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

Supporting information

Enhancing Catalytic Activity of Cr_2O_3 in CO_2-assisted Propane Dehydrogenation with Effective Dopant Engineering: A DFT-Based Microkinetic Simulation

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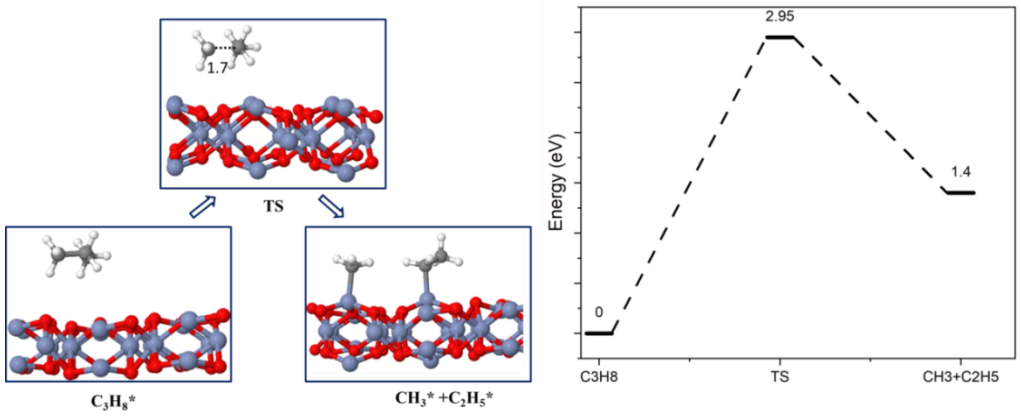

Figure S1 Reaction path for the cracking of C_3H_8 to CH_3 and C_2H_5.

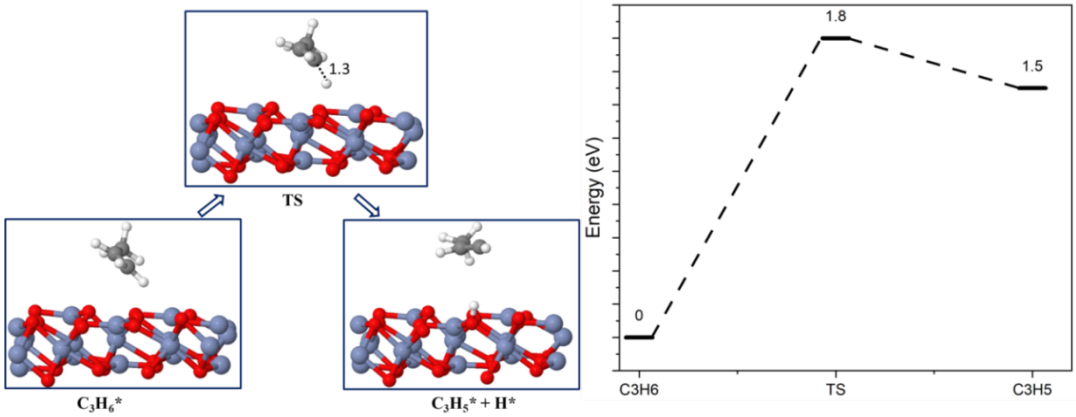

Figure S2 Deep dehydrogenation of C_3H_6 to C_3H_5.

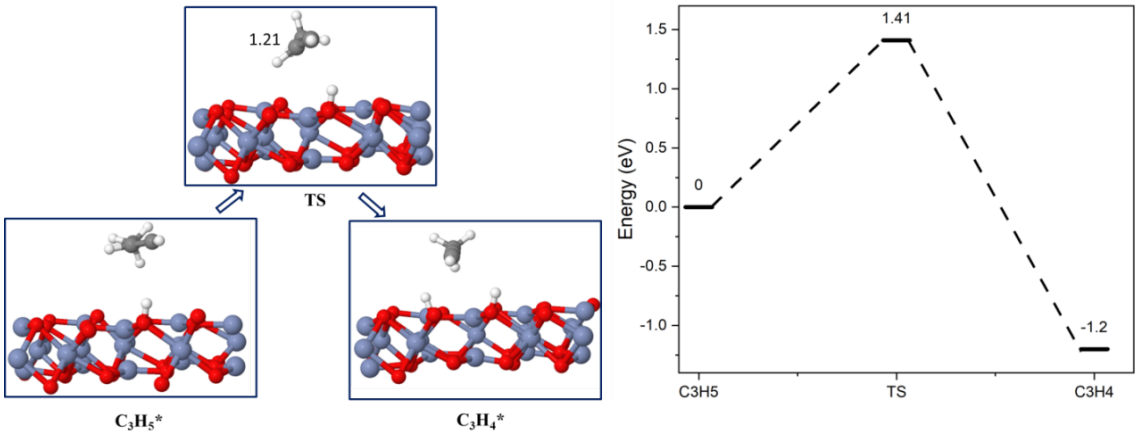

Figure S3 Deep dehydrogenation of C_3H_5 to C_3H_4.

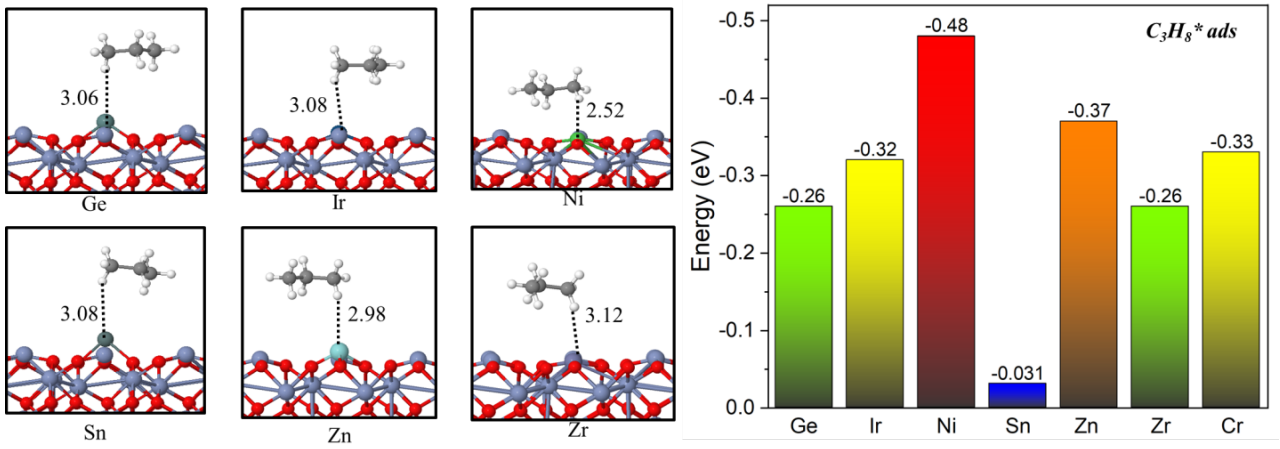

Figure S4 Adsorption energies of propane molecule on Cr_2O_3 and M-Cr_2O_3 surfaces.

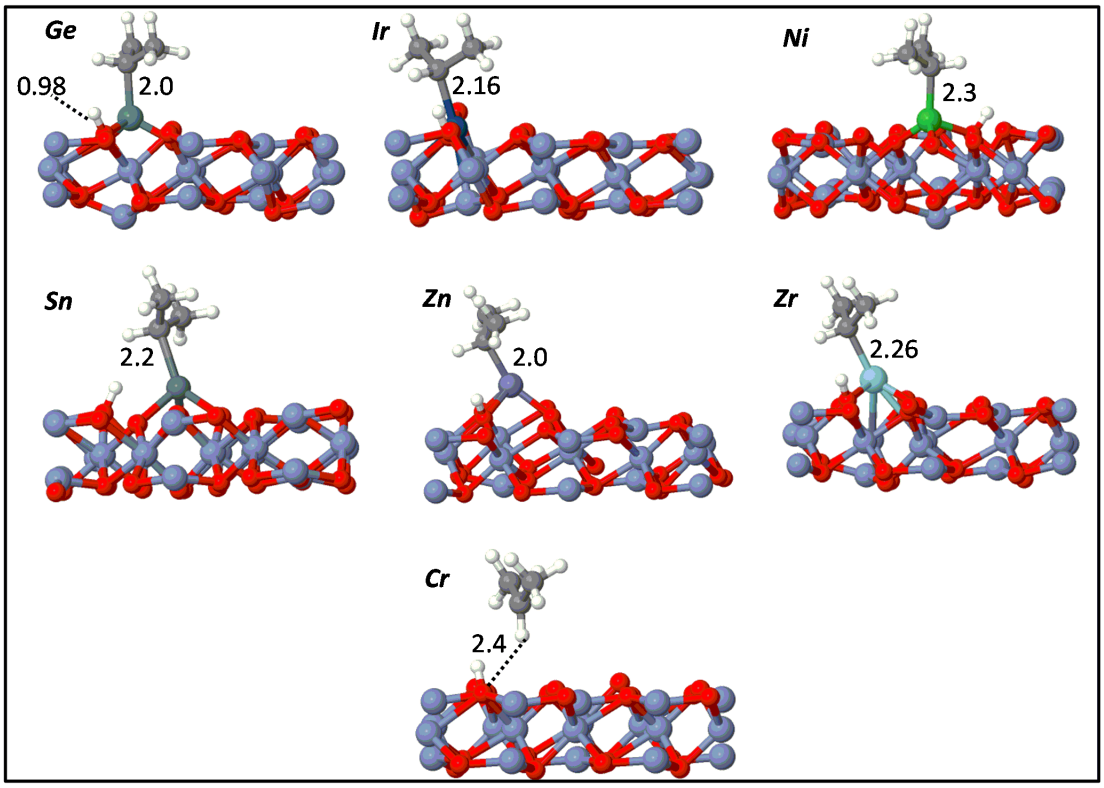

Figure S5. Formation of C_3H_7 specie on all surface.

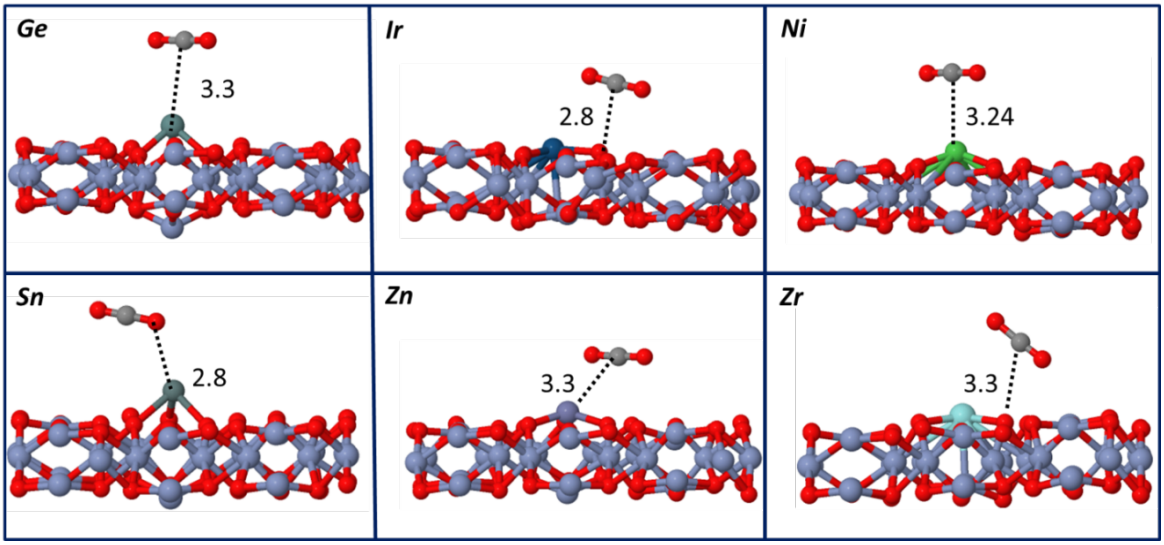

Figure S6. The physisorption of CO_2 molecule on M-Cr_2O_3 surfaces.

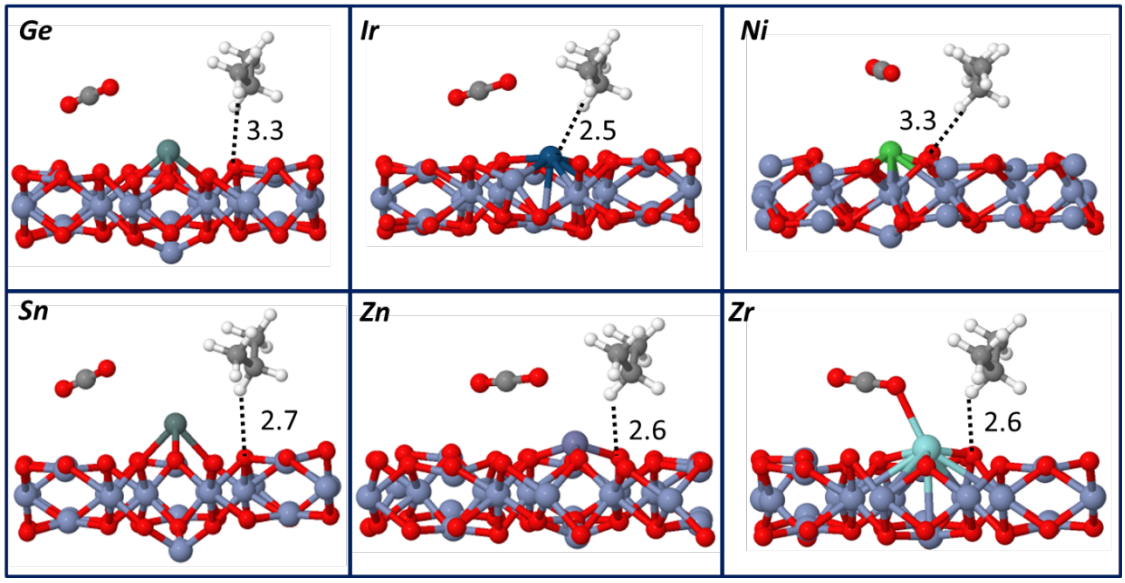

Figure S7. Physisorption adsorption of propane molecule on doped catalytic surfaces.

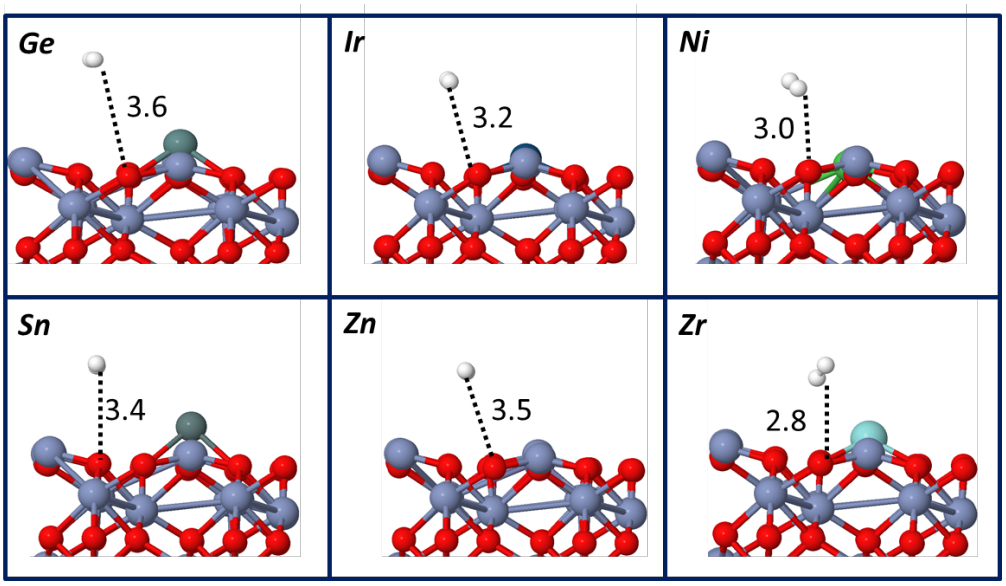

Figure S8. Removal of H-atoms from catalytic surfaces.

Table S1 Formation energies of M-Cr_2O_3 surfaces.

Surfaces	Formation energy
Ge-Cr_2O_3	-2.04
Ir-Cr_2O_3	-0.52
Ni-Cr_2O_3	-2.06
Sn-Cr_2O_3	-1.92
Zn-Cr_2O_3	-1.36
Zr-Cr_2O_3	-2.06

Table S2. The DRC analysis without the CO_2 molecule.

Reactions	**DRC**						
	Ge	**Ir**	**Ni**	**Sn**	**Zn**	**Zr**	**Cr**
$CH_3CH_2CH_3$* + * → CH_3CHCH_3* + H*	8.95E-01	9.95E-01	9.91E-01	9.73E-01	9.82E-01	3.74E-02	9.41E-01
CH_3CHCH_3* + * → CH_3CHCH_2* + H*	6.99E-02	3.54E-03	6.31E-03	1.79E-02	1.17E-02	6.42E-01	3.91E-02
H* + H* → H_2* +*	3.50E-02	1.77E-03	3.17E-03	8.93E-03	5.85E-03	3.21E-01	1.96E-02
$\sum_i xi$	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00

Table S3. The DRC analysis with CO_2 molecule.

Reactions	**DRC**						
	Ge	**Ir**	**Ni**	**Sn**	**Zn**	**Zr**	**Cr**
$CH_3CH_2CH_3$* + * → CH_3CHCH_3* + H*	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.99E-01	9.91E-01	9.08E-01
CH_3CHCH_3* + * → CH3CHCH2* + H*	1.82E-04	4.34E-06	2.35E-07	1.28E-07	3.59E-04	5.97E-03	6.13E-02
H* + H* → H_2* +*	1.32E-04	2.25E-06	4.30E-06	1.04E-07	2.07E-04	3.20E-03	3.07E-02
CO_2* + * → CO* + O*	1.06E-14	3.55E-16	-1.29E-13	-1.78E-16	5.68E-13	5.87E-11	4.44E-16
$CH_3CH_2CH_3$* + O* → CH_3CHCH_3* + OH*	1.06E-14	3.55E-16	4.61E-13	-1.78E-16	6.48E-13	5.86E-11	4.44E-16
CH_3CHCH_3* + OH* → CH_3CHCH_2* + H_2O*	1.06E-14	4.56E-14	4.99E-13	-1.78E-16	5.42E-13	5.86E-11	2.72E-14
$\sum_i xi$	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00

Table S4. The rate constant for the elementary steps.

Reactions	Rate constant	
*Cr_2O_3 surface	k_{fwd}	k_{bwd}
CO_2 + * → CO_2*	1.40E+07	3.17E+17
$CH_3CH_2CH_3$ * → $CH_3CH_2CH_3$*	1.40E+07	5.89E+10
CH_3CHCH_2* → CH_3CHCH_2 + *	1.44E+08	7.24E+17
H_2O* → H_2O + *	2.20E+08	1.46E+18
$CH_3CH_2CH_3$* + * → CH_3CHCH_3* + H*	1.03E+02	2.71E+11
CH_3CHCH_3* + * → CH_3CHCH_2* + H*	4.39E+05	5.60E+09
H* + H* → H_2* + *	1.22E+09	5.92E-01
CO_2* + * → CO* + O*	3.82E+06	1.75E+11
$CH_3CH_2CH_3$* + O* → CH_3CHCH_3* + H*	1.48E+04	2.71E+11
CH_3CHCH_3* + OH* → CH_3CHCH_2* +H_2O*	2.91E+05	5.60E+09

*Ge-Cr_2O_3		
$CO_2 + * \rightarrow CO_2*$	1.36E+07	4.16E+17
$CH_3CH_2CH_3 * \rightarrow CH_3CH_2CH_3*$	1.36E+07	1.97E+17
$CH_3CHCH_2* \rightarrow CH_3CHCH_2 + *$	1.39E+08	9.93E+17
$H_2O* \rightarrow H_2O + *$	2.13E+08	1.92E+18
$CH_3CH_2CH_3* + * \rightarrow CH_3CHCH_3* + H*$	1.81E+09	3.45E+11
$CH_3CHCH_3* + * \rightarrow CH_3CHCH_2* + H*$	2.56E+09	4.53E+12
$H* + H* \rightarrow H_2* + *$	2.13E+09	3.66E+00
$CO_2* + * \rightarrow CO* + O*$	4.93E+08	2.29E+11
$CH_3CH_2CH_3* + O* \rightarrow CH_3CHCH_3* + H*$	7.65E+08	3.45E+11
$CH_3CHCH_3* + OH* \rightarrow CH_3CHCH_2* + H_2O*$	5.31E+09	8.97E+09
*Ir-Cr_2O_3		
$CO_2 + * \rightarrow CO_2*$	1.40E+07	3.17E+17
$CH_3CH_2CH_3 * \rightarrow CH_3CH_2CH_3*$	1.40E+07	1.08E+14
$CH_3CHCH_2* \rightarrow CH_3CHCH_2 + *$	1.44E+08	7.24E+17
$H_2O* \rightarrow H_2O + *$	2.20E+08	1.46E+18
$CH_3CH_2CH_3* + * \rightarrow CH_3CHCH_3* + H*$	1.46E+05	2.71E+11
$CH_3CHCH_3* + * \rightarrow CH_3CHCH_2* + H*$	1.47E+09	5.60E+09
$H* + H* \rightarrow H_2* + *$	9.21E+12	5.92E-01
$CO_2* + * \rightarrow CO* + O*$	9.97E+07	1.75E+11
$CH_3CH_2CH_3* + O* \rightarrow CH_3CHCH_3* + H*$	4.91E+08	2.71E+11
$CH_3CHCH_3* + OH* \rightarrow CH_3CHCH_2* + H_2O*$	2.84E+10	5.60E+09
*Ni-Cr_2O_3		
$CO_2 + * \rightarrow CO_2*$	1.29E+07	6.73E+17
$CH_3CH_2CH_3 * \rightarrow CH_3CH_2CH_3*$	1.29E+07	3.36E+16
$CH_3CHCH_2* \rightarrow CH_3CHCH_2 + *$	1.32E+08	1.74E+18
$H_2O* \rightarrow H_2O + *$	2.01E+08	3.11E+18
$CH_3CH_2CH_3* + * \rightarrow CH_3CHCH_3* + H*$	6.33E+08	5.19E+11
$CH_3CHCH_3* + * \rightarrow CH_3CHCH_2* + H*$	1.67E+13	5.20E+12
$H* + H* \rightarrow H_2* + *$	5.48E+09	7.88E+01
$CO_2* + * \rightarrow CO* + O*$	6.66E+08	3.60E+11
$CH_3CH_2CH_3* + O* \rightarrow CH_3CHCH_3* + H*$	3.41E+10	5.19E+11
$CH_3CHCH_3* + OH* \rightarrow CH_3CHCH_2* + H_2O*$	7.16E+12	1.98E+10
*Sn-Cr_2O_3		
$CO_2 + * \rightarrow CO_2*$	1.40E+07	3.17E+17
$CH_3CH_2CH_3 * \rightarrow CH_3CH_2CH_3*$	1.40E+07	2.65E+11
$CH_3CHCH_2* \rightarrow CH_3CHCH_2 + *$	1.44E+08	7.24E+17
$H_2O* \rightarrow H_2O + *$	2.20E+08	1.46E+18
$CH_3CH_2CH_3* + * \rightarrow CH_3CHCH_3* + H*$	5.59E-03	2.71E+11
$CH_3CHCH_3* + * \rightarrow CH_3CHCH_2* + H*$	5.59E+10	4.18E+12
$H* + H* \rightarrow H_2* + *$	1.22E+09	5.92E-01
$CO_2* + * \rightarrow CO* + O*$	9.97E+07	1.75E+11
$CH_3CH_2CH_3* + O* \rightarrow CH_3CHCH_3* + H*$	6.83E+08	2.71E+11
$CH_3CHCH_3* + OH* \rightarrow CH_3CHCH_2* + H_2O*$	1.67E+13	1.11E+13
*Zn-Cr_2O_3		
$CO_2 + * \rightarrow CO_2*$	1.36E+07	4.16E+17

$CH_3CH_2CH_3$ * → $CH_3CH_2CH_3$*	1.36E+07	1.54E+16
CH_3CHCH_2* → CH_3CHCH_2 + *	1.39E+08	9.93E+17
H_2O* → H_2O + *	2.13E+08	1.92E+18
$CH_3CH_2CH_3$* + * → CH_3CHCH_3* + H*	9.25E+06	3.45E+11
CH_3CHCH_3* + * → CH_3CHCH_2* + H*	1.81E+08	4.53E+12
H* + H* → H_2* + *	2.13E+09	3.66E+00
CO_2* + * → CO* + O*	2.02E+08	2.29E+11
$CH_3CH_2CH_3$* + O* → CH_3CHCH_3* + H*	1.56E+07	3.45E+11
CH_3CHCH_3* + OH* → CH_3CHCH_2* +H_2O*	1.01E+04	8.97E+09
*Zr-Cr_2O_3		
CO_2 + * → CO_2*	1.36E+07	4.16E+17
$CH_3CH_2CH_3$ * → $CH_3CH_2CH_3$*	1.36E+07	2.21E+14
CH_3CHCH_2* → CH_3CHCH_2 + *	1.39E+08	9.93E+17
H_2O* → H_2O + *	2.13E+08	1.92E+18
$CH_3CH_2CH_3$* + * → CH_3CHCH_3* + H*	2.05E+04	3.45E+11
CH_3CHCH_3* + * → CH_3CHCH_2* + H*	1.56E+06	4.53E+12
H* + H* → H_2* + *	2.13E+09	3.66E+00
CO_2* + * → CO* + O*	2.02E+08	2.29E+11
$CH_3CH_2CH_3$* + O* → CH_3CHCH_3* + H*	3.81E+07	3.45E+11
CH_3CHCH_3* + OH* → CH_3CHCH_2* +H_2O*	3.80E+10	8.97E+09

References

[1]. Filot, I.A.., Introduction to Microkinetic Modeling, Technische Universiteit Eindhoven, 2018.