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Maltose hydrogenation over ruthenium nanoparticles impregnated in hypercrosslinked polystyrene

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HIGHLIGHTS

- Hydrogenation of maltose gives maltitol as the main and sorbitol as the side products.
- Ru NPs on hypercrosslinked polystyrene is efficient catalyst.
- Unusual maltitol selectivity dependence on conversion and hydrogen pressure.
- Modeling of reaction kinetics with high accuracy.

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ABSTRACT

The kinetics of maltose hydrogenation using Ru-containing nanoparticles (NPs) formed in the pores of hypercrosslinked polystyrene (HPS) was studied in this work at 110–140 °C and 2–7 MPa. The concept of two sites and non-competitive adsorption of hydrogen and maltose was used due to large differences in the sizes of molecules. The proposed model was able to describe experimental data with sufficient accuracy.

1. Introduction

Saccharide hydrogenation is widely used in industry for various purposes [1–4]. The most important processes are glucose, xylose, lactose and maltose hydrogenation to the corresponding alcohols [1–6]. Several million tons of maltose are produced annually worldwide, therefore it is a low cost and easily available substrate to produce maltitol [6], which is used as a sweetener and a food additive [1–4]. Maltose hydrogenation is commonly performed in a batchwise mode in stirred tank reactors at temperatures ranging from 60 up to 150 °C, pressures of 30–80 bar with sponge nickel or transition metals supported on oxides [7]. Maltose hydrogenation is characterized by the formation of several side products including glucose and sorbitol along with formation of the target product – maltitol (Fig. 1) [8]. Commonly used sponge Ni catalysts have high selectivity up to 96–98%. However, the main problem of this type of catalysts is leaching of nickel and rapid catalyst deactivation. Hydrogenation over ruthenium supported on MgO, SiO_2, Al_2O_3 and TiO_2 gives increased maltose hydrolysis rates and excessive sorbitol formation, therefore selectivity decreased to 20–80% [6,9]. Ru supported on different kinds of carbon shows high activity in maltose hydrogenation with the selectivity up to 96–97% [3]. Ru is more expensive compared to Ni, therefore in order to be feasible for industrial applications it has to provide much higher yields of maltitol and higher selectivity.

Metal nanoparticles formed in different polymers represent an attractive possibility for the modification of catalytic properties and synthesis of efficient and stable catalysts. Stabilization of metal nanoparticles in rigid polymers can be an alternative for commonly used oxides or carbon-supported catalysts, providing high product yields along with the improved catalyst stability [5,10–20]. Hypercrosslinked polystyrene (HPS) is a rigid polymer with high mechanical and chemical stability that can be a good matrix for metal nanoparticle synthesis. This polymer has a high surface area and pore volume consisting of both small and large mesopores. Small mesopores are suitable for metal nanoparticle formation and larger mesopores can provide transport of the substrate to the active sites. The use of the catalysts based on Pd and RuO_2 nanoparticles (NPs) and HPS was reported in the earlier work

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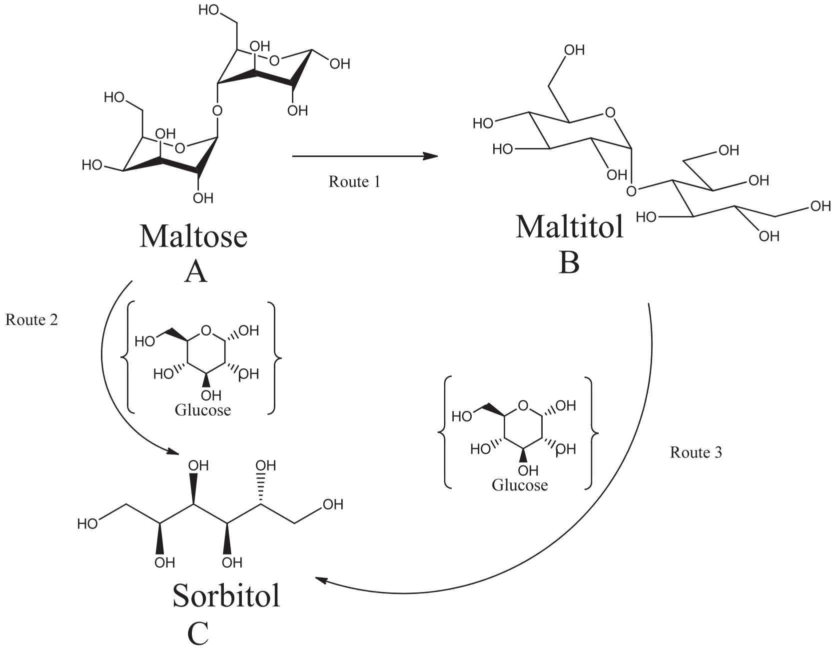

Fig. 1. Scheme of possible reactions during hydrogenation of maltose.

for glucose partial oxidation and lactose hydrogenation [5,13]. These catalysts demonstrated a high selectivity and activity in the formation of the target products. This paper is focused on the kinetic investigation of Ru-containing HPS catalysts in maltose hydrogenation. The study of Ru content and influence of various reaction conditions on the catalyst activity and selectivity is presented.

2. Materials and methods

2.1. Materials

Hypercrosslinked polystyrene (HPS) was purchased from Purolite Int. (U.K.), as Macronet MN 100. The polymer was prepared for the catalyst synthesis as described elsewhere [5,13]. Sodium hydrogen carbonate ($NaHCO_3$), reagent-grade THF, maltose, maltitol (Danisco), sorbitol (Sigma–Aldrich), methanol (J.T. Baker) were used as received. Ruthenium hydroxychloride ($Ru(OH)Cl_3$) was purchased from Aurat Ltd (Moscow, Russia). Reagent grade hydrogen of 99.999% purity was received from AGA. Distilled water was purified with Ultra lab water purification system.

2.2. Catalyst synthesis

The catalysts were prepared according to the methodology described elsewhere [5] by impregnation of HPS with ruthenium hydroxychloride in a complex solution of THF, methanol and distilled water. Three samples with different Ru amounts (4.9 wt%, 2.85% and 1.1% by XRF elemental analysis) were prepared following the same approach. The samples were designated as HPS-Ru-5%, HPS-Ru-3%, and HPS-Ru-1%, respectively. More details are available in reference [5].

2.3. Catalyst testing

The hydrogenation was conducted batchwise in a shaker-type reactor. The reactor was equipped with a heating jacket, a cooling coil, a filter (0.5 μm metal sinter) in a sampling line and a bubbling chamber (for removing dissolved air from the liquid phase and for the saturation of the liquid phase with hydrogen prior to hydrogenation experiments). The liquid volume was 50 mL (total volume 125 mL). The reactor was operated at the overall pressure 20–70 bar and temperature between 110 and 140 °C. The catalysts concentration was 8 g/L in the majority of experiments, which results in ca. 2.38×10^{-3} mol/L for 3 wt% Ru catalyst. The maltose concentration varied between 0.1 and 0.4 mol/L. The suspension of the catalyst (15 mL) prepared at a predetermined concentration was stored in the reactor. A maltose solution (35 mL) saturated with hydrogen in the bubble chamber was rapidly fed into the reactor and the hydrogen pressure and the reactor temperature were immediately adjusted to the experimental conditions.

The shaking frequency rate was set to 174 double movements per minute in all of the kinetic experiments to ensure operation in the kinetically controlled regime. The median particle size of HPS based catalysts was below 50 μm. The high stirring rates and the size of catalyst particles ensured absence of external and internal diffusion limitations respectively as will be further explained in detail. Samples of the reaction mixture were periodically withdrawn for analysis.

2.4. HPLC analysis

The analysis of the reaction media was performed using a Ultimate 2000 HPLC chromatograph equipped with an IR detector. Ion exchange chromatography using a 250 × 4 mm tungsten Reprogel-H carbohydrate column was applied. As a mobile phase H_2SO_4 (1 μM) in deionized water was used. The flow rate was kept constant at 0.5 mL/min at 30 °C. The concentrations of maltose, maltitol, sorbitol and glucose were determined using respective standards and calibration curves.

3. Results and discussion

3.1. Catalyst characterization results

The catalysts structural properties were discussed elsewhere [5]. The formation of NPs is effectively restricted by the HPS

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