ARTICLE

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Reaction Kinetics for Ammonia Synthesis using Ruthenium and Iron based Catalysts under Low Temperature and Pressure Conditions

T.Cholewa[a,b,]*, B.Steinbach[a], C.Heim[a], F.Nestler[a], T.Nanba[c], R.Güttel[b]*, O.Salem[a,] †

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[a.] *Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstr.2 79110 Freiburg.*
[b.] *University of Ulm, Institute of Chemical Engineering, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany.*
[c.] *Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology, AIST, 2-2-9 Machiikedai, Koriyama, Fukushima 963-0298, Japan*
† *Air Company, 407 Johnson Avenue, Brooklyn, New York*

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Supplementary Information

Thermodynamic and Physical Properties

Enthalpy and entropy of formation are calculated using the Shomate Equations according to Eqs. (S.1) and (S.2) respectively, with parameters A-G taken from NIST.[1]

$$\Delta_f H = A\vartheta + \frac{B\vartheta^2}{2} + \frac{C\vartheta^3}{3} + \frac{D\vartheta^4}{4} - E\vartheta^{-1} + F - H \quad (S.1)$$

$$\Delta_f S = A\ln(\vartheta) + B\vartheta + \frac{C\vartheta^2}{2} + \frac{D\vartheta^3}{3} - \frac{E\vartheta^{-2}}{2} + G \quad (S.2)$$

Based on these values the enthalpy and entropy of reaction for NH_3 synthesis are calculated. The Gibbs free energy is calculated according to Eq. (S.3)) using the measured, axially resolved temperature T_f at the respective axial position z. Eq. (S.4) allows the calculation of the equilibrium constant K_{eq}.

$$\Delta_R G(T_f) = \Delta_R H(T_f) - T\Delta_R S(T_f) \quad (S.3)$$

$$K_{eq}(z) = \exp\left(-\frac{\Delta_R G(T_f(z))}{RT}\right) \quad (S.4)$$

The gas phase properties of the non-ideal gas are calculated using the Soave-Redlich Kwong equation of state.[2] Calculations are based on the physical properties of the components given in Table S1. The fugacity coefficients φ_i are calculated according to Eq. (S.5). The Redlich-Kwong parameters a and b and the adapted parameters A_S and B_S according to Soave et al. are calculated according to Eqs. (S.6) to (S.15). Fugacities of the components f_i can then be calculated according to Eq. (S.16). Setting the reference fugacity f^* to 1 bar, allows the calculation of dimensionless activities a_i, used in the kinetic expressions as given in (S. 17).

$$\ln\varphi_i = \frac{b_i}{b}(Z-1) - \ln(Z - B_S) - \frac{A_S}{B_S}\left(2\frac{a_{S,i}^{0.5}}{a_S^{0.5}} - \frac{b_i}{b}\right)\cdot\ln\left(1 + \right. \quad (S.5)$$

$$B_S = \frac{b\,p}{R\,T} \quad (S.6)$$

$$b_i = 0.08664\frac{R\,T_c}{p_c} \quad (S.7)$$

$$b = \sum y_i\, b_i \quad (S.8)$$

$$A_S = \frac{a_S\, p}{R^2\, T^2} \quad (S.9)$$

$$a_S = \left(\sum y_i \cdot a_{S,i}^{0.5}\right)^2 \quad (S.10)$$

$$\beta_i^{0.5} = 1 + m_i\left(1 - \left(\frac{T}{T_c}\right)^{0.5}\right) \quad (S.11)$$

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \quad (S.12)$$

$$a_{c,i} = 0.42747\frac{R^2 T_c^2}{p_c} \quad (S.13)$$

$$a_{S,i} = a_{c,i}\cdot\beta_i \quad (S.14)$$

$$Z^3 - Z^2 + Z\left(A_S - B_S - B_S^2\right) - A_S B_S = 0 \quad (S.15)$$

$$f_i = \varphi_i\, p_i \quad (S.16)$$

$$a_i = \frac{f_i}{f^*} \quad (S.17)$$

Table S1: Physical properties of the gas phase components of the NH_3 synthesis.[1]

	H_2	N_2	NH_3
p_c / Pa	$13.13\cdot 10^5$	$34\cdot 10^5$	$112.8\cdot 10^5$
T_c / K	33.19	126.2	405.65
ω / 1	-0.215993	0.0377215	0.252608

Material Balance

The material balance for the reactor is solved based on the measured fraction y_{NH_3} and the measured total inlet molar flow rate $\dot{n}_{tot,in}$.using Eq. (S.18) to calculate the extent of reaction ξ and Eq. (S.19)) to calculate $\dot{n}_{i,out}$ at the reactor outlet for all components.

$$\xi = \frac{\left(y_{NH_3}\,\dot{n}_{tot,in}\right)}{\nu_{NH_3}\sum \nu_i\, y_{NH_3}} \quad (S.18)$$

$$\dot{n}_{i,out} = \dot{n}_{i,in} + \nu_i\,\xi \quad (S.19)$$

Exclusion of Transport Limitations

The absence of mass transfer limitations was checked based on the criteria given in Eq. (S.20) and Eq. (S.21).The effective diffusion coefficient $D_{i,eff}$ inside the catalyst particle is calculated according to Eq. (S.22) by neglection of Knudsen diffusion and a conservative estimation of 0.05 for the particle porosity to tortuosity ratio (ε_p/τ_p) according to Kapteijn et al. [4]. The mass transfer coefficient k_g was set to typical gas phase values of 7 m s^{-2} for all components according to Fogler et al [5]. The criteria were checked for all experimental points. Yet, the smallest safety margin towards the defined criteria was found at highest temperature and highest pressure, leading to the maximum observed rate of formation for NH_3. Still under these conditions the criterions are fulfilled (Table S 2) proving the absence of internal and external mass transfer limitations.

Mears criterion (internal mass transfer) $$\frac{r_{NH_3} r_p n}{c_i D_{i,eff}} < 0.15 \quad (S.20)$$

Carberry criterion (external mass transfer) $$\frac{r_{NH_3}}{c_i k_{g,i} a} < 0.05 \quad (S.21)$$

Effective diffusion coefficient $$D_{i,eff} = \frac{\varepsilon_p}{\tau_p} D_i \quad (S.22)$$ with $i \in N_2, H_2$

Table S 2: Calculated values for the Mears and Carberry criterion for both catalysts at maximum rate of formation.

	Fe	Ru/CeO$_2$
Mears	$3.7 \cdot 10^{-3} < 0.15$	$2.5 \cdot 10^{-3} < 0.15$
Carberry	$3.11 \cdot 10^{-9} < 0.05$	$1.7 \cdot 10^{-9} < 0.05$

Comparison of Parity Plots

Figure S 1and Figure S 2 compare the parity plots for Fe and RuCeO$_2$ catalyst respectively, considering the different kinetic models considered.

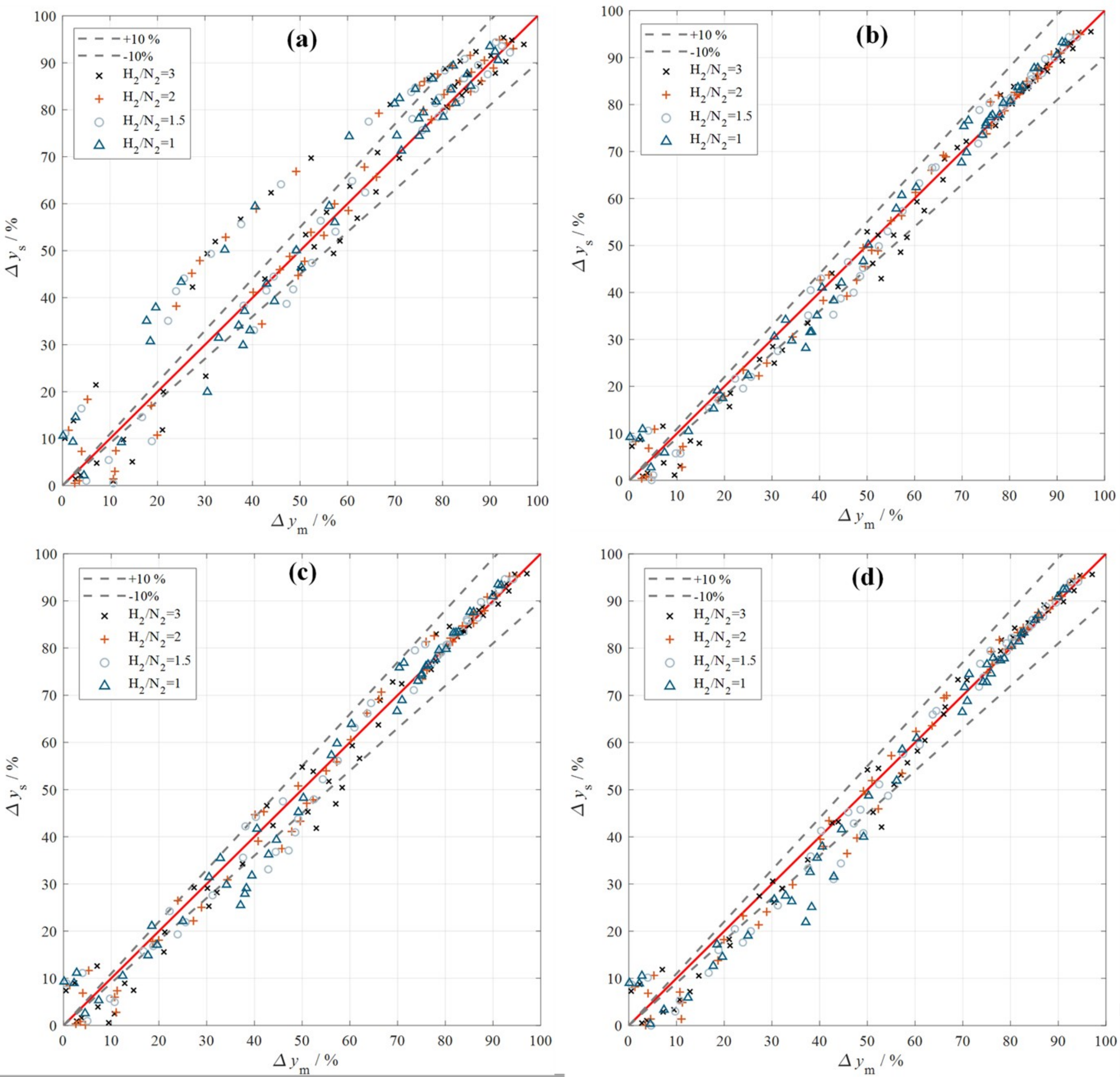

Figure S 1: Parity plots for the different Temkin model variations (Eq. 3 (a), Eq. 11 (b), Eq. 12 (c), Eq.4 (d)) applied to the Fe catalyst. All experimental points are included and classified by the used H_2/N_2 ratio (3 (×), 2 (+),1.5 (o), 1 (Δ)), 0 % (red) and ±10 % deviation lines (black) are given.

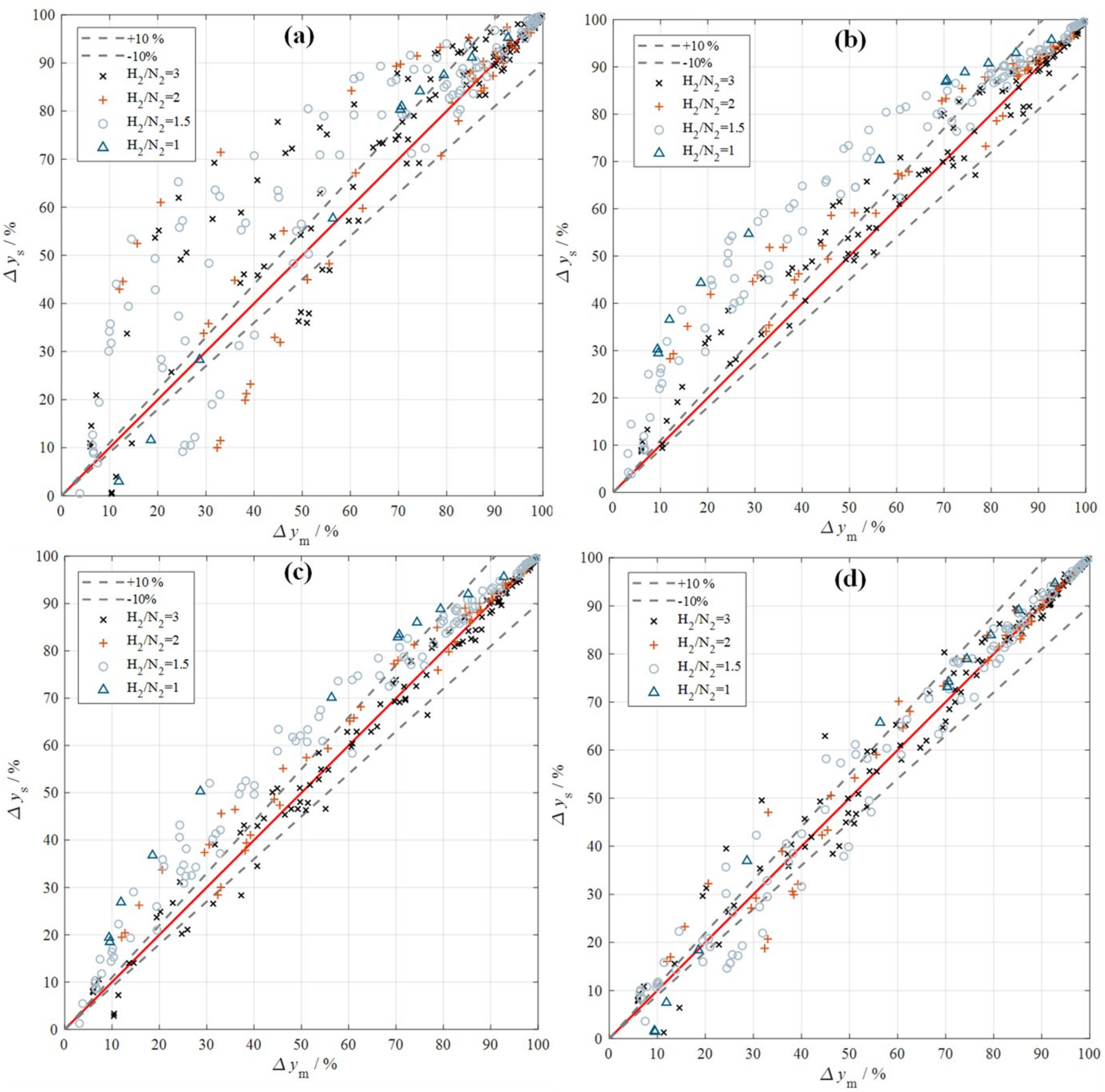

Figure S 2:Parity plots for the different Temkin model variations (Eq. 3 (a), Eq 11 (b), Eq. 12 (c), Eq. 4 (d)) applied to the Ru/CeO_2 catalyst. All experimental points are included and classified by the used H_2/N_2 ratio (3 (×), 2 (+),1.5 (o), 1 (Δ)), 0 % (red) and ±10 % deviation lines (black) are given.

Full Set of Profiles for Fe Catalyst

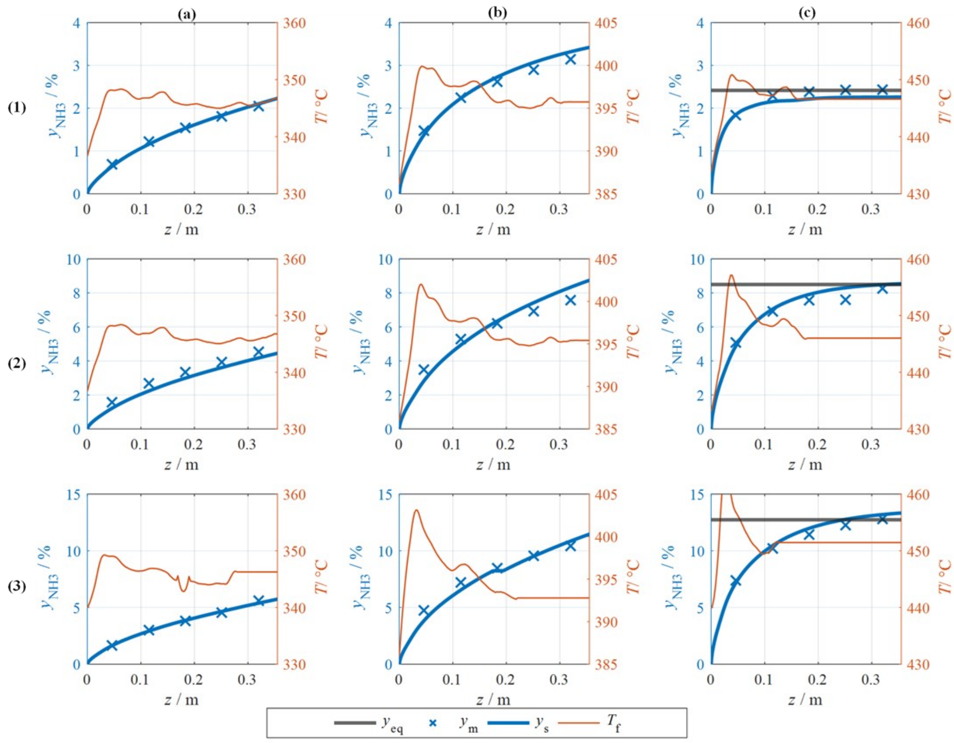

Figure S 3: Measured (markers), predicted (solid blue) and equilibrium (solid black) NH_3 molar fraction (primary axis) as well as temperature (orange, secondary axis) as function of the axial position *z* for the Fe catalyst at reaction pressure of 10 bar (1), 45 bar (2) and 80 bar (3) and temperatures of 350 °C (a), 400 °C (b) and 450 °C (c); reaction conditions: = 2.7 mol/h, H_2/N_2 =1.5.

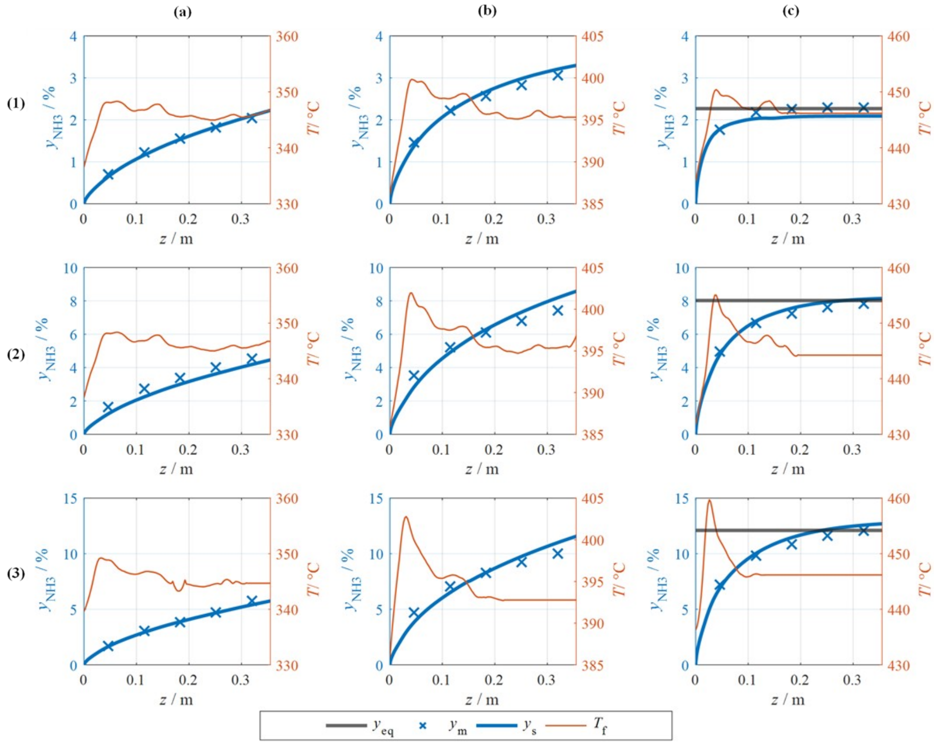

Figure S 4: Measured (markers), predicted (solid blue) and equilibrium (solid black) NH3 molar fraction (primary axis) as well as temperature (orange, secondary axis) as function of the axial position z for the Fe catalyst at reaction pressure of 10 bar (1), 45 bar (2) and 80 bar (3) and temperatures of 350 °C (a), 400 °C (b) and 450 °C (c); reaction conditions: = 2.7 mol/h, H_2/N_2 =2.

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Full Set of Profile for Ru/CeO$_2$ Catalyst

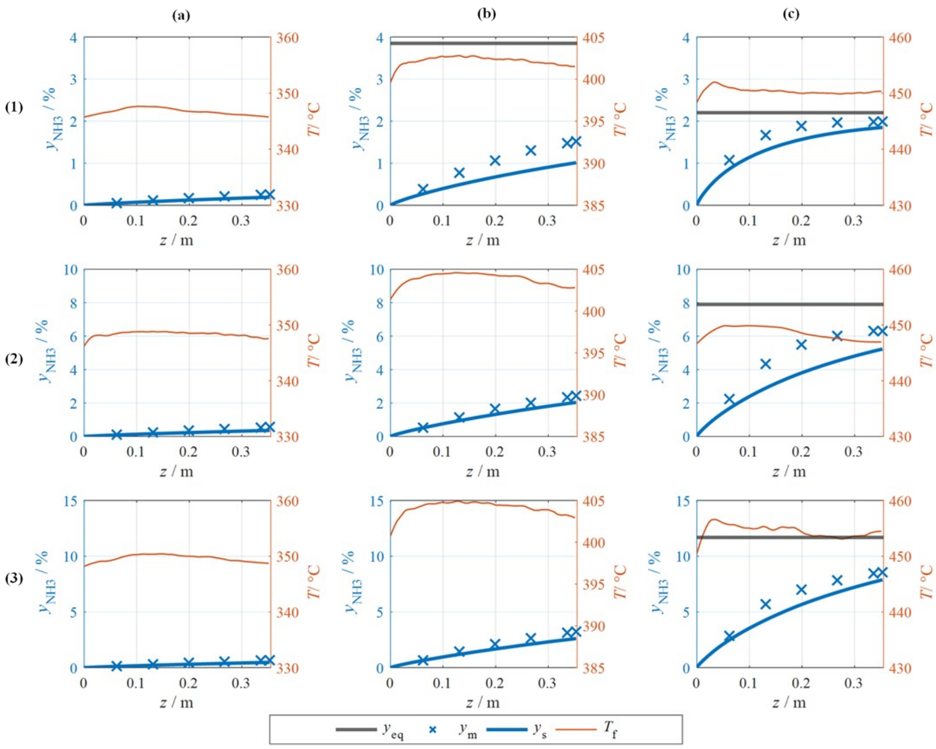

Figure S 5: Measured (markers), predicted (solid blue) and equilibrium (solid black) NH_3 molar fraction (primary axis) as well as temperature (orange, secondary axis) as function of the axial position *z* for the Ru/CeO$_2$ catalyst at reaction pressure of 10 bar (1), 45 bar (2) and 80 bar (3) and temperatures of 350 °C (a), 400 °C (b) and 450 °C (c); reaction conditions: = 2.7 mol/h, H_2/N_2 =1.5.

Experimental Data

Table S 3: Experimental data measured for the Fe catalyst under the reaction conditions given.

Pressure	H_2/N_2 ratio	Catalyst bed length	Molar inlet flow rate	Average temperature	NH_3 molar fraction
bar (gauge)	mol/mol	m	mol h^{-1}	°C	1
10	1	0.363	2.8	346	0.0203
10	1	0.32	2.8	346	0.0196
10	1	0.251	2.8	346	0.0173
10	1	0.183	2.8	346	0.0149
10	1	0.115	2.8	346	0.0120
10	1	0.046	2.8	346	0.0067
10	1.5	0.363	2.8	346	0.0212
10	1.5	0.32	2.8	346	0.0204
10	1.5	0.251	2.8	346	0.0182
10	1.5	0.183	2.8	346	0.0155
10	1.5	0.115	2.8	346	0.0122
10	1.5	0.046	2.8	346	0.0070
10	2	0.363	2.8	346	0.0214
10	2	0.32	2.8	346	0.0205
10	2	0.251	2.8	346	0.0181
10	2	0.183	2.8	346	0.0154
10	2	0.115	2.8	346	0.0122
10	2	0.046	2.8	346	0.0069
10	3	0.363	2.8	346	0.0205
10	3	0.32	2.8	346	0.0197
10	3	0.251	2.8	346	0.0174
10	3	0.183	2.8	346	0.0146
10	3	0.115	2.8	346	0.0116
10	3	0.046	2.8	346	0.0064
45	1	0.363	2.8	346	0.0451
45	1	0.32	2.8	346	0.0433
45	1	0.251	2.8	346	0.0384
45	1	0.183	2.8	346	0.0329
45	1	0.115	2.8	346	0.0267
45	1	0.046	2.8	346	0.0161
45	1.5	0.363	2.8	346	0.0470
45	1.5	0.32	2.8	346	0.0454
45	1.5	0.251	2.8	346	0.0401
45	1.5	0.183	2.8	346	0.0338
45	1.5	0.115	2.8	346	0.0273
45	1.5	0.046	2.8	346	0.0164
45	2	0.363	2.8	346	0.0472
45	2	0.32	2.8	346	0.0454
45	2	0.251	2.8	346	0.0393

45	2	0.183	2.8	346	0.0334
45	2	0.115	2.8	346	0.0268
45	2	0.046	2.8	346	0.0157
45	3	0.363	2.8	346	0.0442
45	3	0.32	2.8	346	0.0423
45	3	0.251	2.8	346	0.0368
45	3	0.183	2.8	346	0.0309
45	3	0.115	2.8	346	0.0248
45	3	0.046	2.8	346	0.0137
45	1	0.363	2.8	396	0.0706
45	1	0.32	2.8	396	0.0691
45	1	0.251	2.8	397	0.0639
45	1	0.183	2.8	396	0.0569
45	1	0.115	2.8	396	0.0492
45	1	0.046	2.8	397	0.0332
45	1.5	0.363	2.8	396	0.0764
45	1.5	0.32	2.8	396	0.0743
45	1.5	0.251	2.8	397	0.0680
45	1.5	0.183	2.8	396	0.0611
45	1.5	0.115	2.8	397	0.0522
45	1.5	0.046	2.8	397	0.0352
45	2	0.363	2.8	396	0.0788
45	2	0.32	2.8	397	0.0757
45	2	0.251	2.8	397	0.0692
45	2	0.183	2.8	397	0.0620
45	2	0.115	2.8	397	0.0529
45	2	0.046	2.8	397	0.0349
45	3	0.363	2.8	396	0.0714
45	3	0.32	2.8	397	0.0740
45	3	0.251	2.8	397	0.0674
45	3	0.183	2.8	397	0.0599
45	3	0.115	2.8	397	0.0511
45	3	0.046	2.8	397	0.0332
10	1	0.363	2.8	396	0.0289
10	1	0.32	2.8	396	0.0282
10	1	0.251	2.8	396	0.0263
10	1	0.183	2.8	396	0.0231
10	1	0.115	2.8	396	0.0208
10	1	0.046	2.8	396	0.0139
10	1.5	0.363	2.8	396	0.0314
10	1.5	0.32	2.8	396	0.0306
10	1.5	0.251	2.8	396	0.0283
10	1.5	0.183	2.8	396	0.0256
10	1.5	0.115	2.8	396	0.0222
10	1.5	0.046	2.8	396	0.0146

10	2	0.363	2.8	396	0.0322
10	2	0.32	2.8	396	0.0314
10	2	0.251	2.8	396	0.0290
10	2	0.183	2.8	396	0.0262
10	2	0.115	2.8	396	0.0225
10	2	0.046	2.8	396	0.0147
10	3	0.363	2.8	396	0.0320
10	3	0.32	2.8	396	0.0312
10	3	0.251	2.8	396	0.0287
10	3	0.183	2.8	396	0.0258
10	3	0.115	2.8	396	0.0219
10	3	0.046	2.8	396	0.0142
10	1	0.363	2.8	446	0.0201
10	1	0.32	2.8	446	0.0200
10	1	0.251	2.8	446	0.0194
10	1	0.183	2.8	446	0.0198
10	1	0.115	2.8	446	0.0192
10	1	0.046	2.8	446	0.0161
10	1.5	0.363	2.8	446	0.0230
10	1.5	0.32	2.8	447	0.0229
10	1.5	0.251	2.8	447	0.0229
10	1.5	0.183	2.8	447	0.0225
10	1.5	0.115	2.8	447	0.0218
10	1.5	0.046	2.8	447	0.0176
10	2	0.363	2.8	447	0.0233
10	2	0.32	2.8	447	0.0243
10	2	0.251	2.8	447	0.0243
10	2	0.183	2.8	447	0.0238
10	2	0.115	2.8	447	0.0229
10	2	0.046	2.8	447	0.0184
10	3	0.363	2.8	447	0.0251
10	3	0.32	2.8	447	0.0250
10	3	0.251	2.8	447	0.0248
10	3	0.183	2.8	447	0.0244
10	3	0.115	2.8	447	0.0232
10	3	0.046	2.8	447	0.0181
45	1	0.363	2.8	447	0.0688
45	1	0.32	2.8	447	0.0684
45	1	0.251	2.8	447	0.0674
45	1	0.183	2.8	447	0.0648
45	1	0.115	2.8	447	0.0594
45	1	0.046	2.8	447	0.0456
45	1.5	0.363	2.8	447	0.0789
45	1.5	0.32	2.8	447	0.0783
45	1.5	0.251	2.8	447	0.0762

45	1.5	0.183	2.8	447	0.0724
45	1.5	0.115	2.8	447	0.0668
45	1.5	0.046	2.8	447	0.0496
45	2	0.363	2.8	448	0.0836
45	2	0.32	2.8	448	0.0826
45	2	0.251	2.8	448	0.0760
45	2	0.183	2.8	448	0.0756
45	2	0.115	2.8	449	0.0691
45	2	0.046	2.8	449	0.0508
45	3	0.363	2.8	450	0.0851
45	3	0.32	2.8	450	0.0840
45	3	0.251	2.8	450	0.0809
45	3	0.183	2.8	450	0.0759
45	3	0.115	2.8	451	0.0684
45	3	0.046	2.8	451	0.0498
45	1	0.363	2.8	297	0.0251
45	1	0.32	2.8	297	0.0240
45	1	0.251	2.8	297	0.0210
45	1	0.183	2.8	298	0.0177
45	1	0.115	2.8	298	0.0134
45	1	0.046	2.8	298	0.0040
45	1.5	0.363	2.8	298	0.0249
45	1.5	0.32	2.8	298	0.0238
45	1.5	0.251	2.8	298	0.0205
45	1.5	0.183	2.8	298	0.0169
45	1.5	0.115	2.8	298	0.0123
45	1.5	0.046	2.8	298	0.0030
45	2	0.363	2.8	298	0.0235
45	2	0.32	2.8	298	0.0224
45	2	0.251	2.8	298	0.0190
45	2	0.183	2.8	298	0.0145
45	2	0.115	2.8	298	0.0107
45	2	0.046	2.8	298	0.0020
45	3	0.363	2.8	298	0.0202
45	3	0.32	2.8	298	0.0189
45	3	0.251	2.8	298	0.0157
45	3	0.183	2.8	298	0.0120
45	3	0.115	2.8	298	0.0075
45	3	0.046	2.8	298	0.0007
10	1	0.363	2.8	298	0.0121
10	1	0.32	2.8	298	0.0116
10	1	0.251	2.8	298	0.0101
10	1	0.183	2.8	298	0.0084
10	1	0.115	2.8	298	0.0063
10	1	0.046	2.8	298	0.0014

10	1.5	0.363	2.8	298	0.0123
10	1.5	0.32	2.8	298	0.0119
10	1.5	0.251	2.8	298	0.0103
10	1.5	0.183	2.8	298	0.0085
10	1.5	0.115	2.8	298	0.0062
10	1.5	0.046	2.8	298	0.0013
10	2	0.363	2.8	298	0.0115
10	2	0.32	2.8	298	0.0116
10	2	0.251	2.8	298	0.0101
10	2	0.183	2.8	298	0.0082
10	2	0.115	2.8	298	0.0059
10	2	0.046	2.8	298	0.0011
10	3	0.363	2.8	298	0.0114
10	3	0.32	2.8	298	0.0108
10	3	0.251	2.8	298	0.0093
10	3	0.183	2.8	298	0.0071
10	3	0.115	2.8	298	0.0052
10	3	0.046	2.8	298	0.0010
80	3	0.363	2.8	299	0.0206
80	3	0.32	2.8	299	0.0188
80	3	0.251	2.8	299	0.0139
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80	3	0.115	2.8	299	0.0035
80	3	0.046	2.8	299	0.0008
80	1.5	0.363	2.8	298	0.0305
80	1.5	0.32	2.8	298	0.0287
80	1.5	0.251	2.8	298	0.0225
80	1.5	0.183	2.8	298	0.0182
80	1.5	0.115	2.8	298	0.0114
80	1.5	0.046	2.8	298	0.0016
80	2	0.363	2.8	297	0.0269
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80	2	0.251	2.8	298	0.0197
80	2	0.183	2.8	298	0.0141
80	2	0.115	2.8	298	0.0075
80	2	0.046	2.8	298	0.0008
80	1	0.363	2.8	297	0.0327
80	1	0.32	2.8	298	0.0310
80	1	0.251	2.8	298	0.0263
80	1	0.183	2.8	298	0.0210
80	1	0.115	2.8	298	0.0144
80	1	0.046	2.8	298	0.0025
80	3	0.363	2.8	346	0.0550
80	3	0.32	2.8	346	0.0516
80	3	0.251	2.8	346	0.0415

80	3	0.183	2.8	346	0.0306
80	3	0.115	2.8	346	0.0230
80	3	0.046	2.8	346	0.0099
80	1.5	0.363	2.8	346	0.0608
80	1.5	0.32	2.8	346	0.0576
80	1.5	0.251	2.8	346	0.0472
80	1.5	0.183	2.8	346	0.0384
80	1.5	0.115	2.8	346	0.0306
80	1.5	0.046	2.8	346	0.0170
80	2	0.363	2.8	346	0.0597
80	2	0.32	2.8	346	0.0560
80	2	0.251	2.8	346	0.0455
80	2	0.183	2.8	346	0.0382
80	2	0.115	2.8	346	0.0300
80	2	0.046	2.8	346	0.0165
80	1	0.363	2.8	346	0.0591
80	1	0.32	2.8	346	0.0560
80	1	0.251	2.8	346	0.0471
80	1	0.183	2.8	346	0.0409
80	1	0.115	2.8	346	0.0334
80	1	0.046	2.8	346	0.0197
80	3	0.363	2.8	396	0.0967
80	3	0.32	2.8	396	0.0935
80	3	0.251	2.8	396	0.0853
80	3	0.183	2.8	396	0.0764
80	3	0.115	2.8	396	0.0653
80	3	0.046	2.8	396	0.0429
80	1.5	0.363	2.8	396	0.1029
80	1.5	0.32	2.8	396	0.1002
80	1.5	0.251	2.8	396	0.0925
80	1.5	0.183	2.8	396	0.0828
80	1.5	0.115	2.8	397	0.0706
80	1.5	0.046	2.8	397	0.0471
80	2	0.363	2.8	397	0.1072
80	2	0.32	2.8	397	0.1042
80	2	0.251	2.8	397	0.0956
80	2	0.183	2.8	397	0.0846
80	2	0.115	2.8	397	0.0721
80	2	0.046	2.8	397	0.0474
80	1	0.363	2.8	397	0.0998
80	1	0.32	2.8	397	0.0972
80	1	0.251	2.8	397	0.0891
80	1	0.183	2.8	397	0.0798
80	1	0.115	2.8	397	0.0685
80	1	0.046	2.8	397	0.0460

80	3	0.363	2.8	446	0.1293
80	3	0.32	2.8	446	0.1273
80	3	0.251	2.8	446	0.1215
80	3	0.183	2.8	446	0.1124
80	3	0.115	2.8	446	0.0991
80	3	0.046	2.8	447	0.0707
80	1.5	0.363	2.8	449	0.1224
80	1.5	0.32	2.8	449	0.1207
80	1.5	0.251	2.8	449	0.1162
80	1.5	0.183	2.8	450	0.1085
80	1.5	0.115	2.8	450	0.0983
80	1.5	0.046	2.8	450	0.0722
80	2	0.363	2.8	452	0.1302
80	2	0.32	2.8	452	0.1281
80	2	0.251	2.8	453	0.1226
80	2	0.183	2.8	453	0.1143
80	2	0.115	2.8	453	0.1020
80	2	0.046	2.8	454	0.0739
80	1	0.363	2.8	454	0.1062
80	1	0.32	2.8	455	0.1054
80	1	0.251	2.8	455	0.1034
80	1	0.183	2.8	456	0.0977
80	1	0.115	2.8	456	0.0892
80	1	0.046	2.8	456	0.0669

Table S 4: Experimental data measured for the Ru/CeO_2 catalyst under the reaction conditions given.

Pressure	**H_2/N_2 ratio**	**Catalyst bed length**	**Molar inlet flow rate**	**Average temperature**	**NH_3 molar fraction**
bar (gauge)	mol/mol	m	mol h^{-1}	°C	1
10	3	0.353	2.7	297	0.0009
10	3	0.336	2.7	298	0.0009
10	3	0.267	2.7	298	0.0008
10	3	0.199	2.7	298	0.0006
10	3	0.131	2.7	298	0.0004
10	3	0.062	2.7	298	0.0002
10	1.5	0.353	2.7	298	0.0015
10	1.5	0.336	2.7	298	0.0014
10	1.5	0.267	2.7	298	0.0011
10	1.5	0.199	2.7	298	0.0009
10	1.5	0.131	2.7	298	0.0006
10	1.5	0.062	2.7	298	0.0003
10	1.5	0.353	2.7	298	0.0004
10	1.5	0.336	2.7	298	0.0004
10	1.5	0.267	2.7	298	0.0003
10	1.5	0.199	2.7	298	0.0002

10	1.5	0.131	2.7	298	0.0002
10	1.5	0.062	2.7	298	0.0001
10	3	0.353	2.7	298	0.0002
10	3	0.336	2.7	298	0.0002
10	3	0.267	2.7	298	0.0002
10	3	0.199	2.7	298	0.0001
10	3	0.131	2.7	298	0.0001
10	3	0.062	2.7	298	0.0000
10	3	0.353	2.7	400	0.0078
10	3	0.336	2.7	400	0.0075
10	3	0.267	2.7	401	0.0064
10	3	0.199	2.7	401	0.0051
10	3	0.131	2.7	402	0.0036
10	3	0.062	2.7	402	0.0017
10	1.5	0.353	2.7	403	0.0119
10	1.5	0.336	2.7	404	0.0115
10	1.5	0.267	2.7	404	0.0101
10	1.5	0.199	2.7	404	0.0083
10	1.5	0.131	2.7	404	0.0058
10	1.5	0.062	2.7	404	0.0029
10	3	0.353	2.7	404	0.0223
10	3	0.336	2.7	404	0.0217
10	3	0.267	2.7	404	0.0192
10	3	0.199	2.7	405	0.0162
10	3	0.131	2.7	405	0.0115
10	3	0.062	2.7	405	0.0058
10	1.5	0.353	2.7	405	0.0280
10	1.5	0.336	2.7	405	0.0277
10	1.5	0.267	2.7	406	0.0252
10	1.5	0.199	2.7	406	0.0221
10	1.5	0.131	2.7	406	0.0168
10	1.5	0.062	2.7	406	0.0088
10	3	0.353	2.7	452	0.0178
10	3	0.336	2.7	453	0.0174
10	3	0.267	2.7	453	0.0161
10	3	0.199	2.7	453	0.0139
10	3	0.131	2.7	453	0.0105
10	3	0.062	2.7	453	0.0055
10	1.5	0.353	2.7	453	0.0191
10	1.5	0.336	2.7	453	0.0190
10	1.5	0.267	2.7	453	0.0182
10	1.5	0.199	2.7	453	0.0170
10	1.5	0.131	2.7	453	0.0142
10	1.5	0.062	2.7	453	0.0083
10	1.5	0.353	2.7	453	0.0198

10	1.5	0.336	2.7	453	0.0198
10	1.5	0.267	2.7	453	0.0199
10	1.5	0.199	2.7	453	0.0199
10	1.5	0.131	2.7	453	0.0196
10	1.5	0.062	2.7	453	0.0172
10	3	0.353	2.7	453	0.0218
10	3	0.336	2.7	453	0.0219
10	3	0.267	2.7	453	0.0218
10	3	0.199	2.7	453	0.0216
10	3	0.131	2.7	453	0.0201
10	3	0.062	2.7	453	0.0146
45	3	0.353	2.7	298	0.0004
45	3	0.336	2.7	298	0.0004
45	3	0.267	2.7	298	0.0003
45	3	0.199	2.7	298	0.0003
45	3	0.131	2.7	298	0.0002
45	3	0.062	2.7	298	0.0001
45	1.5	0.353	2.7	298	0.0008
45	1.5	0.336	2.7	298	0.0008
45	1.5	0.267	2.7	298	0.0006
45	1.5	0.199	2.7	298	0.0005
45	1.5	0.131	2.7	298	0.0003
45	1.5	0.062	2.7	298	0.0001
45	1.5	0.353	2.7	298	0.0028
45	1.5	0.336	2.7	298	0.0026
45	1.5	0.267	2.7	298	0.0022
45	1.5	0.199	2.7	298	0.0018
45	1.5	0.131	2.7	299	0.0012
45	1.5	0.062	2.7	299	0.0005
45	3	0.353	2.7	299	0.0016
45	3	0.336	2.7	299	0.0015
45	3	0.267	2.7	299	0.0013
45	3	0.199	2.7	299	0.0010
45	3	0.131	2.7	299	0.0007
45	3	0.062	2.7	299	0.0003
45	3	0.353	2.7	398	0.0154
45	3	0.336	2.7	398	0.0149
45	3	0.267	2.7	399	0.0127
45	3	0.199	2.7	399	0.0102
45	3	0.131	2.7	399	0.0071
45	3	0.062	2.7	399	0.0032
45	1.5	0.353	2.7	400	0.0266
45	1.5	0.336	2.7	400	0.0259
45	1.5	0.267	2.7	400	0.0222
45	1.5	0.199	2.7	400	0.0180

Please do not adjust margins

45	1.5	0.131	2.7	401	0.0124
45	1.5	0.062	2.7	401	0.0057
45	3	0.353	2.7	396	0.0471
45	3	0.336	2.7	397	0.0459
45	3	0.267	2.7	397	0.0408
45	3	0.199	2.7	398	0.0339
45	3	0.131	2.7	398	0.0235
45	3	0.062	2.7	398	0.0104
45	1.5	0.353	2.7	400	0.0677
45	1.5	0.336	2.7	400	0.0661
45	1.5	0.267	2.7	400	0.0603
45	1.5	0.199	2.7	400	0.0553
45	1.5	0.131	2.7	401	0.0383
45	1.5	0.062	2.7	401	0.0181
45	1.5	0.353	2.7	449	0.0630
45	1.5	0.336	2.7	449	0.0631
45	1.5	0.267	2.7	449	0.0601
45	1.5	0.199	2.7	449	0.0550
45	1.5	0.131	2.7	449	0.0434
45	1.5	0.062	2.7	449	0.0224
45	3	0.353	2.7	452	0.0548
45	3	0.336	2.7	452	0.0541
45	3	0.267	2.7	452	0.0488
45	3	0.199	2.7	452	0.0403
45	3	0.131	2.7	451	0.0290
45	3	0.062	2.7	451	0.0138
45	3	0.353	2.7	452	0.0780
45	3	0.336	2.7	452	0.0777
45	3	0.267	2.7	452	0.0767
45	3	0.199	2.7	452	0.0735
45	3	0.131	2.7	452	0.0663
45	3	0.062	2.7	453	0.0431
45	1.5	0.353	2.7	453	0.0742
45	1.5	0.336	2.7	453	0.0745
45	1.5	0.267	2.7	453	0.0746
45	1.5	0.199	2.7	453	0.0739
45	1.5	0.131	2.7	453	0.0710
45	1.5	0.062	2.7	453	0.0568
30	3	0.353	2.7	432	0.0270
30	3	0.336	2.7	432	0.0259
30	3	0.267	2.7	432	0.0222
30	3	0.199	2.7	432	0.0179
30	3	0.131	2.7	432	0.0126
30	3	0.062	2.7	433	0.0059
80	3	0.353	2.7	295	0.0005

80	3	0.336	2.7	295	0.0005
80	3	0.267	2.7	295	0.0004
80	3	0.199	2.7	295	0.0003
80	3	0.131	2.7	295	0.0002
80	3	0.062	2.7	295	0.0001
80	1.5	0.353	2.7	296	0.0009
80	1.5	0.336	2.7	296	0.0009
80	1.5	0.267	2.7	296	0.0008
80	1.5	0.199	2.7	296	0.0006
80	1.5	0.131	2.7	296	0.0004
80	1.5	0.062	2.7	296	0.0002
80	3	0.353	2.7	296	0.0017
80	3	0.336	2.7	296	0.0017
80	3	0.267	2.7	296	0.0015
80	3	0.199	2.7	296	0.0012
80	3	0.131	2.7	296	0.0008
80	3	0.062	2.7	296	0.0004
80	3	0.353	2.7	396	0.0191
80	3	0.336	2.7	397	0.0184
80	3	0.267	2.7	397	0.0153
80	3	0.199	2.7	397	0.0123
80	3	0.131	2.7	397	0.0084
80	3	0.062	2.7	397	0.0038
80	1.5	0.353	2.7	398	0.0337
80	1.5	0.336	2.7	398	0.0331
80	1.5	0.267	2.7	398	0.0286
80	1.5	0.199	2.7	398	0.0225
80	1.5	0.131	2.7	398	0.0155
80	1.5	0.062	2.7	398	0.0071
30	1.5	0.353	2.7	434	0.0418
30	1.5	0.336	2.7	434	0.0411
30	1.5	0.267	2.7	434	0.0366
30	1.5	0.199	2.7	434	0.0307
30	1.5	0.131	2.7	434	0.0222
30	1.5	0.062	2.7	434	0.0110
80	3	0.353	2.7	453	0.0680
80	3	0.336	2.7	454	0.0672
80	3	0.267	2.7	454	0.0610
80	3	0.199	2.7	454	0.0535
80	3	0.131	2.7	454	0.0375
80	3	0.062	2.7	455	0.0174
80	1.5	0.353	2.7	456	0.0862
80	1.5	0.336	2.7	456	0.0854
80	1.5	0.267	2.7	456	0.0787
80	1.5	0.199	2.7	456	0.0722

80	1.5	0.131	2.7	457	0.0591
80	1.5	0.062	2.7	457	0.0311
45	1	0.353	2.7	399	0.0323
45	1	0.336	2.7	399	0.0319
45	1	0.267	2.7	399	0.0278
45	1	0.199	2.7	399	0.0223
45	1	0.131	2.7	400	0.0160
45	1	0.062	2.7	400	0.0078
45	2	0.353	2.7	400	0.0215
45	2	0.336	2.7	400	0.0204
45	2	0.267	2.7	400	0.0174
45	2	0.199	2.7	400	0.0138
45	2	0.131	2.7	401	0.0096
45	2	0.062	2.7	401	0.0045
45	2.5	0.353	2.7	401	0.0180
45	2.5	0.336	2.7	401	0.0172
45	2.5	0.267	2.7	401	0.0146
45	2.5	0.199	2.7	401	0.0116
45	2.5	0.131	2.7	401	0.0081
45	2.5	0.062	2.7	401	0.0037
80	1	0.353	2.7	457	0.0864
80	1	0.336	2.7	458	0.0859
80	1	0.267	2.7	459	0.0830
80	1	0.199	2.7	459	0.0763
80	1	0.131	2.7	460	0.0665
80	1	0.062	2.7	461	0.0405
80	2	0.353	2.7	462	0.0810
80	2	0.336	2.7	462	0.0800
80	2	0.267	2.7	462	0.0737
80	2	0.199	2.7	463	0.0647
80	2	0.131	2.7	464	0.0522
80	2	0.062	2.7	465	0.0247
45	1.5	0.353	2.7	348	0.0057
45	1.5	0.336	2.7	348	0.0053
45	1.5	0.267	2.7	348	0.0045
45	1.5	0.199	2.7	349	0.0035
45	1.5	0.131	2.7	349	0.0024
45	1.5	0.062	2.7	349	0.0011
45	3	0.353	2.7	349	0.0031
45	3	0.336	2.7	349	0.0029
45	3	0.267	2.7	349	0.0024
45	3	0.199	2.7	349	0.0019
45	3	0.131	2.7	349	0.0013
45	3	0.062	2.7	349	0.0006
80	3	0.353	2.7	349	0.0037

80	3	0.336	2.7	349	0.0036
80	3	0.267	2.7	349	0.0031
80	3	0.199	2.7	349	0.0024
80	3	0.131	2.7	349	0.0017
80	3	0.062	2.7	349	0.0007
80	1.5	0.353	2.7	350	0.0067
80	1.5	0.336	2.7	350	0.0065
80	1.5	0.267	2.7	350	0.0054
80	1.5	0.199	2.7	350	0.0044
80	1.5	0.131	2.7	350	0.0030
80	1.5	0.062	2.7	350	0.0014
10	1.5	0.353	2.7	347	0.0026
10	1.5	0.336	2.7	347	0.0025
10	1.5	0.267	2.7	347	0.0021
10	1.5	0.199	2.7	347	0.0017
10	1.5	0.131	2.7	348	0.0012
10	1.5	0.062	2.7	348	0.0005
10	3	0.353	2.7	348	0.0015
10	3	0.336	2.7	348	0.0014
10	3	0.267	2.7	348	0.0012
10	3	0.199	2.7	348	0.0010
10	3	0.131	2.7	348	0.0006
10	3	0.062	2.7	349	0.0003
80	2.5	0.353	2.7	452	0.0725
80	2.5	0.336	2.7	452	0.0713
80	2.5	0.267	2.7	453	0.0662
80	2.5	0.199	2.7	453	0.0580
80	2.5	0.131	2.7	453	0.0422
80	2.5	0.062	2.7	454	0.0197
10	3	0.353	2.7	299	0.0004
10	3	0.336	2.7	299	0.0004
10	3	0.267	2.7	299	0.0003
10	3	0.199	2.7	299	0.0002
10	3	0.131	2.7	299	0.0002
10	3	0.062	2.7	299	0.0001
10	2	0.353	2.7	299	0.0005
10	2	0.336	2.7	299	0.0005
10	2	0.267	2.7	299	0.0004
10	2	0.199	2.7	299	0.0003
10	2	0.131	2.7	299	0.0002
10	2	0.062	2.7	299	0.0001
10	1.5	0.353	2.7	299	0.0007
10	1.5	0.336	2.7	299	0.0006
10	1.5	0.267	2.7	299	0.0005
10	1.5	0.199	2.7	299	0.0004

10	1.5	0.131	2.7	299	0.0003
10	1.5	0.062	2.7	299	0.0001
45	3	0.353	2.7	300	0.0004
45	3	0.336	2.7	300	0.0004
45	3	0.267	2.7	300	0.0003
45	3	0.199	2.7	300	0.0003
45	3	0.131	2.7	300	0.0002
45	3	0.062	2.7	300	0.0001
45	2	0.353	2.7	300	0.0006
45	2	0.336	2.7	300	0.0006
45	2	0.267	2.7	300	0.0005
45	2	0.199	2.7	300	0.0004
45	2	0.131	2.7	300	0.0003
45	2	0.062	2.7	300	0.0001
45	1.5	0.353	2.7	300	0.0008
45	1.5	0.336	2.7	300	0.0008
45	1.5	0.267	2.7	300	0.0006
45	1.5	0.199	2.7	300	0.0005
45	1.5	0.131	2.7	300	0.0003
45	1.5	0.062	2.7	300	0.0001
10	3	0.353	2.7	400	0.0099
10	3	0.336	2.7	401	0.0096
10	3	0.267	2.7	401	0.0083
10	3	0.199	2.7	401	0.0068
10	3	0.131	2.7	401	0.0048
10	3	0.062	2.7	401	0.0023
10	2	0.353	2.7	402	0.0128
10	2	0.336	2.7	402	0.0124
10	2	0.267	2.7	402	0.0110
10	2	0.199	2.7	402	0.0089
10	2	0.131	2.7	402	0.0064
10	2	0.062	2.7	402	0.0031
10	1.5	0.353	2.7	402	0.0152
10	1.5	0.336	2.7	402	0.0147
10	1.5	0.267	2.7	402	0.0130
10	1.5	0.199	2.7	402	0.0106
10	1.5	0.131	2.7	402	0.0077
10	1.5	0.062	2.7	402	0.0038
45	3	0.353	2.7	403	0.0146
45	3	0.336	2.7	403	0.0140
45	3	0.267	2.7	403	0.0118
45	3	0.199	2.7	403	0.0095
45	3	0.131	2.7	403	0.0065
45	3	0.062	2.7	403	0.0029
45	2	0.353	2.7	403	0.0197

45	2	0.336	2.7	403	0.0192
45	2	0.267	2.7	403	0.0165
45	2	0.199	2.7	404	0.0130
45	2	0.131	2.7	404	0.0090
45	2	0.062	2.7	404	0.0041
45	1.5	0.353	2.7	404	0.0243
45	1.5	0.336	2.7	404	0.0234
45	1.5	0.267	2.7	404	0.0201
45	1.5	0.199	2.7	404	0.0166
45	1.5	0.131	2.7	404	0.0114
45	1.5	0.062	2.7	404	0.0053
10	3	0.353	2.7	449	0.0199
10	3	0.336	2.7	449	0.0197
10	3	0.267	2.7	449	0.0188
10	3	0.199	2.7	449	0.0168
10	3	0.131	2.7	449	0.0135
10	3	0.062	2.7	450	0.0074
10	2	0.353	2.7	450	0.0209
10	2	0.336	2.7	450	0.0207
10	2	0.267	2.7	450	0.0201
10	2	0.199	2.7	450	0.0188
10	2	0.131	2.7	450	0.0158
10	2	0.062	2.7	450	0.0094
10	1.5	0.353	2.7	450	0.0199
10	1.5	0.336	2.7	450	0.0198
10	1.5	0.267	2.7	450	0.0197
10	1.5	0.199	2.7	450	0.0189
10	1.5	0.131	2.7	450	0.0167
10	1.5	0.062	2.7	450	0.0107
45	3	0.353	2.7	451	0.0521
45	3	0.336	2.7	451	0.0509
45	3	0.267	2.7	451	0.0423
45	3	0.199	2.7	451	0.0346
45	3	0.131	2.7	451	0.0246
45	3	0.062	2.7	451	0.0116
45	2	0.353	2.7	451	0.0595
45	2	0.336	2.7	451	0.0586
45	2	0.267	2.7	450	0.0541
45	2	0.199	2.7	450	0.0455
45	2	0.131	2.7	450	0.0329
45	2	0.062	2.7	450	0.0159
80	2	0.353	2.7	299	0.0008
80	2	0.336	2.7	299	0.0008
80	2	0.267	2.7	299	0.0006
80	2	0.199	2.7	299	0.0005

80	2	0.131	2.7	299	0.0003
80	2	0.062	2.7	299	0.0001
80	1.5	0.353	2.7	299	0.0010
80	1.5	0.336	2.7	299	0.0010
80	1.5	0.267	2.7	299	0.0008
80	1.5	0.199	2.7	299	0.0006
80	1.5	0.131	2.7	299	0.0004
80	1.5	0.062	2.7	300	0.0002
80	3	0.353	2.7	402	0.0184
80	3	0.336	2.7	402	0.0174
80	3	0.267	2.7	402	0.0148
80	3	0.199	2.7	402	0.0117
80	3	0.131	2.7	402	0.0080
80	3	0.062	2.7	402	0.0036
80	2	0.353	2.7	403	0.0259
80	2	0.336	2.7	403	0.0247
80	2	0.267	2.7	403	0.0209
80	2	0.199	2.7	403	0.0166
80	2	0.131	2.7	404	0.0113
80	2	0.062	2.7	404	0.0051
80	1.5	0.353	2.7	404	0.0324
80	1.5	0.336	2.7	404	0.0314
80	1.5	0.267	2.7	404	0.0264
80	1.5	0.199	2.7	404	0.0211
80	1.5	0.131	2.7	404	0.0144
80	1.5	0.062	2.7	404	0.0066
80	3	0.353	2.7	453	0.0657
80	3	0.336	2.7	454	0.0651
80	3	0.267	2.7	454	0.0593
80	3	0.199	2.7	454	0.0512
80	3	0.131	2.7	454	0.0344
80	3	0.062	2.7	454	0.0160
80	2	0.353	2.7	454	0.0785
80	2	0.336	2.7	454	0.0774
80	2	0.267	2.7	454	0.0710
80	2	0.199	2.7	454	0.0623
80	2	0.131	2.7	454	0.0477
80	2	0.062	2.7	454	0.0223
80	1.5	0.353	2.7	455	0.0856
80	1.5	0.336	2.7	455	0.0845
80	1.5	0.267	2.7	455	0.0784
80	1.5	0.199	2.7	455	0.0700
80	1.5	0.131	2.7	454	0.0569
80	1.5	0.062	2.7	455	0.0285

Latin Symbols

a_i	Activity of component *i* (1)
a_{ci}	Redlich-Kwong Parameter at critical point
a_S	Redlich-Kwong Parameter
$a_{S,i}$	Modified Redlich-Kwong Parameter
A_R	Cross sectional area of the reactor tube (m^2)
A_S	Adapted Redlich-Kwong Parameter
B_S	Adapted Redlich-Kwong Parameter
b	Redlich-Kwong Parameter
b_i	Redlich-Kwong Parameter at critical point
CI	Relative confidence interval (%)
d_F	Outer diameter of fiber optical temperature sensor (mm)
d_{in}	Inner reactor diameter (mm)
d_p	Particle diameter (µm)
E_A	Activation energy (J mol^{-1})
f_j	Kinetic coefficient for adsorption equilibrium *j* (1)
$\Delta_R G°$	Standard Gibbs free energy of reaction (J mol^{-1})
$\Delta_{Ads} H_i$	Specific enthalpy of adsorption of component i (J mol^{-1})
ΔH_r^o	Enthalpy of formation under standard condition (kJ mol^{-1})
K_{eq}	Equilibrium constant of NH_3 synthesis (1)
k_i	Reaction rate constant (var.)
K_i	Adsorption constant of component (1)
$k_{i,0}$	Pre-exponential factor (var.)
$L_{bed,tot}$	Total length of catalyst bed (m)
$L_{bed}(z)$	Reactor length at sampling position (m)
m_{cat}	Catalyst mass (g)
m_i	Slope of $\beta^{0.5}$ against $\frac{T}{T_c}^{0.5}$
$\dot{n}_{i,in}$	Molar flow of component *i* at reactor inlet (mol h^{-1})
$\dot{n}_{tot,in}$	Total molar flow at reactor outlet (mol h^{-1})
$\dot{n}_{i,out}$	Molar flow of component *i* at reactor outlet (mol h^{-1})
$\dot{N}_{NH_3,out}$	Specific molar flow rate of NH_3 per mass catalyst at reactor outlet (mmol g^{-1} h^{-1})
N	Number of experimental points for each catalyst
p	Pressure (bar (gauge))
p_c	Critical pressure (Pa)
r_{NH_3}	Rate of formation of NH_3 (mol s^{-1} kg_{cat}^{-1})
R	Ideal gas constant (J mol^{-1} K^{-1})
RE	Relative error function (1)
$RSME$	Relative-Square-Mean Error (1)
$\Delta_{Ads} S_i$	Specific entropy of adsorption of component i (J K^{-1} mol^{-1})
T	Temperature (°C)
$T(z)$	Measured Temperature at reactor length z (°C)
T_c	Critical Temperature (K)
y_{eq}	Molar fraction of NH_3 in equilibrium (1)

y_m	Measured molar fraction of NH_3 in the gas phase (1)
y_s	Simulated molar fraction of NH_3 in the gas phase (1)
z	Axial coordinate in the reactor (m)
Z	Compressibility factor (-)

Greek Symbols

α	Kinetic coefficient of Temkin equation (1)
β_i	Correction factor for modified Redlich-Kwong equation
ν_i	Stochiometric coefficient of component *i* in ammonia synthesis (1)
φ_i	Fugacity coefficient of component *i* (1)
ψ_j	Relative rate of formation at H_2/N_2 ratio *j* (1)
ω_i	Acentric factor of component i (1)

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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