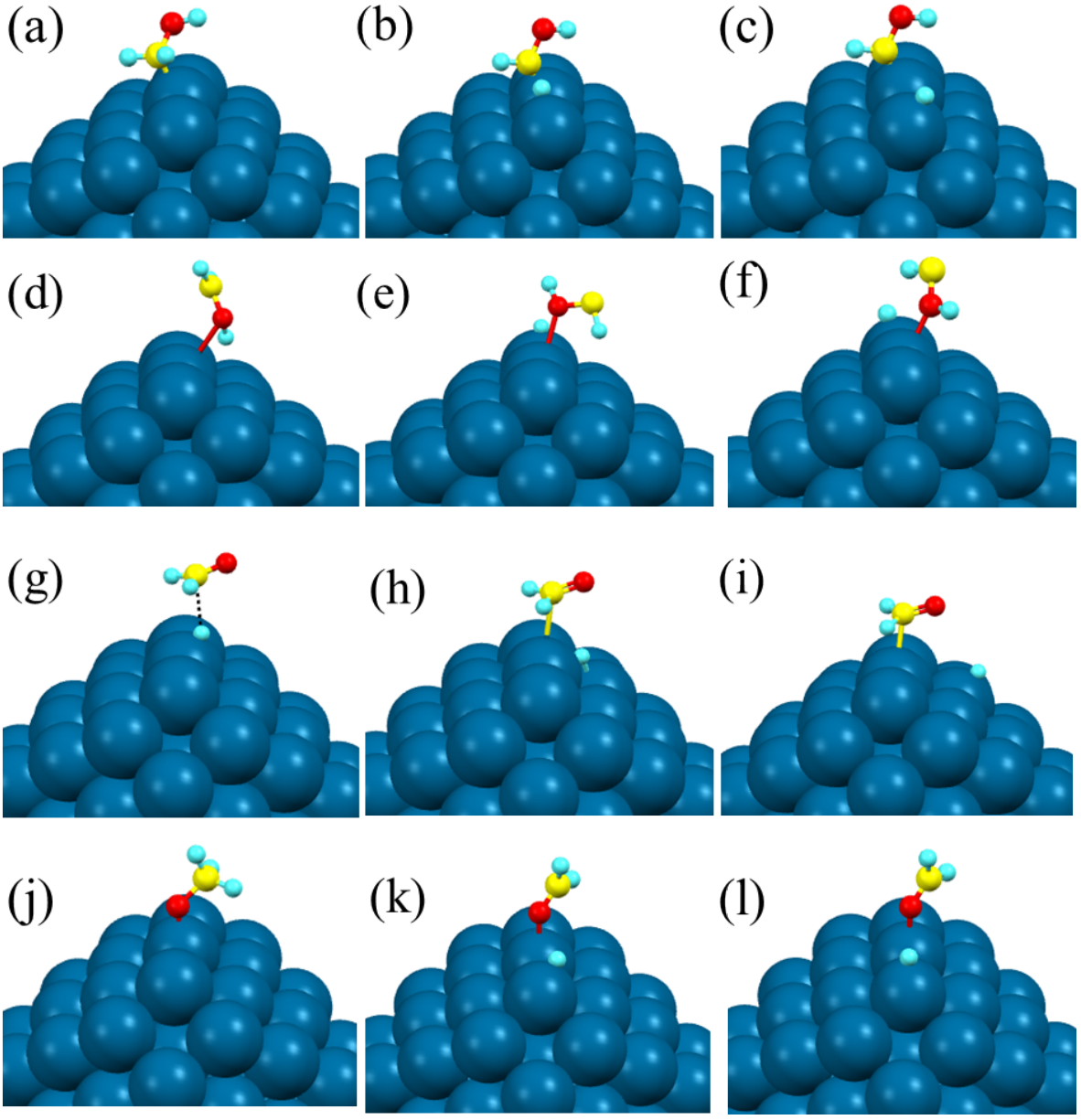


Figure S3: Reaction energy profile for the second C-H/O-H bond dissociation of hydroxymethyl and methoxy at the different active sites (Edge and bridge) of the nanocluster surface. Here TS means transition state.


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
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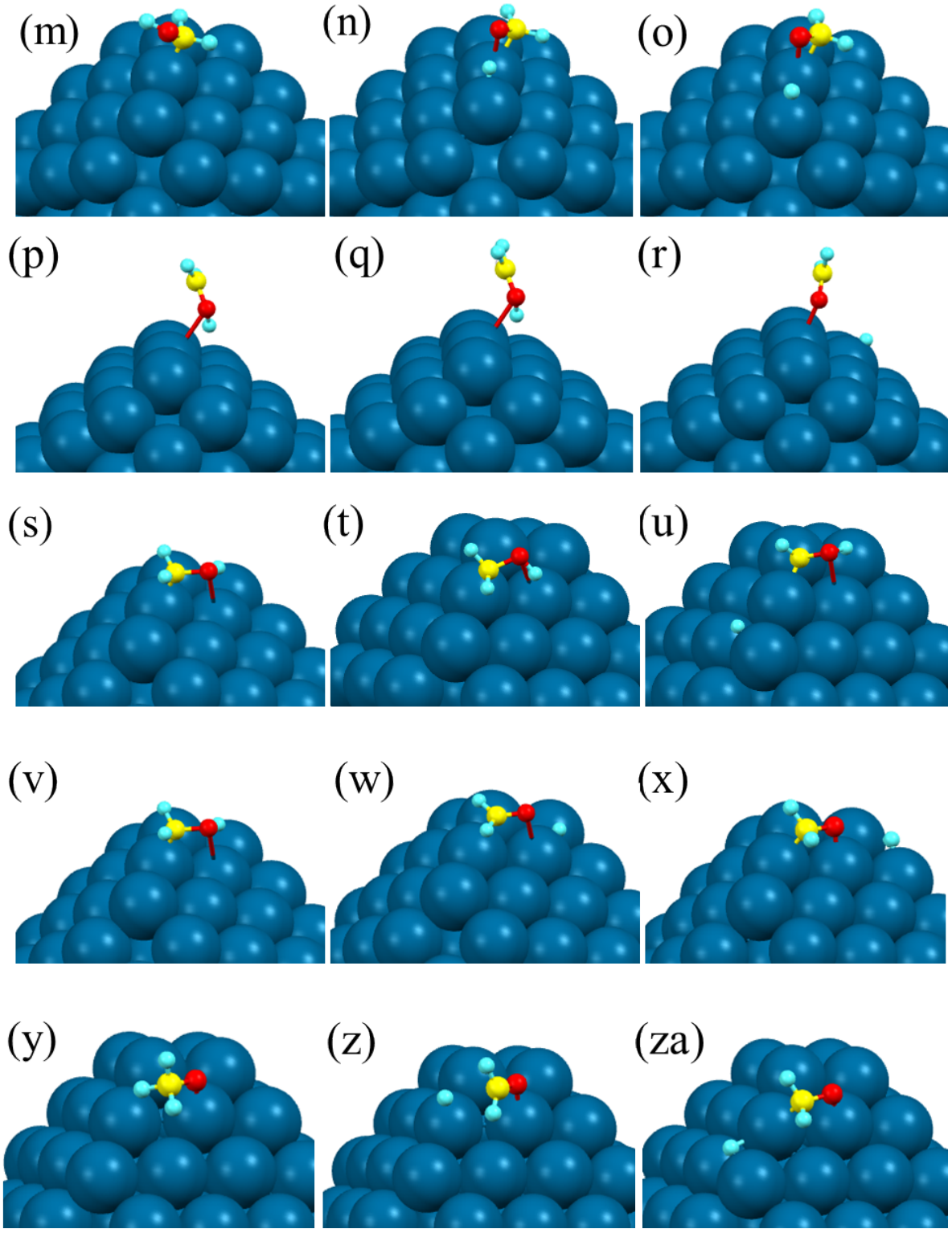


Figure S4: First to third columns are the structures of the initial state, transition state and final state. At edge position, [(a)-(c)] $CH_2OH \rightarrow CHOH\text{-}H$; [(d)-(f)] $OHCH_2 \rightarrow OHCH\text{-}H$; [(g)-(i)] $CH_3O \rightarrow CH_2O\text{-}H$; [(j)-(l)] $OCH_3 \rightarrow OCH_2\text{-}H$; [(m)-(o)] $CH_2OH \rightarrow CH_2O\text{-}H$; [(p)-(r)] $OHCH_2 \rightarrow OCH_2\text{-}H$, and at bridge position [(s)-(u)] $CH_2OH \rightarrow CHOH\text{-}H$; [(v)-(x)] $CH_2OH \rightarrow CHOH\text{-}H$; [(y)-(za)] $CH_3O \rightarrow CH_2O\text{-}H$.

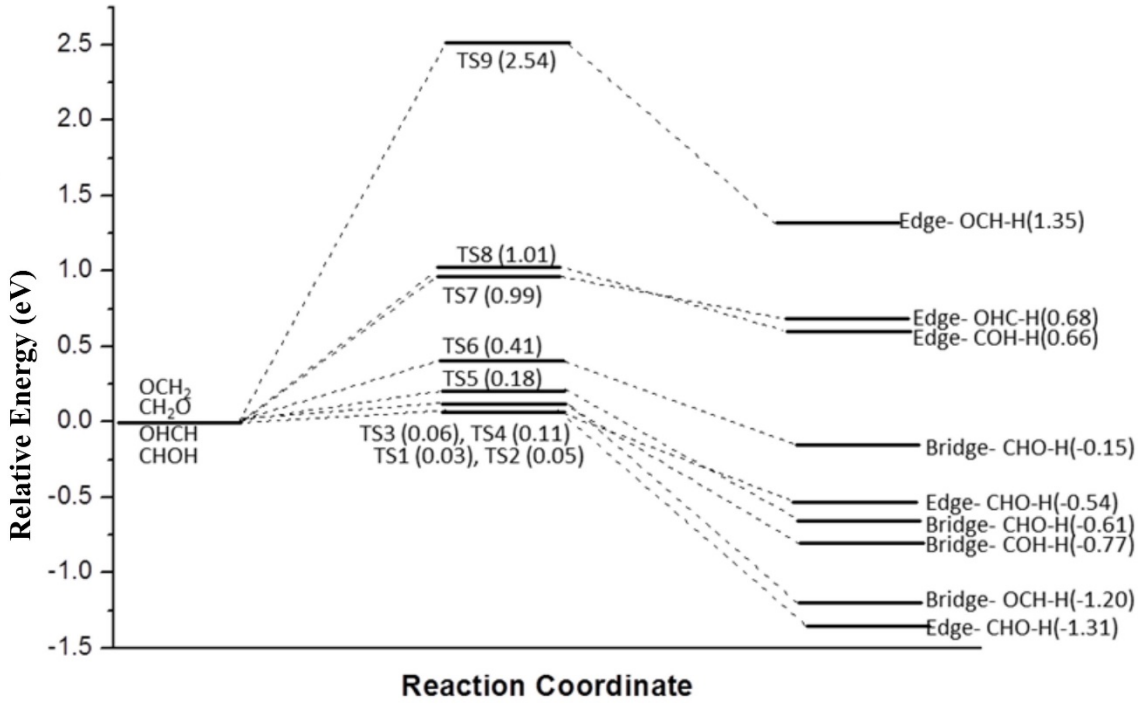
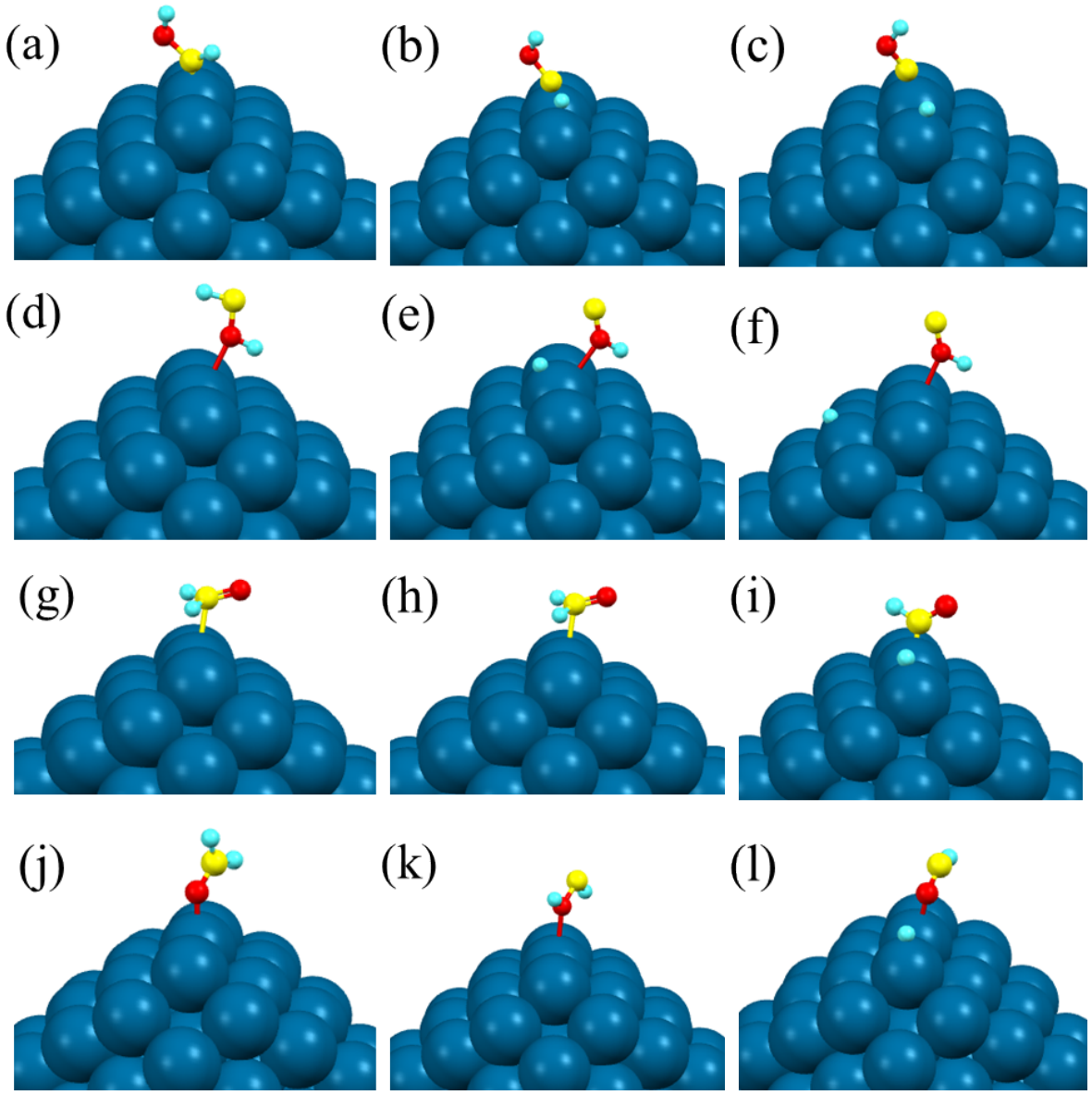


Figure S5: Reaction energy profile for the third C-H/O-H bond dissociation of hydroxymethelene and formaldehyde at the different active sites (Edge and bridge) of the nanocluster surface. Here TS means transition state.


(a)
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(d)
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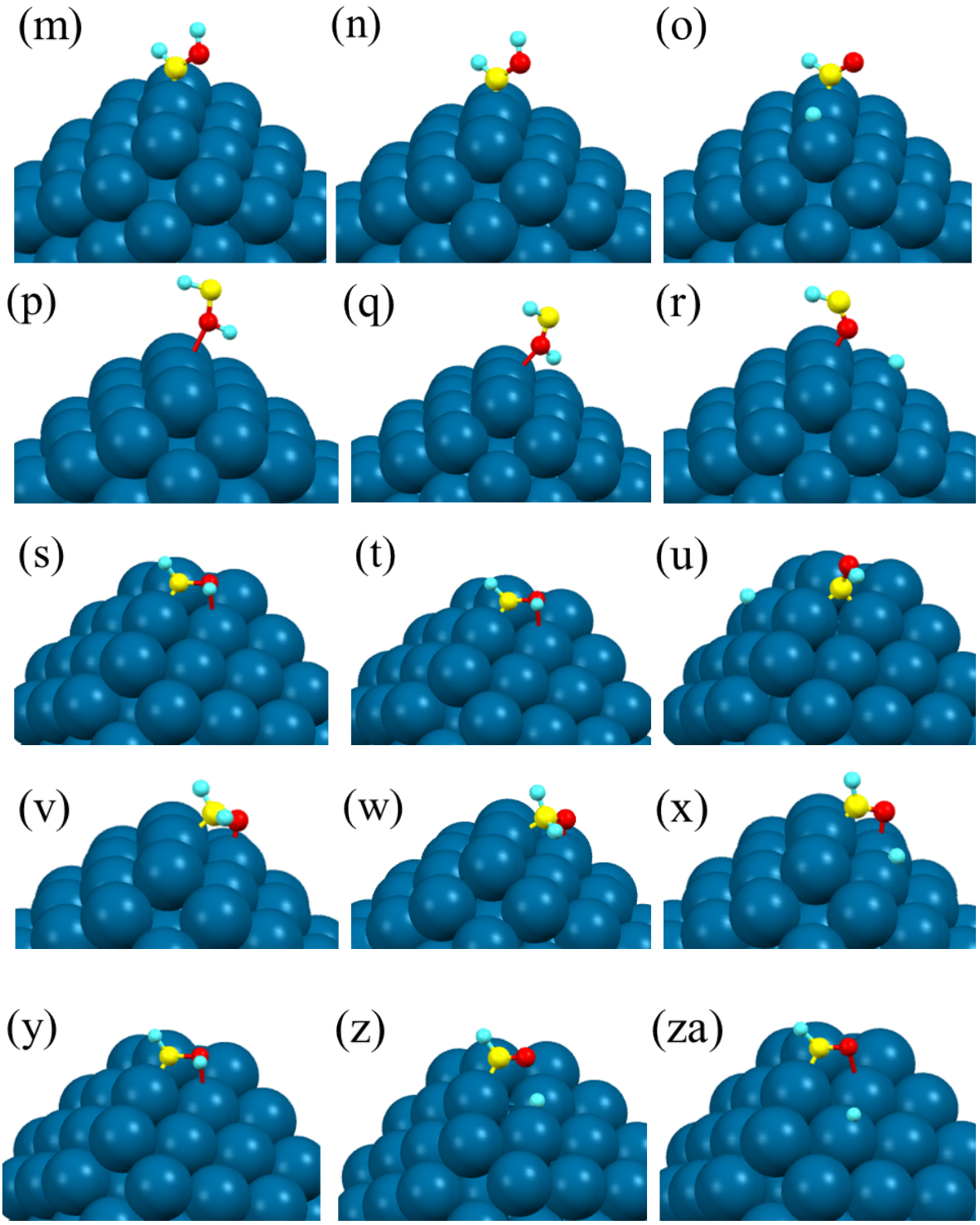

Figure S6: First to third columns are the structures of the initial state, transition state and final state. At edge position, [(a)-(c)] CHOH→COH-H; [(d)-(f)] OHCH→OHC-H; [(g)-(i)] CH_2O→CHO-H; [(j)-(l)] OCH_2→OCH-H; [(m)-(o)] CHOH→CHO-H; [(p)-(r)] OHCH→OCH-H, and at bridge position [(s)-(u)] CHOH→COH-H; [(v)-(x)] CH_2O→CHO-H; [(y)-(za)] CHOH→CHO-H.

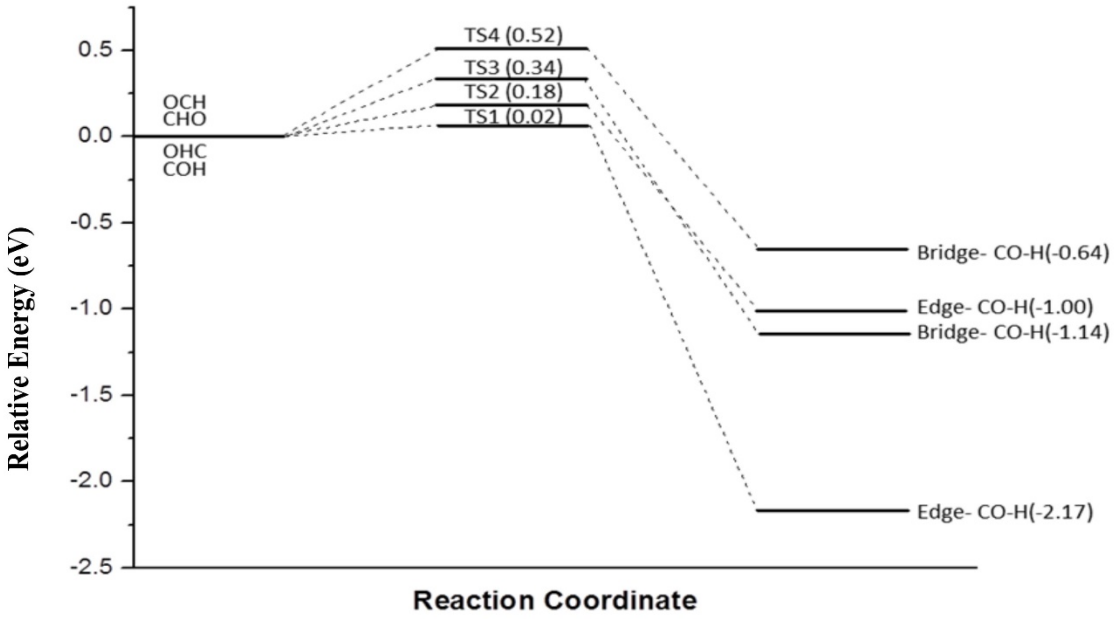

Figure S7: Reaction energy profile for the fourth C-H/O-H bond dissociation of hydroxymethylidyne and formyl at the different active sites (Edge and bridge) of the nanocluster surface. Here TS means transition state.

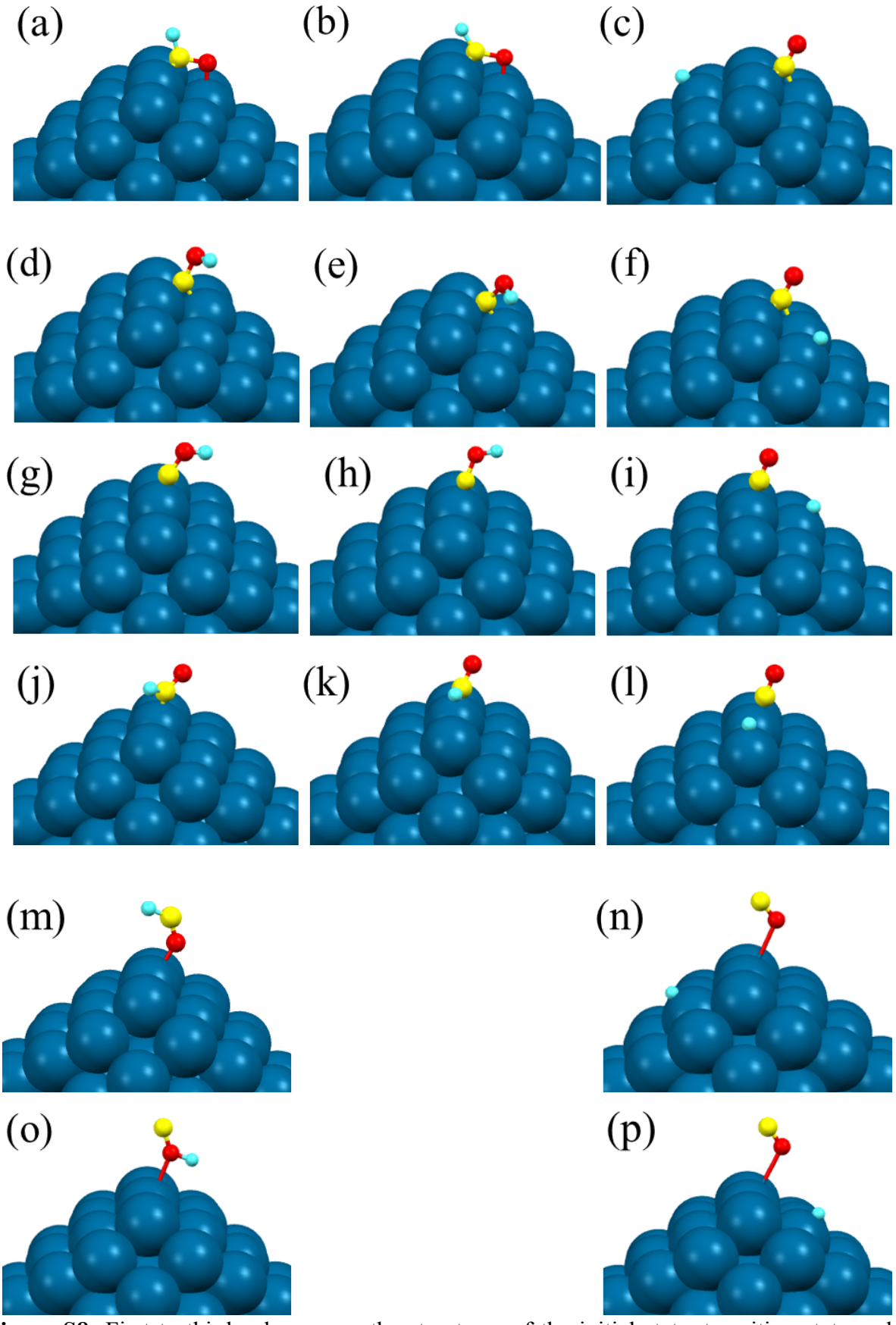

Figure S8: First to third columns are the structures of the initial state, transition state and final state. At bridge position, [(a)-(c)] CHO→CO-H; [(d)-(f)] COH→CO-H, and at edge

position [(g)-(i)] COH→OC-H; [(j)-(l)] CHO→CO-H; [(m)-(n)] OCH→OC-H; [(o)-(p)] OHC→OC-H.