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Highly selective synthesis of Methanol from Glucose in a two step process

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PURPOSE OF THE ABSTRACT

Introduction

Methanol (MeOH) is a high demand chemical due to its versatile usage as a solvent or for the synthesis of various chemicals. Currently, MeOH is produced from fossil-based synthesis gas [1]. In order to reduce CO2-emissions, alternative processes for the MeOH synthesis need to be developed. Besides, CO2 from biogas plants or industrial exhausts, biomass is a regenerative feedstock for the synthesis of MeOH [2]. We herein present a highly attractive two-step process for the synthesis of MeOH starting from glucose.

Focus of research

Within our research we focused on the synthesis of MeOH starting from glucose via a two-step process. In the first step, glucose is oxidized to methyl formate (MF) using an polyoxometalate (POM) catalyst (H8PV5Mo7O40) in methanolic solution. In this process undesired by-products such as CO2 can be completely suppressed, leading to a theoretically possible 100 % carbon efficiency. The reaction from glucose to MF proceeds through a consecutive reaction via methoxymethylfuraldehyde (MMF), glyoxale, glycolaldehyde and erythrose [3]. The target of our research is to develop a continuous liquid phase process for this reaction applying a microreactor system.

In order to achieve high MF-yields, a sufficient reoxidation of the POM-catalyst has to be guaranteed. In our experiments we investigated the influence of the molar fraction of oxygen (xO2) on the reaction performance at constant residence time. In figure 1 the conversion of glucose (XGlucose) and the selectivities (Si, Glucose) are shown.

As can be seen from figure 1, glucose conversions of nearly 100 % can be reached at 90 °C and 15 barO2. For 1 6 mol-% O2 almost no difference between the product distribution can be observed. By further increasing xO2, the selectivities of intermediates decrease leading to a higher MF-yield. Obviously, the reoxidation-rate of the catalyst can be increased by increasing xO2. As MeOH is used as a solvent, its conversion is quite low (3-4 %).

Our target is, to increase the MF yield by adapting process parameters such as residence time, temperature and substrate concentration. Since commercially processed biomass mostly contains water, we want to investigate the influence of water on the MF-yield. Depending on the water content of the biomass, an equilibrium product distribution between MF and formic acid (FA) will be reached due to ester hydrolysis. The latter is important for the second mentioned process step including MeOH synthesis via MF hydrogenolysis.

For this process, we could show that commercial catalysts such as CuO/ZnO/Al2O3/MgO suffer from corrosion building copper formate if FA is present in the substrate. In our research, we investigated a Cu-spinel catalyst (Cu0.9Al2O4) for MF hydrogenolysis and its corrosion resistance against FA. In figure 2 a) the MeOH productivity (PMeOH) for two different Cu-catalysts is shown for different temperatures. Figure 2 b) represents the product solutions of two different catalysts after the contact with 5 mol-% FA solution.

As can be seen from figure 2, the Cu0.9Al2O4 catalyst is more active for MeOH formation over the whole temperature range compared to the CuO/ZnO/Al2O3/MgO catalyst. At 250 °C the MeOH-yield reaches about 72 % concerning the Cu0.9Al2O4?catalyst compared to 25 % using the commercial catalyst. Moreover, we tested the corrosion stability for both catalyst systems, which is shown in figure 2 b). Whereas the solution of the CuO-catalyst showed a blue coloration after contact with FA steaming from the formation of copper formate, the solution of the Cu0.9Al2O4 stayed clear. Beside the remarkably activity of the Cu0.9Al2O4 catalyst we could show, that it is more stable against FA-corrosion. In our further research we will focus on the influence of formic acid on the Cu0.9Al2O4-surface.

FIGURES

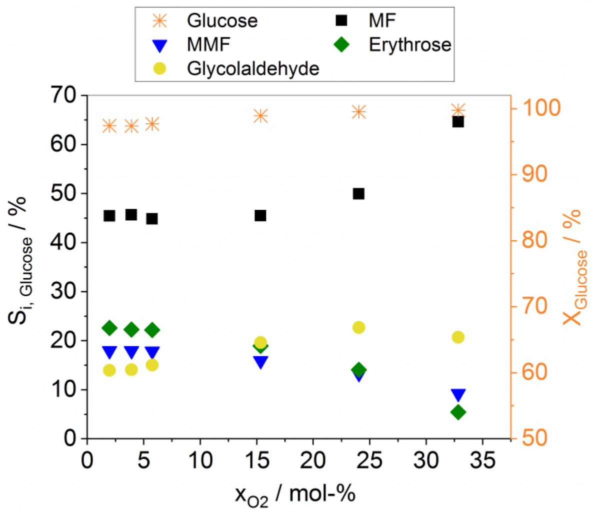

FIGURE 1

XMF and Si, glucose using H8PV5Mo7O40 catalyst in methanolic solution depending on xO2.

Reaction conditions: 90 °C, 15 barg, wGlucose=2.21 wt.-%, wPOM=2.17 wt.-%, residence time=4.9 min, xO2=2 33 mol-%.

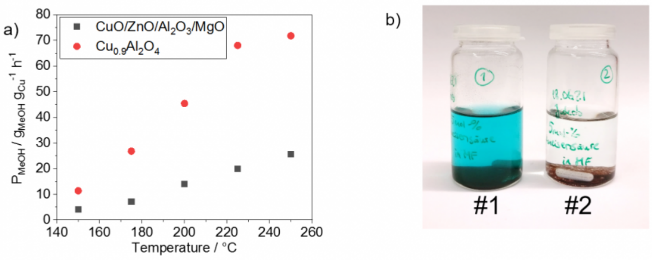

FIGURE 2

MeOH productivity for different Cu-catalysts and resistance against FA

a) MeOH productivity for different temperatures for two Cu-catalysts, conditions: 250 °C, 10 bar(g), 600 mln min-1 H2, 16 g h-1 MF, 0.5 g catalyst, b) Solutions after contact of catalysts with 5 mol-% FA (#1: CuO/ZnO/Al2O3/MgO, , #2: Cu0.9Al2O4).

KEYWORDS

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