Supplementary Information

Accelerating the Identification of the Rate Controlling Steps by Conducting Microkinetic Modeling on Surrogate Networks

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1. Elementary steps of the F-T reaction network on Co(0001)

The network used to demonstrate our strategy and generate testing networks is the network of FT reaction on Co(0001) constructed in our prior work[1]. This network contains the following 67 elementary steps.

R1: $CO + * \leftrightarrow CO*$
R2: $H_2 + * + * \leftrightarrow H* + H*$
R3: $C* + O* \leftrightarrow CO* + *$
R4: $OH* + * \leftrightarrow O* + H*$
R5: $H_2O + * + * \leftrightarrow OH* + H*$
R6: $H_2O + O* + * \leftrightarrow OH* + OH*$
R7: $H* + C* \leftrightarrow CH* + *$
R8: $CH_2* + * \leftrightarrow H* + CH*$
R9: $H* + CH_2* \leftrightarrow CH_3* + *$
R10: $H* + CH_3* \leftrightarrow CH_4 + * + *$
R11: $COH* + * \leftrightarrow CO* + H*$
R12: $CHO* + * \leftrightarrow CO* + H*$
R13: $COH* + * \leftrightarrow C* + OH*$
R14: $CHO* + * \leftrightarrow CH* + O*$
R15: $CHOH* + * \leftrightarrow CHO* + H*$
R16: $CHOH* + * \leftrightarrow CH* + OH*$
R17: $CH_2O* + * \leftrightarrow CHO* + H*$
R18: $CH_2O* + * \leftrightarrow CH_2* + O*$
R19: $CH_2OH* + * \leftrightarrow CH_2O* + H*$
R20: $CH_2OH* + * \leftrightarrow CH_2* + OH*$
R21: $CH_2O* + H* \leftrightarrow CH_3O* + *$
R22: $CH_3O* + * \leftrightarrow CH_3* + O*$
R23: $CH_3OH + * + * \leftrightarrow CH_3O* + H*$
R24: $CHCO* + * \leftrightarrow CH* + CO*$
R25: $CH_2CO * + * \leftrightarrow CH_2 * + CO*$
R26: $CH_3CO * + * \leftrightarrow CH_3* + CO*$
R27: $CH* + CHO* \leftrightarrow CHCHO* + *$
R28: $CH_2* + CHO* \leftrightarrow CH_2CHO* + *$
R29: $CH_2CO* + H* \leftrightarrow CH_2CHO* + *$
R30: $CHCHO* + * \leftrightarrow CHCO* + H*$
R31: $CH_2CO* + H* \leftrightarrow CH_2CHO* + *$
R32: $CH_3CO* + * \leftrightarrow CH_2CO* + H*$
R33: $CH_2CHO* + * \leftrightarrow CHCHO* + H*$
R34: $CHCO* + * \leftrightarrow CCH* + O*$
R35: $CH_2CO* + * \leftrightarrow CCH_2* + O*$
R36: $CH_3CO* + * \leftrightarrow CCH_3* + O*$
R37: $CHCHO* + * \leftrightarrow CHCH* + O*$
R38: $CH_2CHO* + * \leftrightarrow CHCH_2* + O*$
R39: $CH_2OH* + H* \leftrightarrow CH_3OH* + *$
R40: $CHOH* + * COH* + H* \leftrightarrow$
R41: $CH_2OH* + * \leftrightarrow CHOH* + H*$
R42: $CH_3OH* + * \leftrightarrow CH_3* + OH*$
R43: $C* + C* \leftrightarrow CC* + *$
R44: $C* + CH* \leftrightarrow CCH* + *$
R45: $C* + CH_2* \leftrightarrow CCH_2* + *$
R46: $C* + CH_3* \leftrightarrow CCH_3* + *$
R47: $CH* + CH* \leftrightarrow CHCH* + *$
R48: $CH* + CH_2* \leftrightarrow CHCH_2* + *$
R49: $CHCH_3* +* \leftrightarrow CH* + CH_3*$
R50: $CH_2* + CH_2* \leftrightarrow CH_2CH_2* + *$
R51: $CH_2CH_3* + * \leftrightarrow CH_2* + CH_3*$
R52: $CC* + H * \leftrightarrow CCH* + *$
R53: $CCH_2* + * \leftrightarrow CCH* + H*$
R54: $CCH* + H* \leftrightarrow CHCH* + *$
R55: $CCH_3* + * \leftrightarrow CCH_2* + H*$
R56: $CHCH_2* + * \leftrightarrow CCH_2* + H*$
R57: $CHCH_3* + * \leftrightarrow CCH_3* + H*$
R58: $CH_2CH_3* + * \leftrightarrow CH_2CH_2* + H*$
R59: $CH_2CH_3* + * \leftrightarrow CH_3CH_3* + *$
R60: $CHCH_2* + * \leftrightarrow CHCH* + H*$
R61: $CH_2CH_2* + * \leftrightarrow CHCH_2* + H*$
R62: $CHCH_3* + * \leftrightarrow CHCH_2* + H*$
R63: $CH_2CH_3* + * \leftrightarrow CHCH_3 * + H*$
R64: $CH_2CH_2 + * \leftrightarrow CH_2CH_2 *$
R65: $CH_3CHO* + * \leftrightarrow CH_2CHO * + H*$
R66: $CH_3CHO* + * \leftrightarrow CHCH_3* + O*$
R67: $CH_3CHO* + * \leftrightarrow CH_3CO * + H*$

2. A detailed view of the refinement process using our strategy

Figure S1 illustrates iteration 13 as an example to provide a detailed overview of how our workflow identifies the key elementary steps. In the surrogate networks MKM phase, we conducted microkinetic modeling (MKM) across all 16 surrogate networks,

generating kinetic analyses for each. Each elementary step has an associated Degree of Rate Control (DRC) value for each network, yielding a total of 16 DRC values per step. We aggregated these values to calculate the total DRC ($DRC_{(sum)}$) and ranked the elementary steps by $DRC_{(sum)}$ (Figure S1a). Subsequently, in the evaluation phase (Figure S1b), the reaction with the highest $DRC_{(sum)}$ in this iteration was identified as step 22, for which the barrier has already been calculated (highlighted in green, Figure S1c). As the convergence criterion was not yet satisfied, we proceeded to the next most significant elementary step, step 14, whose barrier had not been calculated (highlighted in red, Figure S1c). We then computed the actual barrier for step 14, updating its value in the surrogate networks refinement phase, and initiated a new iteration. All microkinetic modeling calculations mentioned above were carried out via the CATKINAS package, which is a microkinetic simulation package developed by our group and widely used[2–11].

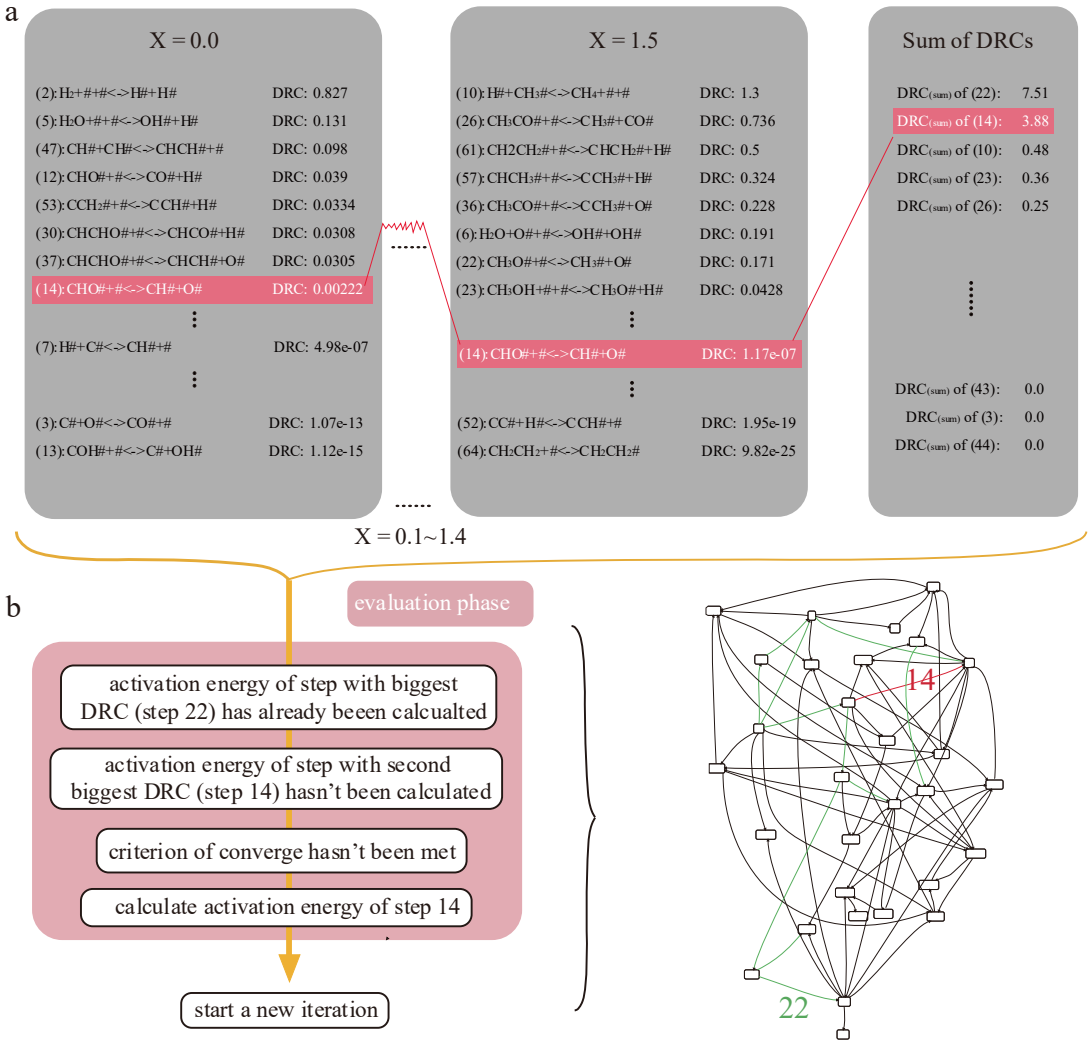

Figure S1. Significant elementary step determination process in a single iteration. (**a**) Elementary steps ranked by the aggregated Degree of Rate Control ($DRC_{(sum)}$). (**b**) Evaluation phase in which the second most significant elementary step, step 14 is selected to be calculated to obtain its activation energy. (**c**) The FT reaction network on Co(0001) calculated in our previous work[1]. The nodes represent reaction intermediates and each line represents an elementary step between the two

nodes. Elementary steps with calculated barriers, uncalculated barriers and barrier selected for calculation in the current iteration are represented in green, black and red lines respectively.

3. Computational cost of the surrogate network calculations

The computational cost of the surrogate network approach primarily stems from the microkinetic modeling (MKM) calculations for all surrogate networks. For the system studied in this work (Fischer–Tropsch reaction on Co(0001), comprising 26 species and 67 reactions), each MKM calculation required approximately 6 min, using Intel(R) Xeon(R) Silver 4210R CPU operating at 2.40 GHz. The relationship between the convergence criterion N and the computational cost is shown in Figure S2. Compared to the transition state calculations (~960 CPU-h), the cost of MKM calculations for surrogate networks is relatively small. This highlights the core strength of our strategy: leveraging low-cost MKM calculations to minimize the need for computationally expensive transition state calculations.

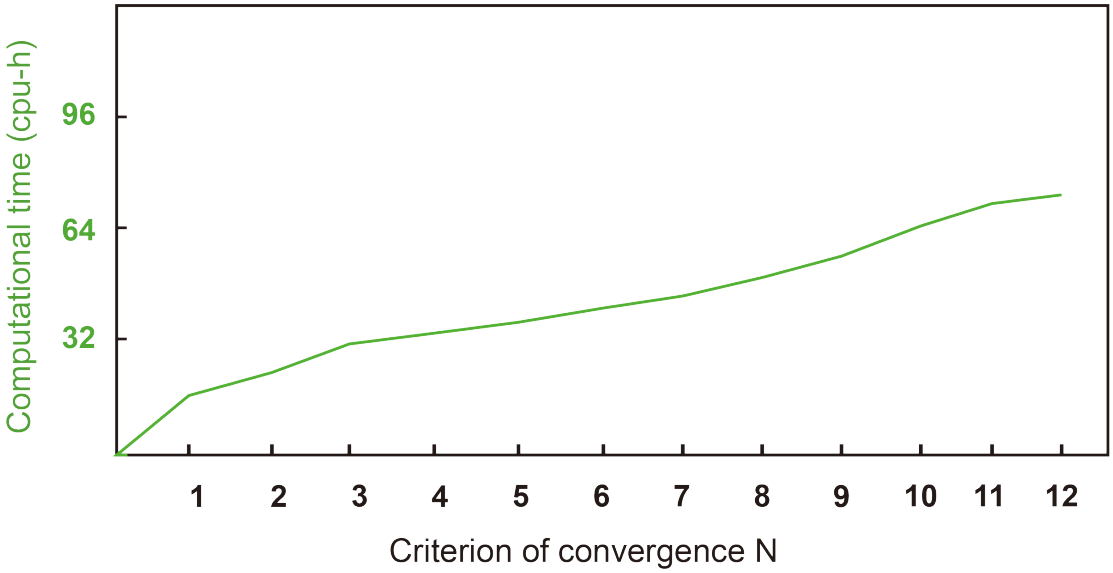

Figure S2. Relationship between the convergence criterion N and the computational cost of the surrogate network calculations.

4. Energy data for elementary steps in the testing networks

Table S1. Activation energies (*Ea*) and reaction energies (ΔE) of elementary steps of testing network T1.

	ΔE(eV)	*Ea*(eV)		ΔE(eV)	*Ea*(eV)
R1	0.000	-0.922	R35	0.530	-0.772
R2	0.000	-0.694	R36	0.625	-0.812
R3	1.242	-0.380	R37	0.866	-1.184
R4	0.810	-0.399	R38	0.915	-0.383
R5	0.335	-0.542	R39	0.579	-0.133
R6	0.829	-0.143	R40	-0.019	-0.715
R7	0.213	-0.067	R41	0.479	-0.320
R8	0.754	-0.371	R42	1.212	-0.936

R9	0.693	-0.026	R43	0.681	-0.273
R10	0.510	-0.159	R44	0.930	-0.505
R11	0.967	-1.091	R45	1.016	-0.417
R12	1.124	-1.218	R46	1.158	-0.388
R13	1.039	-0.312	R47	0.503	-0.532
R14	0.860	-0.905	R48	0.611	-0.042
R15	0.311	-0.588	R49	0.984	-0.296
R16	0.889	-1.094	R50	0.710	-0.338
R17	0.215	-0.287	R51	0.557	-0.177
R18	0.428	-0.821	R52	0.463	-0.299
R19	0.599	-0.621	R53	0.619	-0.459
R20	0.105	-1.043	R54	0.417	-0.094
R21	0.648	-0.088	R55	0.781	-0.003
R22	1.260	-0.759	R56	0.800	-0.308
R23	0.788	-0.576	R57	0.251	-0.617
R24	0.494	-0.370	R58	-0.031	-0.489
R25	-0.045	-0.735	R59	0.617	-0.404
R26	0.442	-0.804	R60	0.699	-0.861
R27	0.818	-0.253	R61	0.688	-0.075
R28	0.414	-0.564	R62	0.392	-0.312
R29	0.528	-0.736	R63	0.706	-0.252
R30	0.477	-0.595	R64	0.000	-0.173
R31	0.811	-0.081	R65	0.503	-0.557
R32	0.576	-0.043	R66	0.626	-0.628
R33	0.993	-0.060	R67	0.366	-0.433
R34	1.288	-0.495			

Table S2. Activation energies (*Ea*) and reaction energies (ΔE) of elementary steps of testing network T2.

	ΔE(eV)	*Ea*(eV)		ΔE(eV)	*Ea*(eV)
R1	0.000	-0.922	R35	1.230	-0.772
R2	0.000	-0.694	R36	0.595	-0.812
R3	0.680	-0.380	R37	0.586	-1.184
R4	0.410	-0.399	R38	0.785	-0.383
R5	0.937	-0.542	R39	0.899	-0.133
R6	0.537	-0.143	R40	0.469	-0.715
R7	1.013	-0.067	R41	-0.079	-0.320
R8	0.754	-0.371	R42	1.082	-0.936

R9	0.493	-0.026	R43	0.781	-0.273
R10	0.870	-0.159	R44	0.670	-0.505
R11	0.367	-1.091	R45	0.896	-0.417
R12	1.194	-1.218	R46	0.468	-0.388
R13	0.739	-0.312	R47	1.013	-0.532
R14	0.320	-0.905	R48	0.241	-0.042
R15	0.781	-0.588	R49	0.464	-0.296
R16	0.799	-1.094	R50	1.030	-0.338
R17	0.595	-0.287	R51	-0.057	-0.177
R18	0.378	-0.821	R52	0.783	-0.299
R19	0.899	-0.621	R53	0.469	-0.459
R20	0.475	-1.043	R54	0.787	-0.094
R21	0.478	-0.088	R55	0.461	-0.003
R22	1.160	-0.759	R56	0.670	-0.308
R23	1.288	-0.576	R57	0.561	-0.617
R24	0.784	-0.370	R58	0.391	-0.489
R25	0.345	-0.735	R59	1.117	-0.404
R26	0.782	-0.804	R60	0.469	-0.861
R27	0.718	-0.253	R61	0.688	-0.075
R28	0.894	-0.564	R62	0.782	-0.312
R29	0.358	-0.736	R63	0.486	-0.252
R30	0.787	-0.595	R64	0.000	-0.173
R31	0.461	-0.081	R65	0.393	-0.557
R32	0.386	-0.043	R66	0.486	-0.628
R33	0.573	-0.060	R67	0.896	-0.433
R34	0.688	-0.495			

Table S3. Activation energies (*Ea*) and reaction energies (ΔE) of elementary steps of testing network T3.

	ΔE(eV)	*Ea*(eV)		ΔE(eV)	*Ea*(eV)
R1	0.000	-0.922	R35	0.830	-0.772
R2	0.000	-0.694	R36	0.325	-0.812
R3	0.342	-0.380	R37	0.466	-1.184
R4	0.410	-0.399	R38	0.515	-0.383
R5	0.935	-0.542	R39	0.379	-0.133
R6	1.129	-0.143	R40	-0.019	-0.715
R7	0.813	-0.067	R41	0.379	-0.320
R8	0.354	-0.371	R42	-0.012	-0.936

R9	0.293	-0.026	R43	0.481	-0.273
R10	0.810	-0.159	R44	0.730	-0.505
R11	0.667	-1.091	R45	1.016	-0.417
R12	1.024	-1.218	R46	1.258	-0.388
R13	0.739	-0.312	R47	0.403	-0.532
R14	0.660	-0.905	R48	0.811	-0.042
R15	0.811	-0.588	R49	0.484	-0.296
R16	0.789	-1.094	R50	0.610	-0.338
R17	1.215	-0.287	R51	0.757	-0.177
R18	0.628	-0.821	R52	0.863	-0.299
R19	0.899	-0.621	R53	0.419	-0.459
R20	0.805	-1.043	R54	0.717	-0.094
R21	0.548	-0.088	R55	0.481	-0.003
R22	1.160	-0.759	R56	0.600	-0.308
R23	0.688	-0.576	R57	0.651	-0.617
R24	0.794	-0.370	R58	-0.031	-0.489
R25	0.745	-0.735	R59	0.417	-0.404
R26	0.342	-0.804	R60	0.799	-0.861
R27	0.418	-0.253	R61	0.988	-0.075
R28	0.314	-0.564	R62	0.792	-0.312
R29	0.828	-0.736	R63	0.406	-0.252
R30	0.677	-0.595	R64	0.000	-0.173
R31	0.411	-0.081	R65	0.203	-0.557
R32	0.276	-0.043	R66	0.826	-0.628
R33	0.693	-0.060	R67	0.166	-0.433
R34	1.188	-0.495			

Table S4. Activation energies (Ea) and reaction energies (ΔE) of elementary steps of testing network T4.

	ΔE(eV)	*Ea*(eV)		ΔE(eV)	*Ea*(eV)
R1	0.000	-0.922	R35	0.830	-0.772
R2	0.000	-0.694	R36	0.325	-0.812
R3	0.743	-0.380	R37	0.966	-1.184
R4	0.390	-0.399	R38	0.415	-0.383
R5	0.575	-0.542	R39	0.879	-0.133
R6	0.349	-0.143	R40	0.319	-0.715
R7	1.123	-0.067	R41	0.179	-0.320
R8	0.454	-0.371	R42	0.512	-0.936

R9	0.893	-0.026	R43	0.381	-0.273
R10	0.670	-0.159	R44	0.430	-0.505
R11	0.707	-1.091	R45	1.116	-0.417
R12	1.024	-1.218	R46	0.858	-0.388
R13	0.809	-0.312	R47	0.403	-0.532
R14	0.430	-0.905	R48	0.811	-0.042
R15	0.781	-0.588	R49	0.484	-0.296
R16	0.949	-1.094	R50	0.810	-0.338
R17	0.675	-0.287	R51	0.357	-0.177
R18	0.348	-0.821	R52	0.863	-0.299
R19	0.899	-0.621	R53	0.419	-0.459
R20	0.345	-1.043	R54	0.717	-0.094
R21	1.208	-0.088	R55	0.381	-0.003
R22	1.010	-0.759	R56	0.500	-0.308
R23	0.568	-0.576	R57	0.951	-0.617
R24	0.904	-0.370	R58	-0.031	-0.489
R25	0.205	-0.735	R59	0.317	-0.404
R26	0.742	-0.804	R60	0.999	-0.861
R27	0.518	-0.253	R61	0.488	-0.075
R28	0.914	-0.564	R62	0.992	-0.312
R29	0.728	-0.736	R63	0.506	-0.252
R30	0.877	-0.595	R64	0.000	-0.173
R31	1.011	-0.081	R65	0.303	-0.557
R32	0.696	-0.043	R66	0.926	-0.628
R33	0.493	-0.060	R67	0.266	-0.433
R34	1.088	-0.495			

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