Electronic Supplementary Material (ESI) for Chemical Communications

Site Regeneration in the Fischer-Tropsch Reaction: A Synchronized CO Dissociation and C—C Coupling Pathway

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1. Computational Details

DFT calculations were performed by the VASP code.[S1] The electronic ground state is calculated by solving the Kohn-Sham equation based on density functional theory. The cut-off energy used for the plane waves is 400 eV. The exchange-correlation functional is expressed by the generalized-gradient approximation (GGA) using the PAW potentials with PBE functionals (PAW-PBE).[S1,S2] *k*-points sampling was generated by the Monkhorst-Pack procedure with a 5×5×1 mesh. In the calculations all the degrees of freedom of the systems have been optimized using the conjugate-gradient technique. The reaction paths have been generated by the nudged elastic band (NEB) as implemented in VASP.[S3] During NEB calculations all the atoms of the images including the transition states have been relaxed. The transition states have been confirmed by the saddle points obtained from the frequency calculations.

2. Model

The optimized Ru$(11\bar{2}1)$ surface is shown in Fig. 1 and was modeled using a 2×2 super-cell. The Ru$(11\bar{2}1)$ surface is modeled with 12 layers slab and 18 layers of vacuum. The same models were also used in our earlier studies.[S4,S5] For a detailed description on the surface models and the CO dissociation reaction on Ru$(11\bar{2}1)$ surfaces we refer to our recent work.[S5] The dipole-dipole interaction between the super-cells has been avoided by adsorption on both sides of the surface retaining a center of inversion. The coverage of the adsorbents is maintained at 25%.

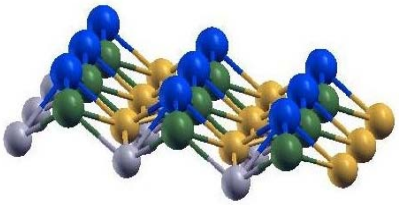

Figure 1. The four layers of the Ru$(11\bar{2}1)$ surface are shown in blue (first layer), green (second layer), yellow(third layer) and grey (fourth layer).[S4,S5]

Table 1. Bond lengths of CH and CO in the transition state involved in the reaction on Ru$(11\bar{2}1)$ surface shown in Figure 1 of the manuscript.

Reactions	C—H (Å)	C—O (Å)
C + H → CH	1.38[a]	-
CH + CO → CH + C + O	-	1.91

[a]Data from reference S6.

Table 2. Bond lengths of CH, C—C and CO in the transition state involved in the reaction on Ru$(11\bar{2}1)$ surface shown in Figure 2 of the main manuscript.

Reactions	C—H (Å)	C—O (Å)	C—C (Å)
CH + C+ H → CH + CH	1.40	-	-
CH+CH → CH—CH	-	-	1.64
CH—CH + CO → CH—CH + C + O	-	1.92	
CH—CH + H → CH—CH_2	1.41	-	-
CH—CH_2 + CO → CH—CH_2 + C + O	-	1.88	-

Table 3. Adsorption energy (E_{ads}) of CH_x adsorbates with respect to CH_4 in the gas phase and the zero-point energy (ZPE) corrections on the Ru$(11\bar{2}1)$ surface (all energies in kJ/mol).

Adsorbate	E_{ads}	ZPE	ZPE from Ref. S7
CH	-100	35	37
CH_2	-65	60	62
CH_3	-63	88	82
CH_4	-9	191	-

Table 4. Energy barriers for the forward (E_{forw}) and reverse (E_{back}) reaction of the CH_x species (x = 0-3) on the Ru$(11\bar{2}1)$ surface (all energies in kJ/mol).

Reaction	E_{forw}	E_{back}
C + H → CH	85	72
CH + H → CH_2	83	48
CH_2 + H → CH_3	34	32
CH_3 + H → CH_4	90	36

Table 5. Adsorption energy (E_{ads}) of CO and forward (E_f) and backward (E_b) activation energies of CO dissociation with and without co-adsorbed species (all energies in kJ/mol).

Reaction	E_{ads}	E_{forw}	E_{back}
CO → C + O	-162	65	86
CH + CO → CH + C + O	-142	70	95
CH—CH + CO → CH—CH + C + O	-157	62	92
CH—CH_2 + CO → CH—CH_2 + C + O	-156	63	97

Table 6: Forward (E_{forw}) and backward (E_{back}) energy barriers of C hydrogenation and CH_x—CH_x coupling on Ru(1121) surface (all energies in kJ/mol).

Reactions	E_{forw}	E_{back}
CH + C + H → CH + CH	88	71
CH + CH → CH—CH	44	33
CH + C → CH—C	142	186
CH—CH + H → CH—CH_2	78	12

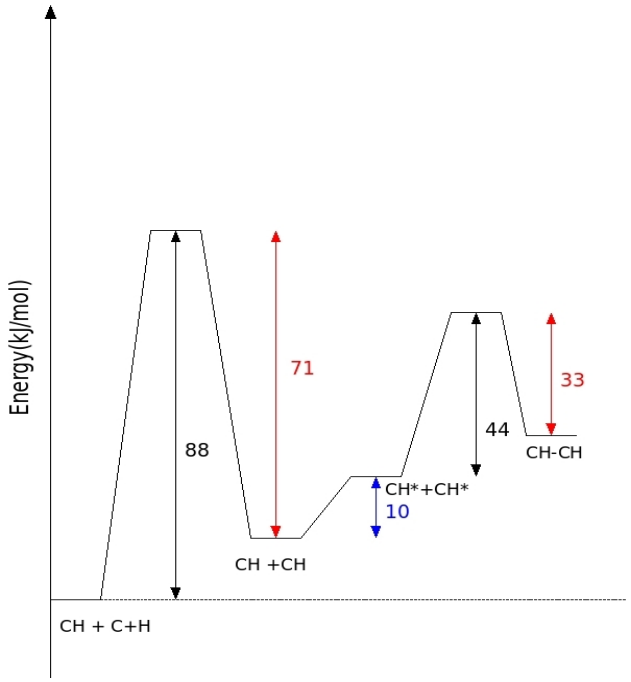

Figure 2. Reaction path for C hydrogenation and CH—CH coupling reaction. Black and red lines correspond to the forward and reverse barriers respectively. Blue line corresponds to the reaction energy for the diffusion of CH intermediates. CH* + CH* correspond to the diffused state.

References

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