SUMMARY OF RESEARCH EXCHANGE AT KIT AND SUMMARY OF WP5.2 WORK

6th researcher’s seminar

Francisco Vidal Vazquez (Paco)

LUT 30.8.2016
CONTENTS

• Research exchange at KIT
• Results since last time.
  – Publication on Power-to-Methanol and Methanol-to-Power.
Research Exchange at KIT: CO production by reverse water gas shift for Fischer-Tropsch synthesis applications
Collaboration background

- Research exchange at Institute of Micro Processing Engineering (IMVT) at Karlsruhe Institute of Technology (KIT).
- Common topics and interests between IMVT and IneraTec, with VTT (Catalyst Technologies team). IMVT is highly focused on Power-to-Gas and Power-to-Liquids technologies (Methanation, FT synthesis, DME synthesis, Storage of $\text{H}_2$ in HC...), specialized in microstructured reactors.
- Direct collaboration with IneracTec GmbH (spin-off company from IMVT). IneracTec specializes in the commercialization of the world’s most compact FT reactors.
Introduction to rWGS for FT applications

- FT synthesis with Co-catalyst (Production of heavier HC): diesel and waxes.
- High pressure (approx. 30 bar) reverse Water-Gas Shift reaction.
  - Endothermic reaction, and equilibrium-limited process.
  - Advantage of high pressure: no need of compression in between rWGS and FT (cooling, water removal, compression and reheating).
  - Disadvantage of high pressure is the methane production.
- Main reactions involved in the HP-rWGS:

\[
\begin{align*}
CO_2 + H_2 & \rightleftharpoons CO + H_2O & \Delta H_{298K}^0 = +41.5 \frac{kJ}{mol} \\
CO_2 + 4H_2 & \rightleftharpoons CH_4 + 2H_2O & \Delta H_{298K}^0 = -165.0 \frac{kJ}{mol} \\
CO + 3H_2 & \rightleftharpoons CH_4 + H_2O & \Delta H_{298K}^0 = -206.1 \frac{kJ}{mol}
\end{align*}
\]
Equilibrium of rWGS

- Initial composition for thermodynamic calculations ($N_2=42.5\%$, $H_2=38.33\%$, $CO_2=19.17\%$).
- rWGS reaction equilibrium is not affected by pressure.
- However, $CH_4$ formation increases with higher pressure and lower temperature.
Research questions

• What are the most optimal operating conditions for CO production? How can be minimized the CH$_4$ production by choosing properly the operating conditions and catalyst?

• How do we size the reactor? What is the optimal operating mode; heat exchanger reactor (co-current or counter current) or adiabatic reactor/s?
Experimental work

- Main target of experimental work was catalyst testing and “kinetic modelling” reactor simulation purposes.
- Fixed-bed tubular reactor.
- Conditions:
  - For catalyst testing:
    - Three commercial catalysts.
    - Fixed Space velocity and gas composition (N₂=42.5%, H₂=38.33%, CO₂=19.17%).
    - Two pressures 1 and 30 barₐ.
    - Temperatures 500-800°C.
  - For “kinetic modelling”:
    - One catalyst.
    - Different SV and H₂/CO₂ ratio.
    - Pressure range 1-30 barₐ and temperatures 500-800°C.
- Gas analysis by online GC of a side stream.
Experimental apparatus, tubular reactor

- Quartz tube inside the Inconel tube. Inner diameter 6 mm.
- Sealing of the gap between the tubes by graphite gasket cord on top and bottom of the tubes. SiC 100-200 µm placed in the gap between tubes to ensure no bypassing.
- Catalyst bed kept in place by SiC 710-850 µm on the bottom of the tube to reduce pressure drop.
Experimental results: catalyst testing

- **Ni/Al$_2$O$_3$** catalyst with low-% Ni content.

- High activity towards formation of products.
- Higher activity towards CO formation.
Experimental results: catalyst testing

- Ni/Al₂O₃ catalyst with high-% Ni content.

- Higher activity towards formation of products but lower selectivity towards CO formation compared to lower Ni-content catalyst.
Experimental results: catalyst testing

- **Rh/CeO$_2$/Al$_2$O$_3$ catalyst**

- Lower activity towards formation of products compared to Ni-based catalysts.
- Similar selectivity towards CO formation.
Experimental results: catalyst testing

- Initial stability of different catalysts.
- Same check point:
  - Fixed SV and composition.
  - At 1 bar and ca. 500°C.
- Run sequences about 20 hr each: 1 bar, 30 bar and 1 bar again. Total operating time ca. 60 hr for each catalyst.
- Generally, catalysts lost activity towards CH₄ formation. Increase of CO selectivity.
- Changes in selectivity and activity seem to be stronger at higher pressures.
Modelling & Simulation work (using Matlab)

- **Assessment of kinetic models from literature**:
  - **rWGS**:
    - Lack of kinetic models for rWGS at relevant conditions. Studies generally focus in rWGS without taking into account CH\(_4\) formation.
    - Bustamante et al. 2004 made a model for homogeneous gas phase kinetics of rWGS. As expected very low activity at reasonable operating temperature using power rate law model. Missed to approach the equilibrium.
  - **WGS**:
    - Quite much more kinetic models available. However, lack of kinetic models for high pressure WGS and studies which consider CH\(_4\) formation. Furthermore, operating temperature of WGS considerably lower.
    - Power rate law models seems not to be able to approach the equilibrium (San et al. 2009 and 2011).
    - LHHW models approached well the equilibrium (Hakeem et al. 2015 and Ding et al. 2008).
  - **Steam reforming of methane**:  
    - Xu and Froment (1989) kinetic model consider also shift reactions.

- **Parameter estimation using experimental data (to be completed)**

- **Assessment of reactor configuration options for rWGS (to be completed)**:
  - Heat exchanger reactor: co-current or counter current.
  - Adiabatic reactor/s: single reactor or reactor in series with “interheating”.
Modelling work

- Xu&Froment kinetic model compared to experimental data using 1D plug-flow reactor model. Both own experiments (with higher-% Ni catalyst) and Xu&Froment experiments used catalyst Ni/Al$_2$O$_3$ with similar Ni-%.

For reaction I of Table 3:

$$r_1 = \frac{k_1}{p_{\text{Ni}}} \left( \frac{p_{\text{CH}_4}p_{\text{H}_2}p_{\text{O}}}{K_1} \right) \left(\text{DEN}\right)^2$$

For reaction II:

$$r_2 = \frac{k_2}{p_{\text{Ni}}} \left( \frac{p_{\text{CO}}p_{\text{H}_2}p_{\text{O}}}{K_2} \right) \left(\text{DEN}\right)^2$$

For reaction III:

$$r_3 = \frac{k_3}{p_{\text{Ni}}} \left( \frac{p_{\text{CH}_4}p_{\text{H}_2}p_{\text{O}}}{K_3} \right) \left(\text{DEN}\right)^2$$

$\text{DEN} = 1 + k_{\text{CO}p_{\text{CO}}} + K_{\text{H}_2}p_{\text{H}_2} + K_{\text{CH}_4}p_{\text{CH}_4} + K_{\text{H}_2O}p_{\text{H}_2O}/p_{\text{H}_2}$

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**Graphs:**

1 bar

- $x_{\text{CO}_2}$ eq (rWGS)
- $x_{\text{CO}_2}$ eq (rWGS+CH4)
- $y_{\text{CH}_4}$ eq (rWGS+CH4)
- $y_{\text{CO}}$ eq (rWGS+CH4)
- $x_{\text{CO}_2}$ exp
- $y_{\text{CO}}$ exp
- $y_{\text{CH}_4}$ exp
- $x_{\text{CO}_2}$ calc (Xu&Froment)
- $y_{\text{CO}}$ calc (Xu&Froment)
- $y_{\text{CH}_4}$ calc (Xu&Froment)

30 bar

- $x_{\text{CO}_2}$ eq (rWGS)
- $x_{\text{CO}_2}$ eq (rWGS+CH4)
- $y_{\text{CH}_4}$ eq (rWGS+CH4)
- $y_{\text{CO}}$ eq (rWGS+CH4)
- $x_{\text{CO}_2}$ exp
- $y_{\text{CO}}$ exp
- $y_{\text{CH}_4}$ exp
- $x_{\text{CO}_2}$ calc (Xu&Froment)
- $y_{\text{CO}}$ calc (Xu&Froment)
- $y_{\text{CH}_4}$ calc (Xu&Froment)
Conclusions

- **Catalyst activity:**
  - Both Ni-based catalysts showed higher activity than Rh-based catalyst.
  - Three catalysts showed higher activity for CO formation than for CH$_4$ formation even at close to equilibrium conditions.
  - CH$_4$ formation increased with increasing Ni-content%.

- **Catalyst initial stability:**
  - Catalyst showed reasonable stable operation while operating at atmospheric pressure.
  - Ni-based catalyst decreased yield towards CH$_4$ formation when operating at 30 bar.
  - Three catalyst maintained or increase CO yield with operating time.

- **Modelling work:**
  - Lack of kinetics models in literature for rWGS.
  - Xu&Froment model seem to give reasonable fitting to experimental data at atmospheric pressure despite of the low number of relevant experimental operating points. Xu&Froment seems to overestimate CH$_4$ formation at high temperature. The deviation from equilibrium at 30 bar is not well fitted by the model.

- **Work still on going.**
- **Joint publication VTT-IMVT-IneraTec will be submitted during Autumn!**
Results of WP5.2 since last time
Summary of latest work

- Research exchange at KIT (Francisco Vidal).
- Publication of article in “Gas for energy” magazine: “Closing energy cycle: Power-to-Methanol and Methanol-to-Power” by Francisco Vidal, Ilkka Hannula and Pekka Simell.
Coated catalyst testing in U-tube reactor

- Objective: testing of methanation coated catalysts operating at low temperature ca. 250°C.
- Work done mainly by Johanna Kihlman and Mari-Leena Koskinen-Soivi.
- Main results: doping of the Ni catalyst with noble metal increased catalytic activity towards methane formation. Coated catalysts could be applied also to methane steam reforming for SOFC application.
Closing energy cycle: Power-to-Methanol and Methanol-to-Power

by Francisco Vidal Vázquez, Ilkka Hannula and Pekka Simell

- Technical and Techno-economical assessment of particular case of the Power-to-Methanol and Methanol-to-Power.
- Combination of expertise gained in NCE project and BeingEnergy project.
- Article published on May 2016 in the Gas for Energy magazine.
Role of lab-technicians

- **Tasks of lab-technicians:**
  - Performing experimental work in laboratory.
  - Installing new experimental set ups and analysis methods.
  - Ordering of equipment and consumables (gas bottles, solvents, reactants...)
  - Teaching and cosupervision of the laboratory work of master’s thesis students.
  - Catalyst preparation.
  - Involved in the work safety in the labs.
  - Technical support for the design of new experimental set ups.
  - ... 

- **Lab-technicians involved in NCE project:**
  - Mari-Leena Koskinen-Soivi.
  - Katja Heiskanen.
  - Päivi Jokimies.
NEO-CARBON ENERGY project is one of the Tekes strategic research openings and the project is carried out in cooperation with Technical Research Centre of Finland VTT Ltd, Lappeenranta University of Technology LUT and University of Turku, Finland Futures Research Centre FFRC.

http://www.neocarbonenergy.fi/