

# Solid Foam Catalysts Applied to Sugar Hydrogenation: Towards Continuous Production of Sugar Alcohols

German Araujo-Barahona<sup>1,2\*</sup>, Alberto Goicoechea-Torres<sup>1,2</sup>, Maria Ciaramella<sup>1,3</sup>, Miriam Cavaliere<sup>1,3</sup>, Kari Eränen<sup>1</sup>, Dmitry Y. Murzin<sup>1</sup>, Juan García-Serna<sup>2</sup>, Vincenzo Russo<sup>3</sup>, Tapio Salmi<sup>1</sup>

*1 Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Åbo Akademi University, FI-20500 Turku/Åbo Finland; 2 Grupo de Tecnologías a Presión (PressTech), Instituto de Bioeconomía de la Universidad de Valladolid (BioEcoUVa), Universidad de Valladolid, ES-47011 Valladolid, Spain; 3 Chemical Sciences Department, Università di Napoli "Federico II", IT-80126 Naples, Italy*

*\* german.araujobarahona@abo.fi*

## Highlights

- An active and selective Ru/C foam catalyst for sugar hydrogenation was synthesized.
- The catalyst was successfully applied on the continuous production of sugar alcohol.
- Advanced kinetic models based on semi-competitive adsorption described the experimental data.
- The flow pattern and liquid holdup in a continuous reactor packed with foam catalysts were studied.

## 1. Introduction

Sugar alcohols are valuable compounds widely used for alimentary and pharmaceutical applications. Sugar alcohols are obtained by hydrogenation of sugars, such as arabinose, galactose, glucose, and xylose, in semibatch three-phase reactors using a finely dispersed Raney nickel powder catalyst. However, Raney nickel catalyst presents several disadvantages, which include metal leaching, catalyst deactivation, pyrophoricity, as well as being limited to semibatch operation. Ru/C solid foam catalysts represent an attractive alternative for continuous sugar hydrogenation, since these catalysts combine the high activity and stability of the Ru/C system with a low pressure drop and suppressed diffusion resistance thanks to their open-foam structure coated with a thin catalytic layer ( $\ll 100 \mu\text{m}$ ).

The objective of this work was to develop a Ru/C solid foam catalyst for selective hydrogenation of sugar monomers and dimers, i.e., xylose, arabinose, galactose, and lactose. The project comprises the following stages: catalyst development and optimization, semibatch experiments to measure intrinsic reaction kinetics, continuous hydrogenation experiments, residence time distribution (RTD) studies, and liquid hold-up experiments aimed at collecting relevant information to describe the hydrogenation process with a detailed mathematical model.

## 2. Methods

The catalyst synthesis was carried out by coating cylindrical foam pieces (porosity=96%) with polyfurfuryl alcohol via a controlled polymerization process. Oxalic acid was used as the polymerization catalyst and polyethylene glycol (PEG; molar mass= 80 kDa) as the pore former. Different amounts of PEG were tested (0-20 wt. %) to tailor the porosity of the resulting carbon layer. The polyfurfuryl alcohol layer was pyrolyzed onto carbon. The carbon layer was activated with oxygen and functionalized with dilute nitric acid. Ruthenium nanoparticles were deposited on the carbon layer through incipient wetness impregnation, followed by a direct reduction with hydrogen.

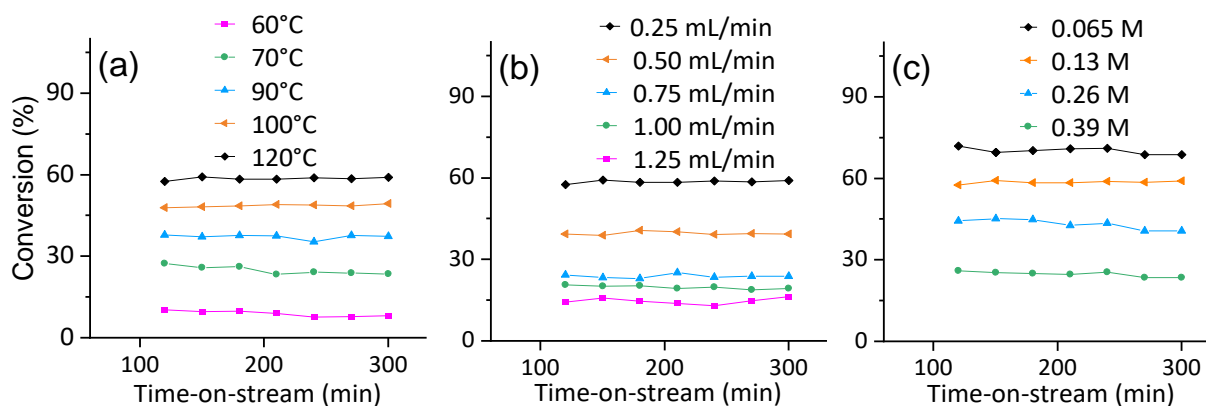
The best catalyst was identified by comparing their activities for xylose hydrogenation in semibatch experiments. The effect of temperature, sugar concentration, and hydrogen pressure on the intrinsic kinetics was studied using the best catalyst. The studied molecules were xylose, arabinose, galactose, and lactose. Continuous experiments were conducted in a parallel screening reactor consisting of six isothermal beds. The investigated parameters in continuous operation were temperature, liquid flow rate, and feed concentration. The liquid flow pattern was characterized with step-response experiments using xylitol as the tracer. The liquid hold-up under different reaction conditions was determined using a close-loop gravimetric method [1] employing helium as the testing gas.

### 3. Results and discussion

The catalyst prepared with 5 wt.% of PEG, exhibited a carbon coating with a meso-to-micropore volume ratio of 1, in contrast to the 0.12 value observed for the foam catalyst prepared without PEG. The introduction of mesoporosity in the 5 wt.% PEG catalyst enabled a more effective dispersion of Ru nanoparticles, resulting in a twofold increase in both the initial rate and the stability for xylose hydrogenation. The obtained Ru loading on the former catalyst was 1.7 wt.% with an average nanoparticle size of 3 nm, maintaining a stable activity for over 200 hours.

In the semibatch experiments with the best catalyst, sugar alcohol selectivity values exceeding 98% were achieved, and sugar conversions ranged from 50% to 99%, depending on the temperature. A kinetic model based on semi-competitive adsorption between sugar molecules and hydrogen gave an excellent description of the intrinsic kinetic data and the effect of the process parameters along with insights on the complex mode of sugar adsorption on the active sites of the catalyst.

The best catalyst was used in continuous xylose hydrogenation experiments. Figure 1 displays the effect of temperature, liquid flow, and feed concentration. The xylitol selectivity exceeded 92%. The catalyst exhibited an excellent stability throughout the time-on-stream (TOS). A slight decrease in the selectivity was observed with increasing temperature due to by-products formation. Furthermore, the decrease in liquid flow rate and feed concentration improved the xylose conversion.



**Figure 1.** Continuous xylose hydrogenation using catalyst F5PEG: (a) effect of temperature, (b) liquid flow, and (c) feed concentration. Conditions: 0.013gRu (three foams), 30 mL/min H<sub>2</sub>.

From the RTD experiments, the cumulative distribution function  $F(t)$  was obtained for different liquid flow rates (0.25-1 mL/min) and effectively fitted to a sigmoidal curve. The fitting allowed the calculation of mean residence times, variances, and Péclet numbers. The Péclet numbers ranged between 40 and 100, depending on the liquid flow rate. These results indicate that the foam structure provides nearly plug flow conditions. Furthermore, the impact of process parameters on the liquid holdup was systematically recorded using the closed-loop gravimetric method. The liquid flow proved to be the predominant factor, i.e., higher flow rates correlate with increased liquid holdups in the reactor.

### 4. Conclusions

This study showcases the viability of employing solid Ru/C foam catalysts for the continuous hydrogenation of primary sugars derived from biomass into sugar alcohols. Critical catalyst preparation parameters were identified and effectively optimized.

### References

- [1] J. García-Serna, G. Gallina, P. Biasi, T. Salmi, *Ind. Eng. Chem. Res.* 56 (2017) 13294–13300

### Keywords

Structured catalysts, sugar alcohols, biorefinery