New structured catalysts for production of sugar alcohols: from experiments to modelling, from batch to continuous operation

Tapio Salmi[1,2]*, Luca Mastroianni[1,2], German Araujo Barahona[1,3], Carl Brunberg[1]

1 Åbo Akademi, Industrial Chemistry and Reaction Engineering (TKR), Turku-Åbo Finland ;2 Università di Napoli 'Federico II', Industrial Chemistry (NICL) Napoli Italy; 3 Universidad de Valladolid, Pressure Technology Group (BioEcoUVa) Valladolid Spain

**Corresponding author: tapio.salmi@abo.fi*

Highlights

- New catalysts are tailored to be active and selective in biomass transformation
- Solid foams and 3D printed structures have high efficiency
- Catalytic hydrogenation of sugars was demonstrated in batch and continuous modes
- Detailed mathematical modelling was applied to batch and continuous data

1. Introduction

The great and demanding shift from fossil resources to renewable raw materials and sustainable products has been a massive vitamin injection for chemistry and chemical engineering. New catalysts have been discovered, characterized and tested. The trinity for a good heterogeneous catalyst is activity, selectivity and durability. Besides the conventional structures of heterogeneous catalysts, new structures have been developed, such as monoliths, fibres, microreactors, solid foams and 3D printed elements. These structures combine the benefits of traditional powder catalysts and catalyst pellets by minimizing the diffusion resistance in the catalyst pores by applying very thin catalyst layers but preserving the open structure in order to minimize the pressure drop. Application of new structures is particularly attractive for new chemical applications appearing in the valorization of biomass components to valuable products. Qualitative approach is, however, not sufficient, since the ultimate goal is to gain deep knowledge of the reaction mechanisms and to progress from laboratory to industrial scale. In situ spectroscopic methods and experiments under transient conditions give a strong impact on the understanding of the behavior of complex molecules appearing in biomass. Chemical reaction engineering plays a key role in reaching the ambitious goal. Understanding and modelling the interplay of thermodynamics, kinetics, transport phenomena and fluid dynamics is the way to breakthrough. The modern trend is to shift from batch and semibatch processes to safe and efficient continuous operation. The successful concept of structured catalysts in batch and continuous modes is illustrated here for hydrogenation of monomeric sugars from biomass to valuable sugar alcohols, which find applications as healthy sweeteners, ingredients in alimentary products, and pharmaceuticals.

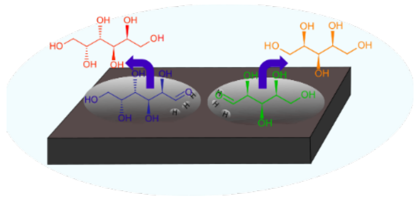
2. Methods

Commercial aluminum foams and 3D printed structures prepared at Åbo Akademi were used in the experiments. Digital Light Processing technology was applied for 3D printing. The solid structures were coated with active carbon, which was obtained by immersing the structures in a polymerization solution. The polymer was pyrolyzed, giving an active carbon layer with a high surface area. Ruthenium was introduced as active metal nanoparticles by wet impregnation, calcination and reduction (Ru/C). The catalyst was characterized with nitrogen physisorption, SEM, HR-TEM, and XPS. Extensive sugar hydrogenation experiments were conducted with arabinose, galactose and xylose to obtain the corresponding sugar alcohols. Data on intrinsic kinetics were obtained from isothermal and temperature-programmed experiments carried out in a laboratory-scale semibatch autoclave (Parr), to which gaseous hydrogen was continuously added to react with aqueous sugar solution. High stirring rate was used to remove the gas-liquid and liquid-solid mass and heat transfer resistances. Continuous operation was demonstrated in parallel screening equipment designed at Åbo Akademi. The continuous reactor system operated at the trickle-flow regime. The flow pattern in the continuous reactor system was determined by using sugar alcohols as inert tracers. The reactants and reaction products were analyzed with High-

Performance Liquid Chromatography (HPLC). The temperature domain of the experiments was 60-120ºC and the hydrogen pressure was varied between 10 and 60 bar.

3. Results and discussion

Excellent catalyst activity (complete conversion of monomeric sugars) and a high sugar alcohol selectivity (>95%) selectivity was obtained in the experiments. The continuous-mode experiments confirmed the catalyst stability. The research approach is sketched in Figure 1. Semi-competitive adsorption model was applied for the sugar and hydrogen molecules, which is motivated by the size difference of the sugar and hydrogen molecules: even after a complete adsorption of sugar molecules, some interstitial sites might be available for sugar adsorption (α = maximum coverage of a sugar molecule, <1). This model described the experimental data obtained from the semibatch experiments very well. The kinetic model was then combined with the RTD experiments obtained with the inert tracer in the continuous reactor system. For the description of the flow pattern, the axial dispersion model was developed, and the solid-liquid mass transfer resistance was included in the mathematical model, which was solved numerically during the parameter estimation process. The model can in future be used for the scale-up of continuous sugar hydrogenation processes carried out in the presence of structured catalysts, which are central elements tin the intensification of this process: toward high selectivity, high effectiveness factor and continuous operation.



$$r_X = \frac{\kappa_X \cdot \boldsymbol{\alpha} \cdot (1 + (1 - \boldsymbol{\alpha}) \cdot K_X \cdot C_X)^2 \cdot C_X \cdot P_{H_2}}{\left(1 + \sqrt{K_{H_2} \cdot P_{H_2}} + K_X \cdot C_X + (1 - \boldsymbol{\alpha}) \cdot \sqrt{K_{H_2} \cdot P_{H_2}} \cdot K_X \cdot C_X\right)^3}$$

Figure 1. From molecular mechanisms to intrinsic kinetics and continuous operation in 3D-printed reactor structures in production of sugar alcohols.

4. Conclusions

The work demonstrated successful preparation and implementation of structured Ru/C catalysts in semibatch and continuous hydrogenation of sugars to sugar alcohols. High activity and selectivity was obtained and mathematical modelling was successful. The proposed approach can in future be applied to hydrogenation of many organic molecules with carbonyl groups or double bonds.

References

[1] G. Araujo-Barahona, A. Goicoechea-Torres, K. Eränen, R.-M. Latonen, T. Tirri, A. Smeds, D. Murzin, J. García-Serna, T. Salmi, *Chemical Engineering Science* 281 (2023) 119130

[2] L. Mastroianni, A. De Jesus Medina Ferrer, A.M. De Domenico, K. Eränen, M. Di Serio, D. Murzin, V. Russo, T. Salmi, *Chemical Engineering Journal* 501 (2024) 157691

Keywords

Biomass conversion, Structured catalysts, From batch to continuous operation