# Supporting information for: Hydrogen-assisted CO dissociation on a Co step site

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## Computational details

All the calculations in this study were performed using the Vienna ab initio simulation package (VASP).[1,2] This code uses periodic DFT with a plane wave basis set and pseudopotentials. The generalized gradient approximation (GGA) with the Perdew and Wang exchange-correlation functional[3] was used. The electron distribution at the Fermi level was modelled by Methfessel and Paxton smearing[4] with $\sigma = 0.2$ eV. A 10 layer slab was used for the Co(211) surface. Ultrasoft pseudopotentials were used in all calculations. The surface is represented by using p($1 \times 2$) surface unitcell. The optimized model has a 10 Å vacuum layer between the two surfaces of the slab. Apart from the constrained bottom three layers of the slab, all the atoms in the configurations were allowed to relax. The k-point sampling was generated by following the Monkhorst-Pack[5] procedure

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with a $6\times7\times1$ mesh for the Co(211) surface. The plane wave basis set cutoff energy was set to 400 eV.

By fitting the energies of a series of bulk Co cells to the Birch-Murnaghan equation of state[6,7] we obtained the equilibrium lattice constant and bulk modulus. For bulk FCC-Co a lattice parameter of 3.538 Å was obtained. This structure has a bulk modulus of 202 GPa and a magnetic moment of 1.67 $\mu_B$ per Co atom. These values are in good agreement with the experimental values of bulk FCC-Co (3.550 Å,[8] 191 GPa[9] and 1.70 $\mu_B$[10] respectively).

The adsorption of the considered species was done on a single side of the Co surface slabs. Dipole corrections have been applied in the calculations to avoid artificial dipole effects. The VASP implementation of the nudged elastic band (NEB) method[11] was used to locate transition states.

## Partial Hessian vibrational analysis

Partial Hessian vibrational analysis was performed on the calculated structures. Perturbations of 0.01 Å in Cartesian space were used. From these calculations we obtained the vibrational frequencies ($\nu_i$) within the harmonic approximation. From these frequencies the vibrational zero-point energy was calculated:

$$E_{ZPVE} = \frac{1}{2}\sum_i h\nu_i \tag{1}$$

The resulting zero-point vibrational corrections were included in the reported energies. The vibrational frequencies of structures in the direct CO dissociation pathways on Co(211) can be seen in Table 2 and Table 3. The frequencies for the considered hydrogen-assisted pathways can be seen in Table 4 and Table 5.

# Simple kinetic analysis

Assuming that the reactions of direct CO dissociation and the hydrogen-assisted pathways are localised at the step sites, and that these reactions are non-reversible and rate limiting in the Fischer-Tropsch synthesis (FTS) reaction, it is possible to set up simple rate equation estimates using the calculated barriers and vibrational frequencies of non-interacting adsorbed H and CO. The values for the reaction temperature and surface coverages of hydrogen and CO were obtained from the experimental SSITKA work by Den Breejen et al.[12] for Co particles with diameters larger than 6 nm.

For direct CO dissociation the FTS turnover frequency (TOF) can be estimated by:

$$r_{CO} = \frac{k_B T}{h} \frac{q_{TS}}{q_{CO}} e^{\frac{-E_a}{RT}} \theta_{CO} \qquad (2)$$

with $k_B$ being the Boltzmann constant, $T$ the reaction temperature, $h$ the Planck constant, $q_{TS}$ the vibrational partition function of the transition state, $q_{CO}$ the vibrational partition function of adsorbed CO, $E_a$ the overall activation energy, $R$ the molar gas constant and $\theta_{CO}$ the coverage of adsorbed CO.

Simlarly the FTS TOF proceeding via the HCO pathway can be estimated by

$$r_{HCO} = \frac{k_B T}{h} \frac{q_{TS}}{q_{CO} q_H} e^{\frac{-E_a}{RT}} \theta_{CO} \theta_H \qquad (3)$$

with $q_H$ the vibrational partition function of adsorbed H and $\theta_H$ the coverage of adsorbed hydrogen.

Using the overal barrier value of 207 kJ.mol$^{-1}$ proposed in literature for the Co(0001) surface[13] we can compare the rate of hydrogen-assisted CO dissociation on the Co(0001) surface to that of the Co(211) surface. The FTS TOF proceeding via the HCO pathway on the Co(0001) surface can be estimated by

$$r_{0001} = \frac{k_B T}{h} \frac{q_{TS}}{q_{CO} q_H} e^{\frac{-E_a}{RT}} \theta_{CO} \theta_H \qquad (4)$$

Since the vibrational frequencies of the species shown in literature are not given, we use a partition

function ratio of 1 which reduces the equation to:

$$r_{0001} = \frac{k_B T}{h} e^{\frac{-E_a}{RT}} \theta_{CO} \theta_H \tag{5}$$

Using the average experimental coverage estimates of $\theta_{CO} = 0.51$ ML and $\theta_H = 0.11$ ML,[12] the estimated FTS rates ware calculated at both 210 °C and 220 °C. The resulting rate estimations, as well as the approximate experimental TOF, can be seen in Table 6.

Table 1: Frequencies of adsorbed H on Co(111)

| Configuration | Frequencies [cm$^{-1}$] |
|---|---|
| H | 1178, 861, 826 |

Table 2: Frequencies of structures in the direct CO dissociation Pathway A on Co(211)

| Configuration | Frequencies [cm$^{-1}$] |
|---|---|
| CO | 1236, 394, 360, 308, 200, 163 |
| CO TS | 528, 482, 438, 308, 303, 359$i$ |
| (C + O) | 679, 603, 486, 384, 295, 278 |

Table 3: Frequencies of structures in the direct CO dissociation Pathway B on Co(211)

| Configuration | Frequencies [cm$^{-1}$] |
|---|---|
| CO | 1518, 350, 246, 195, 164, 100 |
| CO TS | 496, 464, 405, 287, 244, 507$i$ |
| (C + O) | 644, 560, 468, 386, 318, 128 |

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Table 4: Frequencies of structures in the HCO hydrogen-assisted pathway on Co(211)

| Configuration | Frequencies [$cm^{-1}$] |
|---|---|
| TS: CO + H | 1850, 1190, 550, 402, 381, 295, 280, 168, 664$i$ |
| HCO | 2173, 1361, 1006, 689, 449, 339, 330, 240, 201 |
| TS: HCO diss. | 2938, 904, 697, 482, 457, 356, 307, 95, 490$i$ |
| (CH + O) | 2904, 781, 771, 502, 478, 400, 372, 287, 254 |

Table 5: Frequencies of structures in the COH hydrogen-assisted pathway on Co(211)

| Configuration | Frequencies [$cm^{-1}$] |
|---|---|
| TS: CO + H | 1244, 1071, 588, 341, 329, 264, 252, 199, 1474$i$ |
| COH | 3485, 1198, 978, 480, 411, 350, 270, 170, 145 |
| TS: COH diss. | 3645, 790, 583, 526, 500, 361, 223, 125, 346$i$ |
| (C + OH) | 3750, 833, 730, 588, 586, 457, 309, 287, 50 |

Table 6: Estimated FTS turnover frequencies (TOF) for the direct CO and HCO pathways compared to the average experimental TOF for Co particles with diameters larger than 6 nm.[12]

| Temperature [°C] | $r_{CO}$ [$s^{-1}$] | $r_{HCO}$ [$s^{-1}$] | $r_{0001}$ [$s^{-1}$] | Expt.[12] [$s^{-1}$] |
|---|---|---|---|---|
| 210 | 0.0007 | 0.0295 | $2.36 \times 10^{-11}$ | ±0.01 |
| 220 | 0.0014 | 0.0557 | $6.85 \times 10^{-11}$ | ±0.01 |