

Sulfonated Latex Particle as Acid Catalysts for the Continuous Inversion of Sucrose

J. H. KIM, M. S. EL-AASSER, A. KLEIN, and J. W. VANDERHOFF, *Emulsion Polymers Institute and Departments of Chemical Engineering and Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015*

Synopsis

Sulfonated polystyrene latex particles were used as acid catalysts in the continuous inversion of sucrose at 50–70°C. The particles (surface charge 168 $\mu\text{eq/g}$) were confined in a stirred reactor with a semipermeable membrane; sucrose solution was pumped in, and product solution was pumped out. The catalytic activity of the particles was unchanged after 20 days continuous use. Variation of particle size (0.13 and 0.42 μm) and stirring rate showed that internal and external mass transfer was not a controlling factor. The kinetics were pseudo-first-order; the rate constant at 70°C was 2.30/N min as compared with 0.07/N min for macroporous sulfonated ion-exchange resin; the apparent activation energy was 111 kJ/mol as compared with 121 kJ/mol for the homogeneous acid-catalyzed reaction. The faster rate was attributed to the very great surface area, high charge density, and lack of internal diffusional resistance of the latex particles. The proposed mechanism comprised adsorption of sucrose on the particle surface, followed by inversion and desorption of product.

INTRODUCTION

Polymeric particles, larger than a micron in diameter, have often been used as the catalyst itself or as a support, providing the means for using well-defined catalytic groups in a phase separate from that holding the reactants and thereby minimizing the difficulties of product purification and corrosion associated with homogeneous catalysts. The advantages of polymeric reagents are many: They are easily functionalized, easily separated from a reaction mixture, can be reused, can be used in a continuous flow processes, and can be prepared with a wide range of physical properties. The main disadvantages of polymeric reagents or catalysts are the low chemical and thermal stability.¹

Industrial applications until now have used the same acid resin prepared by sulfonation of poly(styrene-co-divinylbenzene) macroporous beads. The synthesis was developed over 40 years ago² to make macroporous ion exchange resins. These acidic beads have been used in chemical processes catalyzed by acids, such as esterification, dehydration, and isomerization. The intensive research in this field has been largely concerned with problems of the macroporous catalytic reactions such as the dehydration of *t*-butyl alcohol,³ formation of olefins and paraffins from butyl alcohol,⁴ benzene propylation,⁵ condensation of phenol and acetone, isopropyl alcohol dehydration,⁶ and toluene alkylation.⁷ These reactions were all catalyzed by a sulfonated styrene-divinylbenzene copolymer resin. One of the most comprehensive discussions of the macroporous catalytic reaction model was presented by

Dooley.⁷ He showed the existence of intraparticle diffusion limitations in crosslinked macroporous resins.

Possible alternatives to crosslinked macroporous polymer supports are colloidal polymers particles. In addition to their well-cleaned surface and well-characterized surface functionality, the latex particles have the advantages of a narrow particle size distribution of spherical particles, and high specific surface area. The latex catalysts promise better activity than the macroporous resin because of its nonporous surface morphology,^{8,9} but because of its colloidal dimensions the product/catalyst separation must be altered from that used for macroporous beads. Little is known about latex catalyzed reactions and suitable reactor systems. In this paper the feasibility of using highly sulfonated latex as catalyst is investigated in a specially designed flow-through reactor.

EXPERIMENTAL

Well-characterized highly-sulfonated polystyrene latexes were used as the heterogeneous catalyst for the model reaction. The reaction kinetic data were determined in a flow-through reactor (FTR). The inversion of sucrose at 50–70°C was carried out at various sucrose concentrations. Reaction temperature was varied.

Sulfonated Latex Catalysts

Two styrene-sodium styrene sulfonate copolymer latexes (SL-1 and SL-2) were used as acid catalysts for this study. The two-stage shot-growth method was used to obtain highly sulfonated polystyrene latex catalysts. The polymerization method and cleaning processes are described elsewhere.¹⁰ Figure 1 shows transmission electron micrograph of latex catalysts SL-1 and SL-2. The number of chemically bound sulfonate surface groups was determined by conductometric titration of the cleaned latexes in the hydrogen form with sodium hydroxide solution. Figure 2 shows the conductometric titration curves for each of the latex catalysts. Both latex SL-1 and SL-2 have the same specific surface charge (168 $\mu\text{eq/g}$ solid). The only difference is their particle size (0.13 and 0.42 μm) and therefore charge density. Various characteristics of the latex catalysts are shown in Table I.

Reactor Setup

The experimental arrangement is shown in Figure 3. The inversion of sucrose was performed in a 70 cm³ serum replacement cell having a filtration membrane diameter of 4.3 cm and filtration area of 11.3 cm². A schematic representation of the filtration cell used for the flow-through reactor (FTR) is shown in Figure 4. The flow-through reactor was continuously fed with sucrose solution, and the hydrolysis product containing unreacted sucrose was drawn off. A membrane filter kept the latex catalyst inside the reactor. Membrane with pore sizes of 0.1 and 0.2 μm were used.

The temperature in this system was controlled by circulating water from a constant-temperature bath. The reactor temperature could be maintained constant within 0.1°C. The sucrose reactant stream was supplied from a

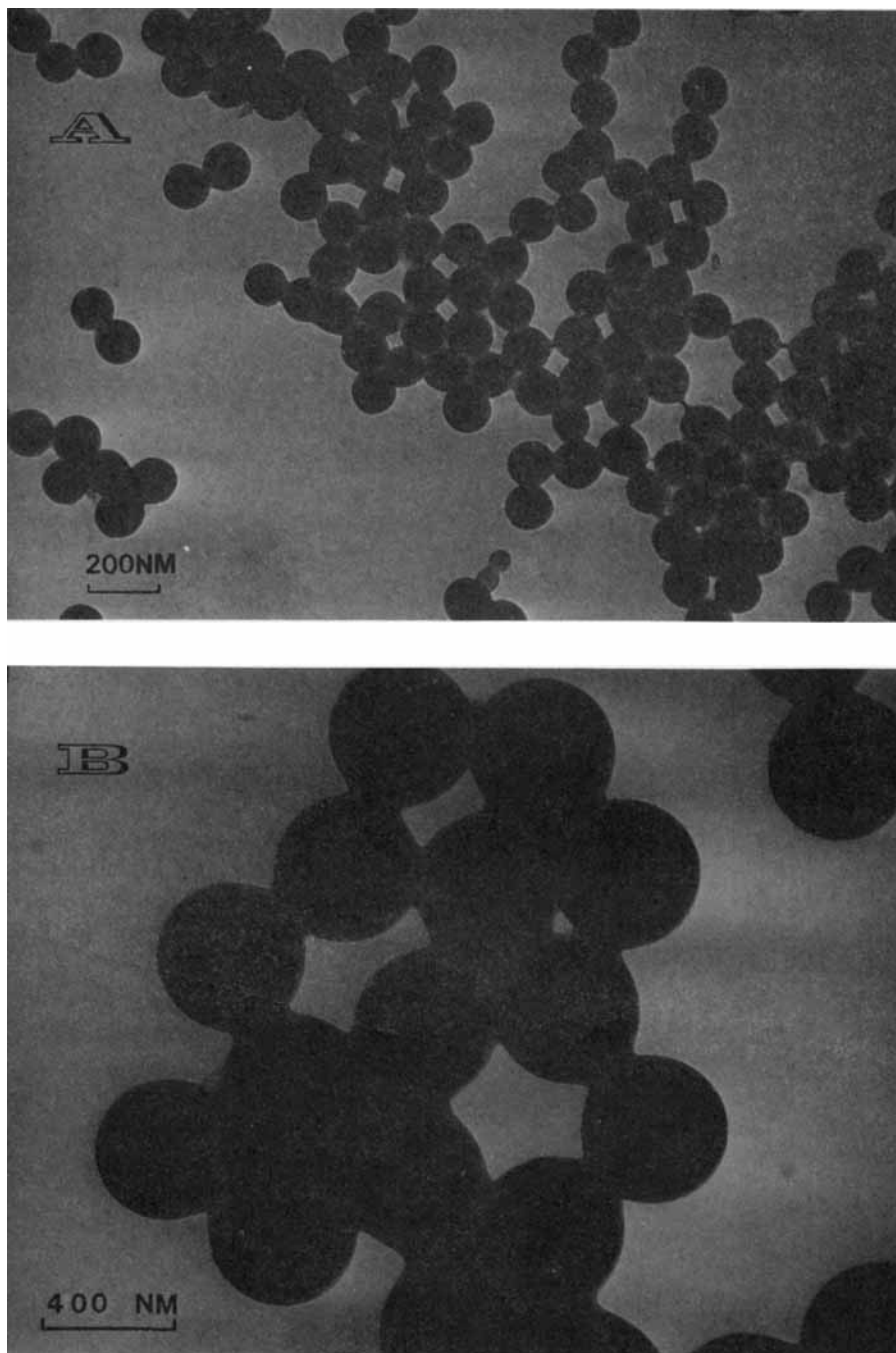


Fig. 1. Transmission electron micrographs of SL-1 and SL-2 styrene-sodium styrene sulfonate copolymer latex catalysts.

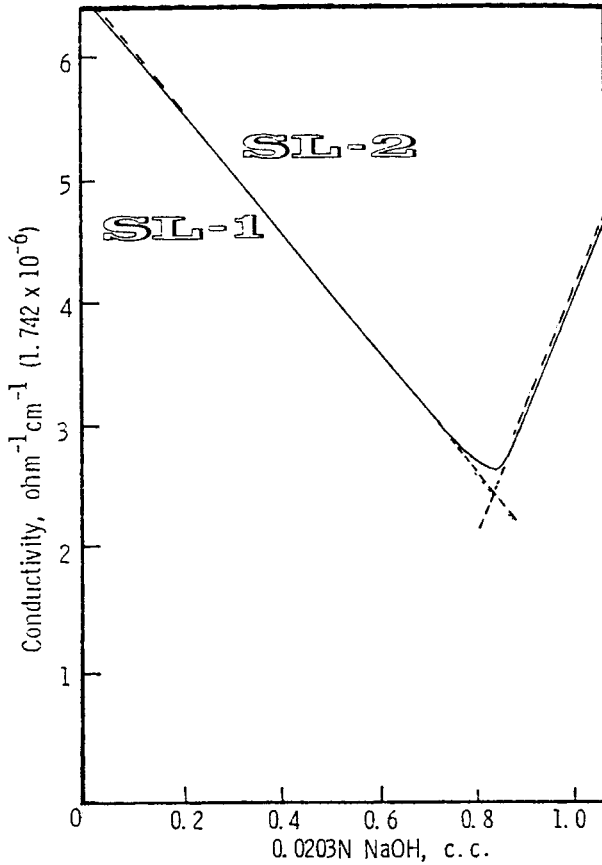


Fig. 2. Conductometric titration curves for SL-1 and SL-2 styrene-NaSS latex catalysts: 0.1 g solid particles in 200 cm³ distilled water.

TABLE I
Physical Characteristics of the Sulfonated Polystyrene Latex Catalysts^a

	SL-1	SL-2
\bar{D}_n (μm)	0.13	0.42
A_p (m^2/g)	43.50	13.90
$N^{(1)}$ ($\mu\text{eq}/\text{g}$)	168	167
$N^{(2)}$ ($\mu\text{eq}/\text{m}^2$)	3.87	11.95
σ ($\mu\text{C}/\text{cm}^2$)	37.3	115.3
P ($\text{\AA}^2/\text{SO}_3^-$)	43.0	14.0

^a \bar{D}_n = number average particle diameter, A_p = specific surface area, $N^{(1)}$ = specific surface sulfonate concentration, $N^{(2)}$ = surface sulfonate concentration per area, σ = surface charge density, and P = packing area per single sulfonate ion.

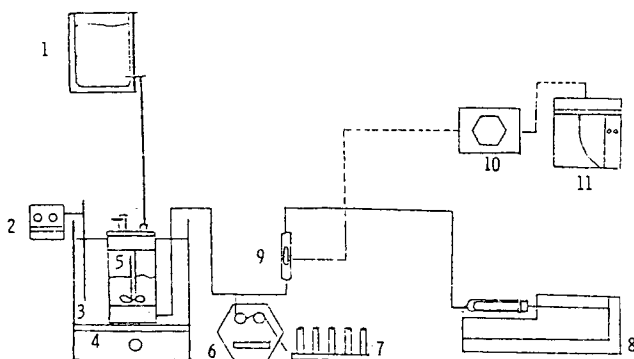


Fig. 3. Experimental arrangement for the continuous acid latex catalyzed inversion of sucrose: (1) reservoir; (2) temperature controller; (3) water bath; (4) magnetic stirrer; (5) FTR; (6) micropump; (7) sampling tube; (8) syringe pump; (9) flow conductance cell; (10) amplifier; (11) recorder.

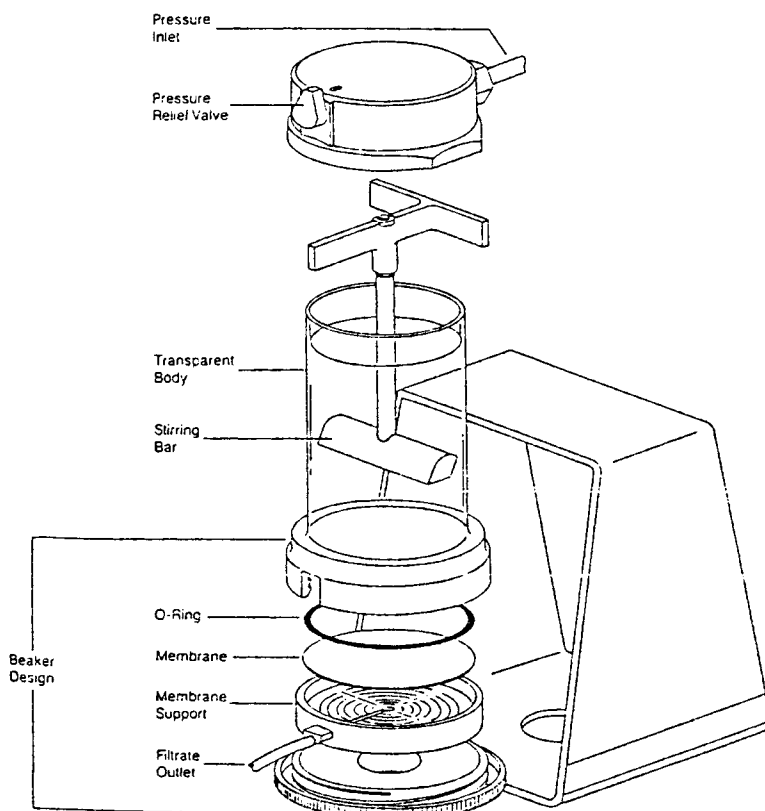


Fig. 4. Schematic representation of the flow through reactor.

reservoir. The flow rate was controlled by a syringe pump located at the reactant outlet.

Sample Analysis

The composition of the effluent stream was analyzed by means of an YSI Model 27 glucose analyzer. The d(+) glucose is selectively oxidized to gluconic acid and hydrogen peroxide by an immobilized glucose oxidase. The hydrogen peroxide formed is oxidized at the platinum electrode and creates a current flow. The current flow in the circuit is linearly proportional to the local concentration of hydrogen peroxide, and, due to the stoichiometry of the oxidation reaction, is also proportional to the glucose concentration.¹¹ All glucose concentrations are the mean of at least three measurements.

RESULTS AND DISCUSSIONS

Stability of the Sulfonated Latex Catalyst

It was possible to carry out the hydrolysis of sucrose in the 75 mL flow through reactor for up to 500 h. The flow-through reactor system was adequate for longer runs because of the great stability of the sulfonated polystyrene latex catalyst. Figure 5 shows the results of continuous 4-h runs with various residence times (different flow rates) of the sucrose solution. The amount of sulfonated polystyrene latex catalyst (SL-1) was kept constant (0.04N) during these runs. A steady state was attained after a period of 3–4 mean residence times.

By monitoring the conductivity of the sulfonated polystyrene latex before and after the reactions, it was possible to determine the extent of catalytic

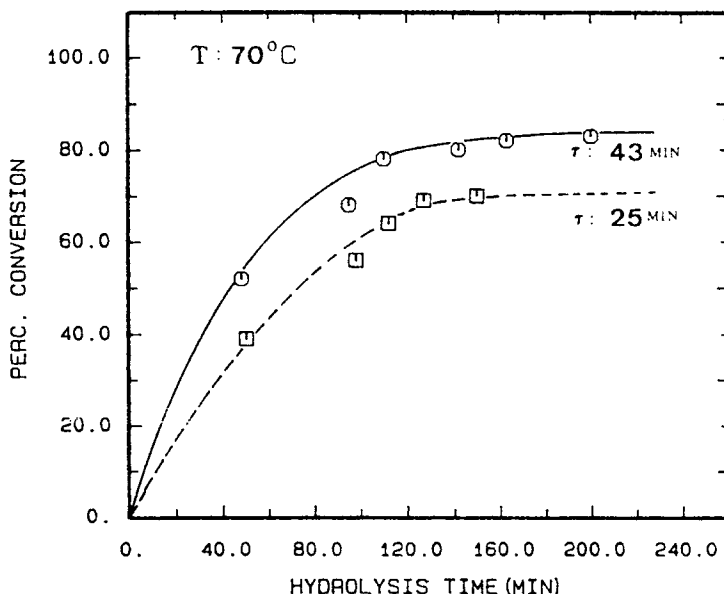


Fig. 5. Transient response for the startup of continuous conversion of the sucrose: $[H^+] = 0.04N$, $[sucrose] = 7.48 \text{ mmol dm}^{-3}$.

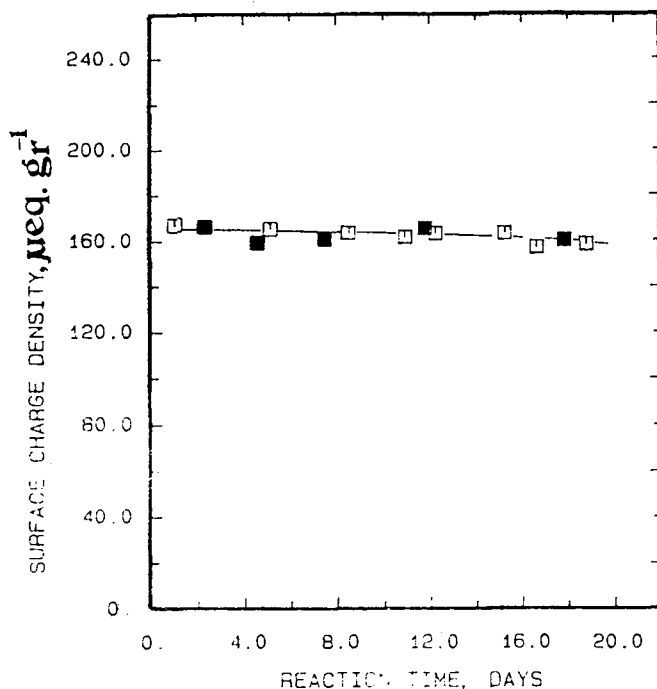


Fig. 6. Effect of reaction time on the activity of sulfonated polystyrene latex catalysts: SL-1[O], SL-2[O].

activity changes. The change in sulfonate functionality with reaction time during conversion of sucrose to glucose is shown in Figure 6. The surface charge density of the sulfonated polystyrene latex catalysts decreased by only about 3% over a period of 400 h, mainly because of the stability of sulfonate groups to hydrolysis, oxidation, and thermal degradation. Both latexes SL-1 and SL-2 showed excellent stability during the long periods of the hydrolysis reactions.

Kinetic Model

Typical batch reaction rate data are shown in Figure 7. The results suggest that the acid latex-catalyzed hydrolysis of sucrose follows pseudo-first order kinetics. Following the surface reaction mechanism shown in Figure 8, three different kinetic models were developed to explain the experimental pseudo-first-order reaction rate. All three are based on the assumption that surface reaction rate is much faster than either the rate of adsorption of the reactants on the acid latex particle surface or the rate of desorption of the products from the latex surface.

In the first model it is further assumed that all the reactants adsorb and all the products desorb with the same equilibrium constant. This leads to the kinetic expression

$$-\frac{1}{V} \frac{dN_s}{dt} = \frac{K}{C_w} C_s S_0^2 \quad (1)$$

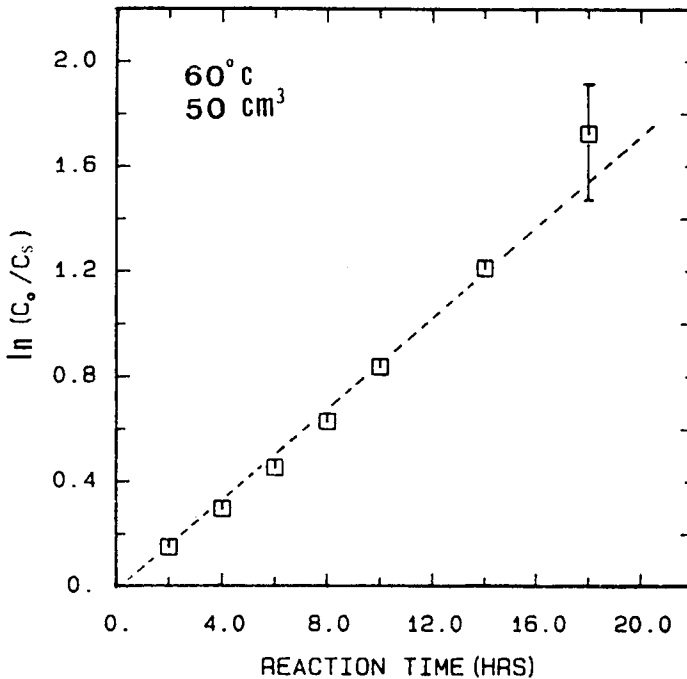


Fig. 7. Pseudo-first order plots for the hydrolysis of sucrose in the presence of SL-1 sulfonated polystyrene latex catalyst at 60°C: $[H^+] = 0.003N$, $[sucrose] = 7.55 \text{ mmol dm}^{-3}$.

where N_s is the number of moles of sucrose in a liquid of volume V in which the molar concentration of water is C_w and that of sucrose is C_s . The reaction rate constant is K and the number of adsorption sites in moles per fluid volume is S_0 .

In the second model, it is assumed that the active particle surface is hydrated and no adsorption of water or fructose takes place. Sucrose, however, is adsorbed and glucose is desorbed. The equilibrium constants are also assumed to be the same for sucrose and glucose adsorption. These assump-

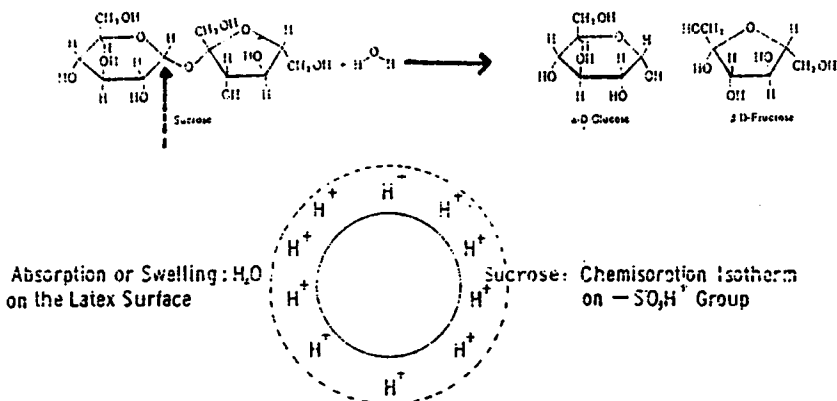


Fig. 8. Heterogeneous surface reaction model for sucrose inversion.

tions lead to the expression

$$-\frac{1^{dN_s}}{V dt} = \frac{KK_1C_sC_wS_0}{1 + K_1C_{s_0}} \quad (2)$$

where K_1 is the equilibrium adsorption constant and C_{s_0} is the initial or feed sucrose concentration.

In the third model, it is assumed the adsorption of sucrose but no product adsorption or desorption is made. This set of assumptions lead to the expression

$$-\frac{1^{dN_s}}{V dt} = \frac{KK_1C_sC_wS_0}{1 + K_1C_s} \quad (3)$$

Model I predicts a reaction rate which is dependent on the square of the active site concentration or S_0^2 . The experimental relationship of reaction rate to active site concentration is shown in Figure 9. The linear relationship found fits the predictions from Models II and III but does not fit Model I. Thus we need to further consider Models II and III. In both of these models the numerator can be expressed as

$$k_0C_w e^{\frac{-E}{RT}} e^{\frac{-\Delta H}{RT}} e^{\frac{\Delta S}{R}} C_s \quad (4)$$

where the first exponential term represents the Arrhenius activation energy and the second and third terms describe the enthalpy and entropy contribution from the adsorption process. (The product of the second and third

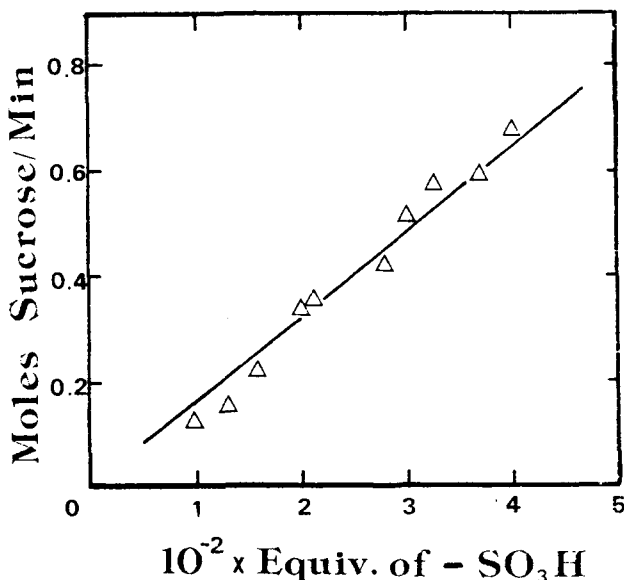


Fig. 9. Dependence of sucrose hydrolysis reaction rate to the active site concentration.

exponential terms is equal to the equilibrium constant.) The apparent kinetic rate constant k_a is expressed as

$$k_a = k_0 C_w e^{\frac{\Delta S}{R}} e^{-\frac{\{E + \Delta H\}}{RT}} = k_{a0} e^{-\frac{\{E + \Delta H\}}{RT}} \quad (5)$$

and the surface reaction rate in moles of sucrose per active site per time is given as

$$-r_{\text{surface}} = \frac{1}{VS_0} \frac{dN_s}{dt} \quad (6)$$

The rate expression for Models II and III are respectively

$$-r_{\text{surface}} = \frac{k_a C_s}{1 + K_1 C_{s0}} \quad (7)$$

and

$$-r_{\text{surface}} = \frac{k_a C_s}{1 + K_1 C_s} \quad (8)$$

The distinction between Models II and III is the rate dependence on the initial or feed concentration of sucrose. The results given in Table II show that doubling the sucrose feed concentration does not change the kinetic rate. Clearly, the data are inadequate to distinguish between the models. However, in both cases, when $1 \gg K_1 C_{s0}$ the reaction models become pseudo-first-order and represent the experimental data. A liquid-phase pseudo-first-order reaction in a continuous stirred tank reactor can be represented by the following relationship:

$$C_{s0}/C_s = 1 + k_a \tau \quad (9)$$

where τ is the space time which is defined as follows:

τ = time required to process one reactor volume of feed measured at specified conditions.

The experimental data are shown to conform to this relationship in Figure 10. The apparent kinetic rate constants were determined from the slopes of

TABLE II
Surface Reaction Rate Constant Dependence on Particle Size and Agitation Speed for Sulfonated Latex Catalysts at 70°C and Total Catalytic Charge of 0.04 N

Latex type (#)	Size (μm)	Stirring rate (rpm)	[Sucrose] (mmol dm^{-3})	k_a [$(\text{N s})^{-1}$]
SL-1	0.13	120 \pm 5	7.48	2.30
SL-1	0.13	20 \pm 1	7.42	2.23
SL-1	0.13	120 \pm 5	13.79	2.25
SL-2	0.42	120 \pm 5	7.25	2.29
SL-2	0.42	20 \pm 1	7.47	2.28
SL-2	0.42	120 \pm 5	13.67	2.24

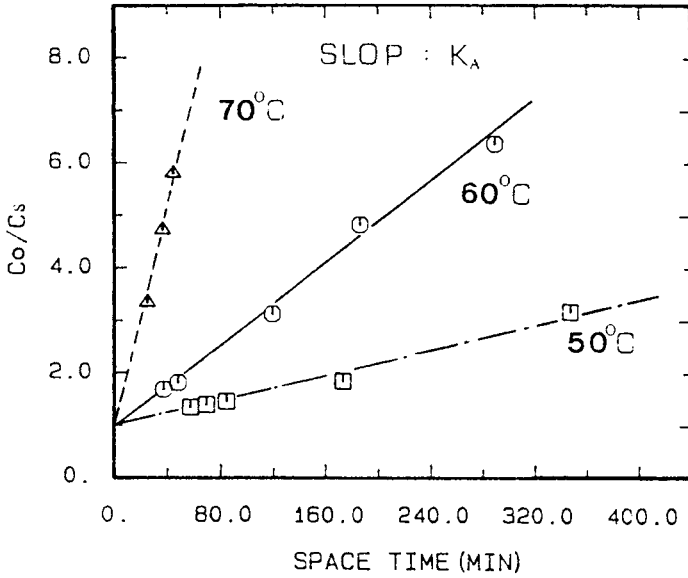


Fig. 10. Relation of space time to $[C_{s0}/C_s]$ at different reaction temperatures with sulfonated polystyrene latex catalyst SL-1.

these curves at three temperatures. The kinetic rate constant vs. temperature relationship is shown in Figure 11, from which an apparent activation energy for the reaction, E_a , was calculated. From the surface reaction model, eq. (5), the following relationship can be obtained:

$$E_{app} = E_{homogeneous} + \Delta H_{adsorption} \tag{10}$$

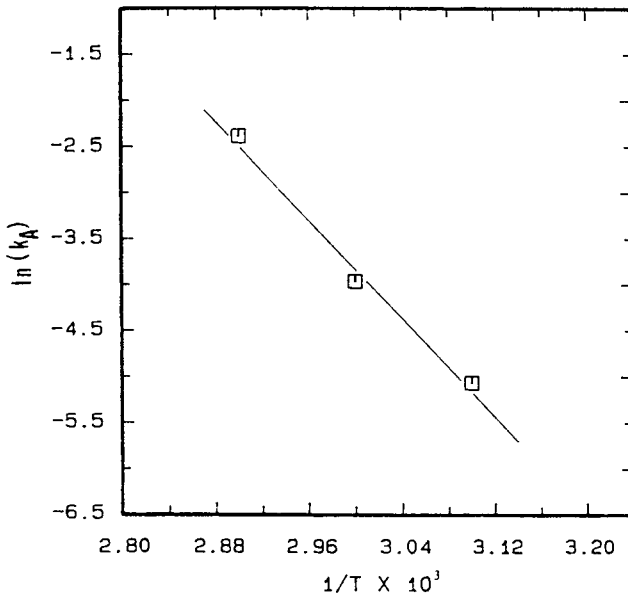


Fig. 11. Effect of temperature on pseudo-first order reaction rate constant; Arrhenius plot.

The apparent activation energy from this study was found to be 111 kJ/mol, and, for the homogeneous case, the value was reported as 121 kJ/mol.¹² The enthalpy of adsorption from eq. (10) is -10 kJ/mol. The enthalpy of physical adsorption is most often exothermic and in the range of 8–22 kJ/mol. Both the magnitude and the sign of the calculated enthalpy of adsorption is reasonable. Whether the assumption of $1 \gg K_1 S_{s0}$ is a reasonable one is more difficult to check. To estimate the equilibrium constant K_1 , the entropy term is needed in addition to the enthalpy term, as shown below:

$$K_1 = e^{-\frac{\Delta H}{RT}} e^{\frac{\Delta S}{R}} \quad (11)$$

The entropy is not available for this system. The entropy data for other systems were used to establish a trend or an estimate for the sucrose system. The entropy of desorption from the air interface into water for the alkyl alcohol series of butanol to octanol varied from 0.42 to -7.54 J/mol.¹³ If we assume that, in adsorption, some entropy is lost owing to the molecules being restricted at the interface and that an estimated lower limit is about 8.37 J/mol, we can estimate K_1 to be about 16. The entropies of desorption for the acid homologs were much higher in the range -29.31 – 58.62 J/mol. A general correlation for the standard state entropy of adsorption, ΔS^0 , as a function of the standard state enthalpy of adsorption, ΔH^0 was determined from physical adsorption data of gases on charcoal at less than monolayer coverage. This correlation is represented as¹⁴

$$\Delta S_a^0 = 0.0014[\Delta H_a^0 - 12.2] \quad (12)$$

From this correlation, an upper limit of the entropy of -62.80 J/mol is obtained, from which K_1 is estimated to be 0.02. It seems reasonable that, for sucrose, the equilibrium constant for adsorption is $0.02 < K_1 < 20$. The concentrations of sucrose in the feed were about 0.1 and at the low end of the K_1 approximation, $K_1 C_{s0} \ll 1$, which is the condition for the reaction model to approximate the pseudo-first-order reaction. Further, one could argue that the entropy of sucrose adsorption is larger than the value used for the approximations. Sucrose is a much larger molecule than the lower alkyl alcohols or acid homologs described above. Therefore, the condition that $1 \gg K_1 C_{s0}$ seems reasonable. The above arguments are used in favor of a sucrose reaction rate model. The hypothesis is that sucrose is physically adsorbed on the hydrated particle surface and adsorption/desorption of the glucose and fructose products is weak. Evidence for the absence of both internal and external mass transfer control is given in Table II. Using small ($0.13 \mu\text{m}$) and large ($0.42 \mu\text{m}$) size particles at low (20 rpm) and high (120 rpm) levels of agitation did not affect the reaction rate constant (2.26 ± 0.04)/N min⁻¹.

It is important to compare the specific rate in this sucrose inversion reaction with those previously reported by others. The sucrose inversion reaction is usually carried out using mineral acids,¹⁵ or high-polymer acids enzymes as catalyst.¹² The heterogeneous catalysis of this reaction by sulfonated ion-exchange resins has also been studied.¹⁶ The most important advantage in using a functionalized high-polymer acids as catalyst is the

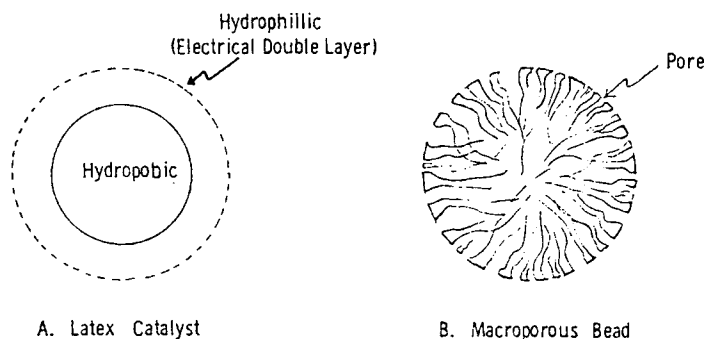


Fig. 12. The different surface morphology of (A) latex catalyst and (B) emacroporous bead.

simplification of product workup, separation, and isolation. However, almost all these studies have been carried out using stirred-tank batch reactors.^{17,18} Saito et al.¹⁹ investigated this reaction using an ion exchange resin (Dowex 50) in a fixed bed. Their kinetic data suggested an effect of external diffusion or mass transfer on the observed reaction rates.

The sucrose inversion reaction was also studied using the acid latex which had been synthesized using as initiator disodium bis(4-sulfomethyl benzoyl) peroxide in the absence of emulsifiers.⁹ In these studies, it was shown that the sulfonated latex particles had good reactivity and selectivity, but no reaction rate model was postulated for those reactions. Moreover, the maximum surface charge density of these latex catalysts was quite low, and therefore they could not be used in a continuous system.

Figure 12 shows the morphological difference between the latex particle and macroporous resin catalysts. Both polymer catalysts have a large surface area, external for the latex particle and internal for the macroporous resin. The comparisons between latex particle and macroporous resin catalyst were illustrated in Table III.

The reported rate constants for the sucrose inversion reaction are shown in Table IV. If the values reported by Hartler et al.¹² and Reed²⁰ were normalized for acid concentrations used, to give comparable reaction conditions, it becomes clear that the sulfonated latex catalysts show higher reaction rates. Based on this information, the order of the pseudo-first-order reaction rate constants for the sucrose inversion reaction is: sulfonated latex particle > polystyrene sulfonic acid > H_2SO_4 > sulfonated ion-exchange resin, indicating the advantage of the latex catalyst.

TABLE III
The Comparison between Latex Catalyst and Macroporous Bead

	Latex catalyst	Macroporous bead
Size	0.1–0.6 (μm)	0.1–0.3 (mm)
Specific surface area	10–50 (m^2/g)	10–25 (m^2/g)
Porosity	None	13–80 vol %
Reaction point	Liq.–particle interface	Pore
Mass transfer limit	No	Yes

TABLE IV
Specific Rate of Sucrose Inversion for Different Type of Acid Catalyst at 70°C

Acid	Concentration N	K_A^a (N min) ⁻¹	R^b	Ref.
H ₂ SO ₄	0.100	1.04	1.00	Hartler ¹²
P-SSA ^c	0.117	1.37	1.32	Hartler ¹²
IER ^d	1.820	0.07	0.07	Reed ²⁰
SL-1 ^e	0.040	2.30	2.21	Table I
SL-2	0.040	2.29	2.21	Table I

^a Surface reaction rate constant.

^b Ratio based on k_{a, H_2SO_4} .

^c Polystyrene sulfonic acid.

^d Ion exchange resin, [Dowex 50W].

^e Sulfonated polystyrene latex catalyst.

CONCLUSIONS

Polystyrene latexes with high surface sulfonation were used as heterogeneous catalysts in the acid-catalyzed inversion of sucrose. The reaction was carried out continuously in a specially designed flow-through reactor in which a membrane filter kept the catalyst inside the reactor. The reaction followed pseudo-first-order kinetics which was consistent with the mechanism in which sucrose was physically adsorbed onto the hydrated latex particle surfaces and the adsorption/desorption of products was weak. Evidence for the absence of internal and external mass transfer control was provided by separate experiments, using small- and large-sized particles at low and high levels of agitation, in which the reaction rate remains invariant.

The reaction rate constant, from this study, was compared to the reaction rate constants for other catalysts in the literature. The pseudo-first-order reaction rate constant was the largest for the latex catalyst, followed by polystyrene sulfonic acid, sulfuric acid, and sulfonated ion exchange resin. The advantage of the latex catalyst lies in the large surface area with large surface charge density and the absence of diffusional resistances. The sulfonated latex particles showed good stability over 400 h of continuous reaction, and the continuous reactor design provided an easy and simple means of separating the catalyst particles from the reactant and products.

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