Supporting information

Revealing role of HBr in propane dehydrogenation on CeO_2 (111) from DFT based microkinetic simulation

Faheem Jan[a,b], Zan Lian[a,b], Shuaike Zhi[a,b], Min Yang[a,b], Chaowei Si[a,b], and Bo Li[a,b*]

[a]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, Liaoning, People's Republic of China

[b]School of Materials Science and Engineering, University of Science and Technology of China, Shenyang 110016, Liaoning, People's Republic of China

Corresponding Author

* B.L.: e-mail, boli@imr.ac.cn; tel, 86-24-83970027; fax, 86-24-83970019.

Lattice parameter

To assure the consistency of computational results, we first calculated the lattice parameter and compared it with experimental values. The lattice parameter was found consistent to stable unit cell through Brich-Murnaghan equation of state. A unit cell is taken to find lattice parameter a_0 of CeO_2 by doing DFT+U calculation. The total energy of the material is changed by changing the lattice parameter. The best value for the lattice parameter is calculated as 5.46 Å, as shown in Figure S1.
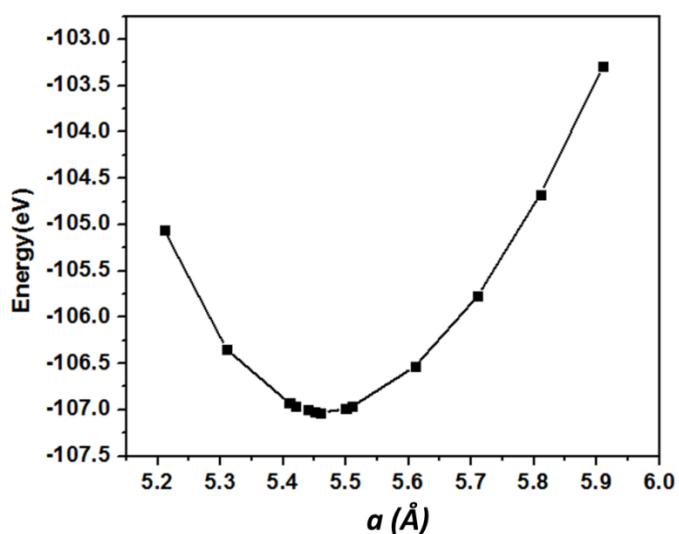

Figure S1. Shows the value of lattice parameter for CeO_2 versus total energy.
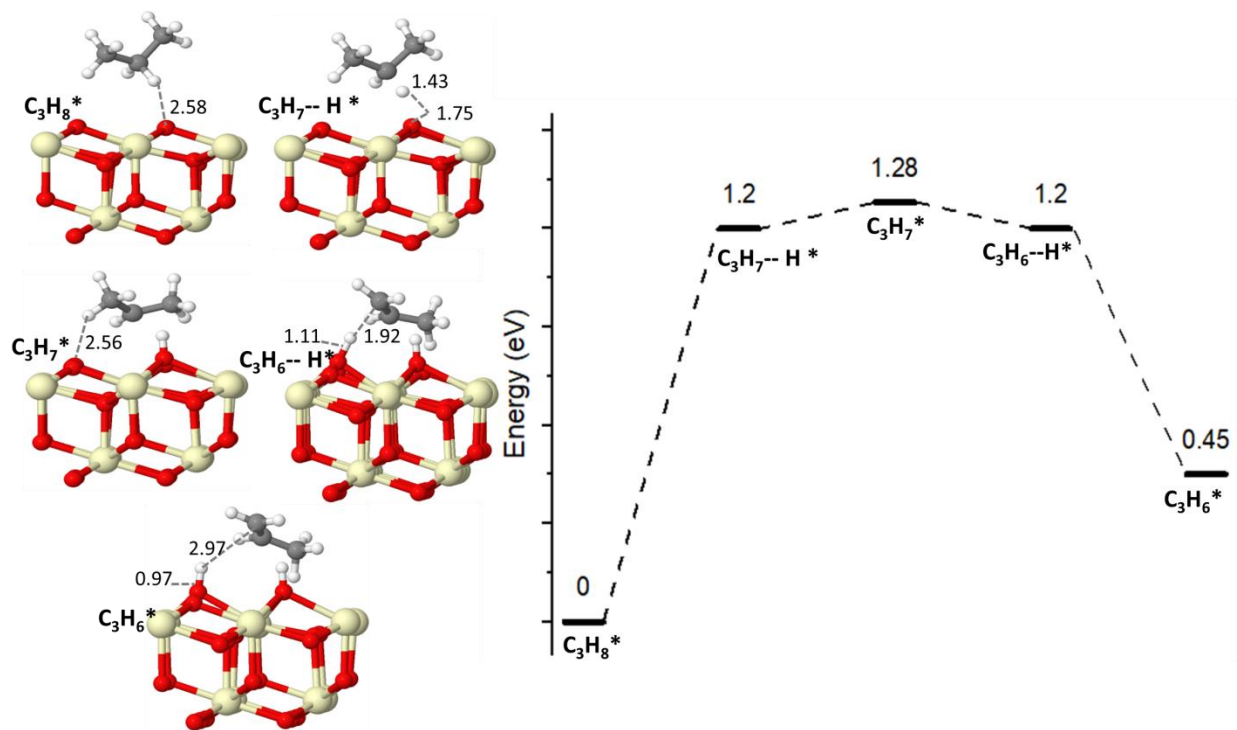
Figure S2. The reaction pathway of propane dehydrogenation on CeO$_2$ surface with a surface vacancy.
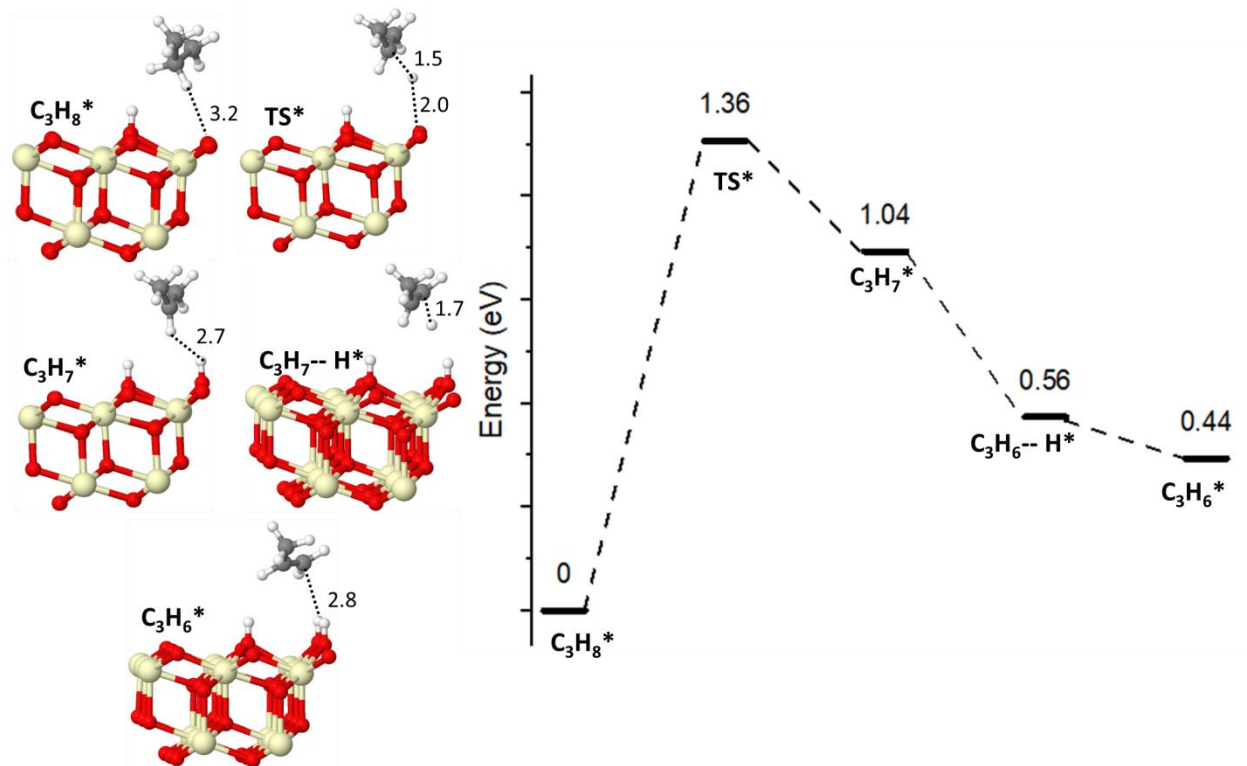

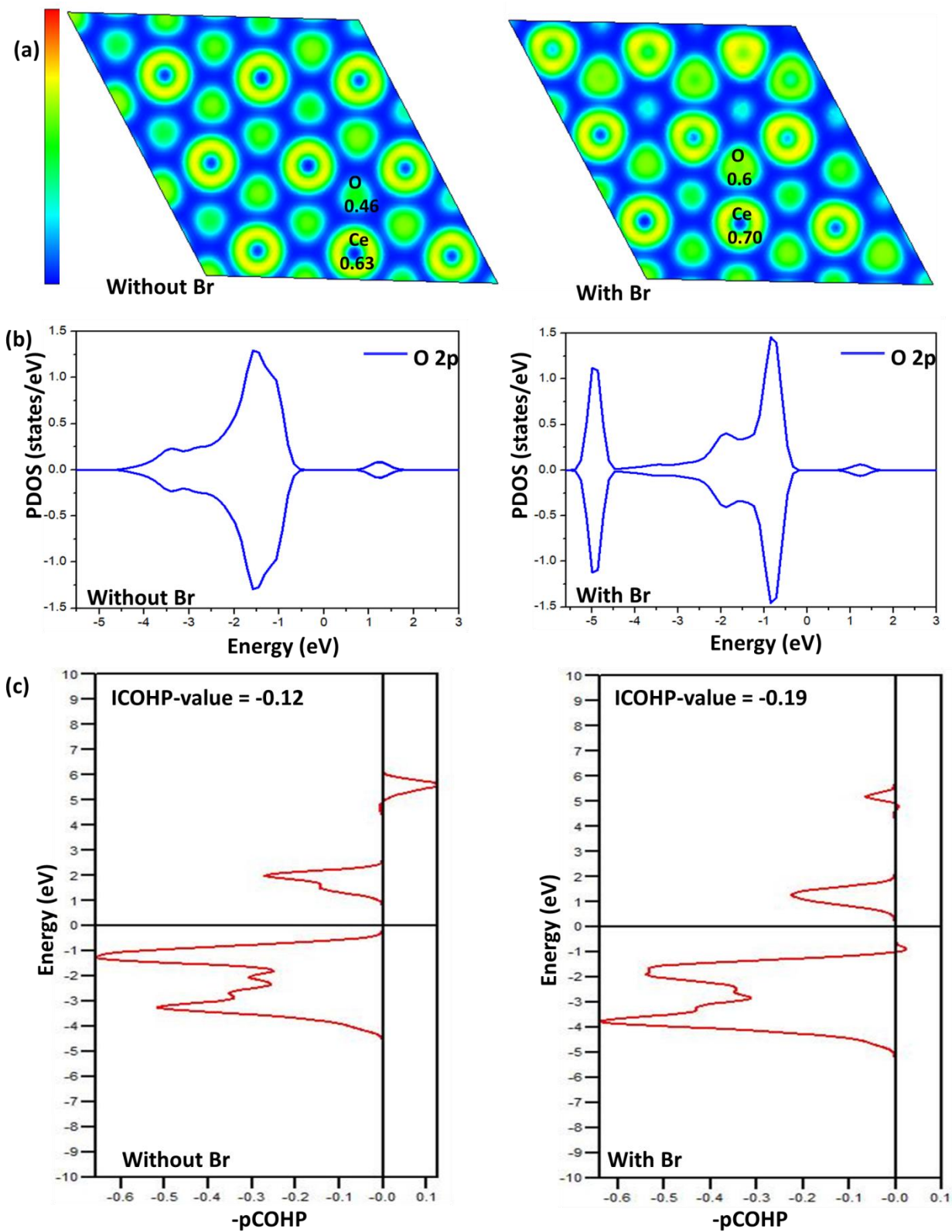Figure S3. The reaction pathway of propane dehydrogenation with a hydroxyl.

Figure S4. (a) Shows the ELF, while (b), and (c) shows the PDOS and COHP analysis.

Formation of water

The adsorb H* atoms on the surface involves in the formation of water as shown in Figure S5.
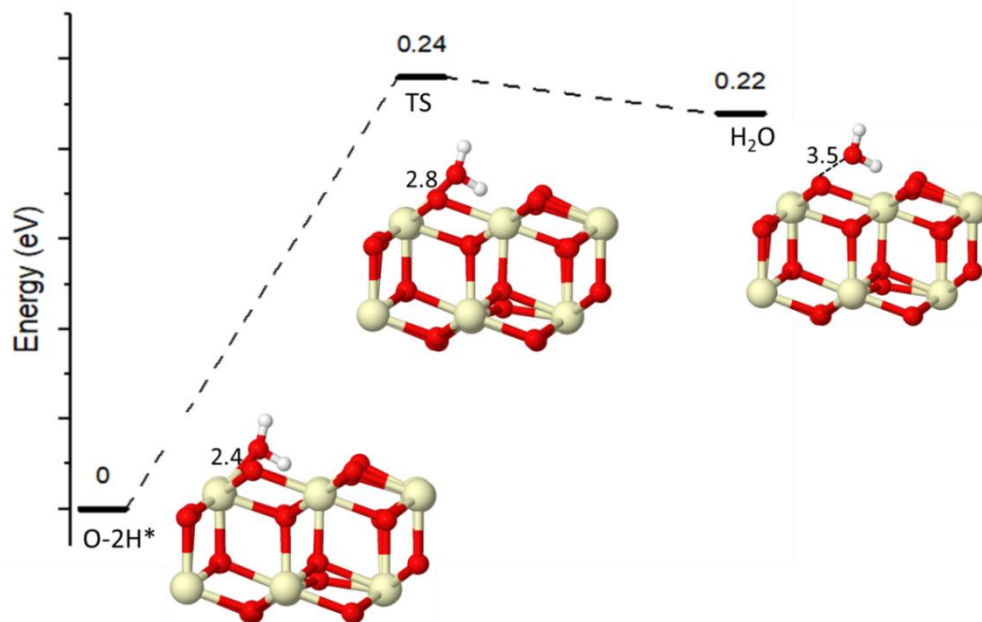

Figure S5. The reaction pathway of water formation.

Regeneration of CeO$_2$ surface

The vacant CeO$_2$ is regenerated by the interaction of O$_2$ with the surface, as given in Figure S6.
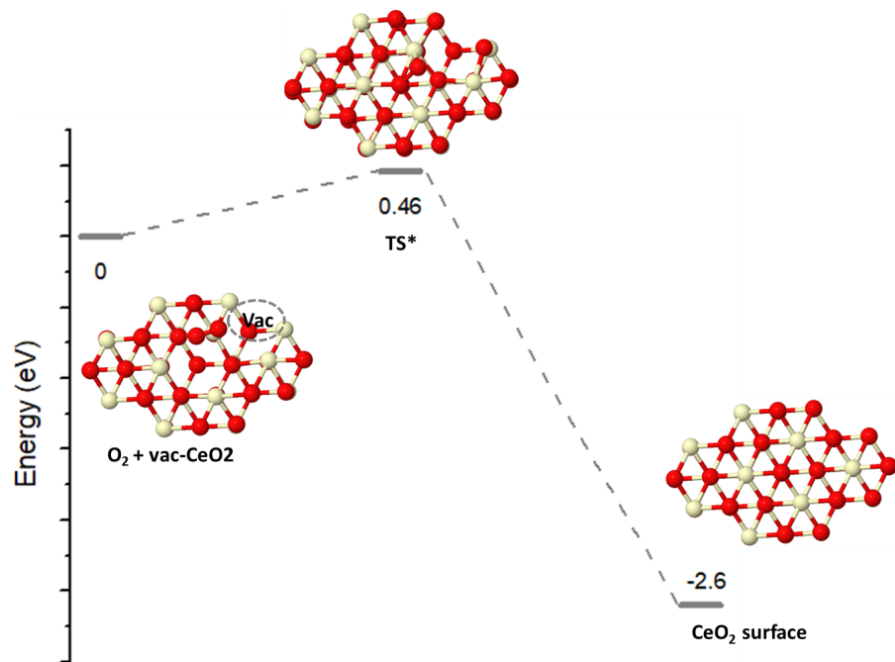

Figure S6. Regeneration of vacant CeO$_2$ surface by the interaction of O$_2$.

Desorption of HBr

The HBr desorb from the surface as shown in Figure S7.
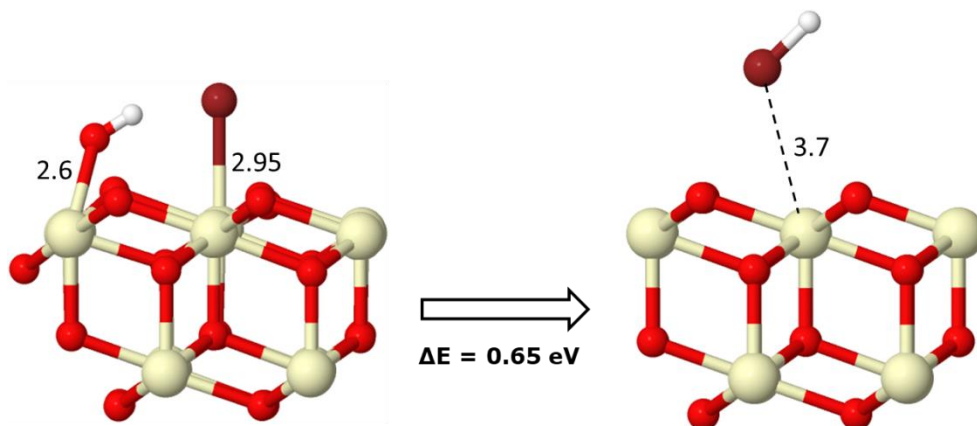

Figure S7. Represent the desorption of HBr from CeO_2 surface.

Degree of Rate Control (DRC)

The DRC analysis is performed for finding the contribution of an elementary step to the overall reaction.

The summation of DRC coefficients for all elementary steps gives unity as given by

$$\sum_i xi = 1$$

The DRC analysis for all elementary steps in absence and presence of HBr as given in tables.

Table S1. Degree of rate control in formation of C_3H_6 in HBr absence at clean surface, at 800K.

No's	Reaction	DRC
R1-P	$CH_3CH_2CH_3$* + * → $CH_3CH_2CH_2$* + H*	1.28E-03
R2-P	$CH_3CH_2CH_2$* + * → CH_3CHCH_2* + H*	4.20E-06
R1-S	$CH_3CH_2CH_3$* + * → CH_3CHCH_3* + H*	9.99E-01
R2-S	CH_3CHCH_3* + * → CH_3CHCH_2* + H*	3.79E-12
	$\sum_i xi$	1.00E+00

Table S2. Degree of rate control in the formation of C_3H_6 in presence of HBr at 800K.

No's	Reactions	DRC

Diss	HBr* + * → H* + Br*	1.46E-04
R3-S	$CH_3CH_2CH_3$*+H*+Br*+*→CH_3CHCH_3* + 2H*+Br*	1.00E+00
R4-S	CH_3CHCH_3* + Br* → $CH_3CHBrCH_3$* + *	-8.21E-08
R5-S	$CH_3CHBrCH_3$* + * → $CH_3CHBrCH_2$* + H*	5.99E-07
R6-S	$CH_3CHBrCH_2$* + * → CH_3CHCH_2* + Br*	-8.62E-08
R3-P	$CH_3CH_2CH_3$*+H*+Br*+*→ $CH_3CH_2CH_2$* + 2H*+Br*	1.16E-03
R4-P	$CH_3CH_2CH_2$* + Br* → $CH_3CH_2CH_2Br$* + *	-7.50E-08
R5-P	$CH_3CH_2CH_2Br$* + * → CH_3CHCH_2Br* + H*	2.67E-07
R6-P	CH_3CHCH_2Br* + * → CH_3CHCH_2* + Br*	1.03E-08
Dehy	H* + H* → H_2O* + Vo *	-2.22E-03
R7-S	$CH_3CHBrCH_3$* + Vo* → CH_3CHCH_3* + VoBr*	-6.54E-05
R8-S	CH_3CHCH_3* + * → CH_3CHCH_2* + H*	6.41E-05
R7-P	$CH_3CH_2CH_2Br$* + Vo* → $CH_3CH_2CH_2$* + VoBr*	-7.59E-07
R8-P	$CH_3CH_2CH_2$* + * → CH_3CHCH_2* + H*	8.64E-07
Des	H* + Br* → HBr* + *	-7.14E-04
Diss 2	HBr* + Ce-O* →Ce-Br* + OH*	-7.92E-09
R9-P	$CH_3CH_2CH_3$* + OH* → $CH_3CH_2CH_2$* + H_2O*	3.98E-06
R10-P	$CH_3CH_2CH_2$* + * → CH_3CHCH_2* + H*	-2.04E-06
R9-S	$CH_3CH_2CH_3$* + OH* → CH_3CHCH_3* + H_2O*	5.06E-06
R10-S	CH_3CHCH_3* + * → CH_3CHCH_2* + H*	-1.89E-06
Des	HBr* → HBr + *	1.97E-04
	$\sum_i x_i$	1.00E+00

Table S3. Coverage of different intermediate species at 800K and different partial pressure of C_3H_8.

Intermediates	10kPa	50kPa	100kPa
HBr Absence			
$CH_3CH_2CH_3$*	2.32E-08	1.16E-07	2.32E-07
CH_3CHCH_3*	8.97E-15	4.48E-14	8.97E-14
$CH_3CH_2CH_2$*	5.85E-12	2.92E-11	0.00E+00

CH$_3$CHCH$_2$*	9.57E-10	4.78E-09	9.56E-09
*	1.00E+00	1.00E+00	1.00E+00
HBr Presence			
CH$_3$CH$_2$CH$_3$*	3.24E-08	1.19E-07	1.79E-07
CH$_3$CHCH$_3$*	1.23E-12	4.56E-12	6.85E-12
CH$_3$CH$_2$CH$_2$*	1.22E-15	4.53E-15	6.81E-15
CH$_3$CHCH$_2$*	3.85E-09	1.43E-08	2.15E-08
CH$_3$CHBrCH$_3$*	9.26E-15	1.32E-14	1.22E-14
CH$_3$CH$_2$CH$_2$Br*	6.91E-16	9.86E-16	9.09E-16
CH$_3$CHCH$_2$Br*	7.18E-17	1.02E-16	9.41E-17
CH$_3$CHBrCH$_2$*	3.10E-11	4.40E-11	4.06E-11
H$_2$O*	1.09E-14	7.75E-14	1.42E-13
OH*	1.84E-08	3.55E-08	4.35E-08
HBr*	3.28E-07	2.42E-07	1.82E-07
H*	3.68E-05	7.09E-05	8.70E-05
Br*	9.60E-03	3.70E-03	2.27E-03
*	9.90E-01	9.96E-01	9.98E-01

Reaction order

The reaction order is calculated at different temperatures and pressure. As the reaction order is linked with the rate determining step, C$_3$H$_7$ formation is explored as rate determining step for all paths. Moreover, the reaction is found as first-order to C$_3$H$_8$ in the presence and absence of HBr. However, the HBr is found as zero-order at all temperatures, as given in Figure S8.
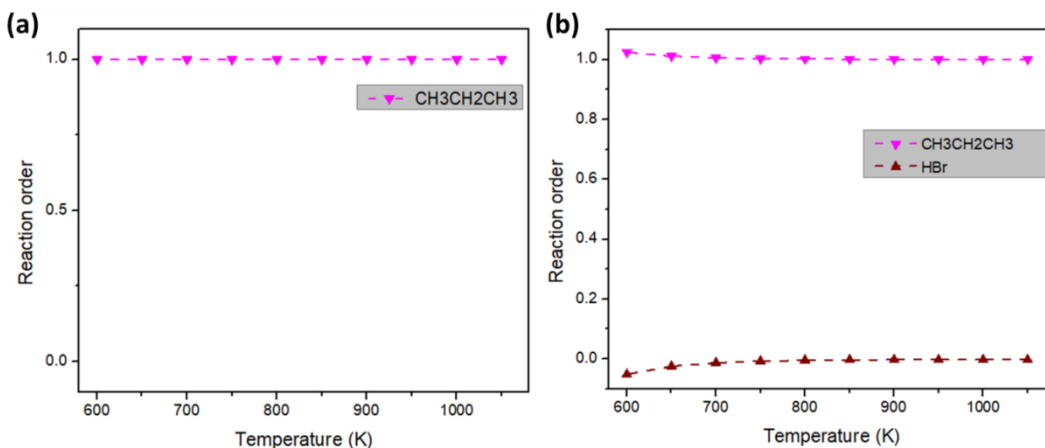
Figure S8. Reaction order at different temperatures (a) shows the order in the absence of HBr while (b) shows the reaction order in the presence of HBr.

Schematic representation.

The Figure S9 and S10 show the schematic representation of coverage and reaction rates of different intermediate species.
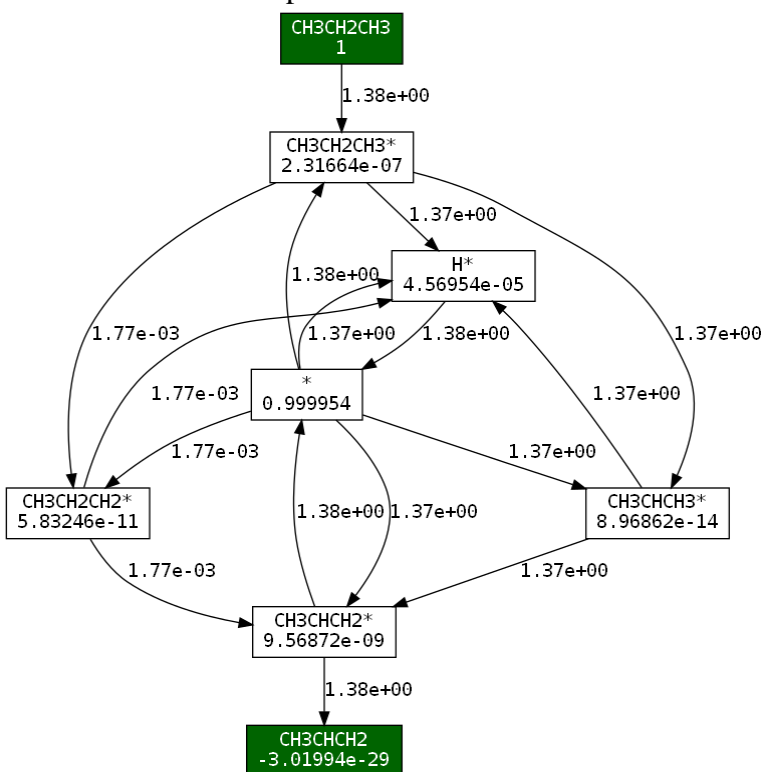

Figure S9. Network of elementary reaction with coverage values inside the square box on the clean surface at 800K and 100kPa. The numbers on arrow lines represent the reaction rates.

Figure S10. Network with coverage of elementary reaction in the presence of HBr surface at 800K and 100kPa. The coverage is indicated inside the box, whereas the reaction rates were labeled on arrow lines.

References

1. Filot, I. A. W. *Introduction to Microkinetic Modeling*; Technische Universiteit Eindhoven, 2018.
2. Sholl, D. S.; Steckel, J. A. *Density Functional Theory: A Practical Introduction*; 2009.