ISGC 2022

N°350 / OC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Mechanism investigations

Homogeneous vs. heterogeneous catalysis: What are the catalytically active species for the isomerization of glucose into fructose in presence of alkaline earth metal (hydr)oxides?

AUTHORS

Peter DRABO / INSTITUTE OF TECHNICAL AND MACROMOLECULAR CHEMISTRY, RWTH AACHEN UNIVERSITY, WORRINGERWEG 2, AACHEN
Matthias FISCHER / INSTITUTE OF TECHNICAL AND MACROMOLECULAR CHEMISTRY, RWTH AACHEN UNIVERSITY, WORRINGERWEG 2, AACHEN
Franziska FLECKEN / INSTITUTE OF INORGANIC CHEMISTRY, KARLSRUHE INSTITUTE OF TECHNOLOGY, ENGESSERSTRASSE 15, KARLSRUHE
Irina DELIDOVICH / INSTITUTE OF CHEMICAL, ENVIRONMENTAL AND BIOSCIENCE ENGINEERING, TECHNICAL UNIVERSITY WIEN, GETREIDEMARKT 9, VIENNA
Regina PALKOVITS / INSTITUTE OF TECHNICAL AND MACROMOLECULAR CHEMISTRY, RWTH AACHEN UNIVERSITY, WORRINGERWEG 2, AACHEN

PURPOSE OF THE ABSTRACT

The isomerization of saccharides is in spotlight of numerous publications as an atom-efficient method for the production of highly demanded or rare sugars.[1] Especially in recent years, the isomerization of readily available glucose into fructose has gained in attention as a key step in the concept of biomass valorization.[2] Currently, the conversion of glucose into fructose is performed biotechnologically [3], though chemo-catalysis presents an economically attractive alternative for bio refining. Due to their high activity and low price, solid base materials have been highlighted in several studies as attractive catalysts for the isomerization reaction.[4] It was shown, that careful adjustment of the reaction conditions allows high fructose yields of up to 42%.[4, 5] However, the contribution of solved as well as surface species is not fully understood, when it comes to the catalytically active species. This hinders the knowledge-driven development of new solid base catalysts, or improvement of existing ones.

In this work, we address the isomerization of D-glucose into D-fructose and the reverse reaction in presence of MgO, CaO, SrO and Ba(OH)2 as catalysts.[6] The isomerization was carried out under batch conditions at 40 °C with 10wt.% aqueous substrate solution and systematic variation of the catalyst amount. The pH values and the concentration of leached metal were monitored over the course of reaction. Reaction rates were determined at low conversions. Revealing of the catalytic active species was supported though application of a kinetic model proposed by Kooymann et al.[7]

Our results indicate homogeneous catalysis by hydroxide ions OH- released by a partial dissolution of the materials. The poorly soluble MgO (pKsp 9.8) continuously generates hydroxide ions during the reaction. Obtained rates for isomerization of glucose into fructose and vice versa are independent of the catalyst loading, as similar pH values are induced. In contrast, the more soluble materials CaO (pKsp 5.3), SrO (pKsp 3.2) and Ba(OH)2 (pKsp 3.6) generate the alkalinity directly upon immersion in the reaction solution. Comparable conversion-selectivity plots were observed during isomerization in presence of the different metal (hydro)oxides, denoting OH- as common catalytically active species. The applicability of filtration tests and contact tests, to estimate the contributions of homogeneous and heterogeneous catalysis, is comprehensively evaluated. For isomerization catalyzed by bases, deceptive results of these tests may be obtained due to in situ generation of hydroxide ions.[6]

FIGURES

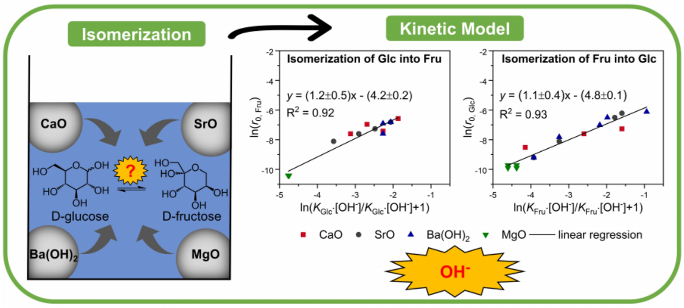

FIGURE 1

Graphical Abstract

Earth-alkaline metal (hydr)oxide catalyzed glucose-fructose isomerization and elucidation of catalytically active species by means of kinetic studies.

FIGURE 2

KEYWORDS

Isomerization | Alkaline earth metal oxides | Fructose | Glucose

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