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Revealing the Contributions of Homogeneous and Heterogeneous Catalysis for Isomerization of D-Glucose into D-Fructose in the Presence of Low-Soluble Basic Salts

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PURPOSE OF THE ABSTRACT

A key aspect of the catalytical valorization of cellulosic biomass is the isomerization of D-glucose (Glc) into D-fructose (Fru). However, a rational catalyst design for the isomerization poses a challenge. Promising catalysts for the isomerization reaction are solid bases as they exhibit high catalytic activity. Though, establishing structure-activity and -selectivity correlations between textural properties of materials and their catalytic performance remains challenging[1].

In general, Glc is transformed into Fru according to the Lobry de Bruyn and Alberda van Ekenstein mechanism with an ene-diol as key intermediate[2]. We recently demonstrated that OH- anions generated by partial dissolution of MgO, CaO, SrO and Ba(OH)2 appear to be the catalytically active species for the isomerization of Glc[3]. On the other hand, the majority of publications report that the isomerization is mainly heterogeneously catalyzed, concluding on only a minor contribution of OH- anions into overall catalytic activity[4]. Due to these contradictions, we systematically explored low-soluble basic salts - carbonates and phosphates - with the aim to reveal the nature of the catalytically active species and to investigate the relationships between catalyst composition and the catalytic performance.

In this study, Li2CO3, MgCO3, Li3PO4, SrCO3, CaCO3, BaCO3 and Mg3(PO4)2 were used as catalysts. These materials generate OH- ions upon contact with aqueous phase owing to a partial dissolution according to Eq.1 followed by the hydrolysis of carbonate/phosphate anions in accordance with Eq.2. The tested solid bases were purchased, except MgCO3 and Mg3(PO4)2 were synthesized by precipitation. The surface areas of the low-soluble basic salts are very small, in a range from 23 to 0.2 m2/g. In aqueous solution, Li2CO3 and MgO can generate an initial pH0 value of 10.2-10.5, MgCO3 and Li3PO4 of ca. 9.7 and SrCO3, CaCO3, BaCO3 and Mg3(PO4)2 of ca. 8. The catalysts were tested for the isomerization using 10 wt% aqueous Glc solution at 60°C and 80°C. MgO was used as reference catalyst. A correlation between the reaction rate and the OH- concentration was examined. Therefore, a model introduced for the initial rate of isomerization in aqueous NaOH solution by Kooyman et al. can be used, to derive a logarithmic relation between the initial reaction rate of Fru formation and the [OH-][5]. Thus, we plotted a dependency of r0,Fru on the concentration of OH- ions in logarithmic coordinates according to Eq.3. Changes of pH values during the reaction were considered by using average values of the [OH-] for the inital time lapse. For both temperatures, linear dependencies were observed (Figure 1). Based on these data, we conclude on OH- released via partial dissolution of the materials followed by hydrolysis (Eq.1-2), as the catalytically active species. The isomerization of Glc is catalyzed thus homogeneously and the rate of Glc isomerization in the presence of low-soluble bases can be predicted based on the pH0 value. Additionally, the homogeneous nature of the catalytic active species was also confirmed by filtration and contact tests[6].

Interestingly, low selectivity could be observed for conversion below ca. 15%, as the steady-state concentration of the intermediate has not been reached yet. Once it is attained, the selectivity for Fru becomes independent on Glc conversion. At Glc conversion over 30%, selectivity for Fru drops again due to decomposition processes. Thus, the highest selectivity for Fru formation is typically reached for 15-30% Glc conversion. Li_2CO_3 showed the highest catalytic activity for the isomerization (25% Fru yield in 10 min. at 80°C). The highest selectivity for Fru was observed by $MgCO_3$ giving rise to 27% Fru yield at 80°C[6].

In summary, the results of the Glc-Fru isomerization with low-soluble basic salts revealed OH^- as catalytical active species. We gratefully acknowledge financial support by the DFG (Projects 397970309 and 450360023).

FIGURES

$$M_2(CO_3)_n \xrightleftharpoons{H_2O} 2\,M^{n+} + n\,CO_3^{2-} \qquad \text{(Eq.1)}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^{-} + OH^{-} \qquad \text{(Eq.2)}$$

$$\ln r_{0,\mathrm{Fru}} = \ln \frac{K_{Glc} \cdot [\mathrm{OH}^-]}{K_{Glc} \cdot [\mathrm{OH}^-] + 1} + \mathrm{const} \qquad \text{(Eq.3)}$$

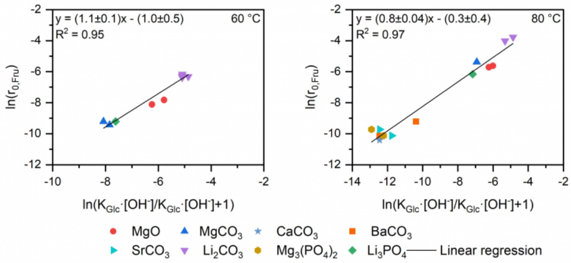

FIGURE 1

Generation of OH- anions through partial dissolution (Eq.1) followed by hydrolysis of carbonate and phosphate anions (Eq.2) and dependency of the initial reaction rate of Fru on the OH- ions in logarithmic form.

Eq.1. Partial dissolution of the catalyst

Eq.2. Hydrolysis of carbonate anion

Eq.3. Dependeny of r0,Fru on the [OH-] in logarithmic form [5]

FIGURE 2

Initial rates of Glc isomerization into Fru plotted in linearized coordinates according to Eq.3 at different temperatures

60 °C (left)

80 °C (right)

KEYWORDS

Glucose | Fructose | Catalysis by bases | Aqueous solution

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