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Supplementary material

SUPPLEMENTARY MATERIAL TO

Density functional theory calculation of propane cracking mechanism over chromium (III) oxide by cluster approach

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LIST OF RELEVANT MODELS EMPLOYED IN THIS STUDY

a) Enthalpy contributions

$$H_{\text{linear}}(T)=\left[\frac{5}{2}RT\right]_{\text{trans}}+[RT]_{\text{rot}}+\left[RT\sum_{\text{i}}\frac{h\nu_{\text{i}}}{k_{\text{B}}T}\frac{e^{-\frac{h\nu_{\text{i}}}{k_{\text{B}}T}}}{1-e^{\frac{h\nu_{\text{i}}}{k_{\text{B}}T}}}\right]_{\text{vib}} \quad (1)$$

$$H_{\text{non-linear}}(T)=\left[\frac{5}{2}RT\right]_{\text{trans}}+\left[\frac{3}{2}RT\right]_{\text{rot}}+\left[RT\sum_{i}\frac{h\nu_{i}}{k_{B}T}\frac{e^{-\frac{h\nu_{\text{i}}}{k_{\text{B}}T}}}{1-e^{\frac{h\nu_{\text{i}}}{k_{\text{B}}T}}}\right]_{\text{vib}} \quad (2)$$

$$\text{ZPE}=\frac{1}{2}\sum\nu_{\text{n, i}} \quad (3)$$

b) Entropy contributions

$$s_{\text{linear}}(T)=R\left[ln\frac{\{(2\pi m/h^2\})^{\frac{3}{2}}(k_{\text{B}}T)^{\frac{5}{2}}}{P_{\text{o}}}+\frac{5}{2}\right]_{\text{trans}}+R\left[ln\frac{8\pi^2k_{\text{B}}TI_{\text{r, linear}}}{h^2\rho_{\text{r}}}+1\right]_{\text{rot}}+$$
$$+\left[R\sum_{i}\frac{\frac{h\nu_{i}}{k_{B}T}}{e^{\frac{h\nu_{\text{i}}}{k_{\text{B}}T}}-1}-R\sum_{\text{i}}ln\left(1-e^{\frac{h\nu_{\text{i}}}{k_{\text{B}}T}}\right)\right]_{\text{vib}} \quad (4)$$

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$$s_{\text{non-linear}}(T) = R\left[ln\frac{(2\pi m/h^2)^{\frac{3}{2}}(k_{\text{B}}T)^{\frac{5}{2}}}{P_{\text{o}}} + \frac{5}{2} \right]_{\text{trans}} + R\left[ln\frac{8\pi^2(2\pi k_{\text{B}})^{\frac{3}{2}}(T)^{\frac{3}{2}}(I_{\text{a}}I_{\text{b}}I_{\text{c}})^{\frac{1}{2}}}{h^3\rho_{\text{r}}} + \frac{3}{2} \right]_{\text{rot}} + \left[R\sum_{\text{i}} \frac{h\nu_{\text{i}}}{k_{\text{B}}T} - R\sum_{\text{i}} ln\left(1 - e^{\frac{h\nu_{\text{i}}}{k_{\text{B}}T}}\right) \right]_{\text{vib}} \quad (5)$$

$$S_{config} = R\left[\ln\left(\frac{1-\theta}{\theta}\right) - \frac{ln(1-\theta)}{\theta} \right] \quad (6)$$

$$S_{\text{config}} = 1.39R \quad (7)$$

TABLE S-I. The activation and reaction energies across Cr-Cr, Cr-O sites for scheme S1

Step	E_a / eV				ΔG / eV			
	CrCr-S1		CrO-S1		CrCr-S1		CrO-S1	
	F	R	F	R	F	R	F	R
ads	-0.37	0.37	-0.37	0.37	-0.37	0.37	-0.37	0.37
suf	0.54	0.18	0.54	0.18	0.36	-0.36	0.36	-0.36
diff	-0.53	0.53	-0.53	0.53	-0.53	0.53	-0.53	0.53
cra1	0.17	0.77	0.22	0.80	-0.60	0.60	-0.58	0.58
cra2	0.52	-0.52	0.58	-0.58	0.52	-0.52	0.58	-0.58
des	0.25	-0.25	0.19	-0.19	0.25	-0.25	0.19	-0.19

TABLE S-II. The activation and reaction energies across Cr-Cr, Cr-O sites for scheme S2

Step	E_a / eV				ΔG / eV			
	CrCr-S2		CrO-S2		CrCr-S2		CrO-S2	
	F	R	F	R	F	R	F	R
Ads	-0.37	0.37	-0.37	0.37	-0.37	0.37	-0.37	0.37
Suf	0.70	0.45	0.72	0.38	0.26	-0.26	0.34	-0.34
Diff	-0.45	0.45	-0.48	0.48	-0.45	0.45	-0.48	0.48
cra1	0.28	0.86	0.24	0.85	-0.58	0.58	-0.61	0.61
cra2	0.52	-0.52	0.58	-0.58	0.52	-0.52	0.58	-0.58
des	0.25	0.25	0.19	0.25	0.25	-0.25	0.19	-0.19

TABLE S-III. Free energies of the species computed

Species	Chemical formula	Symbols	H^o / eV	S^o / eV K^{-1}	G^o / eV
1st Dehy. CrCr	TS (C_3H_7*H)	TS11	3.1223	0.0017	2.6166
1st Dehy. CrO	TS (C_3H_7*H)	TS12	2.9888	0.0016	2.5210
1st Dehy. CrCr	TS (C_3H_7*H)	TS21	3.1213	0.0015	2.6845
1st Dehy. CrO	TS (C_3H_7*H)	TS22	3.1076	0.0014	2.6985
Cracking of propyl-1, CrCr	TS (C_2H_4*CH_3)	TScp1CrCr	2.7798	0.0016	2.2955
Cracking of propyl-1, CrO	TS (C_2H_4*CH_3)	TScp1CrO	2.7942	0.0015	2.3414
Cracking of propyl-2, CrCr	TS (C_2H_4*CH_3)	TScp2CrCr	2.8599	0.0016	2.3795
Cracking of propyl-2, CrO	TS (C_2H_4*CH_3)	TScp2CrO	2.7539	0.0012	2.3903
H Diff., CrO	TS (H*CH_3)	TS_Cat_Cr(M)O(H)_o	1.4611	0.0012	1.1083
Methane	CH_4	M	1.3356	0.0021	0.7112
Cracking of methyl, Cr	TS (H*CH_2)	TS_Cat_Cr(M)	1.3292	0.0008	1.0794
Cracking of methyl, O	TS (H*CH_2)	TS_Cat_O(M)	1.0145	0.0012	0.6684

TABLE S-IV. Free energies of the species computed (Note: "*" signifies that it is surface species)

Species	Chemical formula	Symbols	H^o / eV	S^o / eV K^{-1}	G^o / eV
Catalyst	Cr_2O_3	X	0.3390	0.00031	0.2450
Propane	C_3H_8	R	2.9814	0.0029	2.1062
Phys. Propane	*C_3H_8	RX	3.4571	0.0049	1.9828
Propyl-1&H, CrCr	$CH_3CH_2CH_2$**H	UHX11	3.2556	0.0033	2.2601
Propyl-1&H, CrO	$CH_3CH_2CH_2$**H	UHX12	3.3686	0.0034	2.3418
Propyl-2&H, CrCr	CH_3CH*CH_3H	UHX21	3.2461	0.0034	2.2392
Propyl-2&H, CrO	CH_3CH*CH_3*H	UHX22	3.3644	0.0035	2.3234
Hydrogen, Cr	*H	HX1	0.5841	0.0023	-0.1063
Hydrogen, O	*H	HX2	0.6949	0.0025	-0.0611
Propyl-1, CrCr	$CH_3CH_2CH_2$*	UX11	3.0783	0.0032	2.1216
Propyl-1, CrO	$CH_3CH_2CH_2$*	UX12	3.1534	0.0033	2.1625
Propyl-1, OCr	$CH_3CH_2CH_2$*	UX21	3.0740	0.0033	2.0991
Propyl-1, OO	$CH_3CH_2CH_2$*	UX22	3.1344	0.0033	2.1509
Hydrogen gas	H_2	H2	0.3661	0.0015	-0.0857
Ethylene	C_2H_4	ET	1.5018	0.0024	0.7760
Methyl, CrO	*CH_3	Cat_cr(M)_o	1.4670	0.0028	0.6443
Ethyliene, CrCr	*C_2H_4	Cat_Cr(Ey)Cr_o	1.9491	0.0028	1.1235
Ethyliene, CrO	*C_2H_4	Cat_O(Ey)Cr_o	1.9828	0.0028	1.1400
Methyl & H, OO	H*CH_3	Cat_O(M)O(H)_o	1.7226	0.0030	0.8273
Methyl & H, CrO	H*CH_3	Cat_Cr(M)O(H)_o	1.7482	0.0030	0.8671
H Diff., CrO	TS (H*CH_3)	TS_Cat_Cr(M)O(H)_o	1.4611	0.0012	1.1083
Methane	CH_4	M	1.3356	0.0021	0.7112
Methyliene, Cr	CH_2	Cat_Cr(My)Cr	1.1254	0.0027	0.3339
Methyliene, O	CH_2	Cat_O(My)Cr	1.1671	0.0027	0.3595