ISGC 2022

N°349 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Highly selective glucose oxidation to formic acid and methyl formate

AUTHORS

Dorothea VOSS / UNIVERSITÄT HAMBURG, BUNDESSTRASSE 45, HAMBURG
Anna BUKOWSKI / UNIVERSITÄT HAMBURG, BUNDESSTRASSE 45, HAMBURG
Jakob ALBERT / UNIVERSITÄT HAMBURG, BUNDESSTRASSE 45, HAMBURG

PURPOSE OF THE ABSTRACT

The selective oxidation of biomass to carboxylic acids and -derivatives catalyzed by polyoxometalate (POM) catalysts in the so-called OxFA process shows a promising way to use the energy stored in the primary energy carrier biomass to produce a secondary energy carrier such as formic acid. Using the vanadium-substituted polyoxometalate H8[PV5Mo7O40] (HPA-5) as homogeneous catalyst, this conversion can be performed under mild reaction conditions in aqueous solution. However, the classic OxFA process only leads to a maximum formic acid yield of 60 % in a monophasic reaction system from typical biomass feedstock. This means that approx. 40 % of the carbon present in the biomass substrate gets lost as CO2. [1-4]

Within the scope of a solvent screening, the very remarkable discovery was made that a simple change in the reaction medium of the POM-catalyzed glucose oxidation leads to a step-change in performance. Using a methanolic reaction system in the HPA-5-catalyzed glucose oxidation under mild conditions (90 °C, 20 bar initial O2) an almost perfect yield to methyl formate of > 99 % could be achieved. Undesired side products that have been typically found in the traditional aqueous oxidation system, such as CO or CO2, could be completely avoided in this way. Experiments with labelled 13C glucose confirmed the complete glucose conversion to formic acid which subsequently forms methyl formate by esterification in the excess of methanolic reaction medium. Additionally, stability tests and different water/methanol reaction mixtures were performed as well as detailed analysis of all reaction intermediates formed during glucose oxidation in order to propose a conclusive reaction pathway. [5]

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

biomass oxidation | polyoxometalate | homogeneous catalyst | methyl formate

---

BIBLIOGRAPHY

[1] P. Preuster and J. Albert, Energy Technol. 2018, 6, 501–509.
[2] J. Albert, R. Wölfel, A. Bösmann and P. Wasserscheid, Energy Environ. Sci. 2012, 5, 7956–7962.
[3] J. Albert, D. Lüders, A. Bösmann, D. M. Guldi and P. Wasserscheid, Green Chem. 2014, 16, 226–237.
[4] J. Reichert and J. Albert, ACS Sustainable Chem. Eng. 2017, 5, 7383–7392.
[5] S. Maerten, C. Kumpidet, D. Voß, A. Bukowski, P. Wasserscheid and J. Albert, Green Chem. 2020, 20, 4311-4320.