Physical properties of anion exchangers used as a catalyst in the isomerization of hexoses

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PHYSICAL PROPERTIES OF ANION EXCHANGERS USED AS A CATALYST IN THE ISOMERIZATION OF HEXOSES

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ABSTRACT

Anion exchangers can be used for the conversion of glucose to a mixture of glucose and fructose.

In this paper those chemical and physical properties of a number of ion exchangers are discussed that are necessary to describe the absorption, diffusion and chemical conversion of sugars.

The following physical properties of ion exchangers are used to explain the differences observed in their catalytic activity and selectivity. The particle size as well as the porosity may influence the diffusion of the reaction components inside the resin particle and by that the selectivity of the reaction. The pore volume, combined with adsorption data, determines the concentrations within the ion exchanger. This makes it possible to relate catalytic effects directly to conditions inside the catalyst. To obtain a reproducible catalytic activity, a standardized method of activation of these ion exchangers has been developed.

INTRODUCTION

Ion exchange resins can be used as a catalyst for almost all reactions catalyzed by acids or bases. Kunin [5] gives a survey of the application and the catalyst activity of resins. The alkaline isomerization of glucose and lactose can be considered as one of these applications [1,2]. The heterogeneous catalytic reaction of carbohydrates on a strongly alkaline ion exchanger can be described as taking place in a pseudo-homogeneous solution within the catalyst. The physical properties of a catalyst can influence the catalytic activity and selectivity for a given reaction. For the isomerization of glucose, the fructose formed must be removed from the resin. The concentration gradient, necessary for diffusion, is a function of the physical properties of the resin, such as porosity, pore volume and particle size. When, due to these physical properties, this diffusion is very slow, the concentration of fructose in the catalyst becomes relatively high.

As the rate of alkaline degradation of fructose is much higher than that for glucose, a low rate of diffusion will lower the selectivity of the isomerization under all circumstances.

In this paper, the relevant chemical and physical properties of the resins studied will be described. The adsorption of carbohydrates on, and their diffusion in these ion exchangers will be reported in separate publications [3,4].

CHEMICAL PROPERTIES

The carrier for the active groups of ion exchange resins is generally obtained by homogeneous copolymerization of styrene and 1,4-divinylbenzene. This carrier is of homogeneous structure and is known as a gel-type resin. When the polymerization has been carried out in the presence of an inert solvent/non solvent system, macroreticular carriers are formed. By treating the copolymer with dichloromethyl ether in the presence of a Friedel-Crafts catalyst (ZnCl_2 , AlCl_3 , SnCl_4) and subsequently with a tertiary amine, a strongly basic type I anion exchanger is obtained. To use these ion exchangers as a catalyst for isomerization of carbohydrates, they must be activated with alkali to bring them into the required hydroxyl form. The quaternary ammonium groups, with OH^- counter ions, are the active sites for the isomerization reactions.

The chemical stability of ion exchangers is dependent on the type of resin, the counter ion and the temperature. An ion exchanger is much more stable in the chloride form than in the hydroxyl form [5,6]. At high temperature the resin will lose activity [10-12]. Two types of degradation reactions can be distinguished [6] for type I resins:

- The splitting off of trimethylamine from the ion exchanger. In this case no rest activity is left.
- The Hofmann degradation. In this way the strongly basic function is degraded to a weak one.

Both types of degradation occurs in a ratio of about 1:1.

Activation

The activation procedure comprises the following steps. The ion exchanger is

- brought into a thermostated tubular reactor at a temperature of about 310 K;
- washed with at least 3 bed volumes of distilled water for at least 2 ks;
- activated with a 25-fold excess (relative to the amount of active groups in the resin) of 1 N NaOH solution for about 60 ks;
- and, finally, washed with at least 20 bed volumes of distilled water for at least 10 ks.

During the activation the gel-type exchangers will swell about 25% so that the reactor can be filled to only about 70%. The activated ion exchanger must be stored under N_2 to prevent CO_2 -adsorption from the air.

During use as a catalyst, the resin becomes deactivated. Such a deactivated resin can be reactivated by the same procedure. When the resin is strongly deactivated, a pretreatment with a solution of 2 M NaCl and 1 N NaOH can be applied.

FIGURE 1 Shape of titration curve of a fresh resin in water.

When the resin is so strongly contaminated that this pretreatment is not sufficient, a pretreatment with hydrochloric acid will give better results. Some loss of active groups during reactivation with hydrochloric acid cannot be prevented [5,6]. According to Tilsley [7] the macroreticular resins have better regenerative qualities and Christofides and Smits [8] worked out 4 different regeneration procedures.

Capacity determination

To measure the quantity of active groups (the capacity) of an ion exchange resin, the ion exchange resin is brought in a measuring cylinder with an excess of water and vibrated for 2 ks. During this vibration the particles are compacted towards their densest packing. The water above the bed was sucked off before the weight of the wet compacted resin (W_{WC}) as well as the volume (V_{WC}) was determined. Because Cl^- adsorbs much stronger than OH^- , a 3-fold excess of KCl is sufficient to drive out practically all the hydroxyl ions from the exchanger to the solution. With an automatic titration unit the obtained solution outside the resin can be titrated with HCl. In Figure 1 a titration curve of a fresh catalyst is given.

The titrated Cl^- at the breakpoint (total capacity Cap_{tot}) divided by the weight of the wet compacted resin (W_{WC}) is called the specific capacity (Cap') in $mol\ kg^{-1}$. In Table 1, the specific capacity of the resins used in this study are tabulated. The capacity of dried ion exchangers was also measured by elemental analysis. The C and H amount could be measured precisely while the N-determination is less accurate. Nevertheless, by repeating the analysis a number of times, we could establish that in Amberlite IRA 401 only 50% of the phenyl groups contains quaternary ammonium groups. For each new batch of activated ion exchanger the specific capacity must be determined because there are fluctuations in the propert-

TABLE 1

Experimental physical properties of some ion exchangers in the hydroxyl form.

SB = strongly basic, I = type I, II = type II, G = gel-type, MP = macroreticular.

type	resin	Cap'	x'_{pol}	x''_{pol}	$\bar{d}_{site}$	$PV_{e=0} \cdot 10^3$	$\frac{dPV}{d\theta} \cdot 10^3$	$V'_{tot} \cdot 10^3$
		$\frac{eq}{kg}$	$\frac{kg}{kg}$	$\frac{m^3}{m^3}$	nm	$\frac{m^3}{eq}$	$\frac{m^3}{eq}$	$\frac{m^3}{eq}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SB-I-G	Imac S-5-50	.86	.40	.38	1.07	.49	.038	1.5
SB-I-G	IRA 401	.83	.38	.36	1.09	.52	.070	1.6
SB-I-G	Lew M 504	.93	.31	.29	1.07	.53	.033	2.2
SB-I-MP	Lew MP 500	.78	.29	.27	1.13	.65	.078	2.4
SB-I-MP	IRA 900	.76	.29	.27	1.15	.66	-	2.4
SB-I-MP	IRA 904	.44	.35	.33	1.36	1.05	.127	1.9
SB-I-MP	IRA 938	.38	.19	.18	1.39	1.32	.025	4.3
SB-II-G	IRA 410	1.30	.50	.48	.94	.29	.023	1.0
SB-II-G	Imac S-5-42	1.06	.42	.40	.99	.38	-	1.4
SB-II-MP	Lew CA 9223	1.04	.38	.36	.99	.38	.177	1.6

ies of the commercial resins in the order of 5-10%. Furthermore, it has to be ascertained that the ion exchanger is free of CO_2 . When CO_2 adsorbs, we have:

and in the titration curve we than can distinguish 3 inflection points.

When the specific capacity is known for a certain batch, the total capacity Cap_t can be calculated directly from the weight of the wet compacted resin:

$$Cap_{tot} = Cap' W_{wc} \quad (3)$$

When a component (i) adsorbs, the coverage (θ) is defined as the ratio of the adsorbed component (Ads_i), relative to the total capacity:

$$\theta_i = Ads_i / Cap_{tot} \quad (4)$$

FIGURE 2 Typical titration curve of a resin deactivated by chemical reaction in a sugar solution.

FIGURE 3 Particle size distribution of IRA 401.

To measure the rest activity of a deactivated resin (Ac_r in eq eq^{-1}) the total solution can be titrated in the reactor after adding a 3-fold excess of NaCl. Due to the presence of sugars the inflection point is at about pH 7.5 instead of 7.0 (Figure 2). It has been proven experimentally that for the determination of the specific capacity as well as of the rest activity a 3-fold excess of NaCl is sufficient.

TABLE 2
Particle diameter of several resins

Resin (OH ⁻ -form)	$\bar{d}_p$ mm
Amberlite IRA 401	.47
Amberlite IRA 900	.52
Amberlite IRA 904	.50
Amberlite IRA 938	.40

FIGURE 4 Pore diameter of some materials.

PHYSICAL PROPERTIES

The physical properties of ion exchangers such as porosity, pore volume, pore radius and specific surface can only be influenced by adding special additives during the copolymerization of styrene and divinyl(benzene) [13-15].

The mechanical stability of resins is a function of the porosity, the percentage of crosslinking, the additives, and, to a minor extent, of other production conditions.

The stability of the ion exchanger increases with an increasing percentage of crosslinking but the porosity will generally decrease. In most cases macroreticular resins have a lower mechanical stability than gel-type resins. A high porosity with a reasonable mechanical strength is attained by using a high percentage of

FIGURE 5 Porosity of Amberlite IRA 904: V'_{Hg} ($\bigcirc$) and $d(V'_{\text{Hg}})/d(\log R_{\text{pore}})$ ($\triangle$) as a function of the pore radius.

FIGURE 6 Pictures of Amberlite IRA 904. Figure (b) shows the pores in the macroreticular resin.

FIGURE 7 Porosity of Amberlite IRA 938.

divinylbenzene, combined with monomeric modifications as terpinol [5,6,13]. The mechanical stability of all gell type ion exchangers is more or less the same and is better than that of macroreticular resins. Relative to the other macroreticular resins Amberlite IRA 938 has a very poor mechanical stability.

Particle size

In the introduction we mentioned already that diffusion may influence the selectivity. For this reason the particle diameter may have an influence on the selectivity. The particle size distribution was measured with a microscope. In Figure 3 the particle size distribution of Amberlite IRA 401 in the chloride form is given. The average particle diameter, defined as

$$\overline{d_p} = \sqrt[3]{\frac{\sum n_p \cdot d_p^3}{\sum n_p}} \quad (5)$$

is the most appropriate quantity in theories relating particle size with pore diffusion. In Table 2 the average particle diameters of some resins are presented. They do not exhibit large deviations. An increase of the average diameter of 8% [5] occurs during the conversion of the chloride form to the hydroxyl form.

Porosity

With regard to the pore radius, anion exchangers can be divided into a number of groups. Oehme and Martinola [17] gave a survey of the various pore ranges and compared them with filtering materials (Figure 4).

The porosity has been studied with a mercury penetration porosimeter model 905-1

FIGURE 8 Pictures of Amberlite IRA 938. (a) Survey; (b) 3 particles; (c) large pores; (d) large pores with fusion; (e) small pores; (f) small pores.

[18]. (We gratefully acknowledge the assistance of Mr. N. van Westen of the Delft University of Technology for performing the actual determinations.) The lower limit of this method is about 5 nm, so that it was not possible to measure the porosity of gel-type resins. In Figure 5 the porosity curve of Amberlite IRA 904 is shown.

The line with circles (—○—), determined from right to left during the measurement, gives us the specific pore volume related to the dry weight, available for mercury penetration. The average pore radius of IRA 904 is 0.061 μm . In Figure 6 some pictures of this resin are given, made with a scanning electron microscope, type Stereoscan MK II.

The porosity curve of Amberlite IRA 938 (Figure 7) shows at least 2 types of pores, one with radii about 0.17 μm and another around 8 μm .

There are very few pores with radii between 0.2 μm and 3 μm , so that at least two distinguishable kinds of pores must be present. In Figure 8 (a) and 8 (b) a picture of a narrow sieve fraction of IRA 938 is shown. In these pictures we can distinguish 2 types of particles present in a ratio of about 3:2, one type with large and one type with small pores. In the particle with large macro pores sometimes fusion of the sub-particles is noticed (Figure 8 (d)). In the Figure 8 (c) and (f) the pores can be studied in more detail. The electron microscope pictures confirm the mercury penetration determination.

Pore volumes

To relate differences in catalytic selectivity to differences in concentrations in the catalyst pores, the total pore volume and the adsorption has to be known. The total pore volume was measured at a temperature of 293 K for several ion exchangers in the hydroxyl form. As the temperature influence on the pore volume is very small, the latter can be considered to be independent of the temperature between 295 K and 323 K.

The following procedure was applied: an amount of activated resin with a known W_{wc} and Cap' is filtered for one minute on a suction filter, weighed (W_f) and then dried under vacuum at 400 K until its weight does not change any more (100 ks): W_{pol} . We suppose that all the water has been evaporated. The density of the dry polymer (ρ_{pol}) is about 1100 kg m^{-3} and of the water in the resin (ρ_{H_2O}) it is about 1000 kg m^{-3} . For the exchanger in the hydroxyl form we can calculate:

- the weight fraction of the polymer, relative to the particle:

$$x'_{pol} = W_{pol}/W_f \quad (6)$$

- the volume fraction of the polymer, relative to the particle:

$$x''_{pol} = \rho_{H_2O} \cdot x'_{pol} / (\rho_{pol} \cdot (1 - x'_{pol}) + \rho_{H_2O} \cdot x'_{pol}) \quad (7)$$

FIGURE 9 Pore volume as a function of the degree of coverage with glucose, θ_G .

- the pore volume, relative to the capacity:

$$PV = (W_f - W_{pol}) / (Cap' \rho_{H_2O} \cdot W_{WC}) \quad (8)$$

- the concentration of active groups relative to the pore volume:

$$C_{NR_4} = 1/PV \quad (9)$$

- the average distance between the active sites:

$$\overline{d}_{site} = 10^9 \sqrt[3]{PV / (6.02 \cdot 10^{23} (1 - x''_{pol}))} \quad (10)$$

The differences between the various types of resins are evident, whereas resins of the same type do not differ strikingly. The scavenger IRA 904 and the colloid captor IRA 938, however, have particular high porosities. From the point of low diffusion resistance these two exchangers are to be preferred. When glucose adsorbs on a resin, this resin is converted from the hydroxyl form into the glucose form and a change of the pore volume is expected. With an adsorption experiment [3] the coverage of the resin with e.g. glucose relative to the capacity can be measured (θ_G). As not all the adsorbed glucose has to be dissociated, θ_G can be greater than one. The pore volume of this resin can be determined in analogy with the procedures for a fresh resin. In Figure 9 the final results are given.

All the ion exchange resins swell when glucose adsorbs. The degree of swelling

depends on the physical properties of the polymer skeleton [19]. It can be described by:

$$PV = dPV/d\theta.\theta + PV_{\theta=0} \quad (11)$$

In column (7) and (8) of Table 2, these results are tabulated. In column (9) the total specific pore volume relative to the dry weight (V'_{tot}) is given:

$$V'_{tot} = (1 - x'_{pol})/(\rho_{H_2O} \cdot x'_{pol}) \quad (12)$$

The total pore volume is supposed to be equal to the water content of the resin.

All data, given in this article are necessary to describe the adsorption [3], diffusion [4] and isomerization of sugars with the aid of ion exchangers.

LIST OF SYMBOLS

Ads_i	amount of adsorped component i	mol
$C_{NR_4}^+$	concentration of sites, related to the volume of the pores	mol m ⁻³
Cap	capacity	eq
Cap'	specific capacity, related to the wet compacted weight	eq kg ⁻¹
d	diameter	m
d_{site}	distance between active sites	nm
PV	pore volume relative to the capacity	m ³ eq ⁻¹
pH	acidity: $pH = 3 - \log C_{H^+}$	
R_{pore}	radius of the pores	nm
V	volume	m ³
V'	specific volume, related to the dry weight	m ³ kg ⁻¹
W	weight	kg
X'	weight fraction	kg kg ⁻¹
x"	volume fraction	m ³ m ⁻³
θ_i	coverage of component i	mol eq ⁻¹
ρ	density	kg m ⁻³

SUBSCRIPTS

f	filtered
G	glucose
Hg	mercury penetration porosimetric
p	particle (= pore + polymer)
pol	polymer
pore	pore of

site active site for chemical reaction
 tot total
 wc wet compacted

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