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The one-pot conversion of glucose into (di)andhydrosorbitans using a Ru/Alumina catalyst-H2-CO2 system

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PURPOSE OF THE ABSTRACT

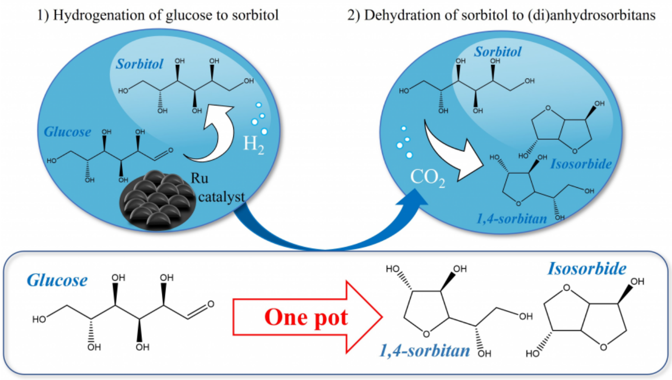
The synthesis of (di)andhydrosorbitans from glucose can be done via several chemical reactions such as hydrogenation of glucose to sorbitol follow by the dehydration of sorbitol to (di)andhydrosorbitans [1]. The aim of this study is to convert glucose to (di)andhydrosorbitans in a one-pot process avoiding a separation step and extra energy-cost by generating in situ the reactive intermediate that undergoes further reaction. In this process, water is commonly used as the reaction medium for both the hydrogenation step and the dehydration with mineral acids (HCl, H2SO4) [2]. In view of a green and convenient application in the one-pot process, the acid-catalyzed dehydration step using gaseous CO2 for the reversible generation of carbonic acid in the aqueous reaction medium seems appropriate for the dehydration of sorbitol [3]. Herein we combine the metal-catalyzed glucose hydrogenation and the successive acid-catalyzed dehydration of the in situ generated sorbitol into (di)anhydro-sorbitans (1,4-sorbitan and isosorbide) using gaseous CO2 (Figure 1). Prior to the development of the one-pot protocol, we have investigated at a first stage the two steps independently and the following results were obtained:

1) Glucose was hydrogenated in aqueous phase in the presence of a Ru/Alumina catalyst commercially available [4]. The glucose (10 wt. %) was selectively converted to sorbitol with a yield around 97 % under optimized conditions (100°C, 30 bar of H2, 150 min) in the presence of 5 wt. % of Ru/Alumina. This catalyst was highly stable up to 10th cycles and without thermal reactivation under gaseous hydrogen between cycles. The reasons for its high stability in water will be presented based on catalyst characterizations.

2) Sorbitol was dehydrated into (di)anhydrosorbitans in aqueous media and in the presence of gaseous CO2. The catalytic effect of carbonic acid enables to enhance 1,4-sorbitan and isosorbide yields and products selectivities can be tuned as the dehydration reaction is time and temperature-dependent. The higher selectivity of 85 % was reached towards the formation of 1,4-sorbitan under selected conditions (220°C, 30 bar of CO2, 72 h) whereas isosorbide can be selectively obtained at higher temperature.

Combining both optimized reactions in a one-pot process was tested afterwards with glucose as starting molecule in combination with H2 and Ru/Alumina for the hydrogenation reaction as well as the addition of CO2 for the dehydration of sorbitol in situ generated. Unfortunately, a systematic drop in the reaction yield and selectivity was observed. The underlying reasons for the limitations of this one-pot protocol were further investigated by in operando infrared and Raman spectroscopic studies. In particular, it is shown that the presence of CO2 in the hydrogenation step leads to the formation of adsorbed carbonates species that passivate the catalyst surface and decrease the catalyst activity (Figure 2). Such investigations allowed us to propose an experimental protocol to limit side effects on the one-pot process.

FIGURES



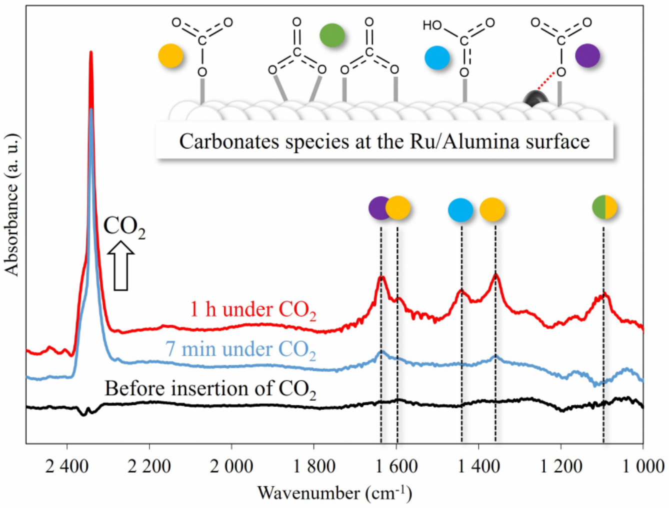


FIGURE 1

The conversion of glucose into 1,4-sorbitan and isosorbide in a one-pot process

The consecutive hydrogenation of glucose in the presence of Ru/Alumina catalyst-H2 (1) and the dehydration of sorbitol in the presence of gaseous CO2 (2).

FIGURE 2

Spectra of the Ru/Alumina in presence of CO2 by in situ spectroscopy

Carbonate species adsorbed at the catalyst surface were detected by in situ Attenuated Total Reflectance (ATR) after the insertion of CO2 during the hydrogenation reaction.

KEYWORDS

One-pot | Hydrogenation | Dehydration | In situ spectroscopy

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