Mass spectrometric investigation of homogeneous gas-phase reactions in combustion-generated exhaust gas

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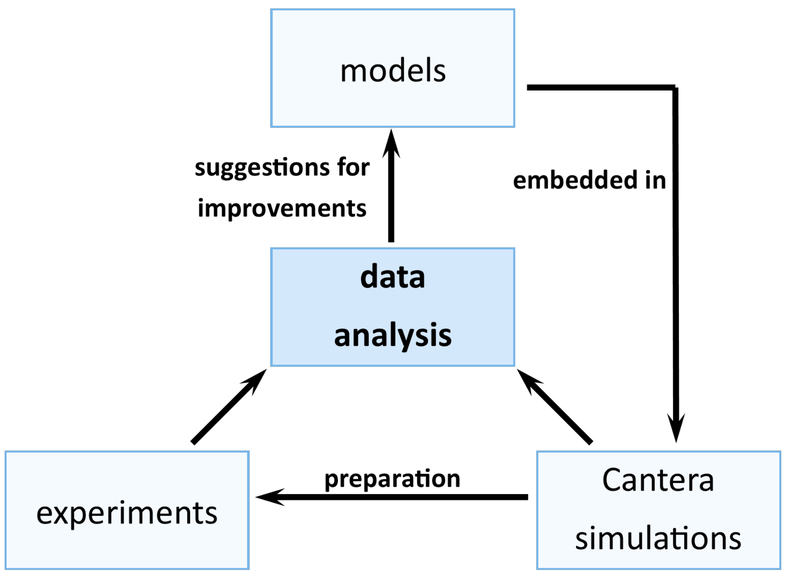
Motivation

- Combustion of fossil and/or renewable fuels remains to be global primary energy source
- Alternative and cleaner combustion processes needed (low temperature)
- More efficient catalysis to lower emission of harmful pollutants and greenhouse gases formed during combustion process
- Reduction of NO_x with NH_3 (selective catalytic reduction, SCR), commonly applied in diesel engines, now tested for heavy duty gas engines

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$



→ Catalyst may be positioned closer to engine

→ Necessary to understand reaction kinetics in exhaust system in detail

→ Systematic evaluation of combustion-generated exhaust streams is needed

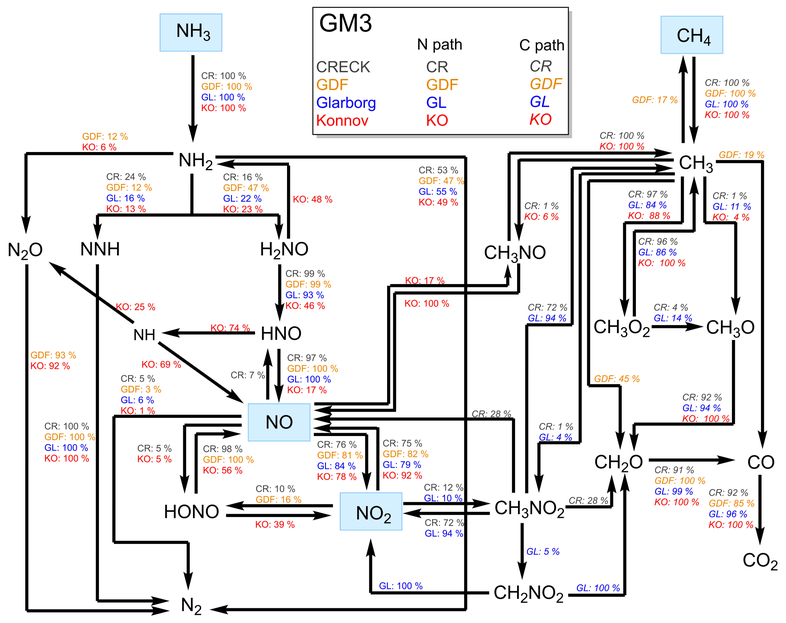
→ Effects of species like CH_4, NO_2, CO and C_2H_4 on NH_3/NO reactivity under these conditions

Kinetic Modeling

- Numeric simulations performed in Cantera with 5 selected mechanisms, chosen because of their nitrogen subset and validated conditions

Mechanism	Year	Number of Species	Number of Reactions
Konnov [3]	2009	129	1231
Curran [4]	2017	44	251
Glarborg [5]	2018	151	1395
CRECK [6-9]	2014	484	19341
GDF [10]	2016	123	934

- For deeper insight into reaction behavior, reaction flow analyses were performed
- They point out differences in describing the reaction kinetics between the mechanisms



- Reduction of NO to N_2 and H_2O is much more complex than **equation (1)** makes it appear
- Many reactions and (reactive) intermediates included

Experimental Procedure

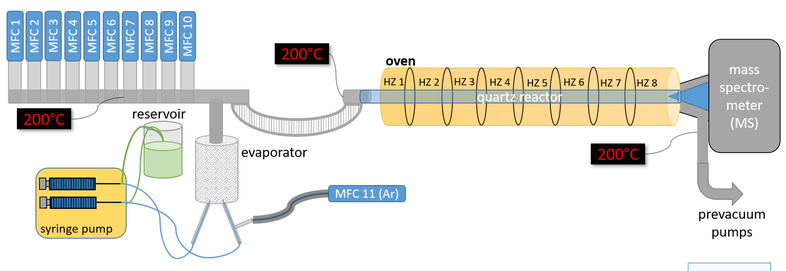
- Investigation in plug-flow reactor (PFR) experiments, at 700 - 1200 K, near atmospheric pressure
- *In-situ* chemical analysis with molecular-beam mass spectrometry (MBMS), simultaneous detection of most chemical compounds

Advantages:

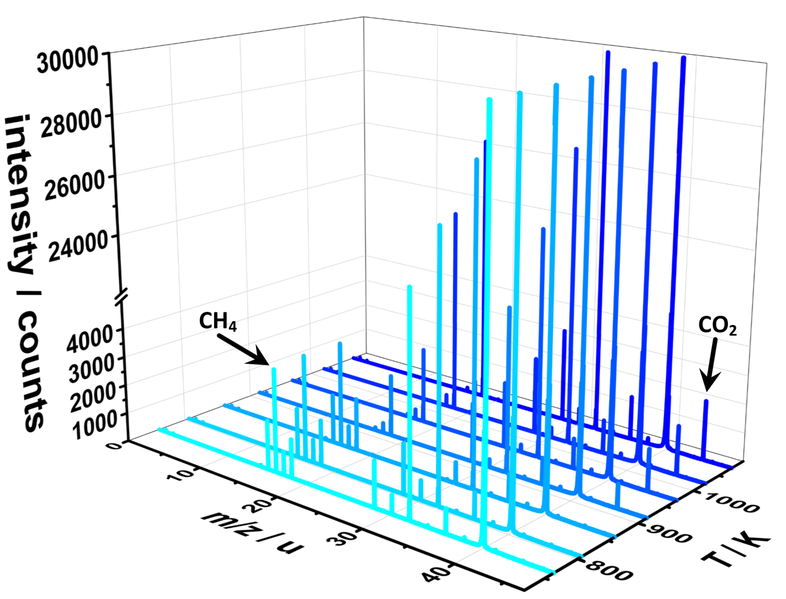
- Sensitive and universal technique
- Conditions close to exhaust-gas conditions accessible

Experimental conditions:

- Starting from NH_3, NO, O_2, successive addition of NO_2, CH_4, CO, and C_2H_4
- Investigation of effects for each individual species to NH_3/NO reactivity



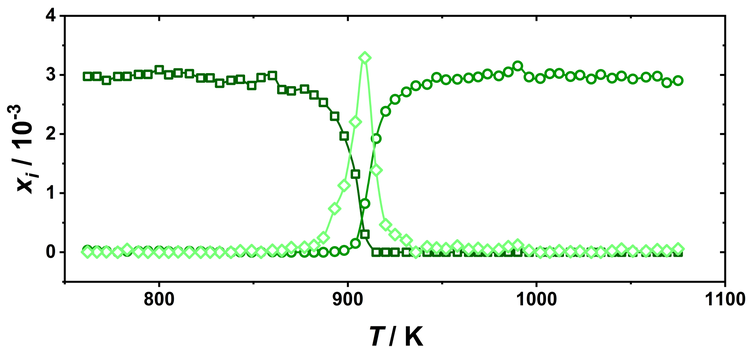
raw data



- MBMS generates one mass spectrum for each temperature point

data evaluation

$$CH_4 + O_2 \rightarrow [CO] \rightarrow CO_2 + H_2O$$

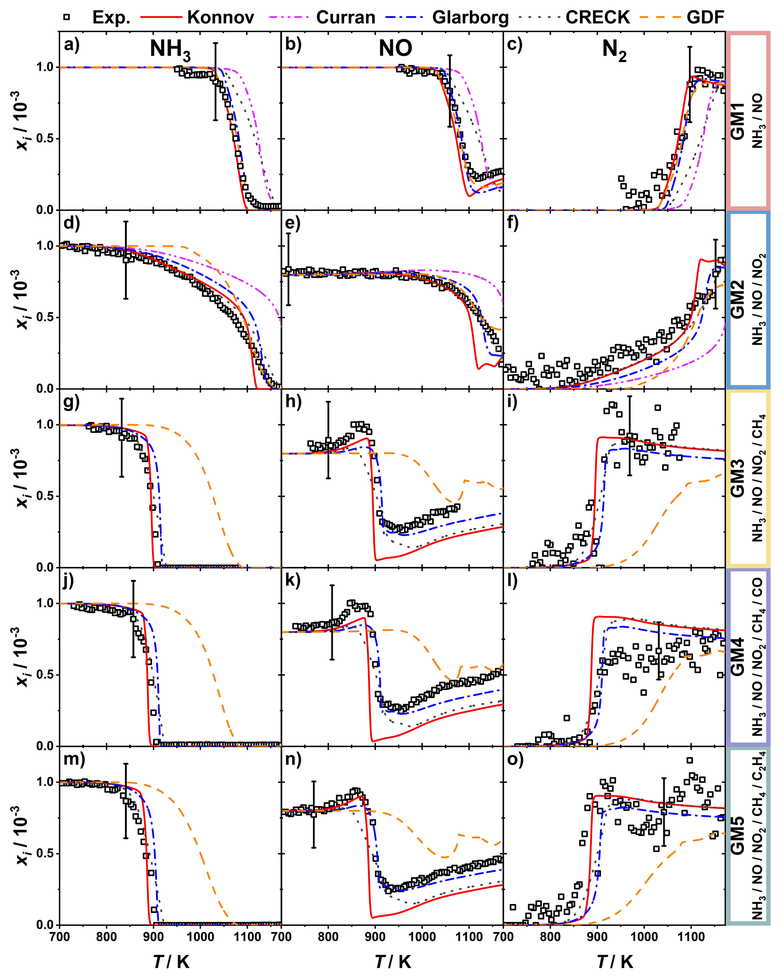


- Temperature-dependent mole fraction profile for each species

		GM1	GM2	GM3	GM4	GM5
inlet mole fraction	Ar	0.939	0.939	0.937	0.934	0.936
	O_2	0.06	0.06	0.06	0.06	0.06
ppm	NH_3	1000	1000	1000	1000	1000
	NO	1000	800	800	800	800
	NO_2	-	200	200	200	200
	CH_4	-	-	3000	3000	3000
	C_2H_4	-	-	-	-	200
	CO	-	-	-	1000	-

Results and Discussion

- Consumption of NH_3 and NO and formation of N_2 for all five gas mixtures



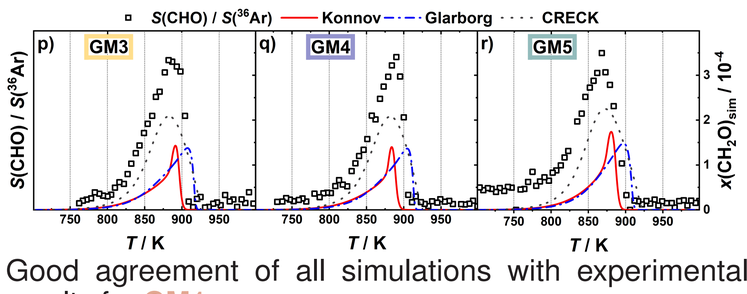
- Addition of NO_2 leads to earlier conversion of NO (cf. **GM1** and **GM2**)

→ Thermal decomposition of NO_2 to NO and O radicals increases reactivity

- Addition of CH_4 decreases NO conversion temperature by nearly 200 K (cf. **GM2** and **GM3**)

→ Decomposition of CH_4 starts with H-abstraction and generates CH_3 radicals

- Further addition of CO and C_2H_4 doesn't show significant effects (cf. **GM3**, **GM4** and **GM5**)
- Partial oxidation of CH_4 forms formaldehyde, CH_2O, a carcinogenic substance
- CH_2O could not be detected, but CHO as a proxy for CH_2O formation



- Good agreement of all simulations with experimental results for **GM1**
- Even addition of NO_2 and especially of CH_4 (cf. **GM2** and **GM3**) results in wide differences

→ Only three mechanisms show good agreement with all experimental results

→ These three mechanisms are not perfect and not identical

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References

[1] S. Schmitt, L. Ruwe, J. Horstmann, S. Schwarz, F. Sabath, L. Maier, O. Deutschmann, K. Kohse-Höinghaus, *PROCI*, **2019**, submitted.

[2] D.G. Goodwin, R.L. Speth, H.K. Moffat, B.W. Weber, *Cantera V. 2.5.0a3*, **2019**.

[3] A.A. Konnov, *Combust. Flame*, 156, **2009**.

[4] Y. Zhang, O. Mathieu, E.L. Petersen, G.Bourque, H.J. Curran, *Combust. Flame*, 182, **2017**.

[5] P. Glarborg, J.A. Miller, B. Ruscic, S.J. Klippenstein, *Prog. Energy Combust. Sci.*, 67, **2018**.

[6] A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, *et al.*, *Combust. Flame*, 156, **2009**.

[7] E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A.P. Kelley, C.K. Law, *Prog. Energy Combust. Sci.*, 38, **2012**.

[8] T. Faravelli, A. Frassoldati, E. Ranzi, *Combust. Flame*, 132, **2003**.

[9] A. Frassoldati, T. Faravelli, E.Ranzi, *Combust. Flame*, 135, **2003**.

[10] N. Lamoureux, H. El Merhubi, L. Pillier, S. de Persis, P. Desgroux, *Combust. Flame*, 163, **2016**.