Supplementary Information

Microkinetic modelling and analysis of CO_2 methanation on Ruthenium

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1. MICROKINETIC MODEL

Table S.1: The microkinetic model, comprising of forward and backward reaction pairs, and the corresponding rate parameters. Pre-exponential factors are expressed in CGS units (cm, mol, s) and the site density is $\Gamma = 2.623 \times 10^{-09}$ mol/cm^2. †These activation energies were taken from DFT literature [1,2].

No.	Reaction	S_i or A_i	β	E_i (kJ/mol)
1	$CO_2 + * \rightarrow CO_2*$	0.85		0.00
2	$CO_2* \rightarrow CO_2 + *$	1.000E+13		10.61
3	$H_2 + * + * \rightarrow H* + H*$	0.25		0.00
4	$H* + H* \rightarrow H_2 + * + *$	4.248E+23	-0.098	101.8
5	$CH_4* \rightarrow CH_4 + *$	1.000E+13		3.86
6	$CH_4 + * \rightarrow CH_4*$	0.073		0.00
7	$H_2O* \rightarrow H_2O + *$	1.000E+13		20.26
8	$H_2O + * \rightarrow H_2O*$	1.0		0.00
9	$CO* \rightarrow CO + *$	6.964E+9	1.5292	-0.1282*T + 189.54
10	$CO + * \rightarrow CO*$	0.8		0.00
11	$CO_2* + * \rightarrow CO* + O*$	3.812E+20		25.14
12	$CO* + O* \rightarrow CO_2* + *$	1.525E+22		73.78
13	$CO_2* + H* \rightarrow COOH* + *$	7.625E+20		96.48†
14	$COOH* + * \rightarrow CO_2* + H*$	1.525E+21		52.99
15	$COOH* + * \rightarrow CO* + OH*$	1.525E+21		22.72
16	$CO* + OH* \rightarrow COOH* + *$	7.625E+21		61.00
17	$CO* + H* \rightarrow COH* + *$	1.525E+22		216.01
18	$COH* + * \rightarrow CO* + H*$	3.431E+21		0.00
19	$CO* + H* \rightarrow HCO* + *$	1.144E+22		153.12

20	HCO* + * → CO* + H*	3.812E+18		0.00
21	HCO* + * → CH* + O*	3.812E+21		91.15
22	CH* + O* → HCO* + *	3.812E+21		170.08
23	C* + H* → CH* + *	7.625E+21		64.28
24	CH* + * → C* + H*	2.287E+21		82.01†
25	CH* + H* → CH_2* + *	3.812E+21		85.74
26	CH_2* + * → CH* + H*	2.287E+21		14.47†
27	CH_2* + H* → CH_3* + *	3.812E+21		45.63
28	CH_3* + * → CH_2* + H*	1.906E+21		41.49†
29	CH_3* + H* → CH_4* + *	1.525E+21		36.76
30	CH_4* + * → CH_3* + H*	7.625E+20		49.20†
31	O* + H* → OH* + *	7.982E+27	-1.678	0.049*T + 83.986
32	OH* + * → O* + H*	2.004E+27	-1.6795	0.0486*T + 30.345
33	OH* + H* → H_2O* + *	1.838E+28	-2.4157	0.0592*T + 38.107
34	H_2O* + * → OH* + H*	1.837E+27	-2.4157	0.0592*T + 36.757
35	COH* + * → C* + OH*	6.176E+24		55.41
36	C* + OH* → COH* + *	7.625E+21		125.65
37	CO_2* + H* → HCOO**	3.812E+20		35.70†
38	HCOO** → CO_2* + H*	1.00E+12		11.68
39	HCOO** → HCO* + O*	7.50E+13		103.79
40	HCO* + O* → HCOO**	3.812E+20		23.33
41	CO* + * → C* + O*	2.473E+28	-0.4494	0.2814*T + 23.766
42	C* + O* → CO* +*	2.825E+25	-0.4516	0.2813*T – 68.102

2. CHEMKIN INPUT FILE FOR 350 °C

The Chemkin input file at 350 °C is attached with this document. Since Chemkin does not support temperature dependent activation energies, the input file at one temperature is provided. For use at other temperatures, activation energies of the sensitive reactions may be calculated and replaced using the formulae given in Table S.1.

```
MATERIAL SABATIERMETH
SITE/RUTHENIUM/    SDEN/2.623E-9/
 (Ru) H2O(Ru) H(Ru) HCOO(Ru)/2/ OH(Ru) CO(Ru) C(Ru)
 CH3(Ru) CH2(Ru) CH(Ru) CH4(Ru) O(Ru) CO2(Ru)
 HCO(Ru) COH(Ru) COOH(Ru)
END
!****************************************************************
REACTIONS  KJOULES/MOLE  MWOFF
CO2 + (Ru) => CO2(Ru)                  0.850E00   0.000     0.000      !1!
      STICK
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```
CO2(Ru) => CO2 + (Ru)                  1.00E+13   0.000     10.61      !2!
H2 + (Ru) + (Ru) => H(Ru) + H(Ru)      0.250E00   0.000     0.000      !3!
      STICK
H(Ru) + H(Ru) => H2 + (Ru) + (Ru)      4.248E23   -0.0981   101.8      !4!
CH4(Ru) => CH4 + (Ru)                  1.00E+13   0.000     3.85       !5!
CH4 + (Ru) => CH4(Ru)                  7.300E-2   0.000     0          !6!
      STICK
H2O(Ru) => H2O + (Ru)                  1.00E+13   0.000     20.26      !7!
H2O + (Ru) => H2O(Ru)                  1.000E00   0.000     0          !8!
      STICK
CO(Ru) => CO + (Ru)                    6.964E9    1.5292    109.65     !9!
CO + (Ru) => CO(Ru)                    0.800E00   0.000     0         !10!
      STICK
CO2(Ru) + (Ru) => CO(Ru) + O(Ru)       3.812E20   0.000     25.13     !11!
CO(Ru) + O(Ru) => CO2(Ru) + (Ru)       1.525E22   0.000     73.77     !12!
CO2(Ru) + H(Ru) => COOH(Ru) + (Ru)     7.625E20   0.000     96.48     !13!
COOH(Ru) + (Ru) => CO2(Ru) + H(Ru)     1.525E21   0.000     52.98     !14!
COOH(Ru) + (Ru) => CO(Ru) + OH(Ru)     1.525E21   0.000     22.72     !15!
CO(Ru) + OH(Ru) => COOH(Ru) + (Ru)     7.625E21   0.000     61.001    !16!
CO(Ru) + H(Ru) => COH(Ru) + (Ru)       1.525E22   0.000     216.01    !17!
COH(Ru) + (Ru) => CO(Ru) + H(Ru)       3.431E21   0.000     0         !18!
CO(Ru) + H(Ru) => HCO(Ru) + (Ru)       1.144E22   0.000     153.12    !19!
HCO(Ru) + (Ru) => CO(Ru) + H(Ru)       3.812E18   0.000     0.00      !20!
HCO(Ru) + (Ru) => CH(Ru) + O(Ru)       3.812E21   0.000     91.15     !21!
CH(Ru) + O(Ru) => HCO(Ru) + (Ru)       3.812E21   0.000     170.08    !22!
C(Ru) + H(Ru) => CH(Ru) + (Ru)         7.625E21   0.000     64.27     !23!
CH(Ru) + (Ru) => C(Ru) + H(Ru)         2.287E21   0.000     82.008    !24!
CH(Ru) + H(Ru) => CH2(Ru) + (Ru)       3.812E21   0.000     85.73     !25!
CH2(Ru) + (Ru) => CH(Ru) + H(Ru)       2.287E21   0.000     14.47     !26!
CH2(Ru) + H(Ru) => CH3(Ru) + (Ru)      3.812E21   0.000     45.63     !27!
CH3(Ru) + (Ru) => CH2(Ru) + H(Ru)      1.906E21   0.000     41.48     !28!
CH3(Ru) + H(Ru) => CH4(Ru) + (Ru)      1.525E21   0.000     36.76     !29!
CH4(Ru) + (Ru) => CH3(Ru) + H(Ru)      7.625E20   0.000     49.20     !30!
O(Ru) + H(Ru) => OH(Ru) + (Ru)         7.982E27   -1.678    114.52    !31!
OH(Ru) + (Ru) => O(Ru) + H(Ru)         2.004E27   -1.6795   60.63     !32!
OH(Ru) + H(Ru) => H2O(Ru) + (Ru)       1.838E28   -2.4157   75.00     !33!
H2O(Ru) + (Ru) => OH(Ru) + H(Ru)       1.837E27   -2.4157   73.65     !34!
COH(Ru) + (Ru) => C(Ru) + OH(Ru)       6.176E24   0.000     55.41     !35!
C(Ru) + OH(Ru) => COH(Ru) + (Ru)       7.625E21   0.000     125.65    !36!
CO2(Ru) + H(Ru) => HCOO(Ru)            3.812E20   0.000     35.69     !37!
HCOO(Ru) => CO2(Ru) + H(Ru)            1.00E12    0.000     11.67     !38!
HCOO(Ru) => HCO(Ru) + O(Ru)            7.50E13    0.000     103.79    !39!
HCO(Ru) + O(Ru) => HCOO(Ru)            3.812E20   0.000     23.3      !40!
CO(Ru) + (Ru) => C(Ru) + O(Ru)         2.473E28   -0.4494   199.12    !41!
C(Ru) + O(Ru) => CO(Ru) +(Ru)          2.825E25   -0.4516   107.19    !42!
END
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3. ADDITIONAL MODEL VALIDATIONS

3.1. Equilibrium Conversion: The final model vs. the initial screening model

Prediction of equilibrium conversion calculated by Gao et al.[3] is compared to the predictions of our model and those of the model by Avanesian et al.[1] in Figure S.1. When the PFR is infinitely long, the system eventually reaches equilibrium. Hence, the simulations were run using the microkinetic model using a large value of reactor length to ensure equilibrium is attained at the corresponding temperature. The lines in Figure S.1 represent equilibrium conversion thus computed from the microkinetic models. The model by Avanesian et al.[1] is unable to predict the equilibrium conversion values.

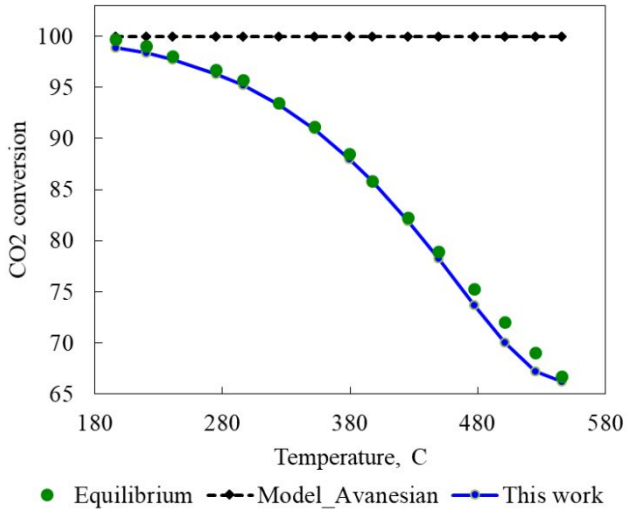

Figure S.1: Equilibrium conversion of CO_2. The green dots represent the equilibrium conversion from Gao et al.[3], the blue solid line indicates model predictions from the model in Table S.1, and the dashed black line indicates model predictions from the kinetic model from Avanesian et al.[1].

3.2. Case 5: Comparison with experimental results from Brooks et al. [4]

Brooks et al. [4] used 3% Ru-TiO_2 catalyst in a microreactor and performed experiments for a wide range of conditions. The PFR is 7 cm long with 1 mm diameter, and the residence times lie in the range 0.21 – 0.1 s. The feed comprises of 20% CO_2 and 80% H_2 and the surface area per unit length was fixed at $a_l = 300$ cm. In addition to the CO_2 conversion, they also reported the inlet and outlet temperatures. The cases of near-isothermal operation reported in their work were simulated using our microkinetic model and are presented in Table S2. The comparison with experimental data shows that the model predicts the data qualitatively. However, it should be noted that the effect of support is not included in the model. Since the support TiO_2 is known to be active for the reaction [4,5], our model which is developed without

considering the effect of support is expected to be inadequate. The reactor temperature is assumed to vary linearly between the inlet and outlet temperatures. When inlet and outlet temperatures are far apart, this assumption is a source of error and can cause deviation in prediction of conversion. Table shows that the model reasonably predicts their data.

Table S.2: A comparison between experimental data from Brooks et al. [4] and model predictions for various conditions.

No.	H_2:CO_2	T_{in} (°C)	T_{out} (°C)	U_{in} (cm/s)	CO_2 conversion (%)	
					Experiments	Model
1	4	251	254	14.62	53.7	62.4
2	4	304	303	32.29	89.4	86.5
3	4	300	300	32.04	80.6	84.7
4	4	353	346	69.97	88.2	84.6
5	4	303	308	64.37	64	62.5
6	6	278	284	61.59	64	58.0

3.3. Comparison with CO methanation data

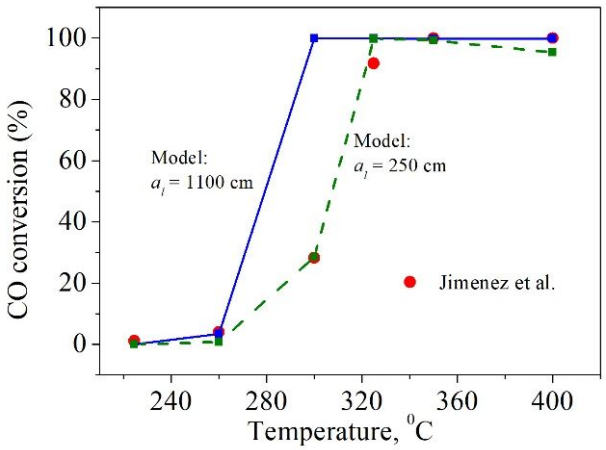

Figure S.2: Experimental data and model prediction of CO conversion vs. reactor temperature. Red dots represent experimental results from Jimenez et al. [6], blue squares with solid line indicate model predictions when a_l = 1100 cm and green circles connected by dashed line shows prediction with a_l = 250 cm.

The microkinetic model was also checked for CO methanation since it is a similar reaction and likely to involve the same elementary steps. The experimental data is taken from Jimenez et al. [6] on 0.5 wt. % Ru on platelet carbon nanofiber catalyst and the comparison with model predictions is shown in Figure S.2. The area per unit length considered in CO_2 methanation for

Case-4 was $a_l = 1100$ cm. With this value, the reaction occurred faster and approached equilibrium at lower temperatures (solid line in Figure S.2). However, when a lower value of $a_l = 250$ cm was used, the model predictions are reasonable (dashed line). Jimenez et al. [6] have reported that CO methanation is sensitive to structure of catalyst support unlike CO_2 methanation and the microkinetic model is not designed to model the effect of support. Moreover, certain surface species such as CHOH*, found to be relevant in CO methanation [1,7] is not included in the model.

4. SENSITIVITY ANALYSIS

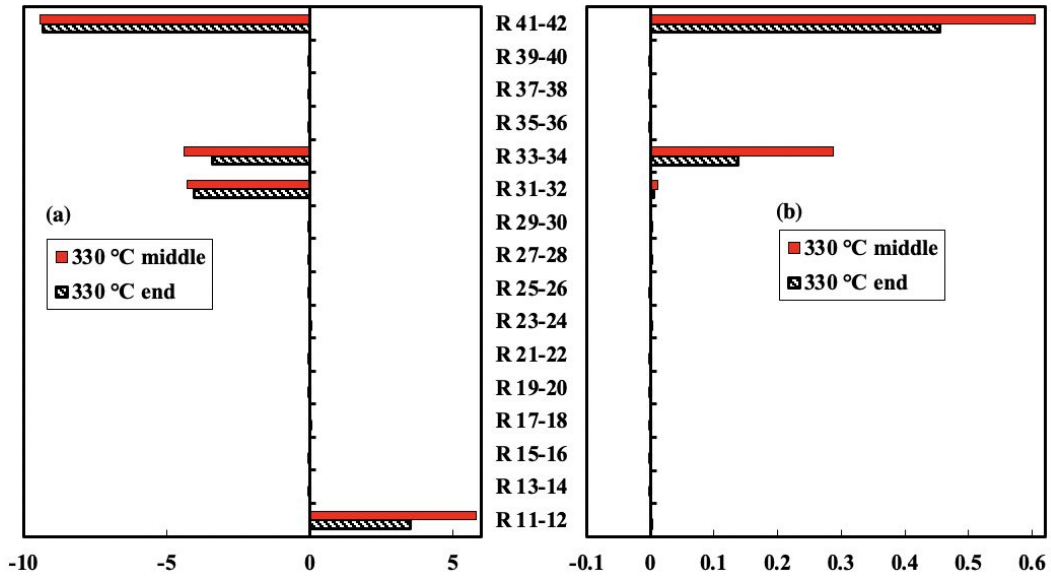

Figure S.3: Sensitivity analysis for the CH_4 mass fraction in the middle and end of the reactor, with respect to (a) activation energy, (b) pre-exponential factor.

Sensitivity analysis was performed by varying activation energies and pre-exponential factors and analyzing their effect on the CH_4 mass fraction at the middle and end of the fixed bed, with inlet conditions as those of Case 1 (for the experiments of Falbo et al.) and with temperature at 330 °C. Figure S.3 shows the pairwise brute-force sensitivity results for a 10% variation in activation energy (Figure S.3-a) and pre-exponential factor (Figure S.3-b). The rate constant for both forward and reverse reaction were varied simultaneously by the same amount and the following quantity was computed:

$$s = \frac{d\ln\left(Y_{CH_4}\right)}{d\ln\left(\phi_i\right)} \approx \frac{\Delta Y_{CH_4}/Y_{CH_4}}{\Delta\phi_i/\phi_i}, \ \phi_i = A_{0i} \text{ or } E_i$$

The same reactions were found to be sensitive at both the locations. Note that the rate constants of the sensitive reactions, with the exception of R11-R12 pair, were the ones varied for fitting the experimental data, as described in Section 3.1 of the manuscript.

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