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Comparison of Activity and Selectivity of Weakly Basic Anion-Exchange Catalysts for the Aldolization of Butyraldehyde with Formaldehyde

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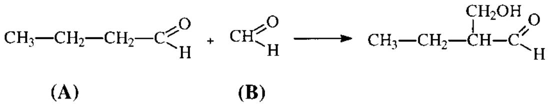
Abstract:

Aldols are important intermediates in the production of polyols, which are raw material for lubricants, surface coatings, and synthetic resins. The activities and selectivities of gel-type and macroporous anion-exchange resin catalysts in the aldolization of butyraldehyde with formaldehyde in an aqueous environment were investigated at 60 °C. The experiments were carried out batchwise in a stirred glass reactor, and the reaction products were analyzed with high performance liquid chromatography. Two main products were observed, 2-ethyl-3-hydroxy-2-hydroxy-methylpropanal (trimethylolpropane aldol) and 2-ethylpropenal (ethylacrolein). The product ratio was strongly dependent on the catalyst. The selectivity with respect to trimethylolpropane aldol varied within the range 2.7−7.3 for the catalysts investigated. Systematic kinetic experiments were carried out at 50−70 °C with the gel-type resin catalyst displaying the highest aldol selectivity. A kinetic model based on molecular mechanisms was able to describe the product distribution.

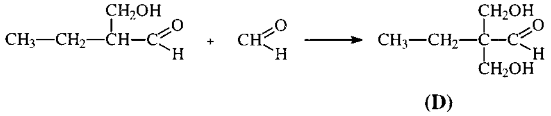
Introduction

Aldols are important intermediates in the production of diols and triols, which are used as reagents for production of lubricants, surface coatings, and resins. The traditional production technology is based on the use of strong alkali catalysts. The aldol condensation is followed by a Cannizzaro reaction which gives directly a diol or a triol, for instance trimethylolpropane, neopentylglycol, and butylethylpropanediol.[1] The conventional technology suffers, however, from a serious drawback: equimolar amounts of sodium formate are generated in the synthesis. The goal of modern chemical industry is to develop cleaner and more selective synthesis technologies, and therefore, alternative routes for diol and triol production are of vital interest.

In the presence of weak bases such as $Ba(OH)_2$, tertiary amines, or an anion-exchange resin, the Cannizzaro reaction is suppressed, and the reaction is stopped at the aldol stage as illustrated below with butyraldehyde (A) and formaldehyde (B):

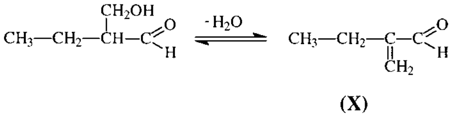


$$\underset{\textbf{(A)}}{CH_3-CH_2-CH_2-CHO} + \underset{\textbf{(B)}}{HCHO} \longrightarrow CH_3-CH_2-\overset{CH_2OH}{\overset{|}{C}H}-CHO \qquad (1)$$



$$CH_3-CH_2-\overset{CH_2OH}{\overset{|}{C}H}-CHO + HCHO \longrightarrow \underset{\textbf{(D)}}{CH_3-CH_2-\overset{CH_2OH}{\overset{|}{\underset{CH_2OH}{\underset{|}{C}}}}-CHO} \qquad (2)$$

Elimination of water always appears as a parallel reaction in the process. In this system, the α-hydroxymethyl-substituted aldehyde which appears as an intermediate (reaction 1) undergoes reversible dehydration, leading to the corresponding unsaturated aldehyde, ethylacrolein (reaction 3).



$$CH_3-CH_2-\overset{CH_2OH}{\overset{|}{C}H}-CHO \underset{}{\overset{-H_2O}{\rightleftharpoons}} \underset{\textbf{(X)}}{CH_3-CH_2-\underset{CH_2}{\underset{\|}{C}}-CHO} \qquad (3)$$

Generally, heterogeneous catalysts should be preferred in aldolization to avoid catalyst separation problems. Almost 50 years ago, Astle and Zaslowsky (1952) proposed the use of anion-exchange catalysts in the aldol condensation of butyraldehyde.[2] Since the development in the field of anion-exchange resins has been enormous since the early 1950s, the subject is worth reevaluation. It is possible to find anion-exchange catalysts which are able to produce 2-ethyl-3-hydroxy-2-hydroximethylpropanal (trimethylolpropane aldol), the aldolization product of butyraldehyde and formaldehyde, with a high yield and high selectivity.

Depending on their matrix, resins can be either gel- or macroporous-type. Gel-type resins have no permanent porosity but swell to a varying degree in polar solvents, thereby opening up their structure. Conversely, macroporous or macroreticular resins have a permanent large internal porosity.

In the present work we studied the aldolization activity and selectivity of 11 anion-exchange catalysts, carried out a physical characterization of them, and determined the reaction kinetics for the most active and selective catalyst with a series of systematic experiments.

Experimental Section

Procedure for Aldolization Experiments. Batchwise aldolization experiments were carried out in a 0.1 dm^3

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(1) Weissermel, K.; Arpe, H.-J. Polyhydric Alcohols. In *Industrial Organic Chemistry*, 3rd ed.; VCH: New York, 1997; p 210.

(2) Astle, M. J.; Zaslowsky, J. A. Aldol Condensation. *Ind. Eng. Chem.* **1952**, *44*, 2869.

10.1021/op000008t CCC: $20.00

Table 1. **Resins investigated**

resin	matrix	type	functional group
GEL1	acrylic-DVB	gel	NR_2
GEL2	acrylic-DVB	gel	NR_2
GEL3	acrylic-DVB	gel	NR_2
GEL4	acrylic-DVB	gel	NR_2
GEL5	acrylic-DVB	gel	NR_2
MACRO1	acrylic-DVB	macro	NR_2
MACRO2	polystyrene-DVB	macro	NR_2
MACRO3	polystyrene-DVB	macro	NR_2
MACRO4	polystyrene-DVB	macro	NR_2
MACRO5	polystyrene-DVB	macro	NR_2
MACRO6	polystyrene-DVB	macro	NR_2

jacketed glass reactor (Normschliff Gerätebau, Wertheim). Formaldehyde, as a freshly prepared aqueous solution of paraformaldehyde (96% Acros), and butyraldehyde (99% Acros), the catalyst, and water were loaded into the reactor at room temperature. Solid paraformaldehyde was dissolved in water by addition of alkali (NaOH). Typically, the molar ratio between formaldehyde, butyraldehyde, and water was 4:1:12. The catalysts are listed in Table 1. The catalyst amount was 30 g, and the total liquid mass was about 120 g. Thereafter, the reactor was heated until the reaction temperature was attained (50−70 °C). A careful temperature control was arranged with a thermostat (Julabo F 32), and the temperature data were stored on a PC. Glycol from the thermostat was used as a heating medium in the reactor jacket. A propeller agitator maintained the liquid-phase well-mixed (800 rpm).

To prevent the escape of volatile compounds a reflux condenser was placed on top of the reactor. The reflux condenser was cooled with recirculating glycol (−25 °C) from a thermostat (B. Braun Biotech International). To prevent the oxidation of aldehydes, the reactor was maintained under nitrogen atmosphere, and an oil trap was installed at the outlet of the condenser to prevent back-diffusion of atmospheric oxygen. Nitrogen (99.999% AGA) was continuously bubbled through a three-way valve through which samples were withdrawn for chemical analysis. The first sample was taken at room temperature before switching on the heating system of the reactor. The reaction temperature was reached within 10−15 min from the beginning of the experiment. The kinetic experiments were carried out with formaldehyde-to-butyraldehyde molar ratios 2:1, 3:1, 4:1 in aquo at temperatures of 50, 60, and 70 °C.

Chemical Analyses. Most of the analyses were carried out with a high performance liquid chromatograph (HPLC, Hewlett-Packard Series 1100) equipped with a LiChrosorb RP-18 column (5 μm, 250 × 4 mm) and diode array (DA) and refractive index (RI) detectors. Two different methods were applied to analyse the compounds: a derivatization method was used for the quantitative determination of aldehydes, aldols, and unsaturated aldehydes, while a direct method[4] was developed for measuring the contents of triols and organic acids.

In the derivatization method, 2,4-dinitrophenyl-hydrazine (DNPH, Acros) was used as a reagent in acetonitrile (ACN, >99.8% J.T.Baker) solution. This procedure is commonly used for the actual purpose.[3] The carbonyl compounds react with acidified DNPH in liquid phase, forming the corresponding hydrazones. The hydrazones can easily be separated by liquid chromatography and detected with the DA detector at the wavelength 360 nm, where the absorption maximum for hydrazones is located. The column temperature was 40 °C.

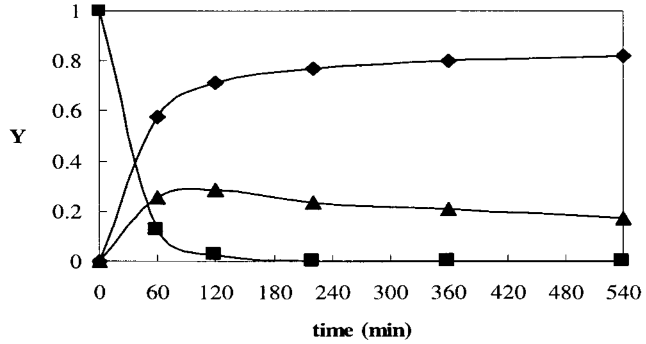

Figure 1. **An example of kinetic curve of the aldolization. Conditions: temperature = 60 °C, formaldehyde-to-butyraldehyde molar ratio = 4:1, catalyst GEL5 (■ butyraldehyde; ▲ ethyl-acrolein; ◆ aldol). ($Y_i = c_i/c_{0A}$; i = A, X, D).**

Triols and acids were analyzed with the straight method. Acids were detected with the DA detector at the wavelength of 210 nm and triols with the RI detector. The temperature in the column was 40 °C.

Characterization of the Resins. For the determination of the volume capacity in the regenerated form (Q_v), the resins were placed in a glass column and converted to the regenerated form (OH-form) with 1.0 mol/dm^3 solution of NaOH. The weakly basic groups were subsequently saturated with an excess of a 1.0 mol/dm^3 solution of HCl, and the excess was titrated with 1.0 mol/dm^3 NaOH until pH 7 was reached. The weight capacity (Q_s) determination was carried out on samples dried at 110 °C overnight. The ratio between the volume of the regenerated resin and the weight of the dried sample (density) gives a measure of the porosity of the material. The swelling of the resin was calculated from the relative volume change when the resin is converted from the OH- to the Cl-form. For the determination of the water retention, the surface-dry resins were dried for 9 h at 110 °C, and the relative weight loss was measured.

Comparison of Catalysts

Aldolization Experiments. The results of the chromatographic analyses were processed to obtain the curves of the normalized concentration of aldol, ethylacrolein, and butyraldehyde as a function of time. Experiments carried out in the absence of the resin catalyst showed that no aldolization took place. The progress of a typical kinetic curve obtained in the presence of a resin catalyst (GEL5) is displayed in Figure 1. Separate analysis of Na-formate was carried out in some experiments, but only traces of it were occasionally observed, which confirmed the absence of Cannizzaro reaction.

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(3) Lipari F.; Swarin S. J Determination of formaldehyde and other aldehydes in automobile exhaust with an improved 2,4-dinitrofenylhydrazine method. *J. Chromatogr.* **1982**, *247*, 297−306.

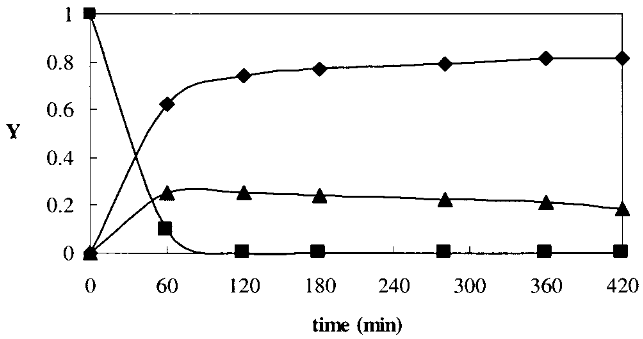


Figure 2. **Aldolization experiments in the presence of GEL3 as catalyst. Conditions: temperature = 60 °C, formaldehyde-to-butyraldehyde molar ratio = 4:1 (■ butyraldehyde; ▲ ethylacrolein; ◆ aldol).**

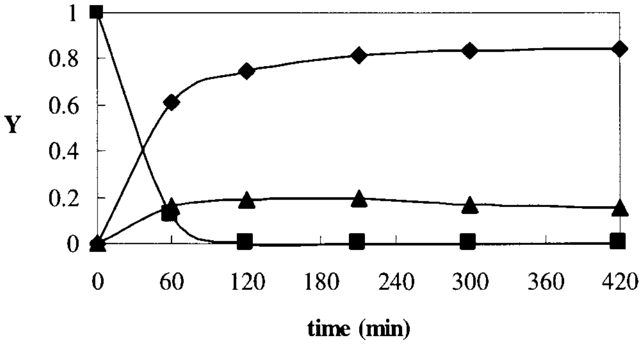


Figure 3. **Aldolization experiments in the presence of MACRO5 as catalyst. Conditions: temperature = 60 °C, formaldehyde-to-butyraldehyde molar ratio = 4:1 (■ butyraldehyde; ▲ ethylacrolein; ◆ aldol).**

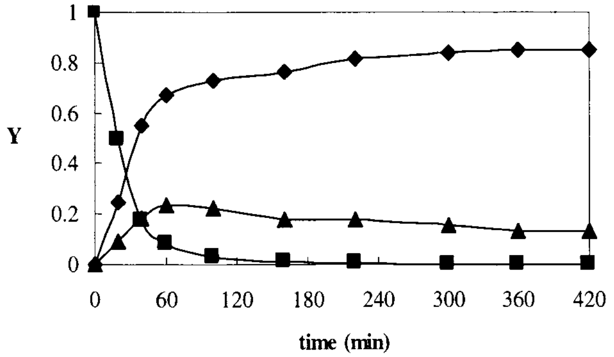


Figure 4. **Aldolization experiments in the presence of MACRO1 as catalyst. Conditions: temperature = 60 °C, formaldehyde-to-butyraldehyde molar ratio = 4:1 (■ butyraldehyde; ▲ ethylacrolein; ◆ aldol).**

Three kinds of resins were investigated, gel-type resins with an acrylic-divinylbenzene matrix and macroporous resins with a styrene-divinylbenzene matrix as well as a macroporous resin with an acrylic-divinylbenzene matrix. Examples of the product distributions obtained with a gel-type resin with acrylic-divinylbenzene matrix, a macroporous resin with styrene-divinylbenzene matrix, and the macroporous resin with acrylic-divinylbenzene matrix are reported in Figures 2, 3, and 4, respectively.

Table 2. **Aldol and ethylacrolein yields as well as the molar ratio between the products after 7 h of reaction**

resin	Y_D (%)	Y_X (%)	Y_D/Y_X
GEL2	85.2	14.7	5.8
GEL4	81.7	18.3	4.5
GEL3	80.8	19.1	4.2
GEL5	80.7	19.3	4.2
GEL1	77.6	21.9	3.5
MACRO1	85.2	13.1	6.5
MACRO5	84.2	15.8	5.3
MACRO3	70.0	17.9	3.9
MACRO2	54.9	19.1	2.9
MACRO6	40.3	18.1	2.2
MACRO4	34.9	12.1	2.9

Y_D = yield of aldol Y_X = yield of ethylacrolein

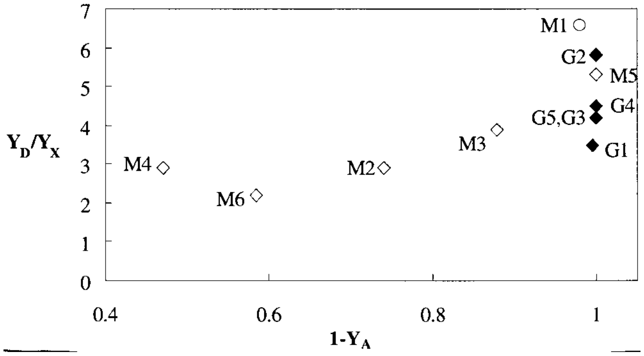


Figure 5. **Selectivity of aldol versus butyraldehyde conversion over macroporous resins with polystyrene matrix (◇) and acrylic matrix (○) as well as over gel-type resins (◆).**

As it can be observed from Figures 2−4, aldol was always the major product, whereas ethylacrolein basically appeared as by-product. The kinetic curve of ethylacrolein yield goes through a maximum and then diminishes, evidently due to a limited degree of back-conversion.

The results obtained from the aldolization experiments on different catalysts are summarized in Table 2, where the aldol and ethylacrolein yields, as well as the molar ratio between the main products after 7 h reaction are reported, and in Figure 5, where the selectivity with respect to the aldol is plotted versus the conversion of butyraldehyde.

A clear trend for macroporous resins with polystyrene matrix (M4, M6, M2, M3, and M5) is visible: when the activity increases, the selectivity increases. On gel-type resins, the conversion is always close to 1, while the selectivity varies in the range 3.5−5.8. As mentioned previously (Table 1), the macroporous resin M1 has a chemical structure (acrylic matrix) different from that of the other macroporous materials.

Catalyst Characterization. The results from the resin characterization are reported in Table 3. No evident correlation is apparent between the catalytic behaviour of the resins investigated and the physical properties measured.

Kinetics on GEL2 Catalyst

Experiments were carried out in aqueous solvents. Only aldol 2 and ethylacrolein were obtained as reaction products, while aldol 1 could not be detected directly, since it is evidently a rapidly reacting intermediate. As mentioned in previous works, the composition of the solvent has a

Table 3. **Results from the resin characterization tests**

resin	Q_s mol/kg	Q_v mol/L	swelling %	density kg/L	water retention %
GEL2	4.43	1.08	−5.9	0.245	61
GEL4	4.68	1.48	20.8	0.316	61
GEL3	4.65	1.43	7.7	0.307	60
GEL5	4.59	1.24	18.6	0.269	68
GEL1	4.70	1.37	21.6	0.292	60
MACRO1	4.29	1.13	2.5	0.263	65
MACRO5	4.05	1.42	21.5	0.350	61
MACRO3	3.87	1.48	25.8	0.381	45
MACRO2	3.91	1.14	19.9	0.292	64
MACRO6	3.87	1.07	17.3	0.277	71
MACRO4	3.88	1.15	18.9	0.297	58

Table 4. **Kinetic matrix for GEL2**

	50 °C	60 °C	70 °C
2:1	●	●	●
3:1	●	●	●
4:1	●	●	●

significant influence on the product distribution.[4,5] In fact, when methanol was used, acetalization of the reacting aldehydes appeared as a side-reaction. By using pure water as solvent, the acetalization was suppressed, and a clearly more favourable product distribution was obtained.[4] The influence of the water concentration on the product distribution was investigated for this system: the aldol yield in the final stage of the experiment went through a maximum, and the corresponding yield of ethylacrolein went through a minimum for a water-to-butyraldehyde molar ratio of 12:1. The aldol yields were 0.79 with a water-to-butyraldehyde molar ratio of 8:1, 0.87 with a water-to-butyraldehyde molar ratio of 12:1 and 0.78 with a water-to-butyraldehyde molar ratio of 16:1 at 60° with a formaldehyde-to-butyraldehyde molar ratio of 4:1.

Aldolization experiments were carried out at temperatures varying from 50 to 70 °C and with formaldehyde-to-butyraldehyde molar ratios varying from 2:1 to 4:1. The matrix of the experiments performed on GEL2 is reported in Table 4.

The effect of temperature on the kinetics and product distribution is illustrated in Figure 6, where the results from two experiments executed with a formaldehyde-to-butyraldehyde molar ratio of 3:1 at 50 and 70 °C are reported.

The influence of the molar ratio of the reactants on the product distribution is enlightened in Figure 7, where the results from two experiments performed at 50 °C with formaldehyde-to-butyraldehyde molar ratios of 2:1 and 4:1 are displayed.

Reaction Mechanisms and Kinetic Model. The modelling of the reaction kinetics is based on the overall reactions in this system as summarized below:

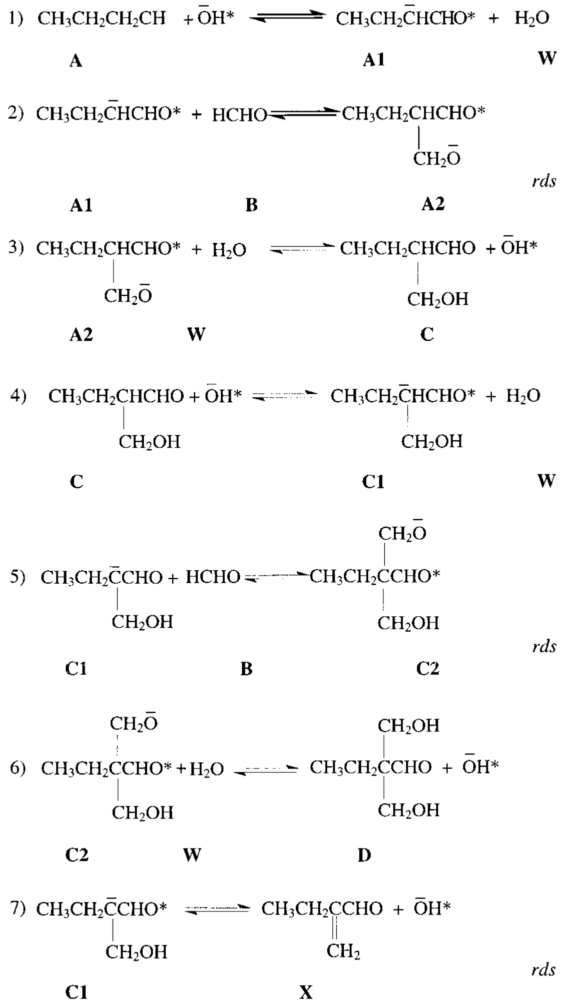
$$A + B \rightarrow C \tag{I}$$

$$C + B \rightarrow D \tag{II}$$

$$C \rightarrow X + W \tag{III}$$

where A = butyraldehyde, B = formaldehyde, C = aldol 1, D = aldol 2, X = ethylacrolein, and W = water.

The interpretation of the product distribution is based on the reaction mechanism presented below. Base-catalyzed aldolization is commenced by a nucleophilic attack of the base catalyst to the α-carbon atom of the aldehyde. A carban ion is formed, which reacts with formaldehyde, giving aldol **1**; the catalyst is regenerated in a reaction with water. The mechanism for the formation of aldol **2** is analogous. The carban ion formed from aldol **1** undergoes elimination which leads to the formation of unsaturated aldehyde and abstraction of water. The proton-transfer steps are presumed to be rapid, whereas the bimolecular reactions between the carban ions and formaldehyde are rate-determining. The elementary steps in the aldolization of propionaldehyde with formaldehyde are summarized below (rds denotes the rate determining step, and * denotes an active site on the catalyst):



It should be kept in mind that the reactions take place at the surface of the catalyst. A complete reaction scheme

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(4) Serra-Holm, V.; Salmi, T.; Multamäki, J.; Reinik, J.; Mäki-Arvela, P.; Sjöholm, R.; Lindfors, L. P. Aldolization of butyraldehyde with formaldehyde over a commercial anion-exchange resin—kinetics and selectivity aspects. *Appl. Catal., A* **2000**, *198*, 207−221.

(5) Serra-Holm, V.; Salmi, T.; Kangas, M.; Multamäki, J.; Reinik, J.; Mäki-Arvela, P.; Lindfors, L. P. Aldolization of propionaldehyde with formaldehyde over a commercial anion-exchange resin—kinetics and selectivity aspects. 2000. Submitted for publication.

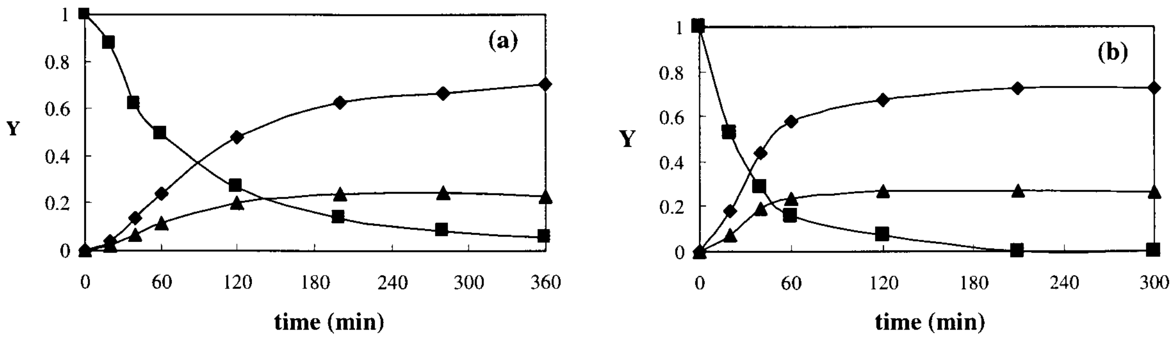

Figure 6. **Aldolization experiments at 50 °C (a) and 70 °C (b) with a formaldehyde-to-butyraldehyde molar ratio of 3:1: ■ butyraldehyde; ▲ ethylacrolein; ◆ aldol.**

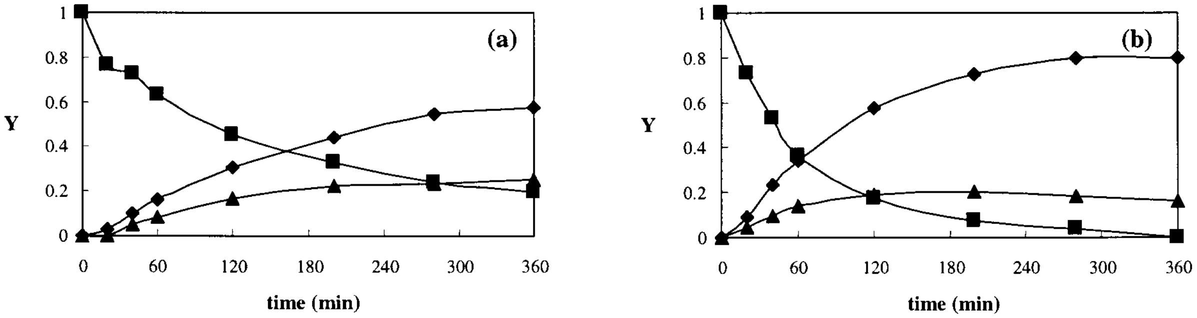

Figure 7. **Aldolization experiments with a formaldehyde-to-butyraldehyde molar ratio of 2:1 (a) and 4:1 (b) at 50 °C: ■ butyraldehyde; ▲ ethylacrolein; ◆ aldol.**

should thus comprise also adsorption and desorption steps of reactants and products. For the sake of simplicity, those steps are discarded for a while. Consequently, the rate equations for the rate-determining steps can be written as follows:

$$r_2 = k_2 c_{A1} c_B - k_{-2} c_{A2} \qquad (1)$$

$$r_5 = k_5 c_{C1} c_B - k_{-5} c_{C2} \qquad (2)$$

$$r_7 = k_7 c_{C1} - k_{-7} c_{OH} c_X \qquad (3)$$

For rapid reaction steps, the quasi-equilibrium hypothesis is applied, giving the simple expressions

$$K_1 = \frac{c_{A1} c_W}{c_A c_{OH}} \qquad (4)$$

$$K_3 = \frac{c_C c_{OH}}{c_{A2} c_W} \qquad (5)$$

$$K_4 = \frac{c_{C1} c_W}{c_C c_{OH}} \qquad (6)$$

$$K_6 = \frac{c_D c_{OH}}{c_{C2} c_W} \qquad (7)$$

The concentrations of the intermediates are solved explicitly from the expressions 4−7 and inserted in the rate eqs 1−3. The final forms of the rate equations become

$$r_1 = r_2 = k_2' \frac{c_{OH}}{c_W}\left(c_A c_B - \frac{c_C}{K_I}\right) \qquad (8)$$

and

$$r_{II} = r_5 = k_5' \frac{c_{OH}}{c_W}\left(c_C c_B - \frac{c_D}{K_{II}}\right) \qquad (9)$$

where $k_5' = k_5 K_4$, $(k_2/k_{-2}) = K_2$, $K_1 K_2 K_3 = K_I$, $k_2 K_1 = k_2'$, and $K_4 K_5 K_6 = K_{II}$

In the equation given above, (c_{OH}/c_W) represents the catalytic driving force. A combination of steps 4 and 7 gives the elimination reaction. The rate equation for elimination becomes

$$r_7 = k_7 \frac{K_4 c_C c_{OH}}{c_W} - k_{-7} c_X c_{OH} \qquad (10)$$

which is easily transformed to the final form

$$r_{III} = r_7 = k_7' \frac{c_{OH}}{c_W}\left(c_C - \frac{c_X c_W}{K_m}\right) \qquad (11)$$

where $k_7' = k_7 K_4$ and $(k_{-7}/k_7 K_4) = (1/K_4 K_7) = (1/K_{III})$

The generation rates of the components are obtained from the rate equations and the stoichiometric relationships, for example:

$$r_A = -r_I$$

$$r_B = -(r_I + r_{II})$$

$$r_D = r_{II}$$

$$r_X = r_{III}$$

The mass balance of the components in the batch reactor can be written as follows

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = \rho_B r_i \tag{12}$$

where and i = A...W and $\rho_B = (m_{cat}/V_L)$ is the bulk density of the catalyst, that is, the mass of catalyst per unit volume of liquid phase. Equation 12 presupposes that the volume of the liquid phase remains approximately constant.

The mass balances are used to obtain relations between the products. By dividing the mass balances of the aldol (D) and of the unsaturated aldehyde (X) we get

$$\frac{\mathrm{d}c_D}{\mathrm{d}c_X} = \frac{r_{II}}{r_{III}} \tag{13}$$

The equilibria of the reactions are heavily shifted to the right-hand side, thus we discard the rates of the backward steps; the ratio ($\mathrm{d}c_D/\mathrm{d}c_X$) is transformed to

$$\frac{\mathrm{d}c_D}{\mathrm{d}c_X} = \frac{k_5'}{k_7'} c_B = \alpha c_B \tag{14}$$

Equation 14 gives a relation between the apparent activation energies of aldolization and elimination

$$\frac{k_5'}{k_7'} = \frac{A_5}{A_7} e^{-(E_{a5}-E_{a7})/RT} \tag{15}$$

Aldol **1** turned out to be a rapidly reacting intermediate, the overall stoichiometry is simplified to

$$\mathrm{A} + 2\,\mathrm{B} \rightarrow \mathrm{D}$$
$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{X} + \mathrm{W}$$

which gives a simple relation between consumed B and produced D and X ($c_{0D} = c_{0X} = 0$)

$$c_{0B} - c_B = 2c_D + c_X \tag{16}$$

After inserting the concentration of B from eq 16 into the differential eq 14 we obtain

$$\frac{\mathrm{d}c_D}{\mathrm{d}c_X} = \alpha(c_{0B} - 2c_D - c_D) \tag{17}$$

The discussion presented hitherto discarded the adsorption effects on the reaction kinetics. Formaldehyde is, however, adsorbed on the surface of the catalyst resin. If we take the adsorption effects into account, the bulk phase concentrations in the rate eqs 8, 9, and 11 are replaced by the surface concentrations of the components. Consequently, the bulk concentration of formaldehyde c_B is replaced by the surface concentration $c_B^* = c_0\theta_B$, where c_0 is the total concentration of the accessible surface sites and θ_B is the surface coverage of formaldehyde. The differential eq 14 is changed to

$$\frac{\mathrm{d}c_D}{\mathrm{d}c_X} = \frac{k_5'}{k_7'} c_0 \theta_B \tag{18}$$

The constants are merged to a dimensionless quantity $\beta = (k_5'/k_7')c_0$ and the surface coverage of B can be expressed with an appropriate adsorption isotherm. For the sake of simplicity, we choose the Langmuir isotherm and neglected the adsorption of other components. The surface coverage of formaldehyde is thus obtained from

$$\theta_B = \frac{K_B c_B}{1 + K_B c_B} \tag{19}$$

The differential eq 18 becomes

$$\frac{\mathrm{d}c_D}{\mathrm{d}c_X} = \beta \frac{K_B c_B}{1 + K_B c_B} \tag{20}$$

After inserting the stoichiometric relationship 16 into 20 we get

$$\frac{\mathrm{d}c_D}{\mathrm{d}c_X} = \frac{\beta K_B(c_{0B} - 2c_D - c_X)}{1 + K_B(c_{0B} - 2c_D - c_X)} \tag{21}$$

A general solution of eq 21 is derived by substituting $z = 2c_D + c_X$.

$$\frac{\mathrm{d}z}{\mathrm{d}c_X} = \frac{2\beta K_B(c_{0B} - z)}{1 + K_B(c_{0B} - z)} + 1 \tag{22}$$

which is readily solved by separation of variables and integration within the limits [0, c_X] and [0, z]. The result becomes

$$(2\beta + 1)c_X = z - \frac{2\beta}{(2\beta + 1)K_B} \ln \frac{(2\beta + 1)K_B(c_{0B} - z) + 1}{(2\beta + 1)K_B c_{0B} + 1} \tag{23}$$

After back-substitution of c_D and c_X and rearrangement, we get

$$c_D - \beta c_X - \frac{\beta}{K_B(2\beta + 1)} \ln \frac{(2\beta + 1)K_B c_{0B} + 1}{(2\beta + 1)K_B(c_{0B} - 2c_D - c_X) + 1} \tag{24}$$

The solution is rewritten to

$$\frac{(2\beta + 1)K_B c_{0B} + 1}{(2\beta + 1)K_B(c_{0B} - 2c_D - c_X) + 1} = \exp[(2\beta + 1)K_B(\beta c_X - c_D)/\beta] \tag{25}$$

A Taylor-expansion of the exponential function on the right-hand side of eq 25 gives

$$\exp[(2\beta + 1)K_B(\beta c_X - c_D)/\beta] = 1 + \frac{z - Bc_X}{A} + \sum_{i=2}^{\infty} \frac{(z - Bc_X)^i}{i!A^i} \tag{26}$$

where $B = 2\beta+1$ and $A = 2\beta/K_B(2\beta+1)$.

After inserting the Taylor-expansion into eq 20, a back-substitution of A and B and rearrangement, we obtain an implicit expression for c_D:

$$c_D = \frac{\beta K_B c_{0B}}{1 + K_B c_{0B}} c_X - ((2\beta + 1)K_B c_{0B} + 1) \sum_{i=2}^{\infty} \frac{(2\beta + 1)^{i-2} K_B^{\,i-1} (c_D - \beta c_X)^i}{\beta^{i-1} i!} \tag{27}$$

At the initial stage of the reaction, the concentrations c_D and

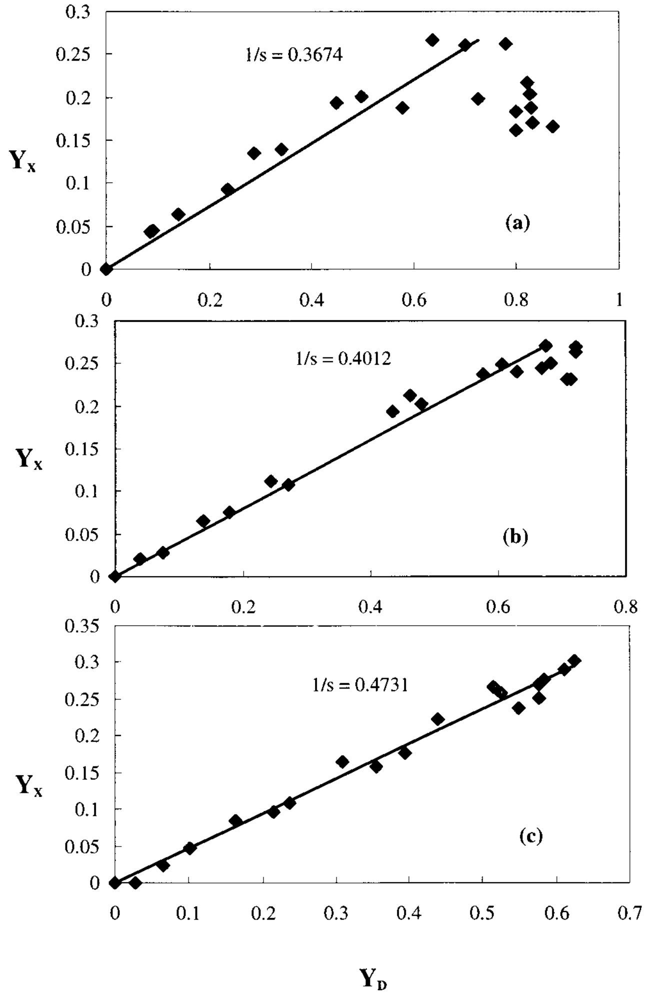

Figure 8. **The concentration of ethylacrolein versus the concentration of aldol for different formaldehyde-to-butyraldehyde molar ratios: (a) formaldehyde:butyraldehyde 4:1; (b) formaldehyde:butyraldehyde 3:1; (c) formaldehyde:butyraldehyde 2:1. Conditions: temperature 50−70 °C.**

c_X are small, $c_B \approx c_{0B}$, and the sum term in eq 27 is negligible. The initial slopes of $c_D - c_X$ plots are thus given by

$$s = \frac{\beta K_B c_{0B}}{1 + K_B c_{0B}} \tag{28}$$

Equation 28 indicates that the inverses of the initial slopes obtained with differential initial concentrations of B are directly proportional to the reciprocal concentrations of B:

$$\frac{1}{s} = \frac{1}{\beta} + \frac{1}{\beta K_B} \cdot \frac{1}{c_{0B}} \tag{29}$$

Modelling Results. The temperature dependence of the product distribution was checked by plotting the concentrations of D and X at different temperatures but at fixed concentrations of B. The results are displayed in Figure 8. The experimental results revealed that the product distribution is essentially independent of the temperature, which indicates that the apparent activation energies of aldolization and elimination are virtually equal (eq 15).

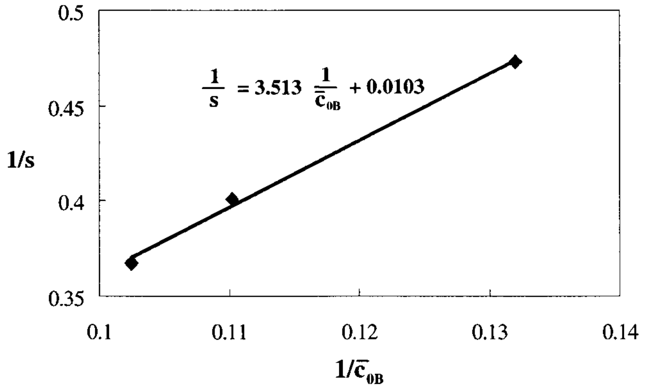

Figure 9. **The inverse of the initial slope of the curves $c_X - c_D$ versus the reciprocal initial concentration of formaldehyde.**

Table 5. **Ratio of the rates of aldol (r_D) and ethylacrolein (r_X) formation at $t = 0$**

formaldehyde:butyraldehyde, 4:1	2.72
formaldehyde:butyraldehyde, 3:1	2.47
formaldehyde:butyraldehyde, 2:1	2.10

The curvature of the product distribution ($Y_X - Y_D$) curves is due to the back-conversion of ethylacrolein. Therefore, the selectivity is constant for most of the reaction, but improves towards the end.

At the next stage the initial slopes of the $c_D - c_X$ curves obtained at different formaldehyde concentrations were tested with the model eq 19. The test plot (eq 29) is displayed in Figure 8, demonstrating that the inverses of the slopes obtained from Figure 6 are directly proportional to the reciprocal initial concentration of formaldehyde ($1/c_{0B}$) (Figure 9). The result gives support to the adsorption of formaldehyde on the solid catalyst. The values of the kinetic parameters were obtained from the test plot (Figure 9): β was 97.1 and K_B was 2.93 g/mol.

The ratios between the initial rates of formation of D and X (r_D and r_X), calculated from eq 20 at $t = 0$ are reported in Table 5.

As Table 5 shows, the aldol rate compared to the ethylacrolein rate can be increased, and therefore the selectivity can be increased by increasing the formaldehyde excess. Nevertheless, due to the adsorption of formaldehyde on the solid catalyst, the D-to-X ratio does not increase linearly as the initial concentration of formaldehyde (c_{0B}) is increased.

Conclusions

Several anion-exchange resin catalysts both gel-type and macroporous were investigated in the aldolization of butyraldehyde with formaldehyde and were characterized. A clear trend for the macroporous resins with polystyrene matrices was visible: the selectivity increased when the activity increased (Figure 5). The kinetic studies carried out on the most active and selective catalyst demonstrated that the selectivity towards aldol can be increased by increasing the butyraldehyde-to-formaldehyde ratio (Table 5). The kinetics of product formation was best described with a rate expression accounting for the adsorption of formaldehyde on the catalyst surface (eqs 20 and 27).

NOTATION

A	preexponential factor
A, B	lumped parameters, eq 26
c	concentration (mol/kg)
c_0	concentration of surface sites
c^*	concentration of a surface species
C	integration constant
E_a	apparent activation energy
k	rate constant
k'	merged rate parameter
K	adsorption constant
m_{cat}	mass of catalyst
Q_s	weight capacity of the resin (mol/kg)
Q_v	volume capacity of the resin (mol/L)
r	rate
R	gas constant
s	slope
t	time
T	temperature
V_L	liquid volume
Y	normalized amount of substance
z	transformed concentration variable, eq 22
α	ratio between rate constants, eq 14
β	dimensionless parameter, eq 18
θ	surface coverage
ρ	ratio, $\rho = m_{cat}/V_L$

Subscripts and superscripts

i	component index or general index in eqs 26−27
0	initial concentration
1, 2	intermediates in reaction mechanism

Abbreviations

A	butyraldehyde
A1... C2	reaction intermediates
B	formaldehyde
C	aldol 1
D	aldol 2
OH	base catalyst
W	water
X	ethylacrolein

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