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# Aqueous-phase reforming – a pathway to chemicals and fuels

Laboratory of Industrial Chemistry and Reaction Engineering Process Chemistry Centre Åbo Akademi





- Short Introduction, biomass, what is APR?
- Main tasks of the doctoral research
- Experimental methods
- Choice of catalytic systems
- Catalytic results
- Summary

### **Introduction - Biomass**



Biomass



Biomass production 200 Gt/y > 75 % of biomass carbohydrates

Fossil fuels extracted 7 Gt/y

huge potential in carbohydrates

Only ~ 4 % of annually produced biomass is used by man. Rest decays and recycles natural pathways.

Carbohydrates C<sub>n</sub>(H<sub>2</sub>O)<sub>n</sub> hydrophilic overfunctionalized with OH<sup>-</sup> groups <u>Hydrocarbons CnH2n+2</u> hydrophobic lacking functional groups

→ due to different nature of carbohydrates compared to fossil resources, different process technology is needed ?





## **Aqueous phase reforming (APR)**



## **Aqueous phase reforming (APR)**



#### The main tasks of the research

- Task 1. Investigation of reaction products and intermediates
- Task 2. Synthesis and characterization of catalysts
- Task 3. Catalyst stability studies
- Task 4. Investigation of reactant structure on process properties
- Task 5. Influence of a second metal (Re)
- Task 6. Modelling of reaction kinetics

#### **Experimental setup**



Reaction conditions:

- 0.5 g of a catalyst
- 225°C
- 30 bar
- Carrier gas N<sub>2</sub> (30 ml/min)

- ✓ Continuous fixed-bed reactor
- ✓ 10 wt.% of xylitol used as a feed

Reagents in the liquid phase

#### **Reactor's scheme**



**Product analysis** 



Volatile compounds were identified by means of Solid-phase microextraction (SPME) + GC-MS

TOC – total organic carbon analysis Mass balance – 95-100% (by carbon analysis)

#### **Important parameters in APR**



- Catalyst activity, stability and selectivity to H<sub>2</sub>
- Product distribution between phases
- Ratio H<sub>2</sub>/CO<sub>2</sub>

Selectivity to H<sub>2</sub> (%) = 
$$\frac{v(H_2)}{v(C_{in gas})} \times 1/RR \times 100\%$$
 RR – reforming H<sub>2</sub>/CO<sub>2</sub> ratio (11/5 fo xylitol)

### **Choice of active metal and support**

Based on catalytic activity in the APR of ethylene glycol

Ni	Pt	
Ru	Pd	

$AI_2O_3$	TiO <sub>2</sub>
С	MgO

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Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/TiO<sub>2</sub>, Pt/C and bimetallic catalyst PtRe/TiO<sub>2</sub>

#### **Catalyst stability**



Catalyst showed stable performance within more than 120 h time on stream

Time. h	$CO_2[\times 10^4]$ . mol	$\sum (X \cdot C_x H_y) [\times 10^5]$ . mol	$\sum C_x H_y / CO_2$
7	1.7	6.9	0.4
123	1.6	6.4	0.4

#### **Distribution of carbon**



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#### **Gas phase composition**

Studied by micro-GC and GC-MS, benchmark catalyst – Pt/Al<sub>2</sub>O<sub>3</sub>



### Liquid phase

Studied by HPLC and SPME benchmark catalyst – Pt/Al<sub>2</sub>O<sub>3</sub>



#### **Influence of reactant structure**



Higher yields of hydrogen for xylitol – substrate with shorter carbon chain

Higher selectivity to alkanes at lower space velocities

Conditions: 225°C, 30 atm.,  $N_2$  30 ml/min, 10 wt.% solution, Pt/Al<sub>2</sub>O<sub>3</sub>

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- 1. Effect of a second metal: series
- $Pt/TiO_2$ ,
- Pt-Re/TiO<sub>2</sub>
- Re/TiO<sub>2</sub>

Prepared by incipient wetness impregnation, from  $HReO_4$  and or  $(NH_3)_4Pt(NO_3)_2$ 

2. Effect of a support material and support structure

one commercial Pt/C (Degussa) four prepared and characterized materials

- 5% Pt/C (Degussa)
- 2.5% Pt/TiC-CDC (CDC carbide-derived carbon)
- 5% Pt/Sibunit from (NH<sub>3</sub>)<sub>4</sub> Pt (HCO<sub>3</sub>)<sub>2</sub>
- 5% Pt/Sibunit H<sub>2</sub>PtCl<sub>6</sub>
- 5% Pt/BAC (Birch active carbon)



- 1. Effect of a second metal: series
- $Pt/TiO_2$ ,
- $Pt-Re/TiO_2$  > To enhance selectivity to hydrocarbons
- Re/TiO<sub>2</sub>

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#### **Example: APR of xylitol over Pt-Re/TiO<sub>2</sub>**



- Higher yields of hydrogen for monometallic Pt catalyst
- ✓ Higher selectivity to alkanes in the presence of bimetallic Pt-Re catalyst

Conditions: 225°C, 30 atm., N<sub>2</sub> 30 ml/min, 10 wt.% solution

In cooperation with prof. C. Hardacre from Queen's University, Belfast



#### **Example: APR of xylitol over Pt-Re/TiO<sub>2</sub>**



Higher yields of hydrogen for monometallic Pt catalyst

Slightly higher selectivity to alkanes in the presence of bimetallic Pt-Re catalyst

Conditions: 225°C, 30 atm., N<sub>2</sub> 30 ml/min, 10 wt.% solution



In cooperation with prof. C. Hardacre from Queen's University, Belfast

#### Characterization

Transmission electron microscopy



#### Particle size distribution Pt/BAC ~2 nm <sup>20</sup> <sup>20</sup>

d, nm

Temperature programmed reduction (H<sub>2</sub>)



Temperature programmed desorption (NH<sub>3</sub>)



#### **APR of xylitol over Pt/C**

Effect of acidity



Supervised visiting PhD student Benjamine Hasse for 2 months

In cooperation with prof. B. Etzold from University of Erlangen-Nürnberg

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#### Based on experimental data



Based on experimental data

Pathway to hydrogen



Based on experimental data

Pathway to hydrogen



#### Based on experimental data



#### Based on experimental data



Based on experimental data

 $\geq$ 



A.V. Kirilin, J. Wärnå, T. Salmi, D. Yu. Murzin, "Kinetic Modeling of Sorbitol Aqueous-Phase Reforming over Pt/Al<sub>2</sub>O<sub>3</sub>", Ind. Eng. Chem. Res., 2014, 53, 4580–4588



Two main pathways are selected



#### Internal mass tranport limitation (pore diffusion)

(P.B. Weisz, C.D. Prater, Adv. Catal. 1954, 6, 143)

Due to Weisz-Prater no pore diffusion limitation occurs, if Weisz modulus:

$$\Phi = \frac{r_{obs} \cdot R^2}{c_s \cdot D_e}$$

 $\Phi < 1$  first order reaction  $\Phi < 6$  zero - th order reaction  $\Phi < 0.3$  second order reaction



coefficient D<sub>e</sub>

$$\phi = R \cdot \frac{k \cdot c_s^{n-1}}{D_e} \quad \rightarrow \quad \phi^2 \cdot \eta = \frac{r_{obs} \cdot R^2}{c_s \cdot D_e} = \Phi$$



Weisz-Prater modulus

$$\Phi = \frac{r_{obs}R^2}{cD_{eff}}$$

for 1-st order reaction  $\Phi < 1$ , for 0 order reaction  $\Phi < 6$ for 2 order reaction  $\Phi < 0.3$  $r_{obs}$  — maximal initial reaction rate R — mean radius of the catalyst particle c —substrate concentration. In our case R =  $1.25 \times 10^{-4}$  m (125 µm)

Wilke-Chang:

effective diffusion coefficient ( $D_{\rm eff}$ ) of substrate (sorbitol) in water

$$D_{ef} = D rac{\xi}{\chi}$$
 porosity (0.3-0.6)  
tortuosity (2-5)

$$D^{o}{}_{AB} = \frac{7.4 \times 10^{-8} (\phi M_{B})^{1/2} T}{\eta_{B} V_{b(A)}^{0.6}} \quad \text{[cm²/s]}$$

 $\phi$  = 2.6 (water),  $M_B$  is molecular weight of solvent,  $\eta_B$  = 0.11888 cP is solvent dynamic viscosity, T (K) = 498K, P=30 bar),  $V_{b(A)}$  = 122.15 cm<sup>3</sup>×mol<sup>-1</sup> is liquid molar volume at solute's normal boiling point.

Assuming  $\xi/\chi = 1/10$  the diffusion coefficient of sorbitol is calculated to be  $D_{ef} = 1.18 \times 10^{-9} \text{ m}^2/\text{s}$  (498 K and 30 bar).

The concentration of the substrate in the solvent is equal to 0.515 mol×l<sup>-1</sup>.  $r_{max}$ = 1.93×10<sup>-4</sup> mol×l<sup>-1</sup>×s<sup>-1</sup> at 2.7 h<sup>-1</sup>

 $\Phi$ =0.005  $\rightarrow$  substrate diffusion inside the catalyst pores does not affect the reaction rate

P=S+W-I, where S is the number of steps, W is the number of balance (link) equations, and I is the number of intermediates

*P*=17+2-11=8 basic routes (no intermediates are there)

**Reaction pathways** 

 $\mathbf{N}^{(1)}: C_6 O_6 H_{14} = C_5 O_5 H_{12} + H_2 + CO$  $\mathbf{N}^{(2)}: C_5 O_5 H_{12} = C_4 O_4 H_{10} + H_2 + CO$  $N^{(3)}: C_4 O_4 H_{10} = C_3 O_3 H_8 + H_2 + CO$ **N**<sup>(4)</sup>:  $C_2O_2H_2 = C_2O_2H_6 + H_2 + CO$ **N**<sup>(5)</sup>:  $CO + H_2O = CO_2 + H_2$ **N**<sup>(6)</sup>:  $C_4 O_4 H_{10} + 4H_2 = C_4 H_{10} + 4H_2 O$ **N**<sup>(7)</sup>:  $C_{2}O_{2}H_{2} + 3H_{2} = C_{3}H_{8} + 3H_{2}O$ **N**<sup>(8)</sup>:  $C_2 O_2 H_6 + 2H_2 = C_2 H_6 + 2H_2 O$ 

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on metal sites:

$$\theta_{C_6 O_6 H_{14}} = K_1 C_{C_6 O_6 H_{14}} \theta_V \qquad \theta_{C_5 O_5 H_{12}} = K_3 C_{C_5 O_5 H_{12}} \theta_V$$
 and so on for each component

on acid sites:

$$\theta_{C_4O_4H_{10}}' = K_{12}C_{C_4O_4H_{10}}\theta_V'$$

Total coverage:

$$\theta_{V} = \frac{1}{1 + K_{1}C_{C_{6}O_{6}H_{14}} + K_{3}C_{C_{5}O_{5}H_{12}} + K_{5}C_{C_{4}O_{4}H_{10}} + K_{7}C_{C_{3}O_{3}H_{8}} + K_{9}C_{C_{2}O_{2}H_{6}} + K_{10}C_{H_{2}O}}$$
  
$$\theta_{V}' = \frac{1}{1 + K_{12}C_{C_{4}O_{4}H_{10}} + K_{14}C_{C_{3}O_{3}H_{8}} + K_{16}C_{C_{2}O_{2}H_{6}}}$$

Rate for basic route 1:

$$r^{(1)} = k_2 \theta_{C_6 O_6 H_{14}} = k_2 K_1 C_{C_6 O_6 H_{14}} \theta_V =$$

$$= \frac{k_2 K_1 C_{C_6 O_6 H_{14}}}{1 + K_1 C_{C_6 O_6 H_{14}} + K_3 C_{C_5 O_5 H_{12}} + K_5 C_{C_4 O_4 H_{10}} + K_7 C_{C_3 O_3 H_8} + K_9 C_{C_2 O_2 H_6} + K_{10} C_{H_2 O}}$$
Generation rate for compound: 
$$-\frac{dC_{C_6 O_6 H_{14}}}{d\tau} = r^{(1)}$$

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D. Murzin & J. Wärnå

- 1. Aqueous-phase reforming of two most abundant polyols has been studied over stable catalysts
- 2. Effect of reactants structure on selectivity to main product formation reveals that higher selectivities to hydrogen can be achieved in APR of xyltiol compared to sorbitol (up to 85%)
- 3. Addition of Re as a second metal component leads to enhanced alkane formation
- 4. Advanced reaction scheme was proposed on the basis of experimental data
- 5. For the first time reaction sensitivity in APR of xylitol was studied over Pt/C
- 6. The reaction kinetics was modeled based on kinetic data and mechanistic considerations for sorbitol transformation during APR.
- $\checkmark$  APR is a powerfull method for hydrogen production from renewables
- ✓ Kinetic model proposed can be further developed and applied to description of APR data for other substrates as well as for APD/H process



- Graduate School in Chemical Engineering (GSCE, 2010-2013)
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- Haldor Topsøe Scholarship Programme (2010-2012)
- COST–Action CM0903 (UbioChem, 2010-2013)





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