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Continuous hydrogenation of sugar monomers and sugar mixtures with ruthenium catalyst supported on carbon-coated open-cell aluminum foam

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1. Introduction

Sugar alcohols are used for production of polyesters, alkyd resins and polyurethanes. In manufacturing pharmaceuticals, sugar alcohols are used as intermediates. Sugar alcohols are very good sweeteners with anticaries and anti-inflammatory properties. Sugar alcohols are produced through reducing the carbonyl group in a sugar molecule either by the means of chemical agents or by molecular hydrogen in the presence of a homogeneous or heterogeneous catalyst. In clean industrial production of sugar alcohols, the catalytic process is preferred. Because of its good activity and excellent selectivity, ruthenium is a preferable metal for sugar hydrogenation¹⁻². Structured catalysts, such as fibres, monoliths and solid foams combine the benefits of catalyst slurries and packed beds. Low pressure drop, large surface-to-volume ratio, suppressed diffusion resistance and good heat conductivity of metal foams make them very attractive for catalytic applications. In this work, ruthenium catalyst supported by carbon-coated open-cell aluminium foams was prepared, characterized and used for the hydrogenation of sugars and sugar mixtures.

2. Methods

Aluminium foams (Goodfellow Cambridge Limited) were used in the experiments. The foam samples were cut into cylindrical pieces with dimensions of 33 × 11 mm and used in a multiphase reactor set-up. The carbon-coating method based on controlled polymerization of furfuryl alcohol as the precursor was applied for the open-celled aluminum foams to obtain a carbon layer on the outer surfaces of the foams.³

The foam sample together with a stirring bar was immersed in the mixture of polyfurfuryl alcohol (PFA), oxalic acid and water was placed on a hot-plate stirrer. The mixture was heated from ambient temperature to 110 °C, while the foam sample was spun constantly. The foam sample was taken from the viscous PFA solution and centrifuged to remove the excess PFA from the foam.³ The sample was pyrolyzed in a tubular furnace in a nitrogen stream. The PFA-coated foams were pyrolyzed at 550 °C for 5 h. The foam samples were activated for 2 h at 380 °C in an air stream to produce a porous carbon layer. Homogeneous Deposition Precipitation (HDP) method was used to precipitate Ru on the active carbon layer. After the HDP process, the temperature of the foam sample was decreased to 450 °C in a hydrogen atmosphere. The foams were characterized by SEM, TEM, XPS, TPR, ICP-MS, CO chemisorption and nitrogen physisorption.

The sugar hydrogenation experiments were conducted in a parallel multiphase reactor set-up comprising six reactor tubes in parallel, operated in co-current trickle flow. The inner diameters of the reactor tubes were 12.5 mm and the lengths of the electrically heated parts were 120 mm. The sugar solution was pumped by individual pumps and hydrogen was fed into the system with the aid of mass-flow controllers. Temperatures 90-120 °C and the hydrogen pressure of 20 bar were used in the catalyst testing. The residence time distributions (RTD) in the foam structures were determined by tracer (KCl) injection using the step response approach. The sugar mixtures were analysed with HPLC.

3. Results and discussion

SEM images of the solid foams before and after coating are shown in Figure 1, which reveals that the open structure of the foam was well preserved during the coating.

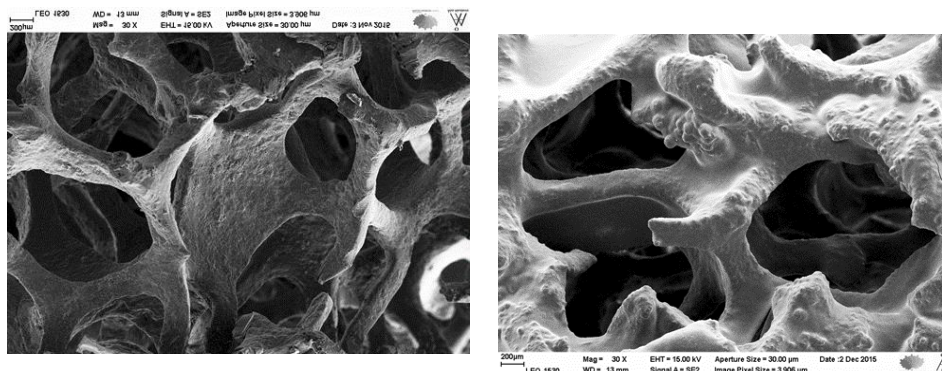


Figure 1. Surface structures of foams before and after coating.

The XPS analysis confirmed that the ruthenium on the carbon surface after HDP was mostly in form of RuO_2 and $\text{Ru}(\text{OH})_3$. To attain elemental ruthenium, the foam catalysts were reduced at $450\text{ }^\circ\text{C}$ under hydrogen flow in a tubular furnace.

The influence of the sugar molar ratios on the hydrogenation kinetics of sugars (L-arabinose and D-galactose) separately and in the mixture were studied at different temperatures ($90\text{--}120\text{ }^\circ\text{C}$), and molar ratios of D-galactose and L-arabinose (1, 2, and 5). The results showed that both individual sugars and sugar mixtures could be hydrogenated with a very high (95% and higher) selectivity to the corresponding sugar alcohols. No catalyst deactivation was detected in the experiments. The Péclet number was determined from the step response experiments with the inert tracer. A mathematical model based on the concept of axial dispersion was developed for the foam structures and the parameters of the model were determined by non-linear regression analysis. The rate equation for the hydrogenation under a constant hydrogen pressure was

$$r = \frac{k e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)} c_A}{1 + K_a c_A}$$

where c_A denotes the concentration of the sugar (e.g. L-arabinose or D-galactose), k is the rate constant at the reference temperature, E_a is the activation energy, K_a is the adsorption parameter and R is the general gas constant. The model gave a good description of the experimental data.

4. Conclusions

Open aluminium foams were coated with an active carbon layer after which ruthenium was deposited on the layer. The foam catalysts were active and selective in the hydrogenation of individual sugars and sugar mixtures to sugar alcohols. The behaviour of the foam structure was described by a dispersion model.

References

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