

Supplementary Materials

Kinetic Model of Catalytic Steam Gasification of 2-Methoxy-4-Methylphenol Using 5%Ni-0.25%Ru/ γ Al₂O₃ in a CREC-Riser Simulator.

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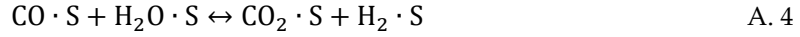
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S1. Water Gas Shift Reaction Mechanism

The water-gas shift mechanism can be considered as a sequence of adsorption and reaction elementary steps as follows [27]



Thus, for every step of the postulated mechanism the following can be considered.

$$r_1 = k_{\text{CO}}^{\text{A}} \left(p_{\text{CO}} C_{\text{v}} - \frac{C_{\text{CO} \cdot \text{S}}}{K_{\text{CO}}^{\text{A}}} \right) \quad \text{A. 7}$$

$$r_2 = k_{\text{H}_2\text{O}}^{\text{A}} \left(p_{\text{H}_2\text{O}} C_{\text{v}} - \frac{C_{\text{H}_2\text{O} \cdot \text{S}}}{K_{\text{H}_2\text{O}}^{\text{A}}} \right) \quad \text{A. 8}$$

$$r_3 = k_{\text{s}} \left(C_{\text{CO} \cdot \text{S}} C_{\text{H}_2\text{O} \cdot \text{S}} - \frac{C_{\text{CO}_2 \cdot \text{S}} C_{\text{H}_2 \cdot \text{S}}}{K_{\text{s}}} \right) \quad \text{A. 9}$$

$$r_4 = k_{\text{CO}_2}^{\text{D}} \left(C_{\text{CO}_2 \cdot \text{S}} - \frac{p_{\text{CO}_2} C_{\text{v}}}{K_{\text{CO}_2}^{\text{D}}} \right) \quad \text{A. 10}$$

$$r_5 = k_{\text{H}_2}^{\text{D}} \left(C_{\text{H}_2 \cdot \text{S}} - \frac{p_{\text{H}_2} C_{\text{v}}}{K_{\text{H}_2}^{\text{D}}} \right) \quad \text{A. 11}$$

where K_{CO}^{A} , $K_{\text{H}_2\text{O}}^{\text{A}}$, $K_{\text{CO}_2}^{\text{D}}$ and $K_{\text{H}_2}^{\text{D}}$ are the equilibrium adsorption and desorption constants, and K_{s} the intrinsic equilibrium superficial reaction

Expressing the concentration of free and adsorbed species on the catalyst, in terms of species partial pressures the following results,

$$r_{\text{WGS}} = \frac{k'_{\text{WGS}} p_{\text{CO}} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}}^A p_{\text{CO}} + K_{\text{H}_2\text{O}}^A p_{\text{H}_2\text{O}} + K_{\text{H}_2}^A p_{\text{H}_2} + K_{\text{CH}_4}^A p_{\text{CH}_4})^2} \left(1 - \frac{p_{\text{CO}_2} p_{\text{H}_2}}{K_{\text{WGS}} p_{\text{CO}} p_{\text{H}_2\text{O}}}\right) \quad \text{A. 12}$$

S2. Rate Equations Using the Centering Temperature Method

Expressing the Arrhenius term of the rate equation using an average temperature reduces cross-correlation for the parameters. Thus, the differential equations of the present study can be re-written as follows, after substitution of Arrhenius term, in order to estimate the pre exponential factor and activation energy parameters:

$$\frac{dp_{\text{H}_2}}{dt} = \frac{\frac{W}{V} RT \left[k_{\text{WGS}}^\circ \exp\left(\frac{E_{\text{WGS}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \right] p_{\text{CO}} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2}^A p_{\text{CO}_2})^2} \left(1 - \frac{p_{\text{CO}_2} p_{\text{H}_2}}{K_{\text{WGS}} p_{\text{CO}} p_{\text{H}_2\text{O}}}\right) \quad \text{B.1}$$

$$+ 3 \frac{\frac{W}{V} RT \left[k_{\text{SRM}}^\circ \exp\left(\frac{E_{\text{SRM}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \right] p_{\text{CH}_4} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2}^A p_{\text{CO}_2})^4} \left(1 - \frac{p_{\text{CO}} p_{\text{H}_2}^3}{K_{\text{SRM}} p_{\text{CH}_4} p_{\text{H}_2\text{O}}}\right) \quad \text{B.2}$$

$$\frac{dp_{\text{CO}}}{dt} = - \frac{\frac{W}{V} RT \left[k_{\text{WGS}}^\circ \exp\left(\frac{E_{\text{WGS}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \right] p_{\text{CO}} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2}^A p_{\text{CO}_2})^2} \left(1 - \frac{p_{\text{CO}_2} p_{\text{H}_2}}{K_{\text{WGS}} p_{\text{CO}} p_{\text{H}_2\text{O}}}\right) \\ + \frac{\frac{W}{V} RT \left[k_{\text{SRM}}^\circ \exp\left(\frac{E_{\text{SRM}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \right] p_{\text{CH}_4} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2}^A p_{\text{CO}_2})^4} \left(1 - \frac{p_{\text{CO}} p_{\text{H}_2}^3}{K_{\text{SRM}} p_{\text{CH}_4} p_{\text{H}_2\text{O}}}\right) \quad \text{B.3}$$

$$\frac{dp_{\text{CO}_2}}{dt} = \frac{\frac{W}{V} RT \left[k_{\text{WGS}}^\circ \exp\left(\frac{E_{\text{WGS}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \right] p_{\text{CO}} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2}^A p_{\text{CO}_2})^2} \left(1 - \frac{p_{\text{CO}_2} p_{\text{H}_2}}{K_{\text{WGS}} p_{\text{CO}} p_{\text{H}_2\text{O}}}\right) \quad \text{B.4}$$

$$\frac{dp_{\text{CH}_4}}{dt} = - \frac{\frac{W}{V} RT \left[k_{\text{SRM}}^\circ \exp\left(\frac{E_{\text{SRM}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \right] p_{\text{CH}_4} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2}^A p_{\text{CO}_2})^4} \left(1 - \frac{p_{\text{CO}} p_{\text{H}_2}^3}{K_{\text{SRM}} p_{\text{CH}_4} p_{\text{H}_2\text{O}}}\right) \quad \text{B.5}$$

$$\frac{dp_{\text{H}_2}}{dt} = \frac{\frac{W}{V} RT \left[k_{\text{WGS}}^\circ \exp\left(\frac{E_{\text{WGS}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \right] p_{\text{CO}} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2}^A p_{\text{CO}_2})^2} \left(1 - \frac{p_{\text{CO}_2} p_{\text{H}_2}}{K_{\text{WGS}} p_{\text{CO}} p_{\text{H}_2\text{O}}}\right) \\ + 3 \frac{\frac{W}{V} RT \left[k_{\text{SRM}}^\circ \exp\left(\frac{E_{\text{SRM}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \right] p_{\text{CH}_4} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2}^A p_{\text{CO}_2})^4} \left(1 - \frac{p_{\text{CO}} p_{\text{H}_2}^3}{K_{\text{SRM}} p_{\text{CH}_4} p_{\text{H}_2\text{O}}}\right)$$

$$\frac{dp_{H_2O}}{dt} = - \frac{\frac{W}{V} RT \left[k_{WGS}^{\circ} \exp \left(\frac{E_{WGS}}{R} \left(\frac{1}{T} - \frac{1}{T_{avg}} \right) \right) \right] p_{CO} p_{H_2O}}{(1 + K_{CO_2}^A p_{CO_2})^2} \left(1 - \frac{p_{CO_2} p_{H_2}}{K_{WGS} p_{CO} p_{H_2O}} \right) - \frac{\frac{W}{V} RT \left[k_{SRM}^{\circ} \exp \left(\frac{E_{SRM}}{R} \left(\frac{1}{T} - \frac{1}{T_{avg}} \right) \right) \right] p_{CH_4} p_{H_2O}}{(1 + K_{CO_2}^A p_{CO_2})^4} \left(1 - \frac{p_{CO} p_{H_2}^3}{K_{SRM} p_{CH_4} p_{H_2O}} \right) \quad B.6$$

S3. CO₂ Adsorption Parameter Calculations

The Langmuir adsorption isotherm equation was fitted to the adsorbed volumes of CO₂.

$$\frac{V_{CO_2}^A}{V_m} = \frac{K_{CO_2}^A p_{CO_2}}{1 + K_{CO_2}^A p_{CO_2}} \quad C.1$$

where $V_{CO_2}^A$ is the volume of CO₂ adsorbed on the catalyst, p_{CO_2} is the CO₂ partial pressure, V_m is the adsorbed volume to form a monolayer and $K_{CO_2}^A$ is the CO₂ equilibrium adsorption constant. Linearizing equation A.1:

$$\frac{1}{V_{CO_2}^A} = \frac{1}{K_{CO_2}^A p_{CO_2} V_m} + \frac{1}{V_m} \quad C.2$$

Figure S1 shows the inverse of CO₂ adsorbed volume ($1/V_{CO_2}^A$), versus the inverse of the CO₂ pressure ($1/p_{CO_2}$). On this basis ($1/V_m K_{CO_2}^A$) slope and $K_{CO_2}^A$ are calculated.

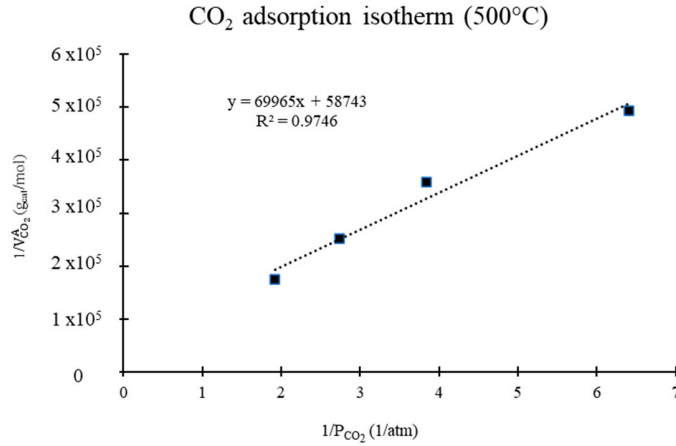


Figure S1. CO₂ adsorption isotherm at 500°C, catalyst 5%Ni-0.25%Ru/γAl₂O₃.

Table S1 reports the $K_{CO_2}^A$ adsorption constants at the four temperature levels using this approach.

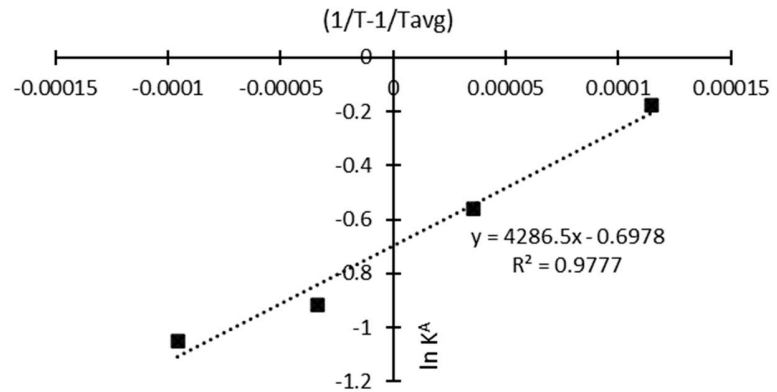
Table S1. CO₂ adsorption constants at different temperatures.

T (°C)	K _{CO₂} ^A (atm ⁻¹)
500	0.84
550	0.57
600	0.4
650	0.35

Furthermore, considering the integrated van't Hoff equations for CO₂ adsorption, one can calculate the CO₂ adsorption intrinsic parameters, K_{CO₂}[°] and the adsorption enthalpy ΔH_{CO₂}^{ads} as follows:.

$$K_{CO_2}^A = K_{CO_2}^{\circ} \exp \left(-\frac{\Delta H_{CO_2}^{ads}}{R} \left(\frac{1}{T} - \frac{1}{T_{avg}} \right) \right) \quad C. 3$$

Figure S2, reports a graphic of the linearized Equation (A.3), with the slope and the ordinate providing K_{CO₂}[°] and ΔH_{CO₂}^{ads} parameters as reported In **Table 7**.

**Figure S2.** Fitting of linearized CO₂ adsorption isotherm to the experimental data at different temperatures, for parameter estimation.

S4. Determination of CO₂ Adsorption Constants

Regarding Calculation of CO₂ adsorption constants Table S2 reports the following:

- Column 1: the argon pressure prior to the experiment,
- Column 2: the injected CO₂ to columns,
- Column 3: the calculated injected CO₂ in moles,
- Column 4: the calculated pressure at the reactor temperature,
- Column 5: the measured pressure following CO₂ injection. T
- Column 6: the pressure difference between calculated measured pressures

- g) Column 7: the CO₂ adsorbed moles calculated using the total pressure difference.
- h) Column 8: the CO₂ adsorbed moles per gram of catalyst (Q), calculated on the basis of the 0.545 g catalyst sample used.
- i) Column 9: the inverse of Q,
- j) Column 10: the calculated CO₂ partial pressure using Dalton's law, with p_{CO2} being the CO₂ partial pressure, y_{CO2} the CO₂ molar fraction and P_T the reactor total pressure.
- k) Column 11: the p_{CO2} inverse.

Table S2. Degree of coverage and partial pressure of CO₂ at different injected amounts of CO₂.

Initial pressure measured of Ar (atm)	Injected volume of CO ₂ (ml)	Moles of CO ₂ (μmol)	Initial pressure measured of Ar (atm)	Theoretical pressure after injection (atm)	Pressure measured after injection (atm)	Pressure difference (Theoretical-Experimental) (atm)	Moles of CO ₂ (μmol)	Q (μmol/gcat)	1/Q (gcat/mol)	p _{CO2} (atm)	1/ p _{CO2} (1/atm)
0.95	3	124.30	0.95	1.11	1.087	0.0268	1.452	2.02	4.94x10 ⁵	0.156	6.40
0.94	5	207.16	0.94	1.2	1.16	0.037	2.00	2.79	1.22 x10 ⁵	0.26	3.84
0.97	7	290.03	0.97	1.34	1.29	0.0525	2.84	3.97	2.52 x10 ⁵	0.364	2.74
0.96	10	414.33	0.96	1.48	1.40	0.0757	4.10	5.72	1.55 x10 ⁵	0.52	1.92

Thus, and on the basis of 1/Q and 1/p_{CO2} plots the adsorption isotherm was established at 550°C, 600°C and 650°C, with the CO₂ adsorption constants obtained as reported in Table S1.