ALDOL CONDENSATION OF BUTYRALDEHYDE IN THE LIQUID PHASE CATALYSED BY ALUMINIUM, IRON AND CHROMIUM SESQUIOXIDES

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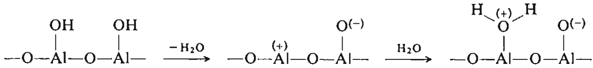
Aldol condensation of butyraldehyde catalysed by aluminium, iron and chromium sesquioxides has been studied in the liquid phase at temperatures from 160°C to 210°C, using a plug-flow stainless steel reactor. Relationships between the activity of the catalysts, surface concentrations of basic sites and the butyric acid concentration in butyraldehyde were determined. The catalytic activity depended both on the surface concentration of basic sites and on their basicity; the latter increased in the sequence $Fe_2O_3 \approx Cr_2O_3 < Al_2O_3$.

Aldol condensations of aldehydes are usually catalysed by bases. An aldehyde carrying a hydrogen atom at the α-carbon interacts with the basic catalyst to form a carbanion which adds in the next step as a nucleophile to the carbonyl group of another aldehyde molecule. The aldol so formed readily undergoes dehydration to give the corresponding α,β-unsaturated aldehyde. Aldol condensations can proceed both as homogeneous and heterogeneous reactions; the latter are catalysed by basic sites localized on the surface of a solid substance, for example, of a metal oxide.

Majority of the heterogeneous catalytic aldol condensations cannot be carried out in the gas phase. The boiling point of products lies usually higher than that of the starting compounds and, moreover, consecutive reactions produce high-boiling by-products. During the gas phase reaction, these substances and the major product are adsorbed on the catalyst surface and decrease rapidly its activity. If the reaction is carried out in the liquid phase, the products of aldolisation and by-products dissolve in the reaction mixture and do not accumulate on the catalyst surface. It was proved that in the gas phase aldolisation of cyclohexanone over iron sesquioxide at 250°C and at a cyclohexanone partial pressure of 0·05 MPa, the catalyst became inactive after two hours. Extraction of the catalyst with acetone renewed partially its catalytic activity and the acetone extract was found to contain higher boiling substances; in the liquid phase reaction the activity of the catalyst decreased after the same period only by 10% (ref.[1]).

In most studies dealing with aldol condensations catalysed by metal oxides, the existence of basic sites on the catalyst surface has been only postulated. For example, composition of products resulting from the autocondensation of methyl ethyl ketone over aluminium oxide led Kozima and coworkers[2] to consider that basic sites are involved in this reaction. Although basic sites were proved to exist on the surface of aluminium, titanium, barium and other metal oxides, their basic properties have been examined to much lesser extent[3] than the acid properties of metal oxide catalysts. Formation of basic sites on the aluminium oxide surface can be described by the general equation (*A*) suggested by Pines and Manassen[4].



$$-O-\overset{\overset{OH}{|}}{Al}-O-\overset{\overset{OH}{|}}{Al}- \xrightarrow{-H_2O} -O-\overset{(+)}{Al}-O-\overset{\overset{O^{(-)}}{|}}{Al}- \xrightarrow{H_2O} -O-\overset{\overset{H\diagdown\overset{(+)}{O}\diagup H}{|}}{Al}-O-\overset{\overset{O^{(-)}}{|}}{Al}- \quad (A)$$

Pairs of basic and acid sites are formed by dehydration of surface hydroxyl groups; Lewis-acid sites initially formed are converted by rehydration into Brönstedt sites. Parallel formation of basic and acid sites on the aluminium oxide surface has been proved experimentally[5]. Krylov and co-workers[6] proposed that three types of basic sites can exist on the surface of magnesium oxide. The most basic sites are thought to be the surface oxygen atoms resulting from proton abstraction by dehydration; their basicity is decreased by the presence of the neighbouring hydroxyl group. A weak basicity is ascribed by Krylov[6] to surface hydroxyl groups. Studies of the relationships between the basic properties and catalytic activity of calcium oxide led to similar conclusions[7,8]. Tanabe and Fukuda[9] investigated the decomposition of diacetone alcohol over calcium, barium and strontium oxides; this reaction, which can be catalysed only by bases, provides a proof for the existence of basic sites on the surface of these catalysts. The basicity of active sites was found to increase in the order $MgO < CaO < < SrO < BaO$; the surface concentration of the basic sites increased in the opposite sequence[9].

The aim of the work presented here was to examine the catalytic activity of iron, chromium and aluminium sesquioxides in the liquid phase aldolisation of butyraldehyde. The reaction was studied in a plug-flow, stainless steel reactor over a broad range of conversions. The construction of the reactor minimized the effect of axial dispersion and that of internal and external diffusion during the kinetic measurements[10].

EXPERIMENTAL

Chemicals. Butyraldehyde (chromatographically pure) was obtained by rectification of the commercial product (Chemické závody ČSSP, Litvínov) under nitrogen. 2-Ethyl-2-hexenal and 3-hydroxy-2-ethylhexanal, which were used as standards for gas chromatographic analysis of reaction mixtures, were prepared by aldol condensation of butyraldehyde and purified by rectification under nitrogen[11]. Butyric acid, phenol and pyridine (Lachema, Brno), all of analytical purity grade, were used as obtained. Purity of all the compounds was checked by gas chromatographic analysis. Aluminium oxide (surface area 110 m^2/g) (Cherox 33—00; Chemické závody ČSSP, Litvínov) and iron sesquioxide (surface area 65 m^2/g) (Girdler G-3B; Girdler-Südchemie Katalyzator G.m.b.H., München, GFR) were commercial catalysts. Chromium sesquioxide was obtained by adding ammonium hydroxide to a chromium(III) nitrate solution and by calcination of chromium(III) hydroxide at 600°C for 6 h; the surface area of the oxide was 8·5 m^2/g. Surface areas of all the catalysts were determined by the BET method. Catalyst particles 30 to 40 μm in diameter were used throughout the kinetic measurements. These particles were obtained by sieving and elutriation of the catalysts in ethanol–water or acetone–water mixtures (1 : 1); after washing with distilled water the catalysts were dried at 400°C for 1 h.

Apparatus. Aldolisation apparatus (Fig. 1) consisted of a butyraldehyde reservoir 1, a pump 2, manometers 3, a reactor inserted into a copper tube and placed in an electrically heated jacket 4, a sampling valve 5, a callibrated tube 6 for measuring flow rate of the reaction mixture on the reactor outlet and of a reaction mixture reservoir 7; this reservoir was connected *via* a reducing valve to a pressure cylinder containing nitrogen. The reactor content was kept liquid by a constant pressure of 1·01–2·03 MPa. Temperature in the reactor jacket was maintained constant within ±0·5°C; the temperature difference between the lower and upper end of the reactor did not exceed 1°C. Charging of the catalyst into the reactor and procedures for testing the effect of the axial dispersion as well as external and internal diffusion effects were described in the preceding work[10].

Aldolisation reactions. Densities and thus also the initial concentrations (c_0) of butyraldehyde were calculated for given temperatures (160–210°C) and pressures (1·01–2·03 MPa) from critical data[12] by the Watson's generalized method[13]. As the density of the reaction mixture changed somewhat with conversion, the concentrations of reaction components were correlated according to a linear relationship recommended by Levenspiel[14]. Density changes were determined from the changes in the volume flow measured at the reactor outlet.

Measurements of the concentration of basic sites. The concentrations of basic sites on the catalyst surface were determined in a through-flow apparatus using a method based on the displacement of preadsorbed benzoic acid with excess acetic acid[15]. The amount of benzoic acid displaced from the catalyst was measured spectrophotometrically.

Analytical methods. Samples of the reaction mixture were analysed on a Chrom 3 gas chromatograph (Laboratorní přístroje, Prague) equipped with a flame-ionisation detector and a 1·7 m × × 3 mm steel column packed with 7% OV 17 on Gas-Chrom Q; column temperature was 160°C and the nitrogen flow rate 40 ml/min.

RESULTS AND DISCUSSION

Aldol condensation of butyraldehyde in the liquid phase that yields 2-ethyl-2-hexenal was investigated up to 75% butyraldehyde conversion. The decrease in the activity of the catalysts with time was negligible. Pure butyraldehyde was fed into the reactor and the experimental data were treated by simple kinetic equations.

Assuming that the aldolisation reaction is taking place on basic sites of metal oxides in a similar way as in the homogeneous base catalysed reaction and that the dehydration of 3-hydroxy-2-ethylhexanal does not affect the total reaction rate, the reaction course can be described by equations (*B*)–(*F*):

$$A + L_B \rightleftharpoons AL_B \qquad (B)$$

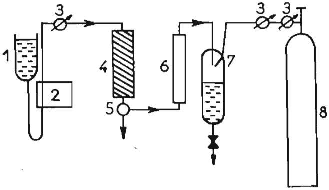


FIG. 1

Scheme of Aldolisation Apparatus

1 Butyraldehyde reservoir, 2 pump, 3 manometers, 4 reactor, 5 sampling valve, 6 calibrated tube, 7 reaction mixture reservoir, 8 nitrogen pressure cylinder.

$$\mathrm{A} + \mathrm{AL_B} \rightleftharpoons \mathrm{A_2L_B} \tag{C}$$

$$\mathrm{A_2L_B} \rightarrow \mathrm{R} + \mathrm{S} + \mathrm{L_B} \tag{D}$$

$$\mathrm{R} + \mathrm{L_B} \rightleftharpoons \mathrm{RL_B} \tag{E}$$

$$\mathrm{S} + \mathrm{L_B} \rightleftharpoons \mathrm{SL_B}\,. \tag{F}$$

Let us suppose that the adsorption of butyraldehyde (*A*) and of reaction products, *i.e.* of water (R) and 2-ethyl-2-hexenal (S), on the basic sites (L_B) is an equilibrium process (Eqs (*B*), (*E*) and (*F*)) and that the rate determining step is the formation of 3-hydroxy-2-ethylhexanal (A_2) (Eq. (*C*)); the time-concentration changes in reactions (*B*)–(*F*) can be then expressed by the rate equation (*1*) of the Langmuir–Hinshelwood type,

$$-r_A = kK_A c_A^2/(1 + K_A c_A + K_R c_R + K_S c_S)\,, \tag{1}$$

where k is the rate constant for the aldolisation reaction, K_A, K_R and K_S are the adsorption coefficients of butyraldehyde, water and 2-ethyl-2-hexenal, respectively, and c_A, c_R and c_S the corresponding concentrations. As these concentrations are given by the initial concentration (c_0) of butyraldehyde in the feed and by the stoichiometry of the reaction, the concentrations can be replaced by the butyraldehyde conversion x. The concentrations of the components in the reaction mixture are high and we therefore adopted the validity of the condition expressed by the relation (*2*):

$$1 \ll K_A c_A + K_R c_R + K_S c_S\,. \tag{2}$$

Modification of the Eq. (*1*) leads to a more simple two-parameter equation (*3*):

$$-r_A = k\, c_0(1 - x)^2/(1 + K_{rel}x)\,, \tag{3}$$

where k is the rate constant for the aldolisation reaction and K_{rel} is the relative adsorption coefficient defined by Eq. (*4*):

$$K_{rel} = (K_R + K_S/2K_A) - 1\,. \tag{4}$$

Dependences of the butyraldehyde conversion (x) on the reciprocal space velocity (W/F) (s $\mathrm{kg_{cat}\,mol^{-1}}$) for aluminium and chromium sesquioxides at temperatures ranging from 160 to 210°C followed quite well the second-order kinetics. The reaction mixtures produced by the aldolisation of butyraldehyde in the presence of both catalysts did not contain any significant amount of 3-hydroxy-2-ethylhexanal. One can therefore assume that, under the given reaction conditions, the rate determining step is the base catalysed formation of aldol A_2 (Eq. (*C*)). Dependences of x on W/F found for the aluminium and chromium sesquioxide catalysts at various temperatures are shown in Figs 2 and 3; the curves which fit the experimental points were calculated by nonlinear regression[16,17] using the Eq. (*3*). Calculated rate constants k and relative adsorption coefficients K_{rel} are summarized in Table I. All the K_{rel}

TABLE I

Rate Constants ($l\ s^{-1}\ kg_{cat}^{-1}$) and Relative Adsorption Coefficients K_{rel} Calculated by Nonlinear Regression from Eq. (*3*) for Aldolisation of Butyraldehyde Catalysed by Aluminium and Chromium Sesquioxides

t, °C	Al_2O_3		Cr_2O_3	
	$k \cdot 10^3$	K_{rel}	$k \cdot 10^5$	K_{rel}
165	2·3	−0·08	3·3	−0·21
180	4·3	−0·01	5·3	−1·06
195	6·7	0·15	7·9	−0·16
210	11·8	−0·04	9·7	0·42

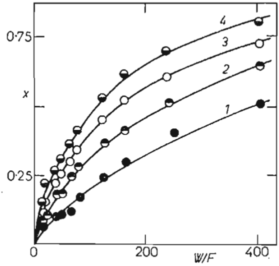


FIG. 2

Dependences of Butyraldehyde Conversion (x) on Reciprocal Space Velocity W/F (s kg_{cat} mol^{-1}) for Aldolisation of Butyraldehyde Catalysed by Aluminium Oxide at Temperatures 165°C *1*, 180°C *2*, 195°C *3*, and 210°C *4* (catalyst weight $W = 2·16$ g)

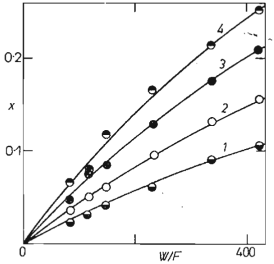


FIG. 3

Dependences of Butyraldehyde Conversion (x) on Reciprocal Space Velocity W/F (s kg_{cat} mol^{-1}) for the Aldolisation of Butyraldehyde Catalysed by Chromium Sesquioxide at Temperatures 165°C *1*, 180°C *2*, 195°C *3* and 210°C *4* (catalyst weight $W = 2·35$ g) values lie close to zero; the adsorption coefficients of butyraldehyde (K_A), water (K_R) and 2-ethyl-2-hexenal (K_S) have thus approximately identical values. It is worthy of note that K_{rel} for the aldol condensation of cyclohexanone over aluminium oxide at 250°C is equal to 8·7; this corresponds to relatively higher adsorption coefficients of the products with respect to the adsorption coefficient of the starting cyclohexanone[1].

The reaction mixtures resulting from the aldolisation of butyraldehyde catalysed by iron sesquioxide contained kinetically important amounts of 3-hydroxy-2-ethylhexanal, and the x *vs* W/F plots show thus different patterns (Fig. 4). This indicates that the dehydration of the intermediate 3-hydroxy-2-ethylhexanal proceeds at a slower rate than the aldolisation reaction, compared to the aluminium and chromium sesquioxide catalysed reactions. The dehydration reaction affects therefore the total rate of the aldol condensation of butyraldehyde ($-r_A$). The formation of 3-hydroxy-2-ethylhexanal (Eq. (*C*)) is reversible and the equilibrium is strongly shifted to the starting butyraldehyde at higher temperatures[18]. Consequently, the kinetic dependences obtained for the iron sesquioxide catalyst could not be analysed by using equations (*B*)–(*F*) and (*3*).

The iron sesquioxide catalysed aldolisation of butyraldehyde has been described by the equilibrium (Eq. (*G*)) and the consecutive irreversible reaction (Eq. (*H*)):

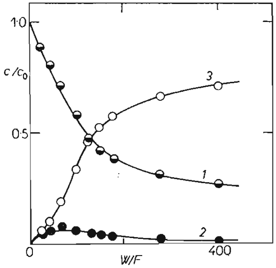


FIG. 4

Dependences of Concentrations of Butyraldehyde *1*, 3-Hydroxy-2-ethylhexanal *2* and 2-Ethyl-2-hexenal *3* in the Product on Reciprocal Space Velocity W/F (s kg_{cat} mol^{-1}) for Aldolisation of Butyraldehyde Catalysed by Iron Sesquioxide at 180°C (catalyst weight $W = 1·95$ g, initial butyraldehyde concentration $c_0 = 8·231$ mol l^{-1})

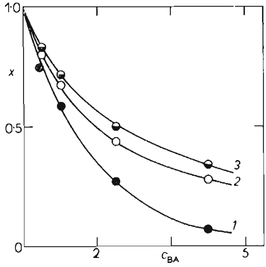


FIG. 5

Effect of Butyric Acid Concentration c_{BA} (mol %) in Butyraldehyde Feed on Relative Catalytic Activity (X) of Aluminium *1*, Iron *2* and Chromium *3* Sesquioxides in Butyraldehyde Aldolisation (temperature 180°C, $W/F = 160$ s kg_{cat} mol^{-1})

$$2\,A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_2 \qquad (G)$$

$$A_2 \xrightarrow{k_3} R + S\,. \qquad (H)$$

The corresponding values of the rate constants k_1 and k_3 and the equilibrium constant $K_{eq} = k_1/k_2$ (Table II) were obtained by nonlinear regression[16,17] using the kinetic equations (*5*) and (*6*).

$$-r_A = k_1 c_A^2 - k_2 c_{A_2} \qquad (5)$$

$$-r_{A_2} = c_{A_2}(k_2 + k_3) - k_1 c_A^2 \qquad (6)$$

To gain evidence that the aldolisation reaction does proceed on the basic sites of the catalyst, we added water, phenol, pyridine and butyric acid (0·5–5% mol) to the butyraldehyde feed. The addition of water, phenol and pyridine did not influence the butyraldehyde conversion regardless of the catalyst used. On the other hand, a concentration of 0·5% mol. butyric acid was high enough to affect significantly the conversion of butyraldehyde catalysed by aluminium, chromium and iron sesquioxides (Fig. 5). However, if pure butyraldehyde was fed again into the reactor, the conversion gradually increased to the original value; butyric acid adsorbs thus reversibly on the basic sites which catalyse the aldolisation reaction. Water and phenol act therefore rather as weaker acids compared to butyraldehyde; their addition in small amounts to the butyraldehyde feed does not affect, *via* a competitive adsorption, the number of the active sites available originally for the aldol formation. As it follows from Fig. 5 individual catalysts show different sensitivity to butyric acid acting as a catalyst poison; the highest decrease in activity was observed in reactions catalysed by aluminium oxide.

In order to compare the activity of all the catalysts studied, the experimental dependences of the butyraldehyde conversion (x) on the reciprocal space velocity

TABLE II

Rate Constants k_1 ($l^2\,mol^{-1}\,s^{-1}\,kg_{cat}^{-1}$) and k_3 ($l\,s^{-1}\,kg_{cat}^{-1}$) and the Equilibrium Constant K_{eq} ($l\,mol^{-1}$) Calculated by Nonlinear Regression Using Eqs (*5*) and (*6*) for Aldolisation of Butyraldehyde Catalysed by Iron Sesquioxide

t, °C	$k_1 \cdot 10^4$	$k_3 \cdot 10^3$	$K_{eq} \cdot 10^3$
165	3·1	11·2	9·3
180	7·2	8·2	17·8

(W/F) determined for aluminium and chromium sesquioxides at 180°C were evaluated according to the simple relation (7).

$$-r_A = k_1 c_A^2 . \tag{7}$$

The rate constant k_1 obtained for iron sesquioxide from Eq. (7) is consistent with the rate constant k_1 calculated for this catalyst and the same temperature from Eqs (5) and (6). Relative catalytic activities related to a surface unit and to an unit concentration of basic sites on the catalyst surface are summarized in Table III; included are also values of activation energies for the butyraldehyde aldolisation which were calculated from dependences of the rate constants k_1 on temperature in the range from 165 to 210°C. The data presented in Table III document that the activity of the catalysts under study does not depend only on the concentration of basic sites but also on their basicity. The fact that the active sites of individual catalysts may differ in basicity is supported by the different sensitivity of these catalysts to poisoning by butyric acid. These conclusions are in accordance with those of Tanabe and Fukuda[9] who found similar differences in both the concentration of basic sites and their basicity also in the series of magnesium, calcium, strontium and barium oxides.

TABLE III

Relative Activities k_{rel} of the Metal Oxide Catalysts in Aldolisation of Butyraldehyde at 180°C Calculated from Eqs (5)–(7), Concentrations of Basic Sites $[L_B]$ (μmol/m^2) and Activation Energies E (kJ mol^{-1}) for the Aldolisation Reaction

Catalyst	$k_{rel}{}^a$	$k_{rel}{}^b$	$[L_B]$	E^c
Al_2O_3	1·0	1·0	1·4	62·0
Fe_2O_3	0·29	0·22	1·8	54·4
Cr_2O_3	0·13	0·36	0·5	48·1^d

[a] Related to a surface unit of the catalyst; [b] related to an unit concentration of basic sites; [c] calculated from the temperature dependences of rate constants k_1; [d] determined from the dependences at two temperature levels.

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