CRITICAL PAPER REVIEW

INTRINSIC REACTIVITY OF Ni, Pd AND Pt SURFACES IN DRY REFORMING AND COMPETITIVE REACTIONS: INSIGHTS FROM FIRST PRINCIPLES CALCULATIONS AND MICROKINETIC MODELING SIMULATIONS

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Course: CL 325

ABSTRACT (THE WHAT?)

1. Activity and intrinsic mechanisms of DRM on various catalysts
2. Analysis done using Density functional theory and Microkinetic calculations
3. Reactions:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

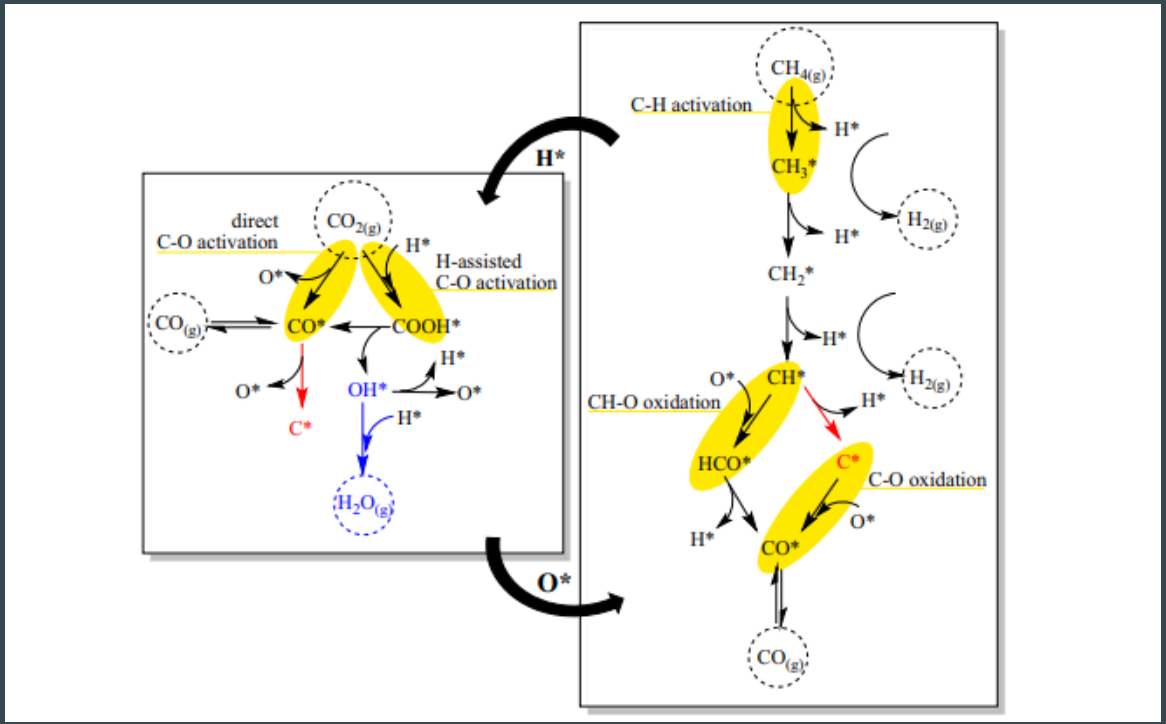
$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$CH_4 \rightleftharpoons C + 2H_2$$

$$2CO \rightleftharpoons C + CO_2$$

THE MECHANISM (THE WHAT?)



NEED (THE WHY?)

- Both Economical and ecological need
- Ecological: Substitute for SRM (Water usage)
- Economical: Controllable ratio of CO and H2O
- Ecological: Consumes CO2
- Economical: Can be used to extract energy from gas hydrates

METHOD (THE HOW?)

- Density Functional Theory
  - quantum mechanical modelling method
  - used to calculate the electronic structure of atoms, molecules, and materials
  - works by solving the quantum mechanical equations
  - Simpler than solving the Schrödinger equations

- Microkinetic Modelling
  - Calculations to guess the rates of different steps based on DFT calculations

THE GOOD PART

- An excellent step by step analysis of various possible elementary steps in the mechanism
- For each step, there is a comparison based on thermodynamic calculations between three catalysts: Ni, Pd, Pt (all from a family)
- DFT calculations were compared with experimental data and were found to match well within acceptable limits
- All possible side reactions along with Coking were also analysed
- Effects of pressure also analysed
- In section 3.5, H* stability was analysed thermodynamically, and a physical explanation was also given. This can be observed throughout the paper

THE DRAWBACKS

- No usable conclusions
- DFT is a strong method and not very computationally expensive but is strongly dependent on the functionals used. This can allow errors
- Defects in catalyst and adsorbate-adsorbate interactions were ignored which might not always be insignificant
- Stability of an intermediate is directly correlated to its adsorption enthalpy which may not be a correct interpretation
- Thermal effects and other sides not analysed

- Continued on next slide

MICROKINETIC MIDELLING

- Model assumes catalyst surface remains constant throughout the reaction which is incorrect, owing to Coking
- It is mentioned that the accurate model is computationally expensive hence approximate models were used
- It is great as it:
  - Provides insight into mechanisms
  - Aids in catalyst design
  - Accounts for Temp and Pressure
- But has disadvantages:
  - Sensitive to assumptions
  - Computationally expensive
  - Can't capture effect of heat and mass transfer (accounted for by adsotption studies)

WRITING STYLE AND OTHER COMMENTS

- Clear and concise
- Final summary is missing
- All interpretations backed by data
- Still has scope of other studies
- An academic paper, not industrially usable

Citations

- Lucas Foppa, Marius-Christian Silaghi, Kim Larmier, Aleix Comas-Vives,
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- 5. Campbell, C. T. Microkinetics: From Heterogeneous Catalysis to Solid-State Chemistry; Wiley-VCH
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THANK YOU