

HETEROGENEOUS SOFT ACID CATALYSIS OF THE SUCROSE HYDROLYSIS

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Using a micro-calorimetric DSC we have compared the acid-catalyzed inversion of sucrose in homogeneous and heterogeneous systems. Acetic acid was chosen as catalyst for homogeneous system, and several carboxylic cationites were used as heterogeneous catalysts. The kinetic apparent parameters (A , E , k_{ap}) for all the systems were calculated from DSC data with Friedmann's method and catalytic constant, k_{cat}^{323} , was further inferred. We found that the specific catalyst efficiency, q_{cat} , in heterogeneous system is over 5000 times higher than in case of homogeneous ones. The activity of heterogeneous carboxylic systems is still about 30 times larger than those of a strong mineral acid in homogeneous catalysis.

The results indicate the high efficiency of heterogeneous systems for soft acid catalysis of the sucrose hydrolysis.

Keywords: carboxylic cationite catalysis, homogeneous/heterogeneous catalysis, sucrose acid hydrolysis

Introduction

Most reactions catalyzed in strongly or weakly acidic solutions are also catalyzed by their corresponding solid acids, i.e. homogeneous acid catalysis may be substituted for the heterogeneous one. This heterogenizing tendency of the homogeneous catalysis is known to have some clear advantages such as an easier separation of the catalyst from the reaction medium, a decrease in the number of secondary products, a lower cost of catalyst per unit of product, reduced corrosion of equipment, etc. [1]. Moreover, some cooperative effects were found among acid $-SO_3H$ groups bonded to a flexible polymer matrix, which contribute to a higher catalytic activity compared to the homogeneous acid catalysis [2, 3]. In anhydrous medium, it was possible to study the general acid catalysis of sulfonic groups, both in homogeneous and heterogeneous systems, leading to a similar result which means that sulfonic groups of the strong acid cationites are much more catalytically active than those of the *p*-toluenesulfonic acid (PTSA) homogeneous phase [4].

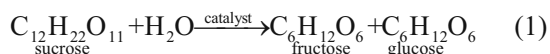
In order to study the heterogenizing of soft acid catalysis it has been chosen as catalyst $-COOH$ groups, in homogeneous system as acetic acid and in heterogeneous phase as carboxylic cationites. As a test reaction, sucrose inversion has been the choice because of its importance in food sweeteners industry [5], especially for the fructose products. Although the

industrial methods used nowadays for fructose type sweeteners are based on enzymatic hydrolysis of starch or sucrose with invertase enzyme (β -*D*-fructofuranosidase, E.C. 3.2.1.2.6) [6], these technologies are laborious and expensive. Therefore, heterogeneous acid catalysis seems to be a good alternative for the sucrose hydrolysis reaction compared to the enzymatic or homogeneous procedures, because of its certain advantages like [7–10]: the rigorous control of the reaction; the possibility of process automation; the higher purity of the reaction products, because of reducing the occurrence of secondary reactions; an easier separation of the catalyst from reaction medium; the absence of the equipment corrosion; the possibility to pilot the reaction at higher temperature than in the enzymatic process, which strongly favours the equilibrium displacement to the reaction products [10]; and also the possibility to re-use, several times, the catalyst. Several studies were dedicated to different aspects of the use of carboxylic cationites in this important process for food industry [11, 12].

Others showed the influence of experimental reaction conditions upon the apparent kinetic parameters in aqueous [13, 14] or non-polar organic medium [15], when using ion exchangers as catalysts.

The purpose of this work is to analyze how the homogeneous/heterogeneous nature of the carboxylic groups ($-COOH$) influences the kinetics of the sucrose acid catalytic hydrolysis:

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The homogeneous catalyst was taken as acetic acid, while various cationic resins were used as heterogeneous catalyst. The Purolite resins were used in this work because of their versatile properties and of their high purity degree, which recommend them as potential catalysts for food industry [16].

Experimental

Materials

The hydrolysis reaction was followed on a sucrose (Merck) aqueous solution of 1 M concentration. We used acetic acid (Merck) for homogeneous catalysis, and a series of carboxylic cationites in H^+ form, of Purolite type (Purolite International Ltd.), for heterogeneous catalysis. The cationite catalysts have polymeric matrix based on acrylic acid, crosslinked with divinylbenzene (DVB). Their characteristics are given in Table 1.

The experiments were performed with several concentrations of catalyst in the reaction medium, expressed as concentration of $-\text{COOH}$ groups (in mEqv COOH/g solution). The concentration of carboxylic groups of catalyst was kept similar for both homogeneous and heterogeneous systems.

In order to measure the real reaction kinetic it is essential to overcome the intraparticle diffusion hindrances [1, 18]. For this reason the resins were used after swelling in deionized water after 24–36 h at 20°C.

All the reagents were of analytic grade.

DSC analysis

The calorimetric measurements were performed in a microDSC III calorimeter – Setaram type, fitted with two identical cells (the reference cell R and the measurement cell S) manufactured from stainless

Table 1 The properties of the cationites used as catalysts in heterogenous systems (granulation 35–50 mesh)

Purolite cationite	Cross-linking degree [16]/% DVB	Exchange capacity ^a / mEqv g^{-1}
Gel type		
C105	7.2	9.38
C106 EP	12.0	9.29
Macroporous type		
C104	10.0	9.42
C106	12.0	9.31
C107 E ^b	9.0	9.69

^aexperimental value; ^bcationite for food industry

steel as cylinders of 1 cm^3 volume. Prior to the reaction in calorimeter, the investigated systems were thermostated at 25°C. The calorimetric calibration, experimental data acquisition, DSC curves processing, temperature program and other experimental details are given elsewhere [1, 17]. During our investigations the temperature ranged from 10 to 90°C, using a heating rate, β , of 0.15 K min^{-1} .

Results and discussion

For evaluating the kinetics of reaction (1) we assume that the heat flow during the time, t , is proportional to the extent of hydrolysis reaction. Following this, the kinetic parameters of the reaction, namely the activation energy, E and the pre-exponential factor, A , are calculated from DSC data by means of Friedmann's relationship, Eq. (2) [19].

$$\ln\beta[(d\alpha/dT) - \ln f(\alpha)] = \ln A - E/RT \quad (2)$$

where the conversion function, $f(\alpha)$ was taken, in line with the literature, of the first order, Eq. (3) [11, 12].

$$f(\alpha) = (1 - \alpha) \quad (3)$$

The conversion degree, α , at different times, t , was calculated directly from calorimetric curve with Eq. (4).

$$\alpha = (a^*/A^*) \quad (4)$$

where a^* = the partial area under the calorimetric curve at time, t and A^* is the total area under the DSC curve. DSC curves were obtained from DSC signals [18] after subtraction of the baseline, and an example is shown in Fig. 1.

The plot of left side member of Eq. (2) calculated at various values of conversion degree, α , vs. the corresponding reciprocal temperature, $(1/T)$, gives a

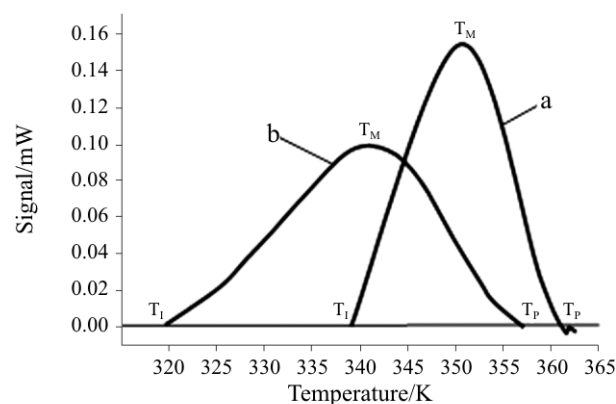


Fig. 1 DSC curves, after subtracting the base line, for a – homogeneous catalysis, b – heterogeneous catalysis, at the same concentration of $-\text{COOH}$ in mixture (DSC recording conditions are given in text)

Table 2 Kinetic parameters and peak temperature for reaction (1) heterogeneously catalysed with Purolite C106 EP at various concentrations, compared to homogeneously catalysed reaction

Catalyst	$C_{\text{cat}}/$ mEqv COOH/ g_{solution}	$T_M/$ K	$E/$ kJ mol ⁻¹	$\ln A/$ s ⁻¹	$k_{323}^{\text{ap}} \cdot 10^6/$ s ⁻¹
Homogeneous	2.08	350.9	193.6±3.5	59.3±1.3	2.7
(Acetic acid)	1.88	353.1	194.2±2.5	59.4±1.8	2.4
	1.63	355.0	195.1±3.5	59.5±0.9	1.9
Heterogeneous	2.09	341.0	122.9±1.5	35.8±0.5	49.0
(Purolite	1.89	342.2	127.9±2.6	37.5±1.0	38.4
C106 EP)	1.64	343.9	128.7±1.7	37.5±0.7	30.0

straight line whose slope equals $(-E/R)$ and the intercept is $(\ln A)$, R standing for the gas constant.

The kinetic parameters obtained for the homogeneous and heterogeneous system with Purolite C106 EP at various concentrations of catalysts are given in Table 2, together with the apparent rate constant, k^{ap} , calculated at 323 K, for easiness of comparison. The peak temperatures, T_M , recorded on DSC curves are also listed and the about 10 K difference between those of homogeneous and heterogeneous reaction supports the difference between the calculated rate constants.

Comparing the values of activation energy, it appears that the homogeneous systems need about 194 kJ mol⁻¹, whilst the heterogeneous systems require only 127 kJ mol⁻¹. These values are higher than those reported for both homogeneous and heterogeneous catalysis of sucrose hydrolysis with sulfonic acids and resins [20, 21].

The effect of the concentration of carboxylic groups on the reaction is noticeable on the peak temperature, T_M . As it indicates the values in Table 2, lesser is the amount of carboxyl group, higher the temperature records, which means slower the reaction is. This is also suggested by the trend of values of rate constant at 323 K in the last column.

Helfferich defined the ionite catalyst efficiency, q , by the Eq. (5) [1].

$$q = k_{\text{ap}}^{\text{het}} / k_{\text{ap}}^{\text{hom}} \quad (5)$$

where both apparent reaction rates constants are calculated for the same concentration of catalyst. Using the data calculated in Table 2 for Purolite C106 EP at the three concentrations, q , gives 18.2 for 2 mEqv cat/g mixture, 16.3 for 1.8 mEqv cat/g mixture and 15.9 for 1.6 mEqv cat/g mixture respectively.

Equation (5) can be also written with the specific rate constants, k_{cat} , which are independent of catalyst concentrations, as Eq. (6) [1].

$$q = (k_{\text{cat}}^{\text{het}} / k_{\text{cat}}^{\text{hom}}) \lambda_R = q_{\text{cat}} \lambda_R \quad (6)$$

In Eq. (6) we defined q_{cat} as the specific catalytic efficiency which, as it appears, it is independent of the concentration of the catalyst and characterise the activity of the catalyst, λ_R , the molar distribution of reactant, is given by Eq. (7).

$$\lambda_R = (m_R^{\text{het}} / m_R^{\text{hom}}) \quad (7)$$

with m being the molar concentration of reactant in solution and in ionite, respectively.

For evaluating the specific catalytic efficiency, q_{cat} , and for comparing further the activity of homogeneous and heterogeneous carboxylic groups, we calculated the kinetic catalyst parameters, namely the reaction catalytic constant, k_{cat} , and reaction catalytic order, n_{cat} , respectively, from the Eqs (8) and (9) [22].

$$k_{\text{ap}}^{\text{hom}} = k_{\text{cat}}^{\text{hom}} C_{\text{acid}}^{\text{h}_{\text{hom}}} \quad (8)$$

$$k_{\text{ap}}^{\text{het}} = k_{\text{cat}}^{\text{het}} C_{\text{COOH}}^{\text{h}_{\text{het}}} \quad (9)$$

where C is the concentration of acid groups.

The data from Table 2 allows inferring the catalytic order, n_{cat} , and catalytic kinetic constant, k_{cat} , as being of 1.4 and $9.5 \cdot 10^{-7}$ (s⁻¹) for homogeneous systems, and 2.0 and $1.1 \cdot 10^{-5}$ (s⁻¹) for Purolite C106 EP system respectively. Following definition of specific catalytic efficiency, q_{cat} , from Eq. (6), the ratio of the catalytic kinetic constants, k_{cat} , calculated from Eqs (8) and (9) equals 11.3. This is smaller than any of the q , values calculated at the three different concentrations, which means $\lambda < 1$ for all the concentrations. Obviously, $\lambda < 1$ means a smaller solubility of sucrose in the cationite matrix than in the reaction solvent, because water is a good solvent of sucrose. Consequently we infer that the high specific catalytic efficiency, q_{cat} , of carboxylic ionite, is not owing to some reactant concentration effect in catalyst matrix, but is due to the cationite catalyst intrinsic activity, similar with what was found out for sulfonic cationites in aqueous, polar [2, 3] and anhydrous, non-polar, organic media [4].

Table 3 The catalytic reaction rate constants and the evaluated specific catalytic efficiency

Catalyst	n_{cat}	$k_{\text{cat}}/\text{s}^{-1}$	$q = k_{\text{ap}}^{\text{het}}/k_{\text{ap}}^{\text{hom}}$
Acetic acid	1.4	$9.5 \cdot 10^{-7}$	1.0
Purolite C105	2	$7.5 \cdot 10^{-5}$	78.7
Purolite C106 EP	2	$1.1 \cdot 10^{-5}$	11.3
Purolite C104	2	$3.5 \cdot 10^{-4}$	369.5
Purolite C106	2	$4.0 \cdot 10^{-4}$	420.0
Purolite C107 E	2	$5.4 \cdot 10^{-3}$	5723.3

Similar calculations of catalytic kinetic constant and catalytic order were carried out for all the Purolite systems and lead to the results from Table 3.

Last column from Table 3 lists the values of specific catalytic efficiency, q_{cats} , for the investigated systems. As it appears, the values may be more than 5000 for Purolite C107E, clearly exhibiting the efficiency of the heterogeneous catalysis.

Summing up, the cationite specific catalytic efficiency, $q_{\text{cat}} \gg 1$, results from its intrinsic structure, being possibly due to an enhancement of the catalytic activity of $-\text{COOH}$ groups from polymer matrix. In comparison, the catalytic activity of carboxyl groups from homogeneous aqueous system is somehow hindered by being trapped in solvent boxes.

Conclusions

We have performed a non-isothermal study of the catalysed sucrose hydrolysis. The micro-calorimetric data of sucrose soft acid inversion reaction in homogeneous and heterogeneous catalysed systems were used for kinetic calculations. We found a significant difference between the two systems, the heterogeneous catalysis, namely the carboxylic cationites, having a specific catalytic efficiency, q_{cat} , up to 5723 times higher than those of $-\text{COOH}$ homogeneous groups.

The results show a higher enhancement of heterogenising soft acid catalysis than it was achieved with strong sulfonic cationites [2–4, 15, 20, 21, 23]. The differences of efficiency between soft and strong acid cationites might be explained by the difference of catalytic groups concentrations in polymer matrix (i.e. exchange capacity), which is about twice higher in carboxylic cationite than in sulfonic ones [4, 15, 20, 21, 23].

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