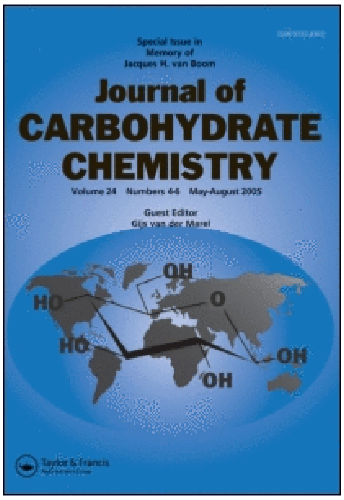

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COMMUNICATION

HYDROLYSIS OF FRUCTOSE AND GLUCOSE PRECURSORS IN THE PRESENCE OF H-FORM ZEOLITES[1]

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We have recently reported on the advantages of the use of microporous catalysts like zeolites compared to macroporous catalytic systems, like ion-exchange resins, to achieve the selective transformation of fructose or fructose precursors sucrose or inulin into 5-hydroxymethylfurfural in water as the solvent.[2-4] However, specific properties of the catalyst (controlled acidity, crystallinity, micropore volume) were required for the reaction to take place with a high selectivity.

If the interest is only to stop at the glucose and/or glucose + fructose step for food and non-food applications, more conventional zeolites like H-Y faujasites are capable of performing the hydrolysis of precursors as is shown in this paper.

Hydrolysis of Fructose and Glucose Precursors. Hydrolysis of fructose and glucose precursors (inulin, sucrose, maltose, cellobiose and starch) was performed in a batch mode in the presence of a commercial dealuminated H-Y faujasite (PQ Zeolites, ZEOCAT) with a Si/Al ratio of 15/1. After a classical screening of catalysts with different structures and dealumination extents, this catalyst was chosen in order to obtain a maximum acidity, and at temperatures ranging from 80 to 150 °C, to maximize hydrolysis to the monosaccharides and minimize formation of 5-hydroxymethylfurfural. Under the operating conditions used, hydrolysis reactions were not controlled by external or internal diffusional limitations.

Hydrolysis of Inulin. Hydrolysis of inulin was performed in water as the solvent (100 g/L) and in the presence of 0.5 to 5 g of catalyst for 50 mL of starting solution at 90 °C. Within 30 to 90 minutes, the hydrolysis was nearly complete giving fructose in a yield as high as 92%. No trace of 5-hydroxymethylfurfural was observed, in agreement with results reported in the recent literature.^{5} This result is to be compared with a H-mordenite catalysed hydrolysis reaction which gave HMF in ≈ 90% yield at 165 °C.

The pseudo first-order kinetics obtained for inulin hydrolysis in the presence of 1.5 g of catalyst at 90 °C and 700 rpm of agitation speed is illustrated in Figure 1.

An additional plot of the observed rate constants as a function of the weight of catalyst shows that the reaction is first order with respect to the catalyst, in accordance with a Langmuir-Hinshelwood equation $rate = \lambda_{inulin} \, x \, [inulin] \, / \, 1 + \lambda_{inulin} \, x \, [inulin]$ in which λ_{inulin} is the adsorption coefficient for inulin (Figure 2). It is also deduced from this figure that the saturation of the catalyst by the substrate does not occur within the range of experimental data reported, and, as a consequence, that the reaction is not subject to inhibition by the products formed.

Hydrolysis of Sucrose. Hydrolysis of sucrose was performed under relatively similar operating conditions (85 °C, up to 800 g/L of sucrose in water, 0.5 to 6 wt % of catalyst and 700 rpm of agitation speed). Under these operating conditions, sucrose is readily transformed into glucose + fructose with a nearly quantitative selectivity, as illustrated in Figure 3.

The important feature to be noted is that a larger amount of catalyst does not increase the reaction rate but retards the appearance of 5-hydroxymethylfurfural (Fig.3,

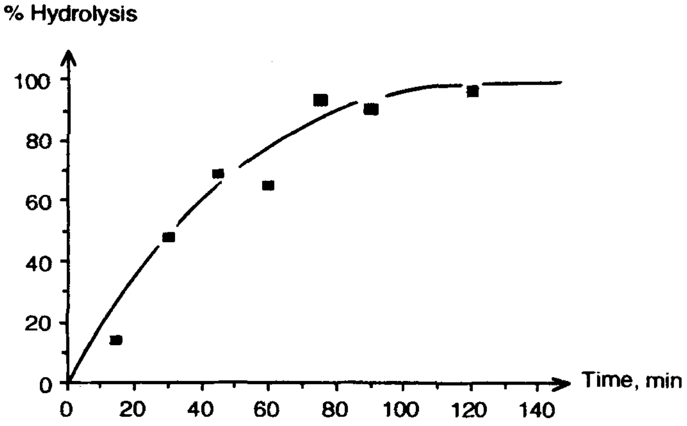


Figure 1. Inulin conversion as a function of time, 1.5 g of catalyst, 90 °C, 700 rpm.

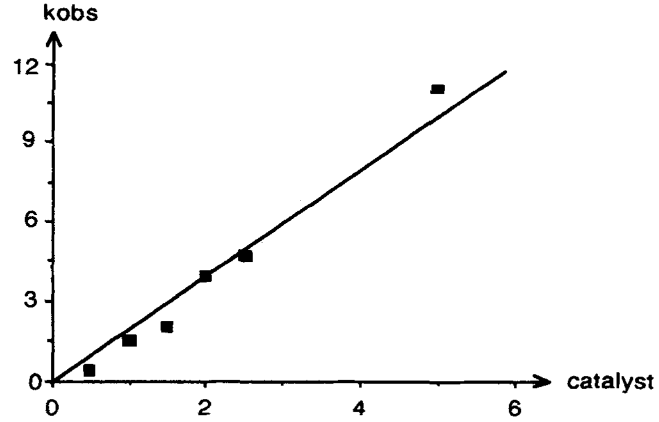


Figure 2. Plot of pseudo first-order rate constants (x 10^2 min^{-1}) as a function of catalyst weight (g) for inulin hydrolysis at 90 °C, 700 rpm.

dashed line). This excess of catalyst is therefore acting as an adsorbent. In a continuous process, 5-hydroxymethylfurfural will then be removed with the catalyst and the catalyst easily regenerated by thermal treatment under air flowing at 773 K. The amount of 5-hydroxymethylfurfural is reduced by a factor of 10 in comparison with what occurs in the presence of macroporous catalysts like resins under similar experimental conditions.

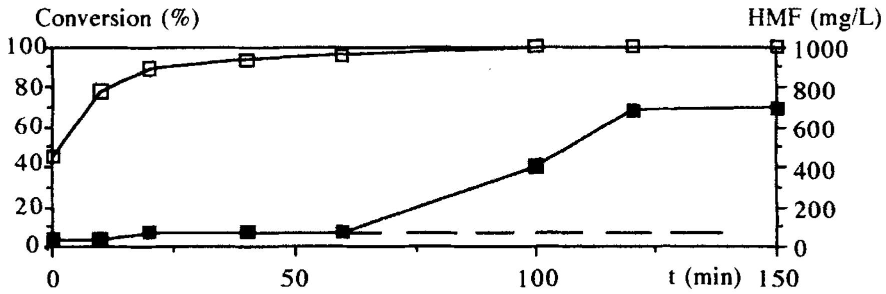
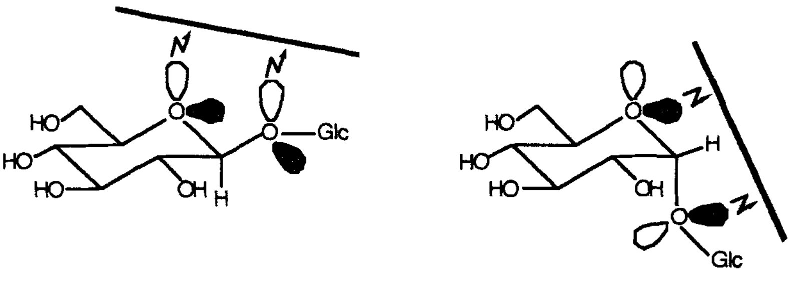


Figure 3. Sucrose conversion (□) and corresponding 5-hydroxymethylfurfural amount (■) as a function of time, 3 wt % of catalyst, 85 °C, 700 rpm.

The low amount of by-products may result from the better adsorbent capacity of faujasites compared to resins; it may also result from differences in the structures between both catalyst families, the formation of by-products being less important in microporous zeolites than in macroporous resins.[2] Indeed, in spite of the relatively important molecular size, sucrose may enter H-Y zeolites,[7] leading to intracrystalline catalysis and to a reduced amount of by-products, thus ensuring a better control of the formation of colored impurities nonacceptable in food industry.

Hydrolysis of Cellobiose and Maltose. Hydrolysis of cellobiose and maltose was performed under identical operating conditions (50 g/L, 150 °C, 2.5 g of catalyst). They are both readily transformed into glucose with selectivities as high as 98 and 92%, respectively, at conversions close to 90%. Higher conversions lead to a significant decrease in the selectivities. Their relative reactivity is also interesting to compare as far as they are capable of being subject to stereoelectronic effects due to the β-1,4 and α-1,4 linkages in cellobiose and maltose, respectively.[8] It was effectively shown that β-D-alkyl glucopyranosides are hydrolyzed faster than α-D-alkyl glucopyranosides by a factor of 2 to 3. The low reactivity of the α-anomer was attributed to a reverse anomeric effect.[9] However, hydrolysis of rigid models of α- and β-D-alkyl glucopyranosides led to opposite results, the α-anomer being hydrolyzed faster than its β counterpart. The relative rates of hydrolysis of α and β glycosides were then rationalized in terms of



Cellobiose Maltose

Figure 4. Adsorption through oxygen electron lone pairs for β and α anomers.

differences in the energies of both anomers in their ground and transition states for non rigid models, and in terms of differences in the energies of both anomers in their transition states only for rigid models.[8] In the presence of microporous catalytic systems such as zeolites, the ratio of the initial hydrolysis rates maltose/cellobiose is equal to 2.8 and in agreement with what could be expected if stereoelectronic effects were present with rigid anomers. This contrasts with the results obtained in the presence of resins where hydrolysis rates were found to be nearly identical and close to the α/β ratio of 1.5 observed for the homogeneous catalyzed reaction.[10] Here again the presence of microporous structure would be capable of differentiating between the two anomers through selective adsorption. Maltose and cellobiose may adopt a conformation in which adsorption onto a surface would involve two oxygen electron lone pairs in both cases as illustrated in Figure 4.

The rigidity of those models is then reinforced and the reactivity of maltose increased as compared to cellobiose. On the contrary, in macroporous systems, there is space enough within the macropores for conformational changes both in ground and transition states as observed for the homogeneous catalyzed reaction.

Hydrolysis of Starch. Finally, starch (soluble quality) is readily hydrolyzed to glucose in the presence of 2.5 g of catalyst for 50 mL of the starting (40 to 120 g/L) solution at 150 °C. Under these conditions, yields in glucose are up to and higher than

95% after a period of 150 minutes. It should be worth noting that damaging effects on the glucose yield are obtained by further increasing the reaction temperature and/or the initial quantity of starch.

In conclusion, whatever the food or non food applications are for fructose and glucose, it is clear that significant improvements in such hydrolyses are obtained by using heterogeneous processes, particularly those involving microporous H-form zeolites instead of macroporous protonic ion-exchange resins. In addition, as for ion-exchange resins, the reaction is not subject to product inhibition, which is not always the case for reactions catalyzed by enzymes.[11] Higher reaction temperatures can be used with the former catalysts, and improvement of both activity and selectivity can be obtained from their adsorbent and shape selective properties.

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