Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Tuning the transition barrier of H_2 dissociation in the hydrogenation of CO_2 to formic acid on Ti-doped Sn_2O_4 cluster

Plaban J. Sarma[1], Dikshita Dowerah[1], Nand K. Gour[1], Andrew J. Logsdail[2], C. Richard A. Catlow[2,3,4] and Ramesh Ch. Deka*[1]

[1]Department of Chemical Sciences, Tezpur University, Tezpur, Assam, India

[2]Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK

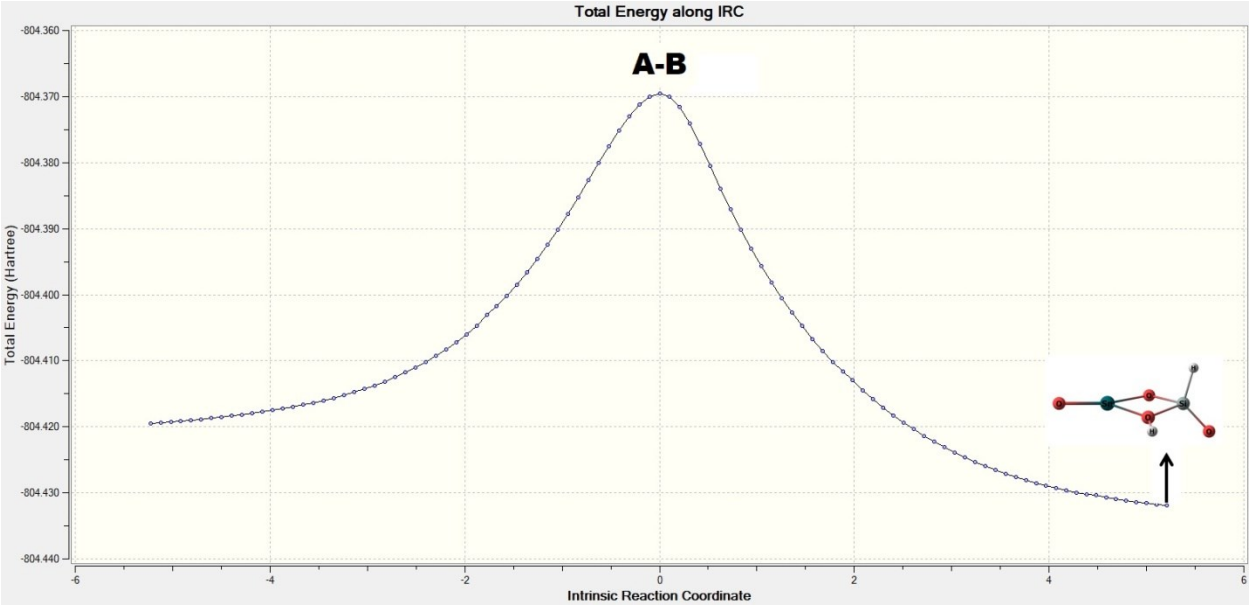
[3]Department of Chemistry, University College London, 20 Gordon St., London WC1HOAJ, UK

[4]UK Catalysis Hub, Research Complex at Harwell, RAL, Oxford, OX11 0FA, UK

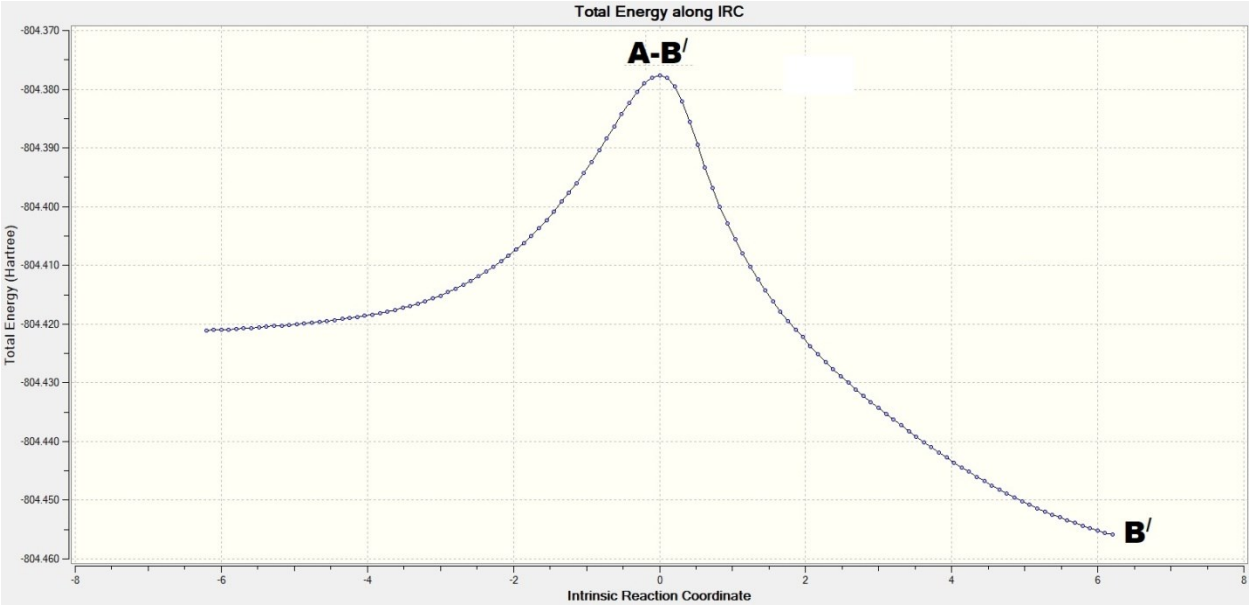
E–mail: ramesh@tezu.ernet.in

Fig. S1 Intrinsic reaction coordinate (IRC) path for the transition states involved in the H_2 dissociation calculated at MN-12SX/def2TZVPP level of theory.

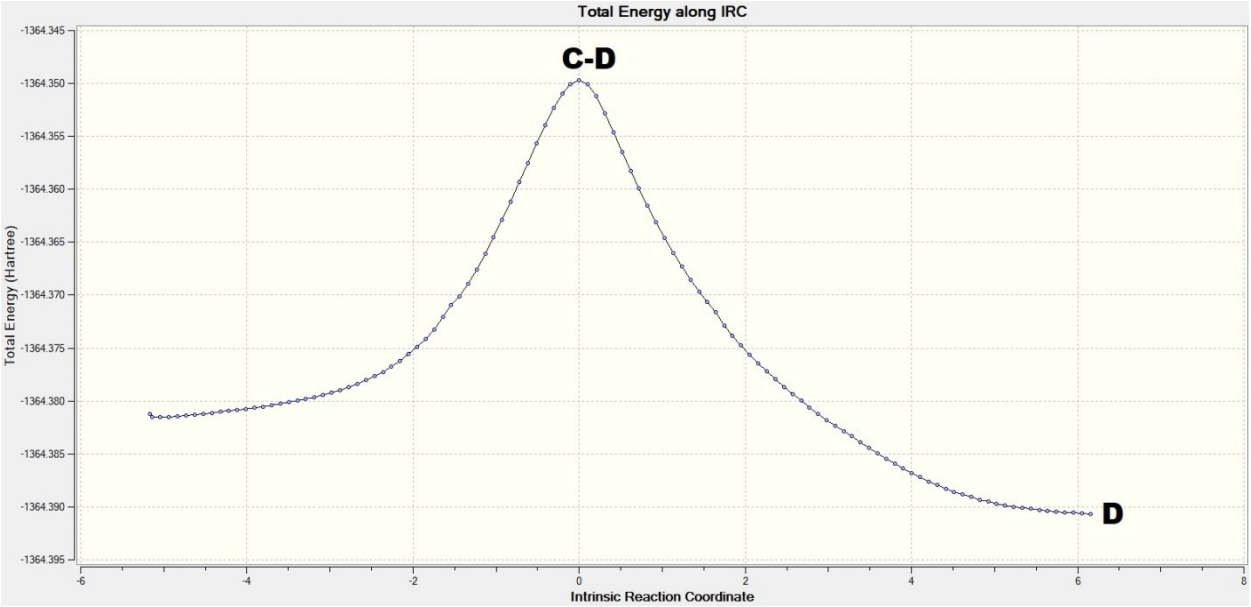
For the path A→ (A-B) →B



For the path A→ (A-B′) →B′



For the path C→ (C-D) →D



For the path C→ (C-D/) →D/

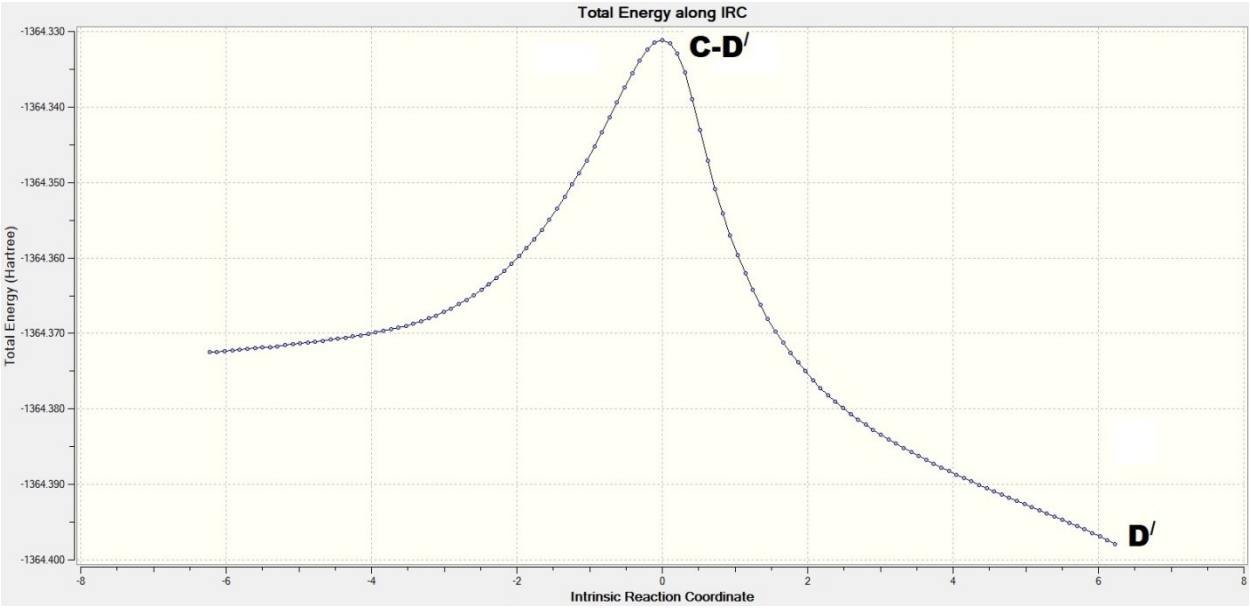
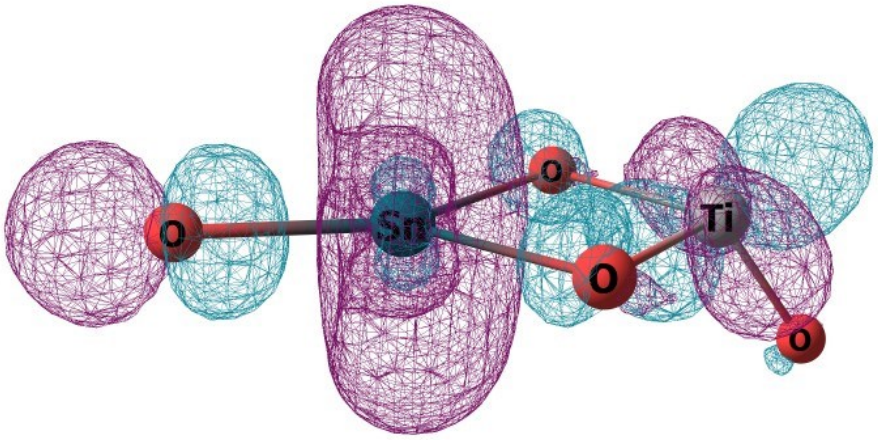


Fig. S2 The LUMO+1 of the SnTiO4 cluster for the description of H_2 dissociation over Sn-O bridge calculated via NBO at MN-12SX/def2TZVPP level of theory.



Geometrical coordinates

Sn_2O_4

Sn	1.474858000	0.000049000	-0.000005000
O	0.000046000	-1.299128000	0.000034000
O	3.280633000	-0.000205000	0.001257000
Sn	-1.474855000	-0.000009000	-0.000070000
O	-0.000093000	1.299179000	0.000033000
O	-3.280607000	-0.000098000	-0.000858000

CO_2

O	0.000000000	0.000000000	1.152763000
C	0.000000000	0.000000000	0.000000000
O	0.000000000	0.000000000	-1.152763000

H_2

H	0.000000000	0.000000000	0.372559000
H	0.000000000	0.000000000	-0.372559000

HCOOH

C	-0.132679000	0.395592000	0.000834000
H	-0.103499000	1.497537000	0.000381000
O	-1.124587000	-0.263012000	-0.000384000
O	1.105628000	-0.089132000	-0.000750000
H	1.051250000	-1.053942000	0.003694000

$SnSiO_4$ (A)

O	-0.717279000000	-1.219657000000	-0.000001000000
O	-3.305751000000	-0.000200000000	0.000011000000
Sn	0.841841000000	0.000037000000	-0.000006000000
O	-0.717388000000	1.219729000000	-0.000001000000
O	2.643090000000	-0.000194000000	0.000028000000
Si	-1.808104000000	0.000050000000	0.000002000000

$SnSiO_4 – H_2$ TS (A-B)

O	0.662572000000	-1.263755000000	-0.021173000000
O	3.177726000000	0.121755000000	-0.552807000000
Sn	-0.877829000000	0.050522000000	-0.026241000000
O	0.677175000000	1.160719000000	0.297689000000
O	-2.667086000000	-0.103661000000	-0.151556000000
Si	1.853554000000	0.005376000000	0.141058000000
H	1.918481000000	-0.678141000000	1.631598000000
H	1.220095000000	-1.243705000000	1.128425000000

$SnSiO_4 – H_2$ P (B)

O	-2.828889000000	-0.082330000000	0.836517000000
O	-0.657781000000	1.236462000000	-0.191949000000
Sn	0.856449000000	0.001061000000	0.019455000000
O	-0.665242000000	-1.215498000000	-0.255138000000
O	2.646667000000	-0.014284000000	0.251243000000
Si	-1.759685000000	0.013687000000	-0.369991000000
H	-2.436215000000	0.083175000000	-1.658045000000
H	-3.708672000000	0.277360000000	0.739796000000

$SnSiO_4 – H_2$ TS (A-B$^/$)

O	0.723990000000	-1.150857000000	0.199435000000
O	3.349745000000	-0.135241000000	-0.195493000000
Sn	-0.891707000000	-0.037441000000	0.083897000000
O	0.853278000000	1.268221000000	-0.156398000000
O	-2.580630000000	-0.030706000000	-0.558828000000
Si	1.861517000000	-0.017502000000	-0.081003000000
H	0.222669000000	1.390081000000	1.012223000000
H	-0.469617000000	1.115662000000	1.617246000000

$SnSiO_4 – H_2$ P (B$^/$)

O	0.679831000000	-1.094269000000	-0.136524000000
O	3.378555000000	-0.132734000000	-0.302685000000
Sn	-1.053239000000	-0.093165000000	0.193865000000
O	1.060295000000	1.257948000000	0.385119000000
O	-1.889315000000	0.477839000000	-1.298052000000
Si	1.896135000000	-0.087483000000	-0.082630000000
H	1.483482000000	2.117219000000	0.440243000000
H	-1.202344000000	-0.304485000000	1.840470000000

$SnTiO_4$ (C)

O	0.484376000000	-1.312601000000	0.193589000000
O	2.899264000000	-0.000289000000	-0.858829000000
Sn	-0.965418000000	0.000060000000	-0.017345000000
O	0.484336000000	1.312718000000	0.193289000000
O	-2.760022000000	-0.000344000000	-0.254516000000
Ti	1.791239000000	0.000051000000	0.303590000000

$SnTiO_4$ –H_2 TS (C-D)

O	-0.429580000000	1.334600000000	-0.117612000000
O	-3.009366000000	-0.184142000000	-0.825360000000
Sn	1.029938000000	-0.059627000000	-0.017224000000
O	-0.425437000000	-1.276304000000	0.322190000000
O	2.813738000000	0.135147000000	-0.222615000000
Ti	-1.824820000000	-0.003519000000	0.235819000000
H	-1.081113000000	1.609681000000	0.893504000000
H	-1.864566000000	1.374657000000	1.526846000000

$SnTiO_4$ –H_2 P (D)/ IM1

O	-0.385079000000	1.331482000000	0.293083000000
O	-2.874429000000	0.108333000000	-1.028377000000
Sn	1.063434000000	-0.134264000000	-0.014813000000
O	-0.423310000000	-1.260294000000	0.140433000000
O	2.759531000000	0.422894000000	-0.248765000000
Ti	-1.935409000000	-0.012220000000	0.262082000000
H	-0.298188000000	2.259526000000	0.069943000000
H	-2.908251000000	-0.096823000000	1.653930000000

$SnTiO_4$ –H_2 TS (C-D$^{/}$)

O	0.507671000000	-1.017674000000	0.841428000000
O	2.624701000000	-0.541866000000	-1.050651000000
Sn	-0.983062000000	-0.033799000000	0.061393000000
O	0.625011000000	1.381339000000	-0.257754000000
O	-2.583962000000	-0.250761000000	-0.758850000000
Ti	1.858477000000	0.085786000000	0.211331000000
H	-0.927569000000	1.529773000000	1.325872000000
H	-0.193177000000	1.704566000000	0.761817000000

$SnTiO_4 – H_2$ P (D/)

O	0.547563000000	-1.176482000000	-0.396130000000
O	2.932780000000	0.337898000000	-0.881123000000
Sn	-1.144370000000	-0.157382000000	0.099309000000
O	0.591390000000	1.115149000000	0.955843000000
O	-1.871924000000	0.939136000000	-1.149380000000
Ti	1.848279000000	-0.134897000000	0.204708000000
H	-1.546679000000	-0.942432000000	1.524396000000
H	0.504541000000	2.053657000000	0.772904000000

TS1 (Transition state corresponding to hydride transfer)

O	0.169790000000	-0.828889000000	1.367211000000
O	2.878765000000	-1.766833000000	-0.088594000000
Sn	-1.196864000000	-0.220268000000	-0.147574000000
O	0.276613000000	-0.729356000000	-1.243917000000
O	-2.930865000000	-0.025635000000	0.306310000000
Ti	1.660536000000	-0.736921000000	0.042680000000
H	-0.042141000000	-1.111042000000	2.256782000000
H	2.065515000000	0.994776000000	0.147526000000
O	1.689464000000	3.198144000000	-0.048178000000
C	0.950883000000	2.319379000000	0.061203000000
O	-0.135923000000	1.830775000000	0.165697000000

IM2 (Formate intermediate)

O	0.663600000000	-0.342898000000	1.416874000000
O	3.341062000000	-0.764951000000	-0.094079000000
Sn	-0.948007000000	-0.559709000000	-0.113175000000
O	0.696191000000	-0.481624000000	-1.209238000000
O	-2.241294000000	-1.765156000000	0.287375000000
Ti	1.938452000000	-0.006376000000	0.002123000000
H	0.651705000000	-0.829861000000	2.242590000000

H	0.717005000000	1.968725000000	-0.111196000000
O	-0.508270000000	3.526998000000	0.078815000000
C	-0.353944000000	2.355822000000	-0.016002000000
O	-1.262620000000	1.434123000000	-0.032664000000

IM2$^{/}$ (Intermediate with respect to the configuration change)

O	-1.075140000000	0.448132000000	-1.102209000000
O	-3.545193000000	0.185277000000	0.304408000000
Sn	0.678571000000	0.504424000000	-0.068137000000
O	-0.634485000000	-0.720088000000	1.127715000000
O	1.368348000000	2.095407000000	0.483622000000
H	-0.349939000000	-0.901743000000	2.024894000000
H	2.815478000000	-2.450315000000	-0.394452000000
O	1.520155000000	-1.079310000000	-1.153693000000
C	2.182033000000	-1.576308000000	-0.181281000000
O	2.102358000000	-1.086456000000	0.944175000000
Ti	-2.153392000000	-0.507045000000	-0.089457000000

TS2 (Transition state corresponding to HCOOH formation)

O	-0.491758000000	0.758748000000	-0.953866000000
O	-3.318054000000	-0.093110000000	-0.465545000000
Sn	0.615193000000	-0.742446000000	-0.014071000000
O	-1.006012000000	-0.799361000000	1.112216000000
O	1.835856000000	-1.900354000000	-0.696655000000
Ti	-1.963276000000	0.449230000000	0.197832000000
H	0.324164000000	1.697462000000	-0.896011000000
H	2.572754000000	2.698867000000	0.781824000000
O	1.150007000000	2.460937000000	-0.613410000000
C	1.808476000000	2.026729000000	0.362427000000
O	1.665540000000	0.908459000000	0.903616000000