

Mechanistic and microkinetic study of non-oxidative methane coupling on a single-atom iron catalyst

Seok Ki Kim,^{1,2,*} Hyun Woo Kim,³ Seung Ju Han,¹ Sung Woo Lee,¹ Jungho Shin,³ Yong Tae Kim^{1,*}

¹ C1 Gas & Carbon Convergent Research Center, Korea Research Institute of Chemical Technology, Daejeon 34114, Republic of Korea

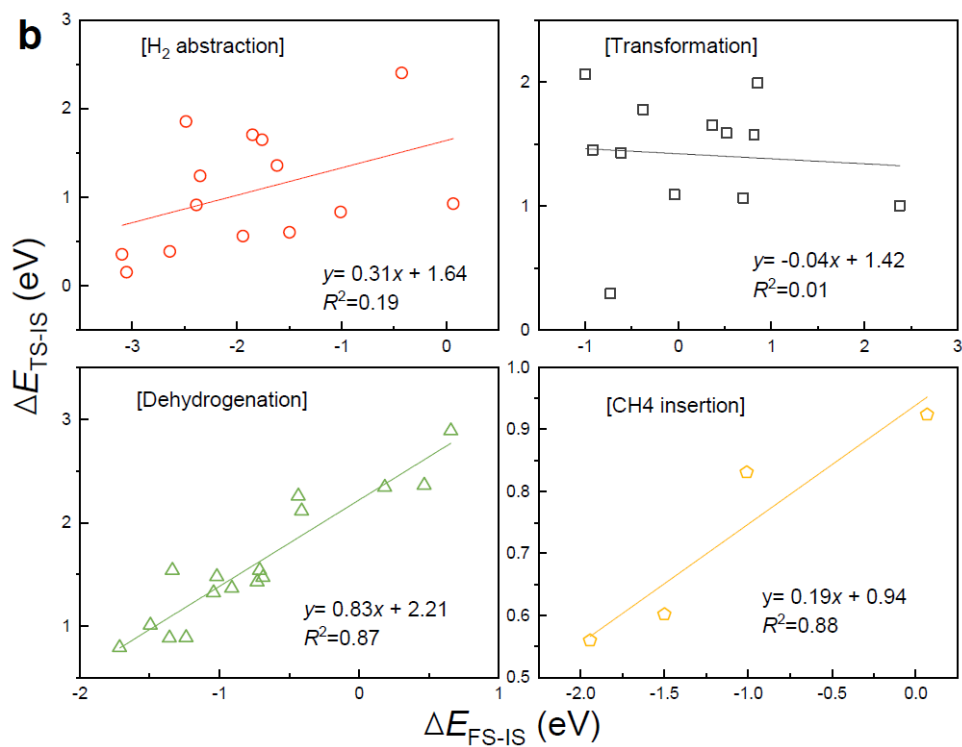
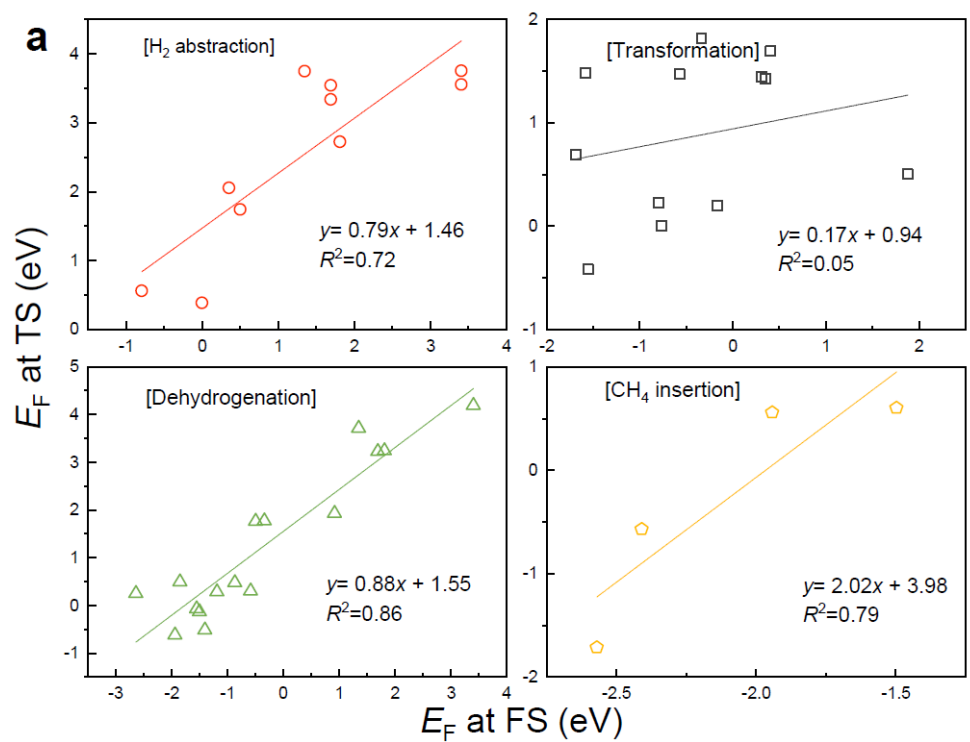
² Advanced Materials and Chemical Engineering, University of Science and Technology, Daejeon 34113, Republic of Korea

³ Chemical Data-Driven Research Center, Korea Research Institute of Chemical Technology, Daejeon 34114, Republic of Korea

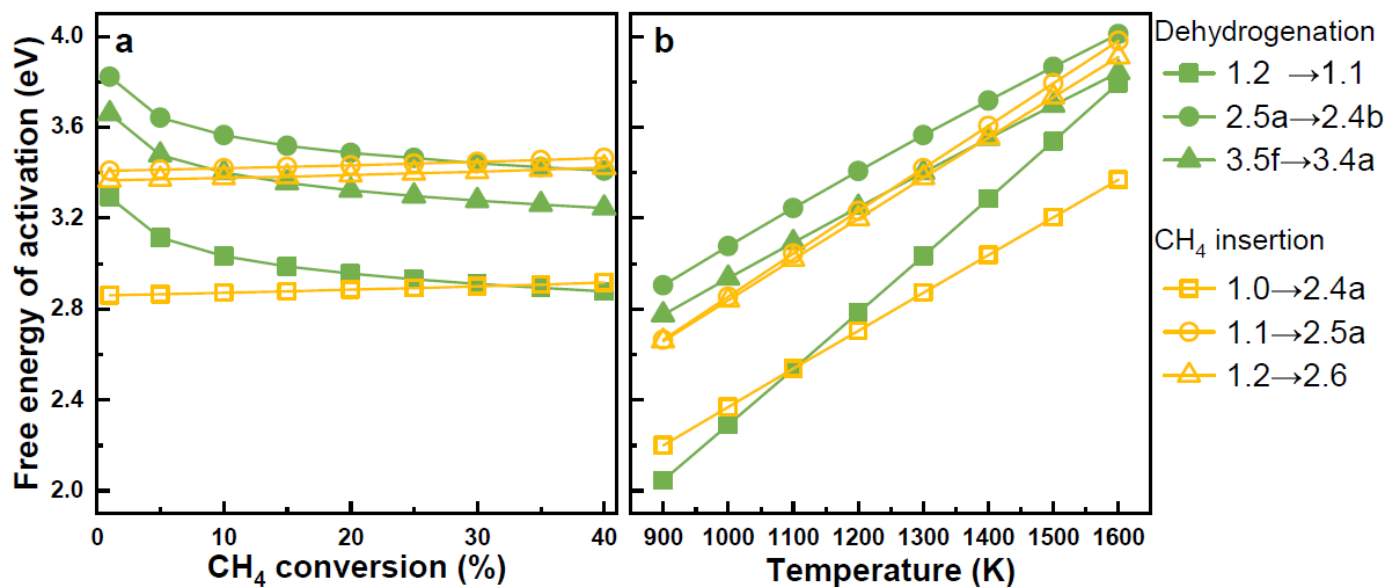
*Corresponding authors: skkim726@kriict.re.kr, ytkim@kriict.re.kr

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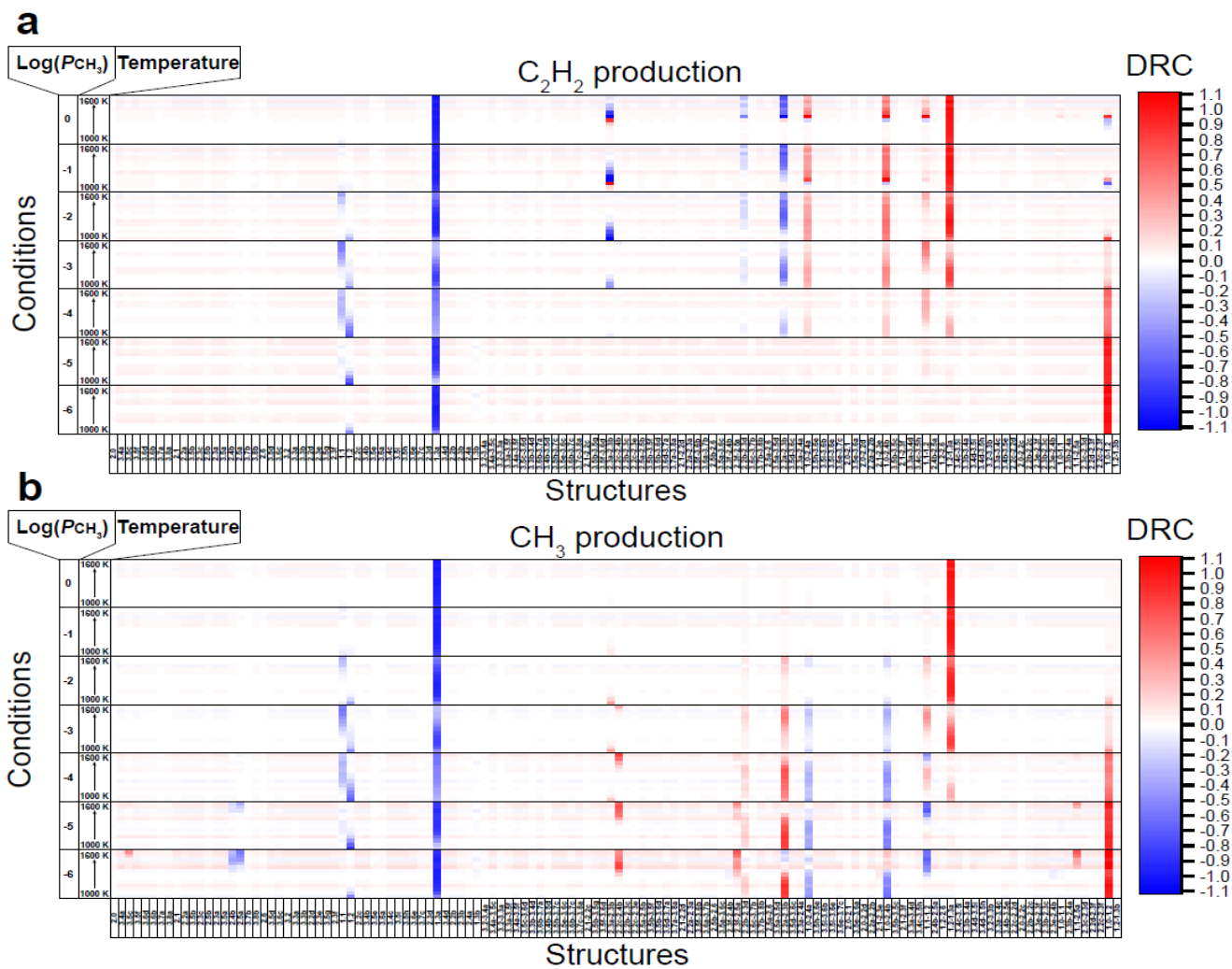
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Supplementary Figure 1. a, Transition-state scaling with formation energy at final state (E_F at FS). **b**, Brønsted-Evans-Polanyi (BEP) relation.



Supplementary Figure 2. Change in free energies of activation for dehydrogenation and CH₄ insertion reactions. a, Effect of CH₄ conversion at 1300 K and 1 bar. **b,** Effect of reaction temperature at CH₄ conversion of 10% and 1 bar. CH₄ was assumed to be converted to CH₃ and 1/2 H₂.



Supplementary Figure 3. Degree of rate control calculated for all states calculated under different reaction conditions. **a**, DRC values for the production of C_2H_2 . **b**, DRC values for the production of CH_3 .

Supplementary Table 1. Hydrocarbon distributions obtained using the Fe@CRS catalyst under various reaction conditions.

$t_{\text{gas}}^{\text{a}}$ (s)	$t_{\text{cat}}^{\text{b}}$ (s)	X^{c} (%)	Selectivity (%)										
			C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃	C ₄	C ₅	C ₆ H ₆	C ₇ H ₈	C ₁₀ H ₈	Alkyl benzenes	Coke
1.7	0.0	1.0	20.0	38.4	8.9	8.0	9.5	1.8	2.0	0.0	0.0	3.1	8.3
2.3	0.0	1.8	13.1	34.5	12.0	7.9	12.8	2.8	6.0	1.4	0.9	3.2	5.4
2.8	0.0	2.9	9.6	32.3	14.8	7.6	12.7	2.8	11.6	2.9	3.2	2.4	0.0
11.3	0.0	24.3	1.0	15.9	11.3	1.2	1.1	0.5	22.4	1.7	11.4	3.3	30.3
1.8	0.0	4.7	6.0	28.1	16.9	6.1	9.5	2.1	9.9	2.3	2.2	3.8	13.0
2.4	0.1	7.3	3.9	23.6	17.3	4.5	1.8	1.8	12.5	2.7	3.7	3.8	24.5
11.7	0.3	26.6	0.8	14.9	11.4	1.0	1.0	0.5	19.0	1.3	5.9	2.5	41.8
40.4	1.1	42.3	0.8	9.1	4.6	0.3	0.2	0.1	13.1	0.4	5.5	1.0	64.9
1.8	0.1	6.5	4.4	26.9	18.7	5.0	7.6	1.6	11.8	2.5	3.3	2.8	15.3
2.4	0.1	9.5	2.8	22.1	18.1	3.6	5.2	1.4	12.8	2.4	4.3	3.1	24.2
3.0	0.2	11.0	2.3	21.3	18.5	3.3	4.5	1.2	15.3	2.6	5.5	3.9	21.5
12.0	0.6	27.2	0.8	14.2	11.0	0.9	0.8	0.3	16.5	1.1	4.7	2.0	47.6
41.5	2.1	41.5	0.8	9.5	4.7	0.3	0.2	0.1	12.5	0.4	4.9	1.0	65.6
2.2	0.2	7.9	3.4	24.6	18.0	4.4	6.2	0.0	10.1	2.1	2.5	5.3	23.4
2.9	0.3	10.6	2.2	20.4	17.1	3.2	4.5	0.0	10.4	1.8	3.0	4.5	32.9
3.7	0.3	12.2	2.0	19.3	17.4	2.8	3.8	0.0	11.9	1.9	4.0	3.8	33.2
14.6	1.2	26.3	0.8	13.8	11.3	1.0	0.9	0.0	13.4	0.9	4.5	2.1	51.5
50.5	4.3	40.4	0.8	10.0	5.1	0.3	0.2	0.0	11.2	0.4	4.1	1.1	66.8

^a Gas-phase residence time

^b Catalyst contact time

^c Methane conversion