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Multiscale microkinetic modelling of carbon monoxide and methane oxidation over Pt/γ-Al_2O_3 catalyst

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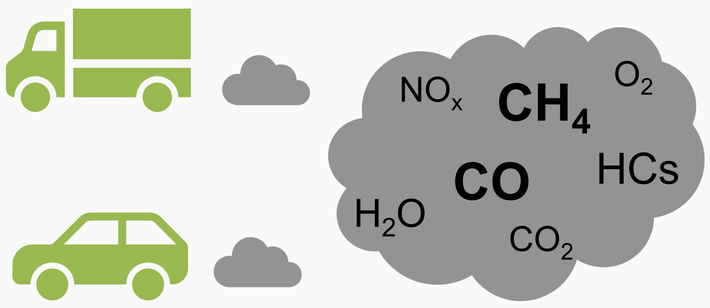
Introduction and goals

- Emissions from vehicles contain many harmful components - must be efficiently converted.
- Improvements of the catalyst require the knowledge of the **microkinetics**, but the complexity of the exhaust gas mixture makes it very challenging to unravel them.
- The catalyst has been shown to undergo modifications under the highly **dynamic** operation of the catalytic converters [1, 2].



Scope

Detailed surface reaction mechanism ⟷ Catalyst structure ⟷ Affected by chemical environment/conditions

CH_4 oxidation – method and results

- Microkinetic mechanisms present in literature are assessed through the simulation of dynamic experimental campaigns (light – off curves) performed in very different operative conditions.
- Understanding what are the key parameters suitable for a dynamic description of the catalyst:
  - First attempt: $F_{cat/geo}$.
    Starting from the characterization of the fresh and fully reduced catalyst, the value is optimized in order to reproduce the experimental data in the ignition area.

$$F_{cat/geo} = D \cdot \frac{m_{cat}}{M_{cat} \cdot \Gamma_{cat} \cdot A_{geo}}$$

CO oxidation			
Microkinetic models		Chan et al. [3]	Mhadeshwar et al. [4]
Thermodynamic consistency		Yes, 0 – 1000 °C	Yes, 0 – 1400 °C
Reaction pathways	O_2 ads	• Molecular • Dissociative	• Molecular
	CO ox	• LHHW • ER	• LHHW

CH_4 oxidation			
Microkinetic models		Koop et al. [5]	Quiceno et al. [6]
Thermodynamic consistency		Yes, 150 – 600 °C	No
Reaction pathways	O_2 ads	• Dissociative	• Dissociative
	CH_4 ads	• Dissociative • Oxydative dehydrogenation	• Dissociative
	CH_4 ox	• Pyrolitic	• Pyrolitic • Oxidative dehydrogenation

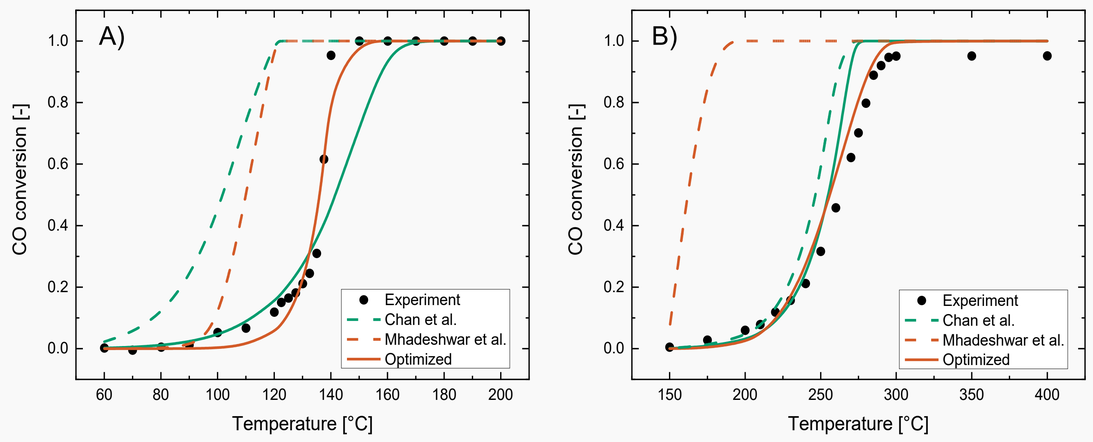


Fig. 1: *CO oxidation light-off curves. A) Packed-bed reactor with the following inlet conditions: 1000 ppm CO, 8% O_2, N_2 balance, GHSV = 36430 1/h. Simulations using* DETCHEM^{PBR} [7]. *B) Monolithic reactor (400 cpsi) with the following inlet conditions: 5000 ppm CO, 2500 ppm O_2, N_2 balance, GHSV = 30000 1/h. Simulations using* DETCHEM^{CHANNEL} [7].

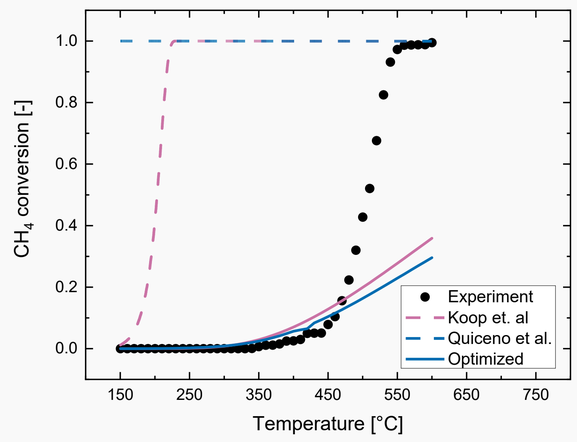


Fig. 2: *CH_4 oxidation light-off curves. Monolithic reactor (400 cpsi) with the following inlet conditions: 3000 ppm CH_4, 6000 ppm O_2, N_2 balance, GHSV = 30000 1/h. Simulations using* DETCHEM^{CHANNEL} [7].

Conclusions

- When the $F_{cat/geo}$ value is derived from the characterization of the fresh catalyst, the model predicts ignition at much lower temperature than experimentally observed.
- The adjustment of $F_{cat/geo}$ is not sufficient to well reproduce the light-off curve in the whole range of temperatures.
- When the ignition dynamics is not well reproduced, modifications of the reaction pathways and kinetic parameters are needed.

Outlook

- Improvement of the high temperature area may be sensibly reached via implementation of transient plug-ins available in DETCHEM package.
- Assess other microkinetic mechanisms to verify the impact of alternative reaction pathways and DFT-based kinetic parameters.
- Operando studies within CRC-1441 project are going to provide models to forecast the structural changes of the catalyst, enabling a fair description of the particles through values of $F_{cat/geo}$ linked with the dynamic structure.

References and Acknowledgements

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