Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Quantum chemistry of the Fischer-Tropsch reaction catalysed by a stepped Ruthenium surface

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Table S1: Top view of the initial, transition and final states of the calculated reactions. The number of the reaction refer to the numbers as provided in the Table 1, 2 and 3 in the main article.

1. $CO + * \rightarrow C* + O*$		
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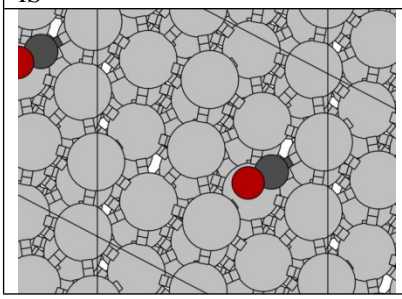	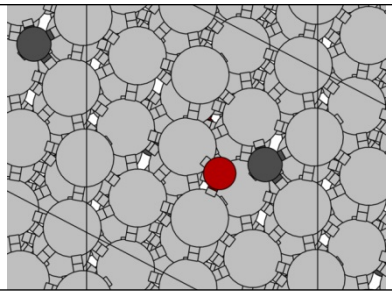	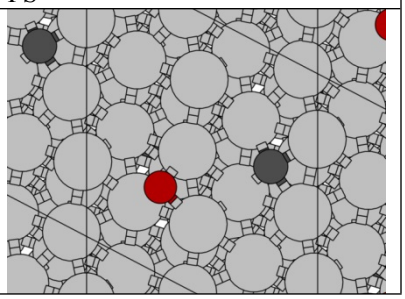

2. $C* + H* \rightarrow CH* + *$		
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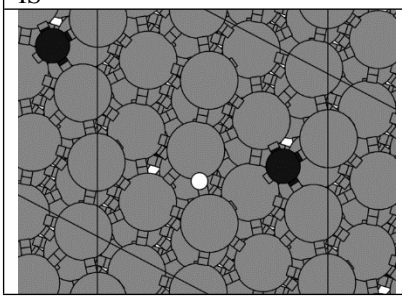	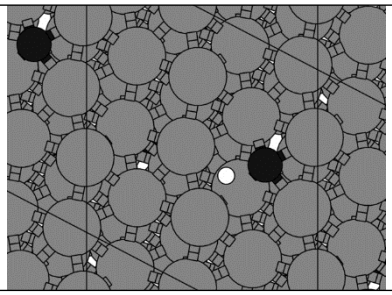	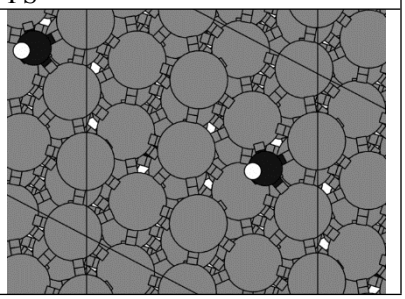

3. $CH* + H* \rightarrow CH_2* + H*$		
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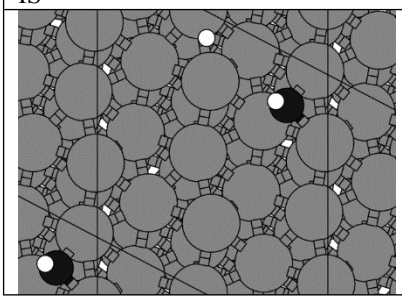	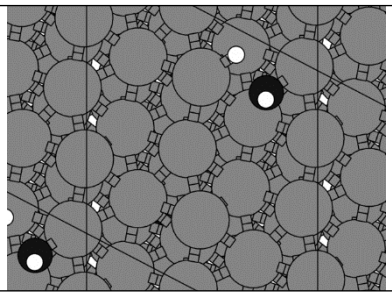	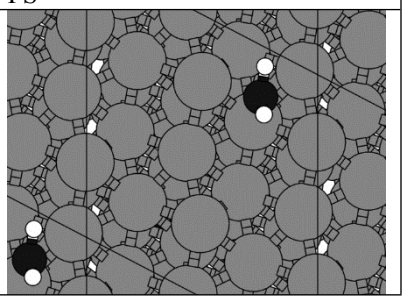

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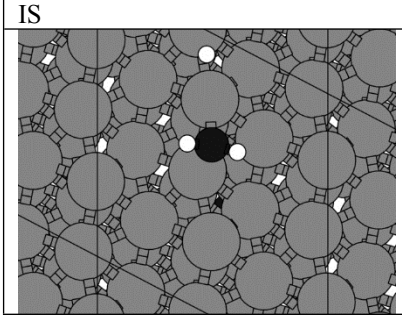	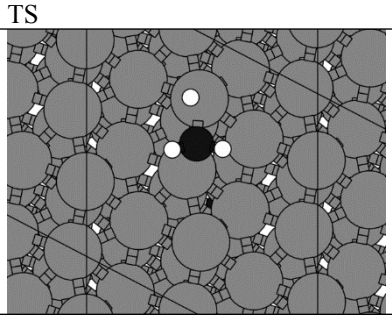	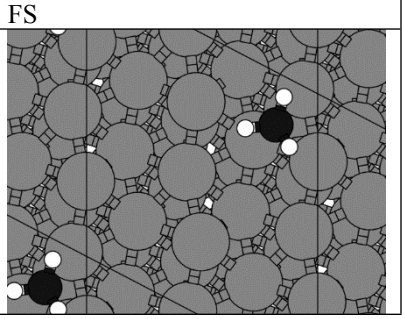

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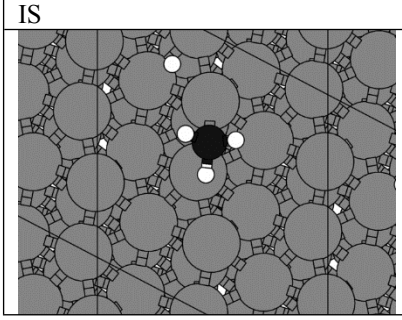	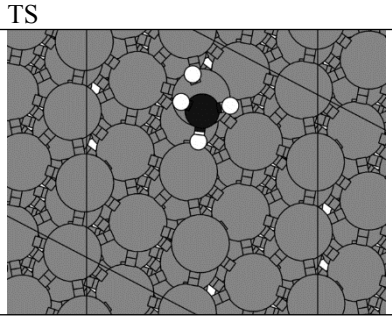	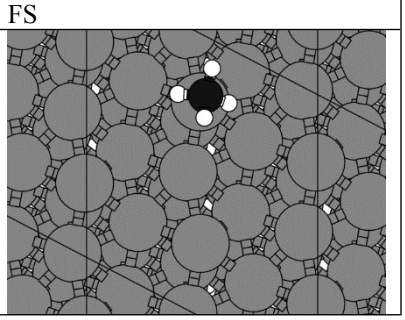

6. C*+C* → CC* + *		
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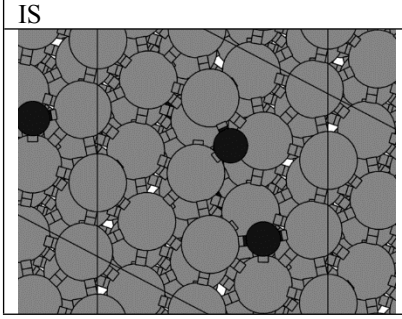	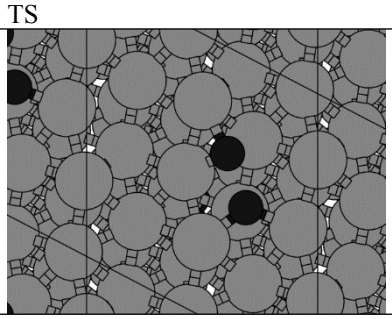	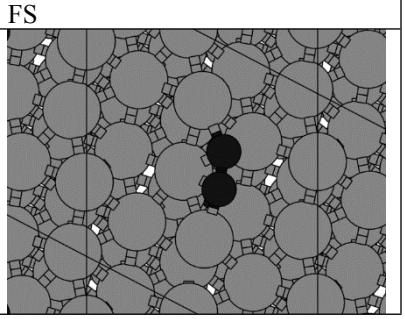

7. C* + CH* → CCH* + *		
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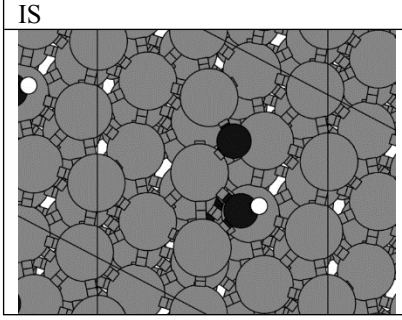	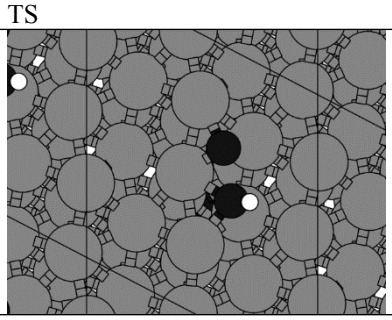	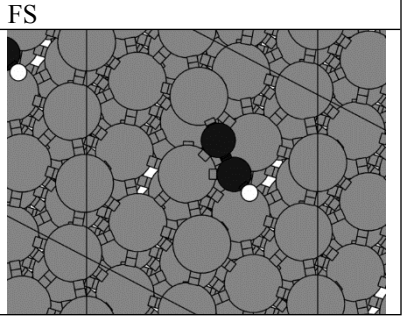

9. C* + CH_3* → CCH_3* + *		
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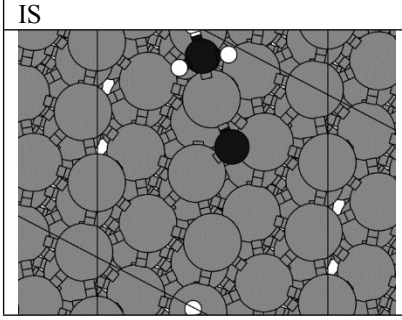	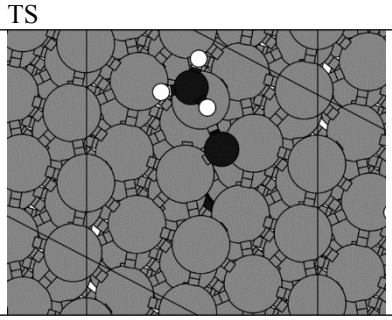	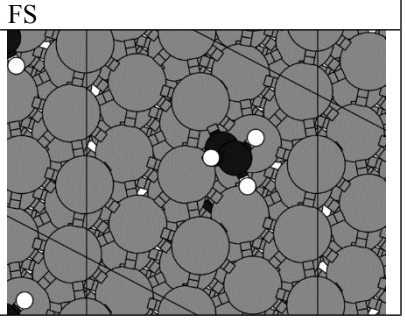

10a. CH* + CH* → CHCH* + * (terrace)

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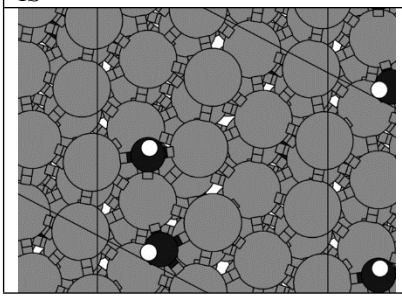	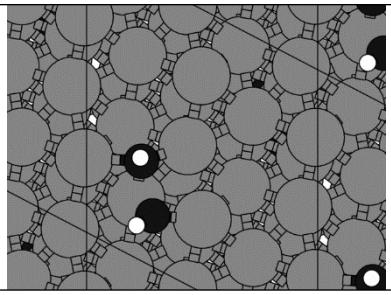	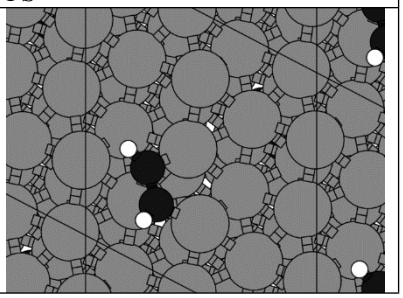

10b. CH* + CH* → CHCH* + * (step)

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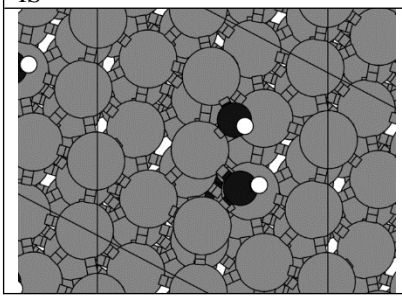	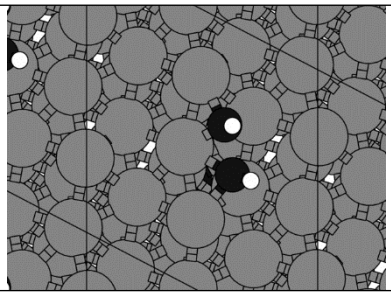	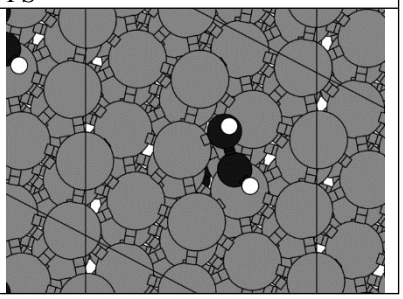

13. CH_2* + CH_2* → CH_2CH_2* + *

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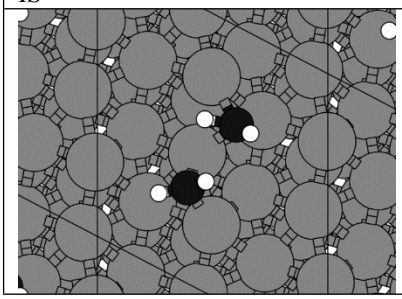	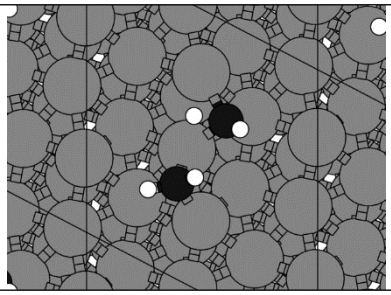	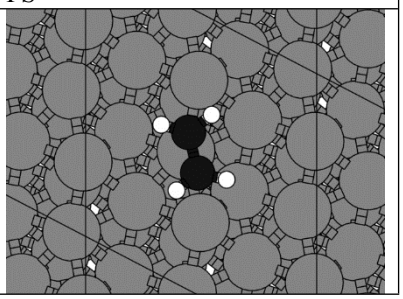

16. CC* + H* → CCH* + *

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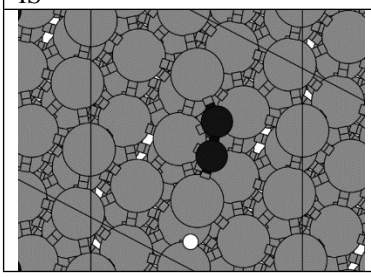	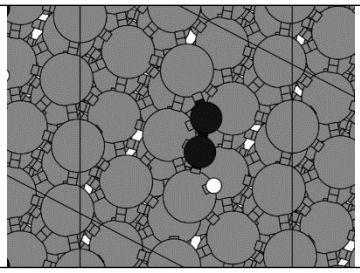	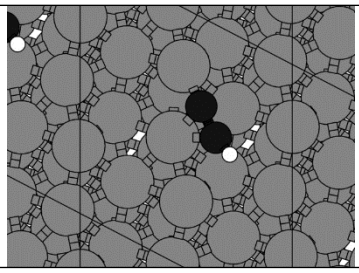

17. $CCH^* + H^* \rightarrow CCH_2^* + *$

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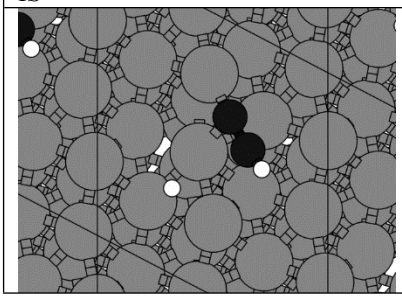	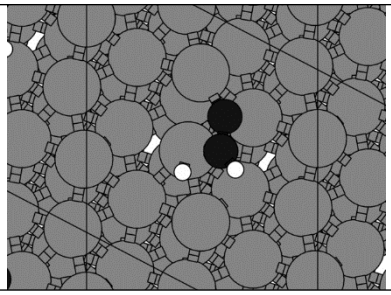	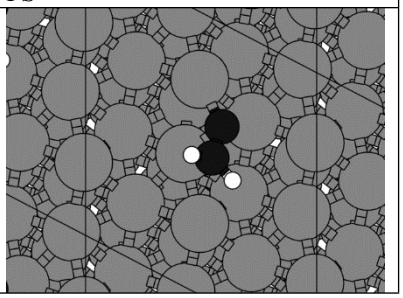

18. $CCH_2^* + H^* \rightarrow CCH_3^* + *$

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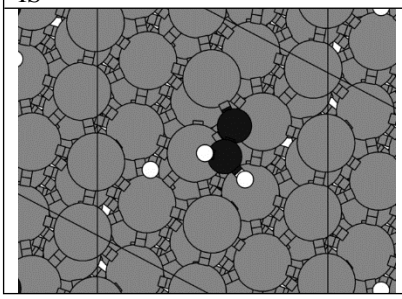	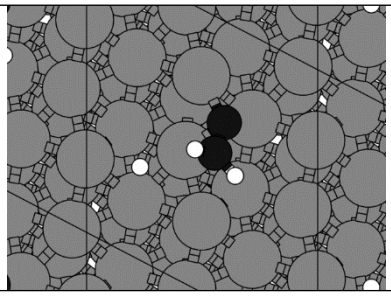	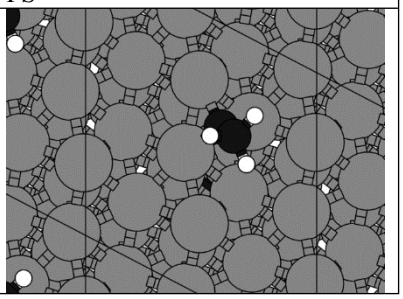

19. $CHCH^* + H^* \rightarrow CHCH_2^* + *$

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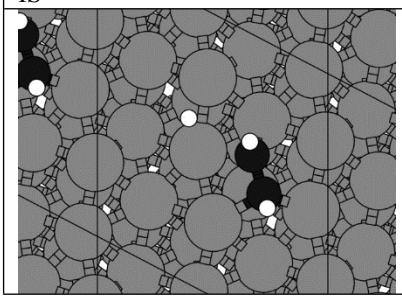	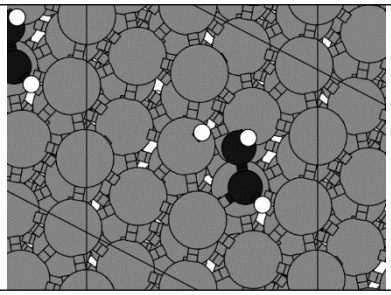	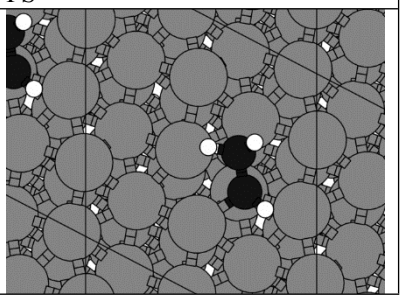

20. $CHCH_2^* + H^* \rightarrow CHCH_3^* + *$

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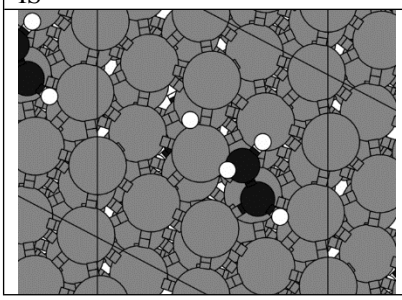
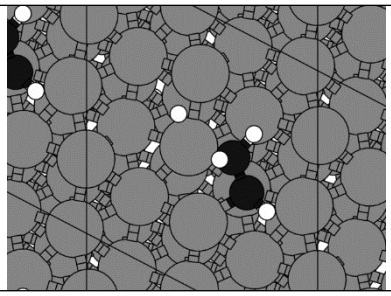
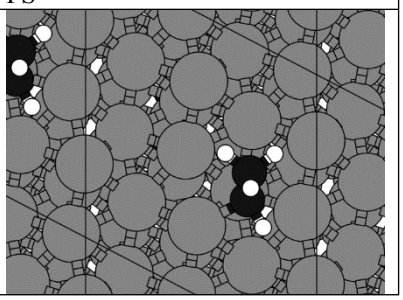
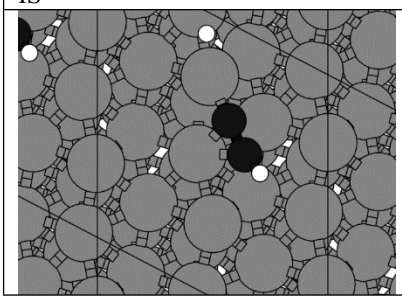
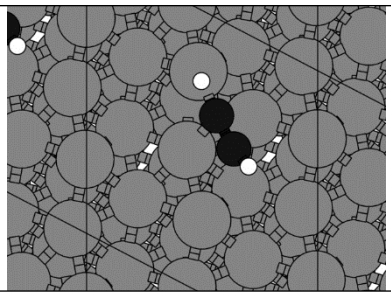
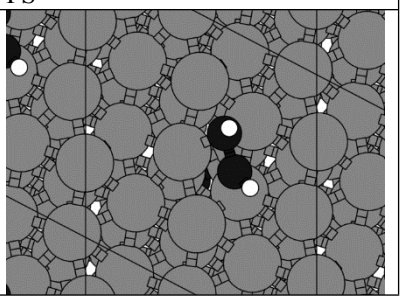
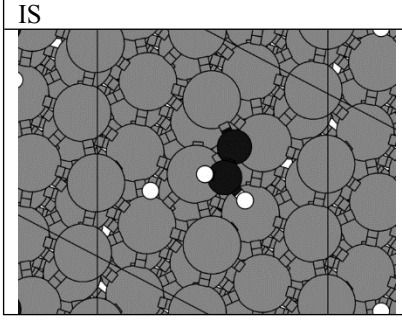
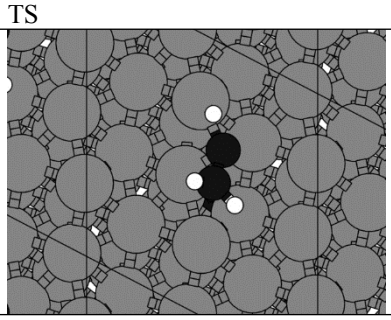
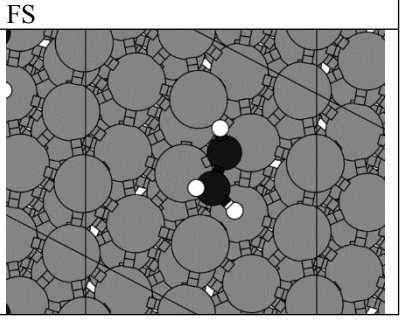
		

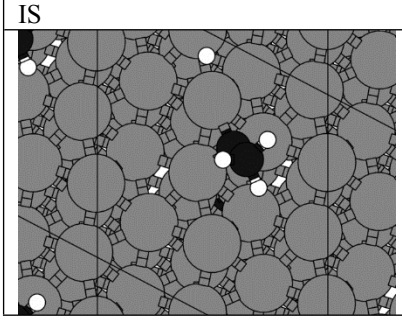
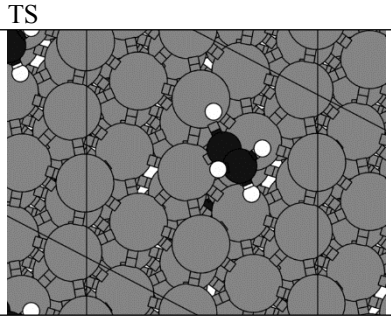
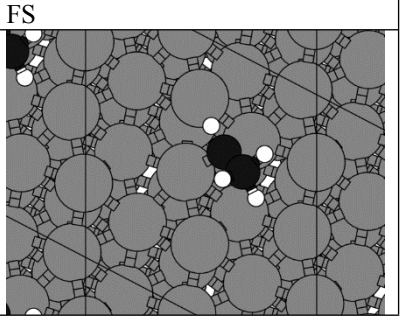
21. $CCH^* + H^* \rightarrow CHCH^* + *$

IS	TS	FS
		

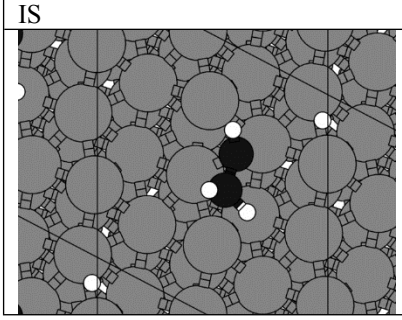
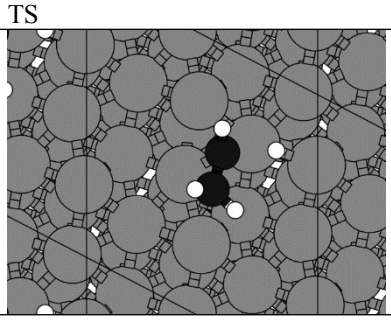
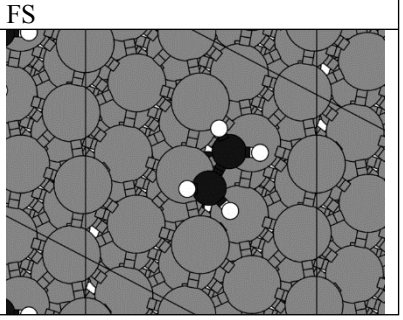
22. $CCH_2^* + H^* \rightarrow CHCH_2^* + *$

IS	TS	FS
		

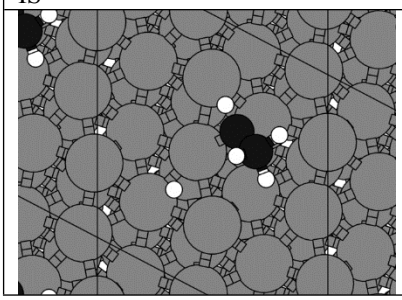
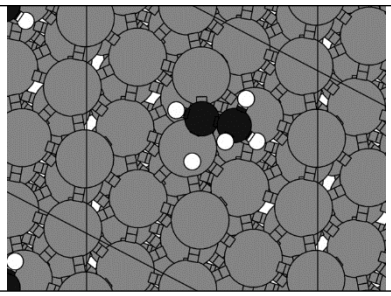
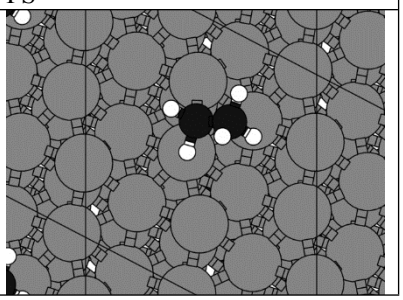
23. $CCH_3^* + H^* \rightarrow CHCH_3^* + *$

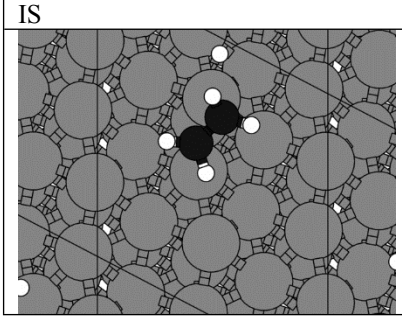
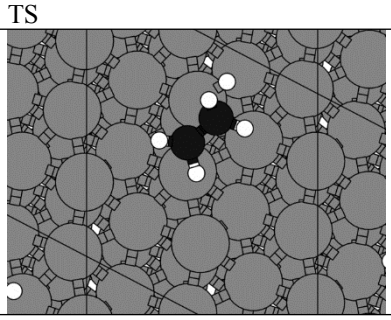
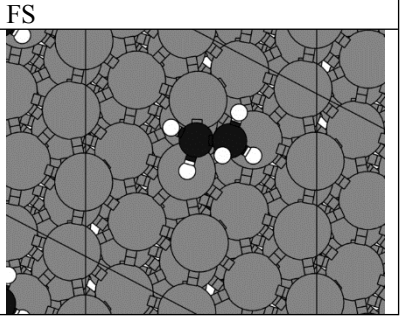
IS	TS	FS
		

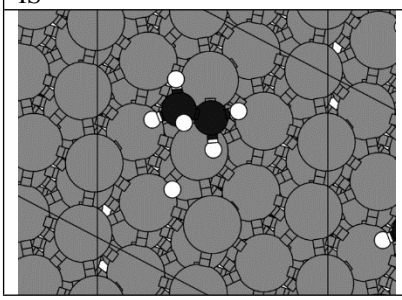
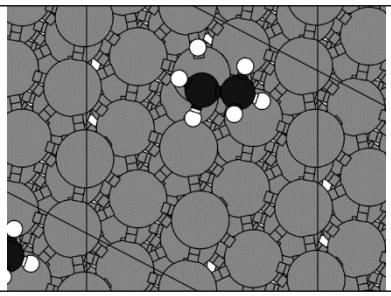
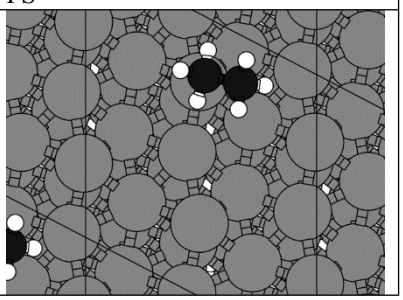
24. $CHCH_2^* + H^* \rightarrow CH_2CH_2^* + *$

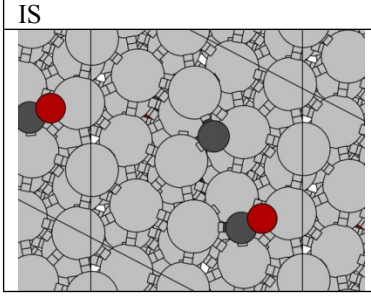
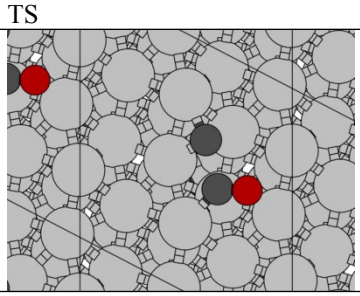
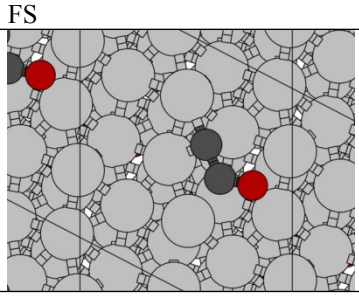
IS	TS	FS
		

25. $CHCH_3^* + H^* \rightarrow CH_2CH_3^* + *$

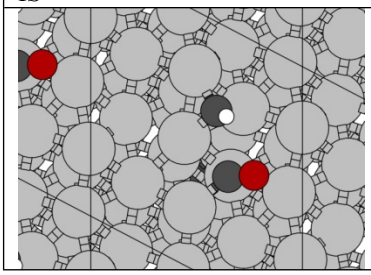
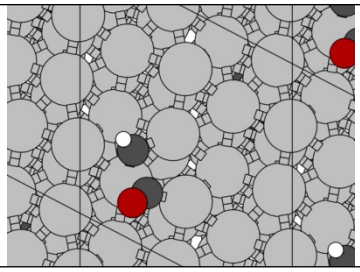
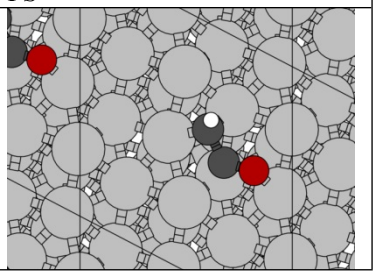
IS	TS	FS
		

26. CH_2CH_2* + H* → CH_2CH_3* + *		
IS	TS	FS
		

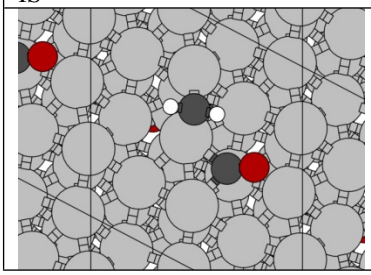
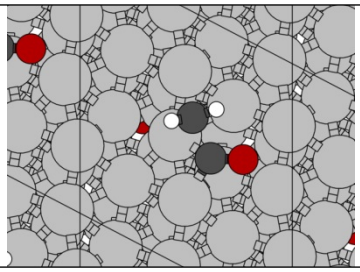
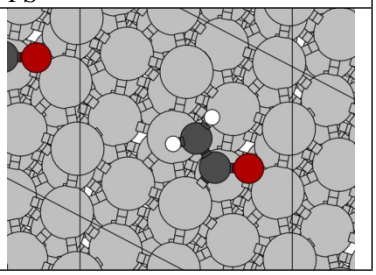
27. CH_2CH_3* + H* → CH_3CH_3* + *		
IS	TS	FS
		

28. C* + CO* → CCO* + *		
IS	TS	FS
		

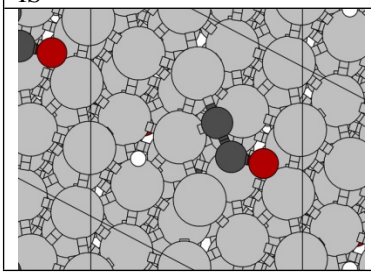
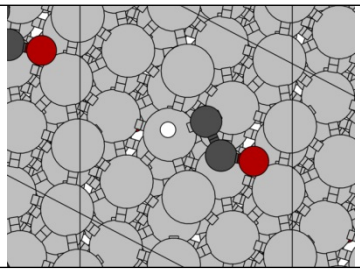
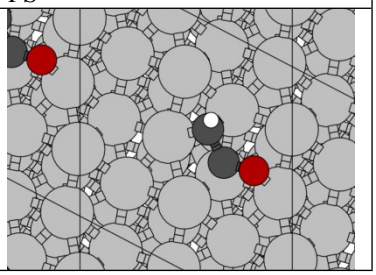
29. CH* + CO* → CHCO* + *

IS	TS	FS
		

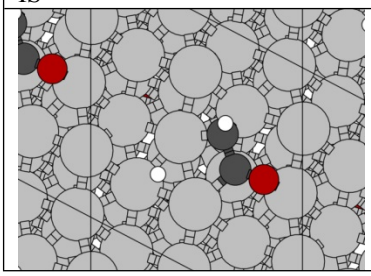
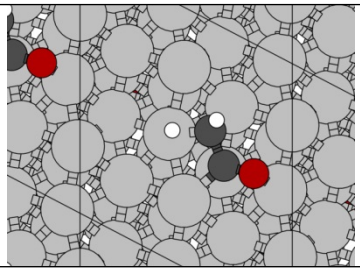
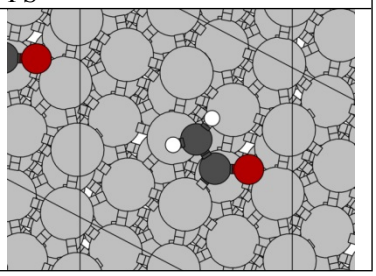
30. CH_2* + CO* → CH_2CO* + *

IS	TS	FS
		

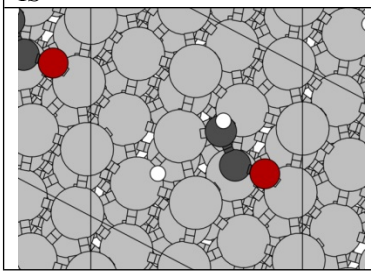
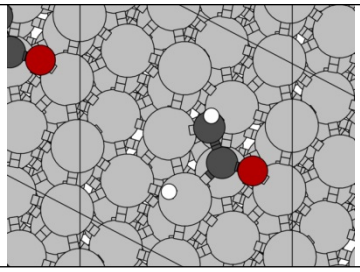
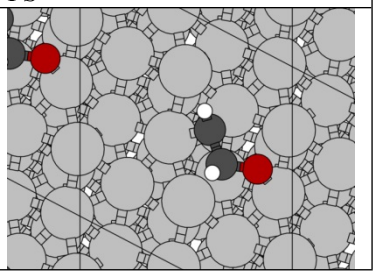
32. CCO* + H* → CHCHO* + *

IS	TS	FS
		

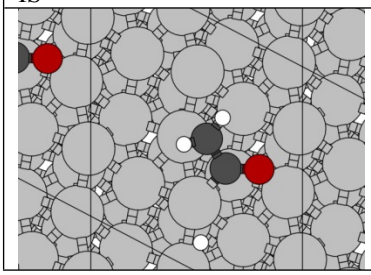
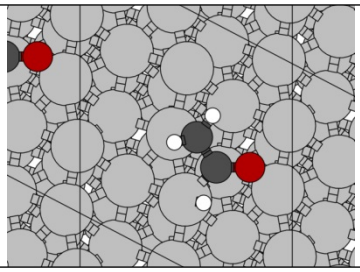
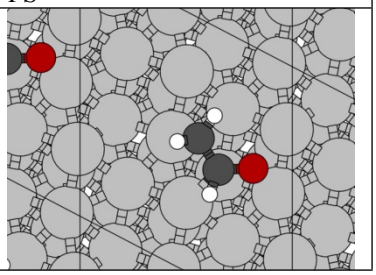
34. CHCO* + H* → CH_2CHO* + *

IS	TS	FS
		

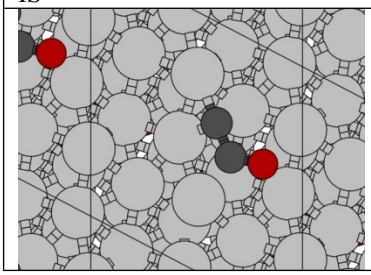
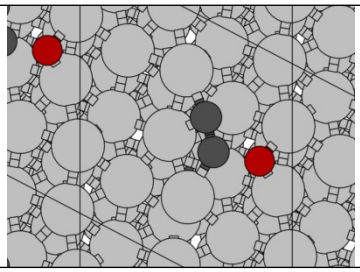
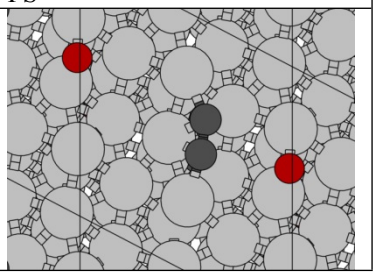
35. CHCO* + H* → CHCHO* + *

IS	TS	FS
		

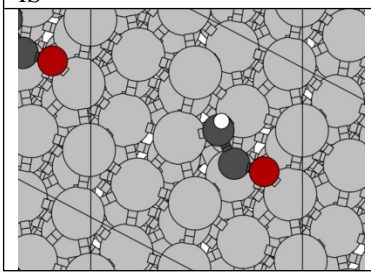
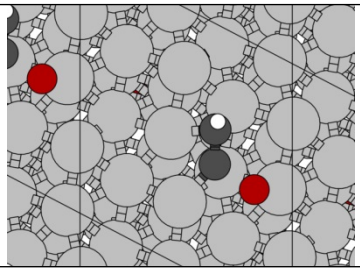
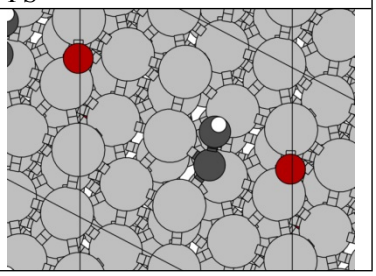
36. $CH_2CO^* + H^* \rightarrow CH_2CHO^* + *$

IS	TS	FS
		

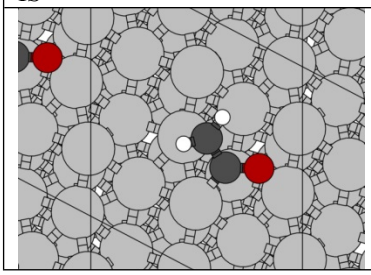
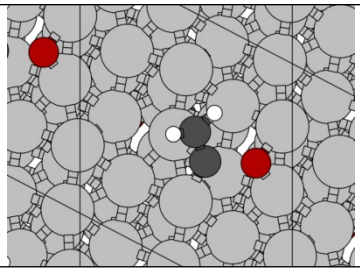
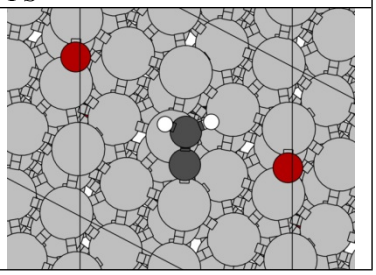
37. CCO* + * → CC* + O*

IS	TS	FS
		

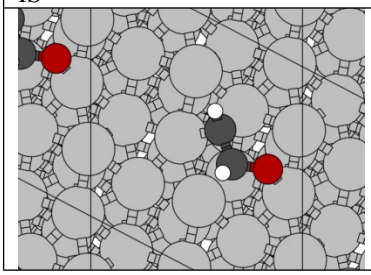
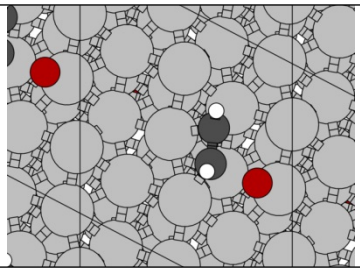
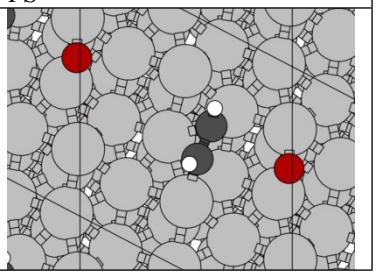
38. CHCO* + * → CCH* + O*

IS	TS	FS
		

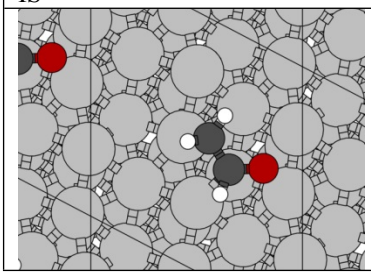
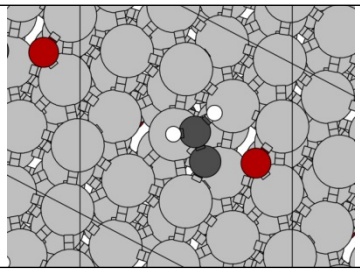
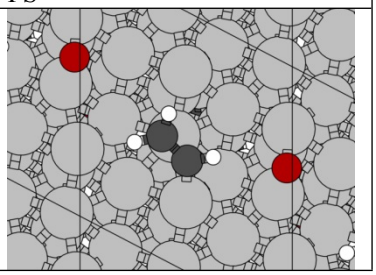
39. $CH_2CO^* + * \rightarrow CH_2C + O^*$

IS	TS	FS
		

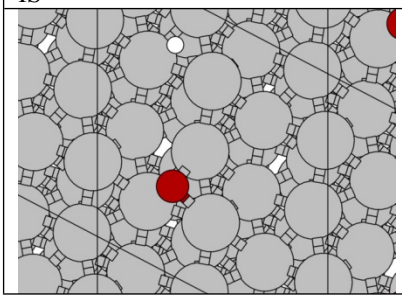
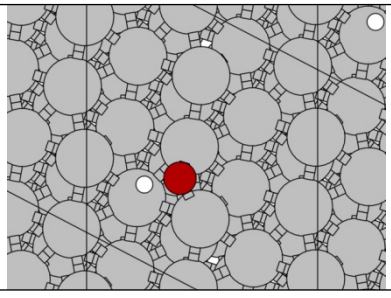
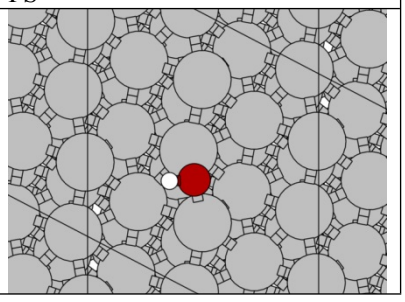
40. $CHCHO^* + * \rightarrow CHCH^* + O^*$

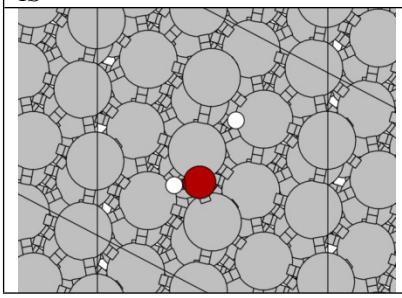
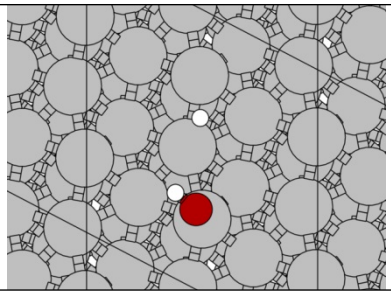
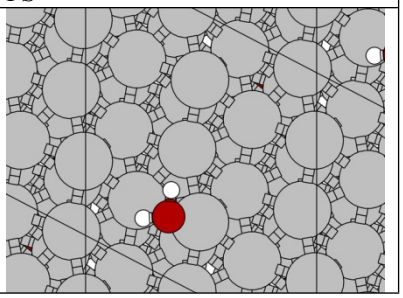
IS	TS	FS
		

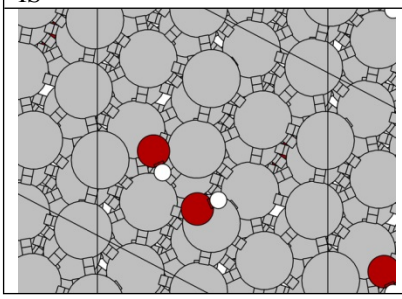
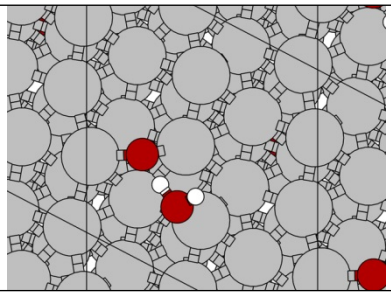
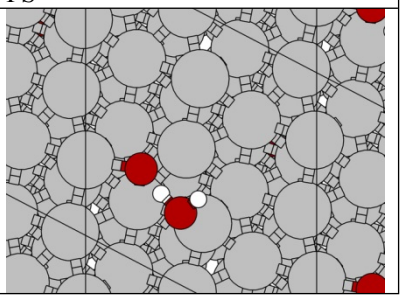
41. $CH_2CHO^* + * \rightarrow CH_2CH^* + O^*$

IS	TS	FS
		

42. $O^* + H^* \rightarrow OH^* + *$

IS	TS	FS
		

43. $OH^* + H^* \rightarrow H_2O^* + *$		
IS	TS	FS
		

44. $OH^* + OH^* \rightarrow H_2O^* + O^*$		
IS	TS	FS
		

Derivation of formula 2 and 3

Considering the following approximations:

- C_1 species are generated from direct CO dissociation. Upon dissociation of CO, C and O will occupy two different sites and oxygen is assumed to be removed from the surface at a very fast pace as compared to the other reaction steps.
- A single type of C_n species is assumed (n>0) that will serve as the C_n intermediate.

The rate of C_n generation is then:

$$\frac{\mathrm{d}}{\mathrm{d}t}\theta_{C_n} = -k_{\mathrm{t}}\theta_{C_n} + k_{n-1\to n}\theta_{C_1}\theta_{C_{n-1}} - k_{n\to n+1}\theta_{C_1}\theta_{C_n} \qquad \text{* MERGEFORMAT (1.1)}$$

where θ_{C_1} is the surface concentration of C_1 species, θ_{C_n} is the surface concentration of C_n species, $k_{n-1\to n}$ is the rate of C-C coupling to C_n, $k_{n\to n+1}$ the rate of C-C coupling to C_{n+1} and k_{t} the rate of chain-termination by hydrogenation to the alkene or the alkane.

Under steady-state conditions, this yields:

$$\theta_{C_n} = \frac{k_{n-1\to n}\theta_{C_1}\theta_{C_{n-1}}}{k_{n\to n+1}\theta_{C_1} + k_{\mathrm{t}}} \qquad \text{* MERGEFORMAT (1.2)}$$

Given the definition of the chain-growth probability as

$$\alpha_n = \frac{\theta_{C_n}}{\theta_{C_{n-1}}} \qquad \text{* MERGEFORMAT (1.3)}$$

we obtain the following expression

$$\alpha_n = \frac{k_{n-1\to n}\theta_{C_1}}{k_{n\to n+1}\theta_{C_1} + k_{\mathrm{t}}} \qquad \text{* MERGEFORMAT (1.4)}$$

Assuming that all the coupling rates are independent of chain length, this generalizes to:

$$\alpha = \frac{k_p \theta_{C_1}}{k_p \theta_{C_1} + r_t} \qquad \text{* MERGEFORMAT (1.5)}$$

For the CO insertion mechanism, the exact same formula is obtained under the assumption that the rate of CH_xC-O bond scission is very fast. From our DFT calculations it was found that this is the case.