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Oxidation of monomeric sugars and sugar mixtures on gold catalysts: from batch to continuous operation, from qualitative kinetics to modelling

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1. Introduction

Utilization of lignocellulosic biomass is an essential part in the global trend to shift to a sustainable technology based on renewable raw materials for the production of chemicals, fuel components and materials. Hemicelluloses are rich – but often forgotten – sources of valuable sugar monomers and oligomers. The wood material contains up to 20-30% hemicelluloses, which are branched polymers with various sugar units [1-2]. For instance, the dominating hemicellulose in Norway spruce (*Picea abies*) is galactoglucomannan while arabinogalactan is the most abundant hemicellulose in Sibirian larch (*Larix sibirica*). By controlled hydrolysis of hemicelluloses in the presence of acid catalysts, the valuable sugar monomers, the building blocks of the hemicelluloses can be obtained: arabinose, galactose, glucose, mannose etc. The monomers can be valorized via catalytic treatment, for example, by hydrogenation and oxidation to obtain sugar acids and sugar alcohols. Typical hydrogenation catalysts for obtaining sugar alcohols are sponge nickel and supported ruthenium, while palladium and gold are active in the oxidation of sugars to sugar acids. Recent research has revealed [3] that gold is a very selective catalytic metal for sugar oxidation; therefore the present work is devoted to the oxidation of selected monomeric sugars and sugar mixtures to sugar acids on gold catalysts. The research comprises catalyst screening and kinetic aspects as well as the shift from semibatch to continuous technology. Mathematical modelling is incorporated on several levels, from the active sites on gold nanoparticles to the coupled reaction-diffusion phenomena in porous catalyst particles and flow pattern in continuous fixed beds.

2. Methods

An extensive series of experiments was carried out in an isothermal and isobaric semibatch reactor (liquid volume 200 ml). The catalyst was immersed in the aqueous phase which contained the sugar solution and a controlled gas flow of oxygen was fed in the reactor in semibatch mode keeping the partial pressure of oxygen constant. High rotation speeds (1000 rpm) were used to guarantee the absence of external mass transfer limitations. The pH of the reaction was controlled using an automatic titration device by addition of a NaOH solution. Pure D-arabinose and glucose as well as mixtures of them were oxidized in the presence of several finely dispersed gold catalysts (particle size ca 60µm; gold nanoparticle size around 2nm) after which larger catalyst particles (ca 1.0mm) were immobilized in a rotating stirrer and a series of kinetic and mass transfer experiments were conducted. The reactor temperature was maintained constant (50-80°C) by water flow in the reactor jacket. A reflux condenser was placed on top of the reactor to prevent the evaporation of water from the system.

After completing the experiments with the semibatch reactor, the system was rebuilt to allow continuous operation. A jacketed glass tube was used as the fixed bed, through which a continuous flow of the sugar solution and the oxygen-argon mixture was continuously fed. The residence time distribution (RTD) of the liquid phase was determined with tracer experiments using step changes and pulse inputs. The concentration profiles of the reactants and products were obtained by the chemical analysis of samples periodically withdrawn from the reactor with high-performance liquid chromatography (HPLC, Hewlett Packard Inc. Bio Rad Aminex HPX-87C carbo-hydrate column).

3. Results and discussion

The reaction stoichiometry is displayed in Figure 1 using L-arabinose as an example. The open-chain forms of the sugar monomers are transformed directly to arabinonic acid while the ring forms are oxidized to arabinolactone. Increasing basicity of the medium favors the opening of the arabinolactone ring and arabinonic acid is neutralized, producing arabinonate anion.

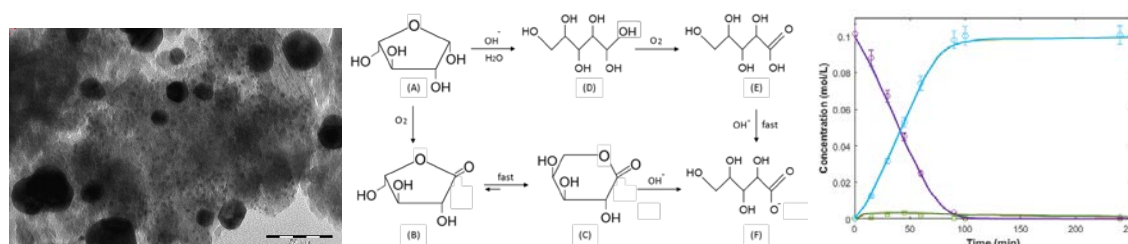


Figure 1. HR-TEM image of a gold catalyst. Two pathways for arabinose (A) oxidation, which can be converted to arabinolactone (B,C) then to arabinonate (F) or the sugar can be converted to aldehydol (D) oxidized to arabinonic acid (E) and finally neutralized to arabinonate, (F). Experimental (dots) and calculated (lines) concentrations (diamond \rightarrow D-arabinose, square \rightarrow arabinolactone, circle \rightarrow arabinonate) for arabinose oxidation in semibatch reactor on 2 wt% Au/Al₂O₃, m = 0.5g, T = 60°C, P_{O₂} = 0.125 bar and pH 8.

A typical kinetic curve obtained from the semibatch reactor experiments is displayed in Figure 1, which reveals that the reaction route through the open form of the sugar is the dominating one. In general the selectivity to sugar acids was very high and binary sugar mixtures were oxidized very well to the desired final products. A detailed kinetic model was derived based on the reaction scheme (Figure 1) and plausible surface reaction mechanisms. The kinetic parameters were estimated by non-linear regression analysis. The larger catalyst particles were modelled by a dynamic reaction-diffusion model for porous media. This model was extended to the fixed bed system to predict the experimental behavior of the bed.

4. Conclusions

Selected sugar monomers and monomer mixtures were oxidized in semibatch and continuous reactors. High yields and selectivities of sugar acids were obtained. The experimental results were modelled mathematically by applying a multiscale modelling approach.

References

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