

REESTERIFICATION OF ETHYL ACETATE BY PROPANOL CATALYSED BY GLYCIDYL METHACRYLATE COPOLYMERS CONTAINING SULPHONIC ACID GROUPS

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A series of differently crosslinked macroporous 2,3-epoxypropyl methacrylate-ethylenedimethacrylate copolymers with chemically bonded propylsulphonic acid groups were used as catalysts for the kinetic study of reesterification of ethyl acetate by *n*-propanol in the liquid phase at 52°C and in the gas phase at 90°C. Analysis of kinetic data by the method of nonlinear regression for a series of equations of the Langmuir-Hinshelwood type showed that kinetic equations which describe best the course of the reaction are the same as for the earlier studied sulphonated macroporous styrene-divinylbenzene copolymers. Compared types of catalysts differ, however, in the dependence of their activity on the degree of crosslinking of the copolymer used.

Reesterification of aliphatic esters by alcohols has been frequently used in our laboratory as model reaction for determining catalytic properties of organic ion exchangers in gas and liquid phase¹⁻⁶. In these works the catalysts were ion exchangers derived from sulphonated styrene-divinylbenzene copolymers with different degree of crosslinking and were used as both standard (gel) and macroporous particles. Copolymers of this type provide the basis of strongly acidic commercial ion exchangers which have been utilized for many years as catalysts of chemical reactions both in laboratory and in industry⁷.

Recently, a new type of ion exchangers based on glycidylmethacrylate copolymers in the form of macroporous particles with different degree of crosslinking, containing chemically bonded sulphonic acid groups has been synthesized⁸. The aim of this work was to determine the catalytic properties of these copolymers which differ principally from styrene-divinylbenzene copolymers and that chemically, by texture, by the structure of macromolecular skeleton and also by the chemical bonding of the acidic functional groups. For this purpose, the same model catalytic reaction and analogical procedure were used as in the case of styrene-divinylbenzene ion exchangers.

EXPERIMENTAL

Polymer catalysts. A series of differently crosslinked macroporous 2,3-epoxypropyl methacrylate-ethylenedimethacrylate copolymers⁹ with bonded sulphonic acid group⁸ (designated as GM polymers) were used in this study. Sulphonated macroporous styrene-divinylbenzene copolymers

(designated as MS) were used in our earlier works¹⁻⁶. Properties of all the catalysts are summarized in Table I. GM catalysts were washed in the column with the excess 0.1N-HCl before use and then by distilled water until negative test on the presence of Cl^- ions. After drying on air, the catalysts were dried at 80°C/0.1 kPa for 6 h.

Apparatus and procedure. For liquid phase reactions at 52°C, a flow stirred glass differential microreactor, described in our earlier work³ was used. The reaction mixture with the required molar ratio of components, *i.e.* reactants and solvents, was fed through a pre-heater into the reactor and its flow rate was controlled by weighing the mixture which had passed through the reactor. Gas phase reactions were carried out in a glass flow microreactor with fixed catalyst bed at a temperature of 90°C. Before each experiment, the catalyst was dried in the reactor for 1 h in a stream of nitrogen at the reaction temperature. Liquid reaction mixture was introduced *via* a feeding device to an evaporator in which it was mixed with nitrogen and after evaporation and pre-heating it passed through the reactor. Gaseous products were then condensed.

Kinetics. Data were obtained by the method of initial reaction rates; these were calculated from conversion to 10% and reciprocal values of space velocity of the starting ester. For each catalyst, 30 values were obtained for the partial pressure range 10–30 kPa of each of the reaction components in gas phase reactions and for the range of mole fractions 0.1–0.8 in liquid phase reactions.

Analytical methods. Gas chromatographic analyses of reaction products were carried out on a chromatograph equipped with a flame ionization detector, using a column (3 400 × 4 mm)

TABLE I
Properties of catalysts used

Designation	Content of crosslinking agent, %	Specific surface m^2/g	Specific pore volume cm^3/g	Porosity %	Titration exchange capacity mequiv. H^+/g
GM-30	30 ^a	31	1.13	61	0.71
GM-40	40 ^a	63	0.90	54	1.09
GM-55	55 ^a	117	0.92	54	0.99
GM-60	60 ^a	83	0.79	50	0.92
GM-85	85 ^a	228	1.25	69	0.30
MS-10	10 ^b	16	0.10	13	4.00
MS-15	15 ^b	35	0.60	45	3.81
MS-25	25 ^b	44	0.95	58	3.80
MS-40	40 ^b	120	1.04	59	3.20
MS-60	60 ^b	227	1.20	63	3.02

^a Crosslinking agent was ethylenedimethacrylate, ^b crosslinking agent was divinylbenzene. Density of polymer mass as such for GM samples $d = 1.30 \text{ g/cm}^3$, MS $\alpha = 1.41 \text{ g/cm}^3$. Data for MS catalysts are taken from our earlier work³.

packed with 12% dinonyl sebacate and 4% diglycerol on Celite at 75°, with nitrogen as a carrier gas.

RESULTS AND DISCUSSION

For kinetic analysis of reesterification of ethyl acetate by n-propanol, three of the glycidymethacrylate catalysts (GM) specified in Table I were chosen and a procedure analogous to the previous work⁶ dealing with sulphonated styrene-divinylbenzene copolymers (MS) was adopted. In the liquid phase reactions, kinetic equations used involved also other forms which included the kinetic effect of solvent on the reaction course¹⁰. Experimental data were confronted with all of the kinetic equations considered and by using the method of nonlinear regression the sequence of their fit was obtained separately for gas and liquid phase reactions. As the criterion of suitability of the equations for describing the kinetics of the studied reaction,

TABLE II
Values of constants of best kinetic equations

Constants	Copolymer			
	GM-30	GM-60	GM-85	MS-25 ^a
Liquid phase, Eq. (1)				
k ($\text{h}^{-1} \text{kg}_{\text{cat}}^{-1}$)	5.77 (3.55) ^b	9.00 (10.36) ^b	4.79 (6.97) ^b	11 —
K_B (l mol^{-1})	0.66 (1.3) ^b	2.04 (1.4) ^b	2.77 (1.4) ^b	4.4 —
K_S (l mol^{-1})	0.09 (0.26) ^b	1.00 (0.24) ^b	0.63 (0.21) ^b	0.2 —
Gas phase, Eq. (2)				
k ($\text{mol h}^{-1} \text{kg}_{\text{cat}}^{-1}$)	705 (343) ^b	10 000 (1 600) ^b	605 (619) ^b	284 —
K_A (kPa^{-1})	0.70 (1.1) ^b	0.16 (0.5) ^b	1.45 (1.4) ^b	1.0 —
K_B (kPa^{-1})	0.22 (0.57) ^b	0.13 (0.50) ^b	1.75 (1.7) ^b	2.8 —

^a Taken from works^{6,13}; measured at 120°C. ^b The values corresponding to such combination of the constants acceptable on 95% level of significance which would give the closest as possible adsorption coefficients for all three GM copolymers.

the sum of squared deviations of experimental from calculated initial reaction rates was utilized. For purposes of further discussion, from the sequence of kinetic equations, only those relations were considered which had lesser than the critical sum of deviations, defined¹¹ on the level of significance $\alpha = 0.05$. Under these conditions it was found that for all three catalysts, kinetic equations which fulfil these requirements are the same as in the case of this model reaction carried out in the presence of sulphonated styrene-divinylbenzene copolymers^{6,10}, *i.e.* Eq. (1) for the liquid phase reaction and Eq. (2) for the gas phase reaction, where r^0 is the initial reaction rate,

$$r^0 = kK_B c_A c_B / (1 + K_B c_B + K_S c_S) \quad (1)$$

$$r^0 = kK_A K_B p_A p_B / [1 + K_A p_A + 2(K_B p_B)^{1/2}]^3 \quad (2)$$

k is the rate constant, K_i is the adsorption coefficient, c_i , p_i is the concentration and partial pressure of reactants, respectively, and indices i designate A ethyl acetate, B propanol and S solvent (dioxane). Values of the constants of the above equations are presented in Table II; data without parentheses are those corresponding to the

TABLE III

Initial reaction rates of model reaction. Reaction were carried out with molar ratio of reaction components A : B : S = 2 : 2 : 1, in liquid phase at 52°C and in gas phase at 90°C. Data for MS catalysts were taken from our earlier work²

Catalyst	r^0 , mol h ⁻¹ kg _{cat} ⁻¹			
	gas phase		liquid phase	
GM-30	2.6	(84) ^a	0.49	(16) ^a
GM-40	6.0	(95)	1.30	(21)
GM-55	9.3	(80)	1.50	(13)
GM-60	14.8	(178)	1.45	(17)
GM-85	7.2	(32)	0.92	(4)
MS-10	5.9	(370)	4.44	(280)
MS-15	9.8	(280)	3.85	(110)
MS-25	13.5	(310)	3.60	(82)
MS-40	17.5	(150)	4.51	(38)
MS-60	16.3	(70)	4.38	(19)

^a Reaction rates calculated per 1 m² of specific surface of the catalysts. 10⁶ (mol h⁻¹ mm_{cat}²)⁻¹ are given in parentheses.

smallest values of the regression criterion and data in parentheses are the values selected with the possibility of combination for 95% level of significance with tendency to retain, if possible, the same values of adsorption coefficients for all three copolymers under study. This approach is based on the assumption, the validity of which was verified experimentally in one of our previous works¹², that on catalysts with chemically, and hence also catalytically, equivalent functional groups (in our case sulphonic acid groups), the adsorption coefficients (equilibrium constants of adsorption) of a given compound should have the same value in all cases. As it is evident from data given in Table II, we succeeded in determining the statistically admissible values of adsorption coefficients corresponding to the just mentioned assumption only for liquid phase reactions. The constants of kinetic equations for the gas phase reactions exhibit greater deviations from this assumption, which can be due to the greater experimental errors observed for this system. For comparison of copolymers of both types, the constants of the same kinetic equations are also given for a macroporous sulphonated styrene-divinylbenzene copolymer with 25% of divinylbenzene (MS-25)^{6,13}.

The results thus showed that changes in the type of copolymers do not reflect in the kinetics of the model reaction on acidic functional groups. One can even state that neither differences in the obtained adsorption coefficients of kinetic equations are significant, particularly if one considers the accuracy achieved in their determination and the scatter in the reproducibility of the properties of polymers, which is demonstrated best in Table I and in the report on the synthesis of these catalysts⁸.

For investigation of the effect of the type of copolymer and of properties thereof on the course of the model reaction it was therefore possible to use the initial reaction rates obtained at the constant molar ratio of components, $A : B : S = 2 : 2 : 1$ (Table III). The values show that these two types of the catalysts studied differ in the dependence of their activity on the degree of crosslinking of their skeleton. In the case of MS catalysts and gas phase reactions, the reactivity increases with specific surface, while in the liquid phase reactions the reactivity does not change. This was explained³ by compensation effect of swelling of particles and of the degree of the crosslinking. In the case of GM catalysts, the activity varies considerably with crosslinking. This can be due to the fact that specific surface, specific pore volume and exchange capacity do not change regularly with the degree of crosslinking. This was reflected also in Table II in the values of the rate constants for differently crosslinked GM catalysts.

In Table III are presented initial reaction rates recalculated to 1 m^2 of the catalyst surface (in parentheses). These data should correlate with the activity, providing that the transformation proceeds exclusively on the surface. In the case of the MS catalysts, this presumption is apparently in accordance with the values found for the most crosslinked MS-60; the increase in the activity in going to less crosslinked samples is caused by increasing swelling of particles and thus by increasing number

of functional groups located within the polymer mass which by this way become more accessible. In the case of GM catalysts, which, in average, are substantially more crosslinked, the activity is essentially independent of crosslinking (except for GM-85 catalyst). One can therefore assume that the swelling exerts negligible effect. The low activity observed for GM-85 can be caused by the fact that during sulphonation, even the surface layers of the catalyst particles were not fully saturated.

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