

# Ammonia-methane interaction in Jet-Stirred and Flow reactors: an experimental and kinetic modeling study

Suphaporn Arunthanayothin<sup>a</sup>, Alessandro Stagni<sup>b</sup>, Yu Song<sup>a,c</sup>, Olivier Herbinet<sup>a</sup>,  
Tiziano Faravelli<sup>b</sup>, Frédérique Battin-Leclerc<sup>a</sup>

<sup>a</sup> *Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, ENSIC, Nancy Cedex, France*

<sup>b</sup> *CRECK Modeling Lab, Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133 Milano, Italy*

<sup>c</sup> *Laboratoire PRISME, Université d'Orléans, Polytech Vinci – 45072 Orléans cedex, France*

## Supplementary Material

Additional information about experimental setups .....	2
Global schemes of the two setups .....	2
Temperature profiles in the flow tube reactor .....	2
Calculation of the Reynolds and Peclet numbers .....	3
Experimental conditions for experiments .....	4
JSR experiments .....	4
Flow tube experiments .....	4
Atomic balances .....	5
Additional model validations for CH <sub>4</sub> /NH <sub>3</sub> /O <sub>2</sub> .....	6
Ignition delay times [1] .....	6
Laminar burning velocities [2] .....	6
Flow reactor [3] .....	7
Flow reactor [4] .....	10
References .....	11

## Additional information about experimental setups

### Global schemes of the two setups

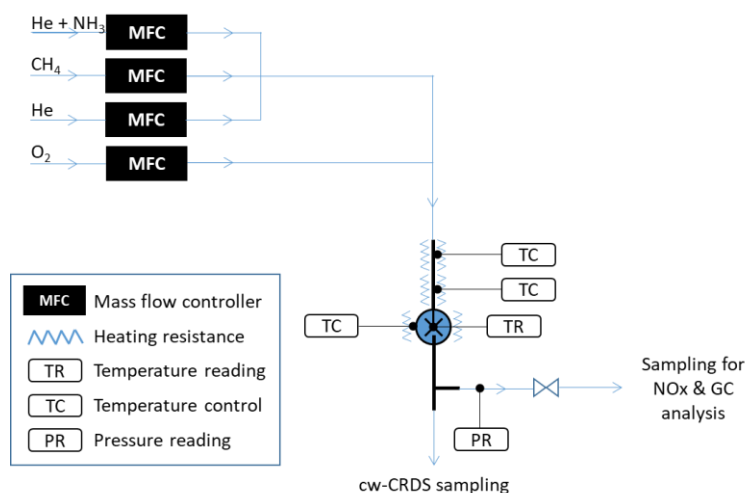


Figure S1. Scheme of the experimental apparatus (Setup 1).

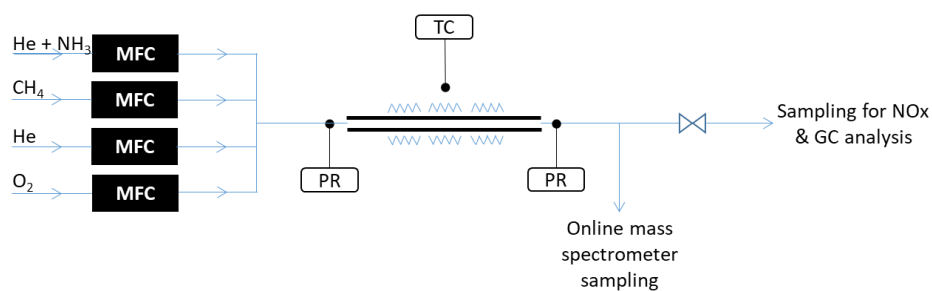


Figure S2. Scheme of the experimental apparatus (Setup 2).

### Temperature profiles in the flow tube reactor

Temperature profiles were measured for the different reaction temperature setpoints. Raw data are given in an excel spreadsheet associated with this paper. Figure S3 displays the profile measured for a setpoint of 1600°C.

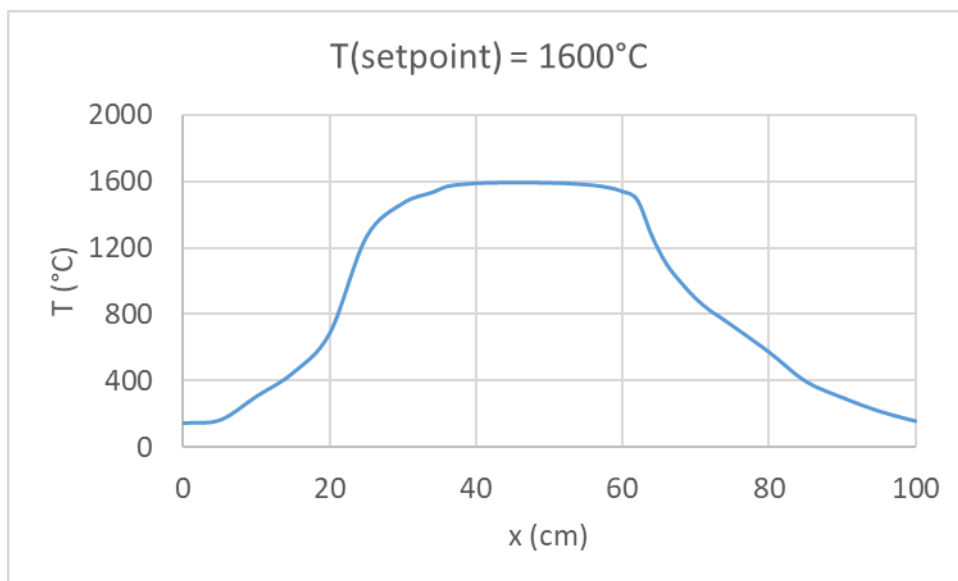


Figure S3. Example of temperature profile measured in the flow tube reactor.

### Calculation of the Reynolds and Peclet numbers

The Reynolds number,  $Re = \rho \times u \times d / \mu$ , was calculated to verify if the flow is laminar or turbulent ( $\rho$  is the density of the fluid,  $u$  is the linear velocity of the fluid,  $d$  is the internal diameter of the tube and  $\mu$  is the kinematic viscosity of the fluid). The calculation gives  $Re$  between 146 and 75, which far below the limit value of 2500. The flow can be considered laminar.

The Peclet number,  $Pe = u \times d / D$ , was calculated as a function of the temperature ( $u$  is the linear velocity of the gas,  $d$  is the internal diameter of the tube, and  $D$  is the molecular diffusivity of helium). The calculation provides large values ranging from 852 at 1073.15 K to 441 at 2073.15 K. We can assume that the diffusion has a minor impact on the flow and that the reactor can be modelled as a plug flow reactor.

## Experimental conditions for experiments

Tables S1-S3 summarized the experimental conditions used for the JSR and flow tube experiments. Flow rate calculations is described for the flow-tube experiments.

### JSR experiments

Table S1. Experimental conditions of experiments performed in the JSR.

Parameter	Value(s)
Inlet methane mole fraction	0.01
Inlet ammonia mole fraction	500 ppm
Equivalence ratio, $\phi$	0.5, 1 and 2
Pressure (kPa)	106.7
Residence time (s)	1.5
Temperature (K)	500-1200
Dilution	helium

### Flow tube experiments

Table S2. Experimental conditions of experiments performed in the flow tube reactor.

Parameter	Value(s)
Inlet methane mole fraction	1000 ppm
Inlet ammonia mole fraction	1000 ppm
Equivalence ratio, $\phi$	1*
Inlet dioxygen mole fraction	3250 ppm
Pressure (kPa)	126.7
Flow rate (m <sup>3</sup> /s)**	$1.51 \times 10^{-4}$
Temperature (K)	1223.5-1973.15
Dilution	helium

\* Reaction products of complete combustion reaction considered for the calculation of the equivalence ratio: CO<sub>2</sub>, H<sub>2</sub>O and NO.

\*\* Flow rate given under the conditions of pressure and temperature of the reaction, the temperature being that in the central zone of the reactor where it is constant. It was chosen to maintain the flow rate constant to have the same residence time for each temperature.

Table S3. Inlet flow rate in cubic centimeter per minute under standard conditions.

T(K)	Q (sccm)	T(K)	Q (sccm)	T(K)	Q (sccm)
1223.15	2205	1523.15	1771	1823.15	1480
1273.15	2119	1573.15	1715	1873.15	1440
1323.15	2039	1623.15	1662	1923.15	1403
1373.15	1965	1673.15	1612	1973.15	1367
1423.15	1896	1723.15	1566		
1473.15	1831	1773.15	1521		

## Atomic balances

The atomic balance for an atom X was defined as the number of atoms X at the outlet of the reactor (in the unconverted fuels and reaction products) divided by the number of atoms X at the inlet of the reactor in the fuels and oxidizer. Balance for N, C, H and O atoms are displayed in Table S4 for experiments in the flow tube reactor.

Table S4. Atomic balances in the flow tube reactor.

T (K)	balance N	balance C	balance H	balance O
1223.15	1.00	1.00	1.00	1.00
1273.15	1.00	0.99	0.99	1.00
1323.15	0.98	0.98	0.98	1.00
1373.15	0.96	0.98	0.97	0.98
1423.15	0.95	0.98	0.96	0.95
1473.15	0.98	0.99	0.94	0.93
1523.15	1.09	0.83	0.80	0.94
1573.15	0.85	0.98	1.06	1.02
1623.15	1.02	0.98	1.05	1.02
1673.15	1.01	0.96	1.03	1.02
1723.15	1.02	0.97	0.99	1.00
1773.15	1.03	0.98	1.00	1.01
1823.15	1.02	1.00	1.00	1.01
1873.15	1.01	1.01	0.99	1.01
1923.15	1.00	1.01	0.99	1.01
1973.15	1.00	1.02	1.00	1.03

Table S5. Carbon atom balances in the jet-stirred reactor<sup>1</sup>.

T (K)	$\varphi = 0.5$	$\varphi = 1.0$	$\varphi = 2.0$
800	1.03	1.03	
900	1.03	1.04	
950	1.02		
975	1.02		
1000	1.02	1.04	1.04
1025	1.00	1.02	
1050	1.02	1.03	
1075	1.02	1.03	
1100	1.03	0.61	1.02
1125	1.03		
1150	1.04	1.00	1.03
1175	1.02		
1200	1.02	1.07	1.12

<sup>1</sup> Nitrogen and oxygen atom balances were not calculated as some products like N<sub>2</sub> and water were not quantified during the JSR study.

## Additional model validations for CH<sub>4</sub>/NH<sub>3</sub>/O<sub>2</sub>

### Ignition delay times [1]

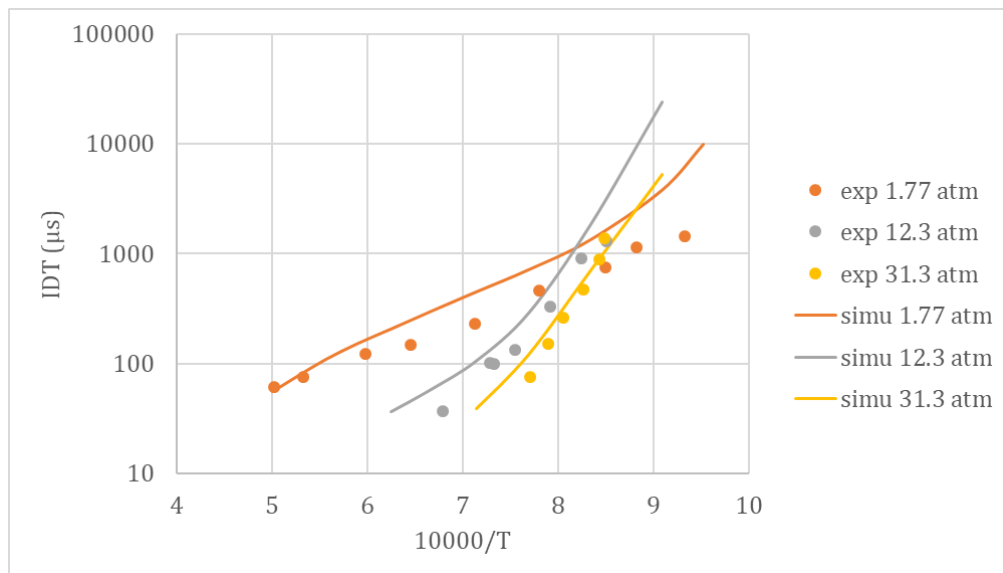


Figure S4. Ignition delay times of bio-syngas (molar composition: 0.02%NH<sub>3</sub>, 0.08924%CH<sub>4</sub>, 0.29659%H<sub>2</sub>, 0.29659%CO, 0.20997% H<sub>2</sub>O, 0.15748%CO<sub>2</sub>, 0.95013%O<sub>2</sub>, 97.9798%Ar) in a shock tube [1].

### Laminar burning velocities [2]

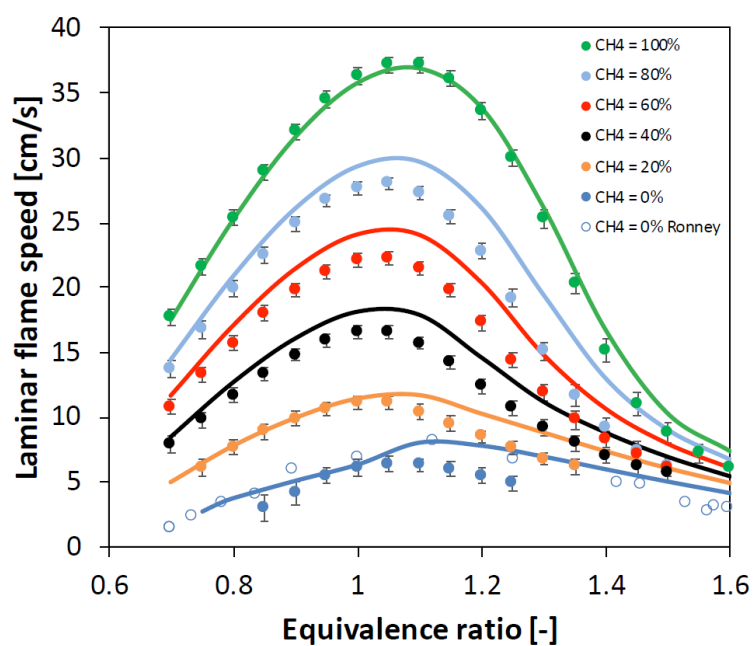


Figure S5. Laminar burning velocity of NH<sub>3</sub> + CH<sub>4</sub>/air flames at the temperature of 298 K and pressure of 0.1 MPa [2].

## Flow reactor [3]

Methane/ammonia oxidation in a flow reactor as a function of temperature [3],  $N_2$  or  $CO_2$  used as bath gas.  $P = 1.05$  atm.

Table S6. Summary of the experimental conditions

ID	Figure	CH <sub>4</sub> [ppm]	O <sub>2</sub> [ppm]	NH <sub>3</sub> [ppm]	CO <sub>2</sub> [%]	N <sub>2</sub> [%]	Res. time [s]
1	S6	2515	3479	484	0	99.35	1296/T[K]
2	S7	2513	5036	468	0	99.20	1296/T[K]
3	S8	2508	40062	468	0	95.69	1293/T[K]
4	S9	2519	3505	468	90.21	9.14	1299/T[K]
5	S10	2512	5014	460	88.55	10.65	1296/T[K]
6	S11	2512	40133	450	90.10	5.59	1296/T[K]

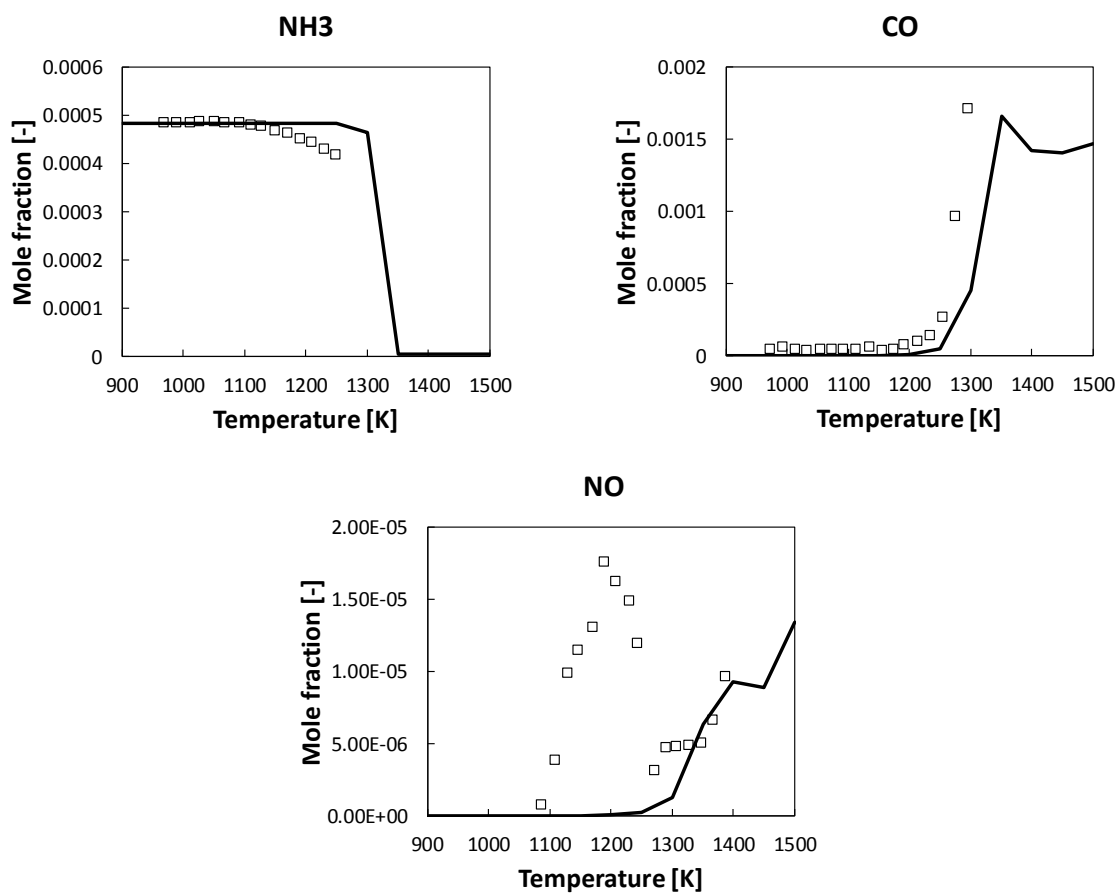


Figure S6. Test case 1 (see conditions in Table S5).

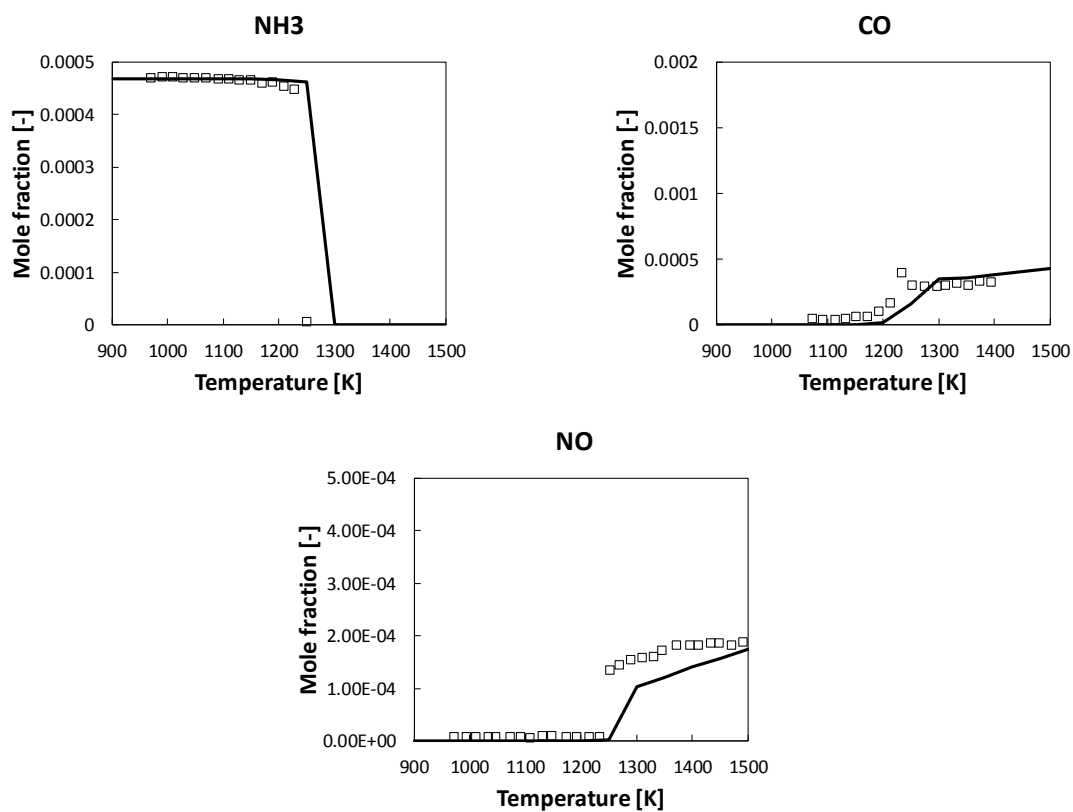


Figure S7. Test case 2 (see conditions in Table S5).

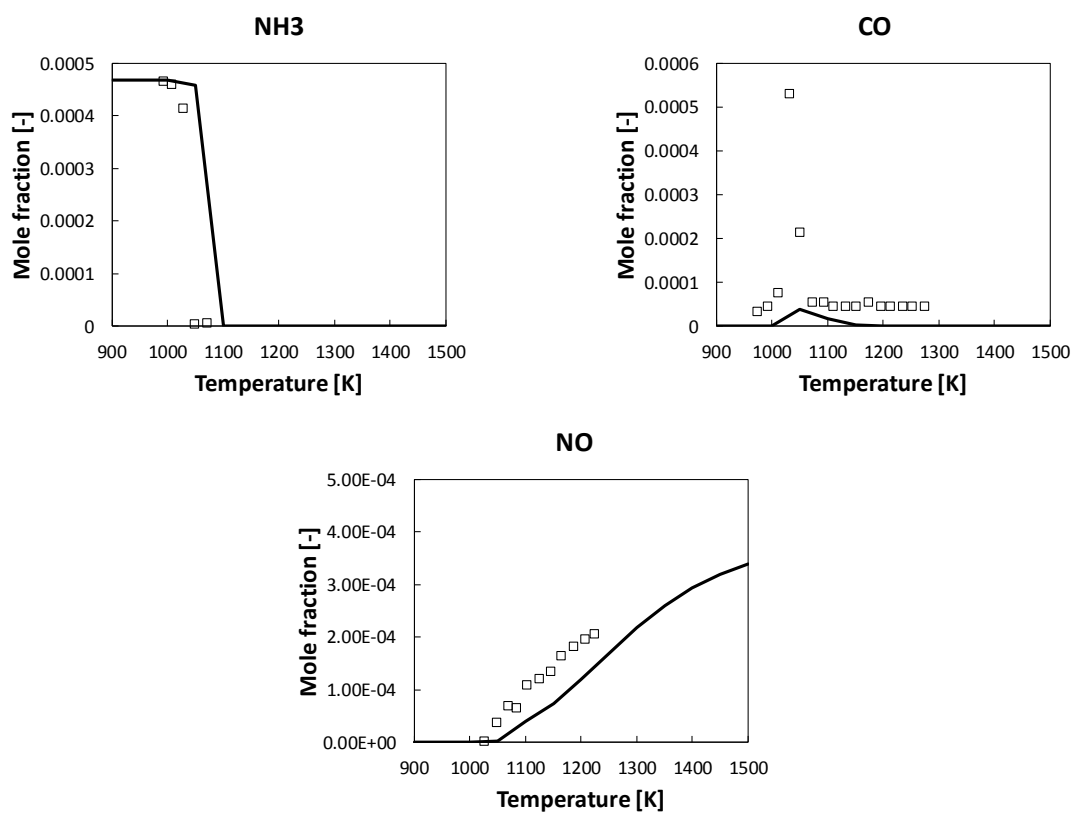


Figure S8. Test case 3 (see conditions in Table S5).

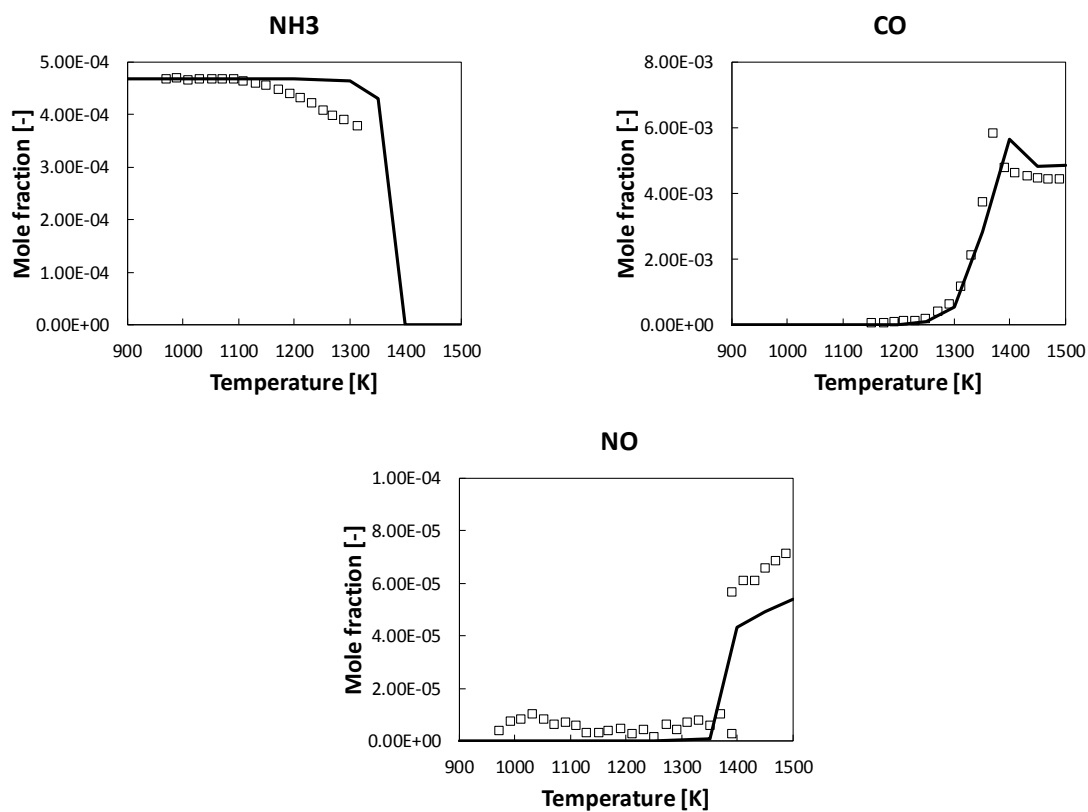


Figure S9. Test case 4 (see conditions in Table S5).

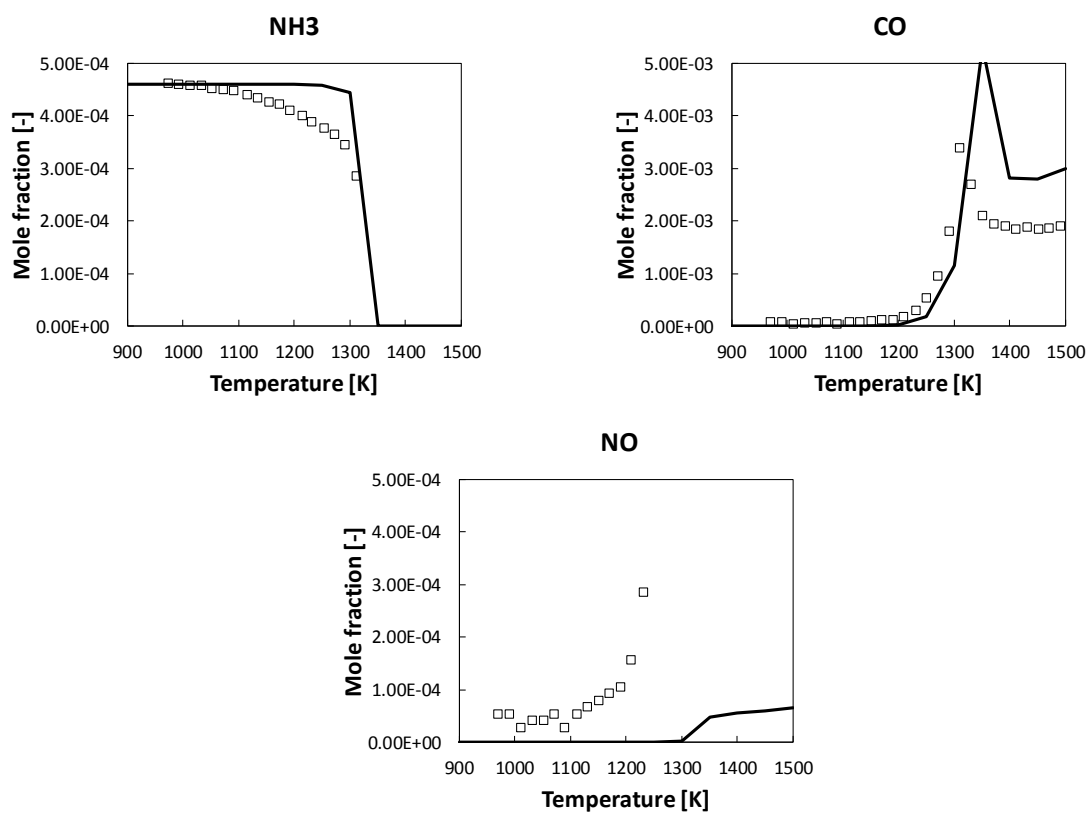


Figure S10. Test case 5 (see conditions in Table S5).

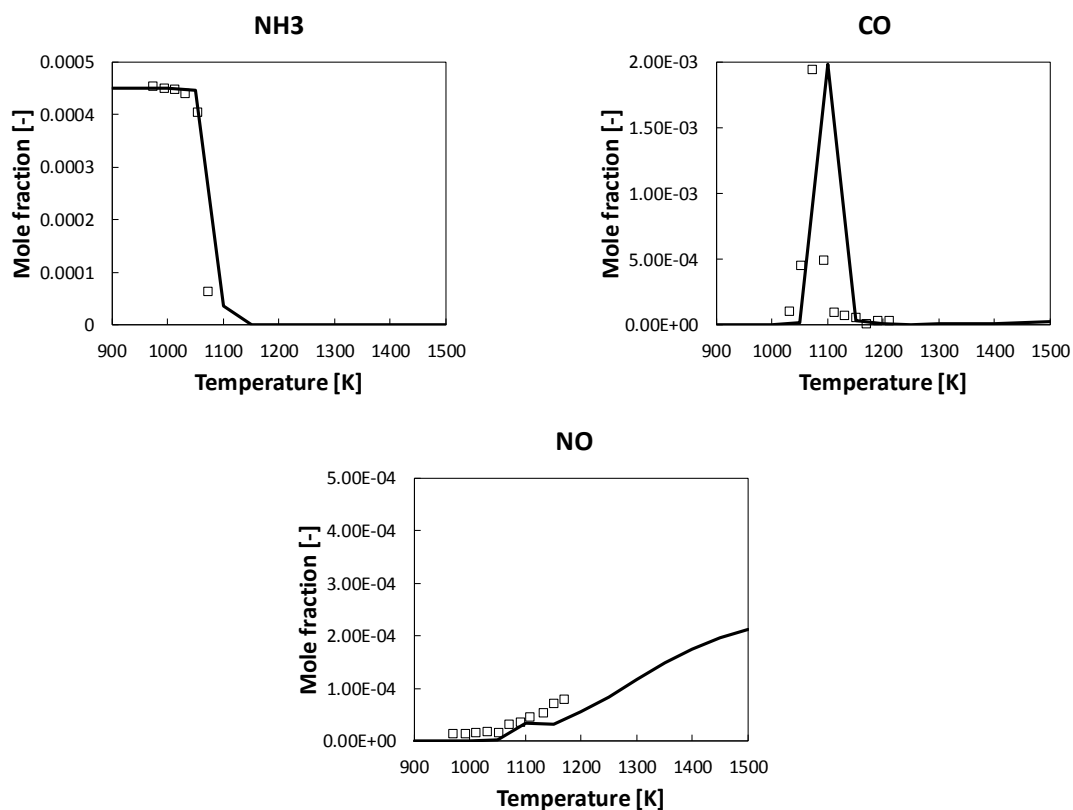


Figure S11. Test case 3 (see conditions in Table S5).

## Flow reactor [4]

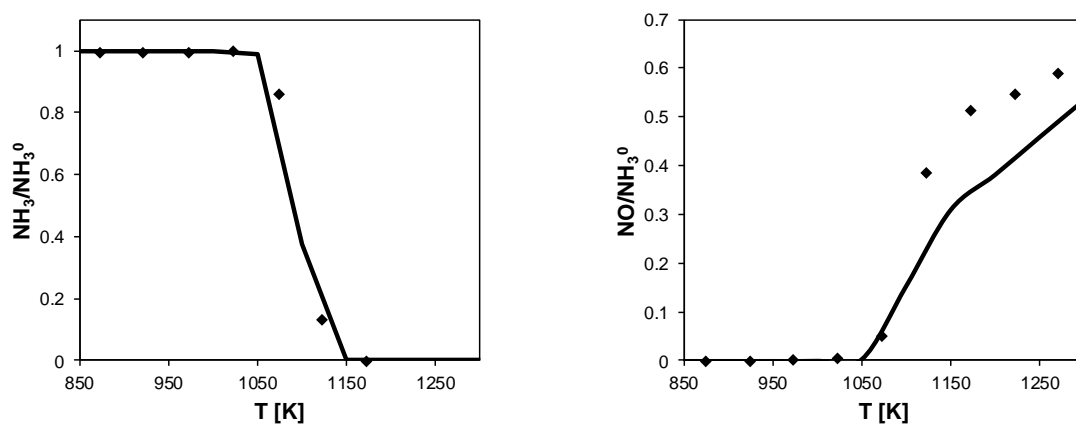


Figure S12. Ammonia conversion and NO formation in the oxidation of 200 ppm  $\text{NH}_3$  with 1000 ppm  $\text{CH}_4$  and 10%  $\text{O}_2$ . Balance gas:  $\text{N}_2$ .  $P = 1$  atm [4]

## References

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- [4] V.J. Wargadalam, G. Löffler, F. Winter, H. Hofbauer, Homogeneous formation of NO and N<sub>2</sub>O from the oxidation of HCN and NH<sub>3</sub> at 600–1000°C, *Combust. Flame*. 120 (2000) 465–478. [https://doi.org/10.1016/S0010-2180\(99\)00107-8](https://doi.org/10.1016/S0010-2180(99)00107-8).