

LIQUID-PHASE ALDOL CONDENSATION OF CYCLOHEXANONE ON ALUMINIUM AND IRON OXIDES

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The kinetics of the aldol condensation of cyclohexanone in decalin were investigated at 210°C on catalysts prepared by drying and calcining the aluminium and iron hydroxides at 110–850°C. The effect of catalyst poisoning by benzoic acid and pyridine on the course of the condensation reaction and aldol retroaldolisation was also examined. The kinetics of the cyclohexanone condensation can be described by means of Langmuir–Hinshelwood equations which are in agreement with a mechanism involving adsorption of cyclohexanone on a basic site to form a transient complex, reaction of this complex with a cyclohexanone molecule affording the aldol, the rate determining interaction of the aldol with free basic and acid sites yielding 2-(1-cyclohexen-1-yl)cyclohexanone and water and desorption of these products from the catalyst surface. The proposed kinetic model is supported by the results of catalyst poisoning. The activity of aluminium and iron oxides in the condensation of cyclohexanone is a complex function of their basicity and acidity depending strongly on the calcination temperature.

The aldol condensations of carbonyl compounds in the homogeneous phase belong to typical acid–base catalysed reactions, whose kinetics and mechanism have been investigated most extensively^{1,2}. The course of these reactions in the presence of solid acid–base catalysts is, however, relatively less known. Malinowski and coworkers^{3–5} have studied the gas-phase aldol condensation of aliphatic aldehydes and ketones on silica gel impregnated by alkali metal hydroxides. The activity of these catalysts depended on the site concentration controlled by the base content and on the site strength influenced by the cation nature⁴. The reactivity of substrates increased with the acidity of the α -hydrogen and the mechanism of the heterogeneous catalytic aldol condensation was analogous with that suggested for the homogeneous catalytic reaction⁵. The kinetics of the formation of 2-butenal and 2-propenal could be described by means of Langmuir–Hinshelwood equations provided that the rate determining step was a reaction between the aldehyde molecule adsorbed on the catalyst surface and that in the gas phase³. The gas-phase aldol condensation of cyclohexanone on aluminium oxide and lithium phosphate carried out at low conversions and at 237–258°C yielded⁶ 2-(1-cyclohexen-1-yl)cyclohexanone with a selectivity of 80–90%; when the same reaction was performed at 250°C over aluminium

oxide impregnated with sodium hydroxide, the formation of polymeric products and particularly that of cyclohexene decreased with increasing content of the sodium cation in the catalyst⁷. In the gas-phase aldol condensation of cyclohexanone on ferric oxide a rapid catalyst poisoning was observed due to a strong adsorption of products on the catalyst surface⁸. There are also a few examples of the liquid-phase aldol condensation in the presence of solid catalysts. Watanabe and coworkers⁹ have determined the kinetics of the formation of 2-methyl-2-penten-4-one from 2-propanone on zirconium phosphate at 35–50°C with use of the method of initial reaction rates; a surface reaction between two 2-propanone molecules was supposed to be the rate determining step. The composition of products of the liquid-phase aldol condensation of benzaldehyde with 2-propanone or 2-butanone on aluminium oxide at 60–160°C led to a conclusion that both acidity and basicity of the catalyst apply in this reaction; the aldol formation was here the slowest step¹⁰. The course of the liquid-phase aldol condensation of butanal on aluminium oxide at 160–210°C indicated that also in this case the aldol formation was the rate determining step; on the other hand, the same reaction catalysed by ferric oxide proceeded by way of the aldol dehydration as the slowest step¹¹. When compared with a homogeneous catalytic aldol condensation, the reaction on solid catalysts follows generally a more complicated course; the condensation can proceed on basic as well as acid sites according to different mechanisms and the reaction kinetics can be influenced by the basicity to acidity ratio of catalysts.

The aim of this work was to gain a more profound knowledge of the kinetics and mechanism of aldol condensation in the liquid phase over solid acid-base catalysts. The aldol condensation of cyclohexanone over aluminium oxide and ferric oxide was chosen as the model reaction. Under the above conditions cyclohexanone is a more suitable model substrate than the aliphatic aldehydes or benzaldehyde, which can undergo oxidation to form carboxylic acids poisoning basic sites of solid catalysts.

EXPERIMENTAL

Chemicals. Reagent grade cyclohexanone (Lachema, Brno) was dried over molecular sieve and distilled before use. Commercial decalin was stirred with conc. sulphuric acid at 90°C for 8 h, the organic layer was separated, washed with aqueous sodium hydroxide and water, dried over metallic sodium and distilled; pure decalin was a mixture of 70% trans and 30% cis isomers. An authentic sample of 2-(1-hydroxycyclohexyl)cyclohexanone was prepared by condensation of cyclohexanone in the presence of potassium hydroxide¹²; after crystallisation from decalin, m.p. 33.5°C. An authentic sample of 2-cyclohexylidenecyclohexanone was obtained according to known procedures^{13–15}; m.p. 55°C. Reagent grade pyridine (Lachema, Brno) was dried over potassium hydroxide and distilled under nitrogen. Reagent grade benzoic acid (Lachema, Brno) was used without further purification.

Catalysts. Samples of aluminium oxide and ferric oxide were prepared by adding aqueous ammonia to a solution of the corresponding nitrate at 70°C and by drying and calcining the hydroxide gel at 110–850°C for 3 h. The catalysts were ground and sieved to obtain a particle size of 10–70 µm; all samples were rehydrated by standing in the moist air and dried before each measurement at 110°C. The content of magnesium, silicon, potassium and phosphorus impurities in catalysts did not exceed 0.1%. The surface concentrations of basic or acid sites in samples of both catalysts were measured by using the displacement method based on the preadsorption of benzoic acid or pyridine (or benzylamine) and their displacement by acetic acid or n-butylamine, respectively^{16,17}. The surface areas of aluminium oxide and ferric oxide and radius or distribution of pores in selected catalyst samples were determined as described in a previous work¹⁸.

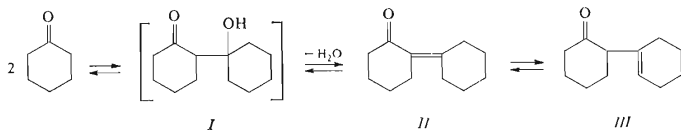
Kinetic measurements. The kinetics of the liquid-phase aldol condensation of cyclohexanone in decalin were measured in a batch, isothermal, stainless steel micro-reactor¹⁹ under an overall pressure of 0.6 MPa and at 210 ± 0.5°C by using the method of initial reaction rates. The organic volatile components of the reaction mixture were kept in the liquid phase by means of compressed nitrogen. Catalysts with a particle size of 10–70 µm were used for all measurements. The concentration of aluminium oxide corresponded to 4 g l⁻¹ and that of ferric oxide to 13.2 g l⁻¹. The catalytic retroaldolisation of the aldol in decalin at 20°C was carried out in a stirred 10 ml glass reactor at an aldol concentration of 0.228 mol l⁻¹ and at catalyst concentrations of 13.2 to 132.0 g l⁻¹; the values of the initial reaction rates were obtained by evaluating the aldol conversions as a function of time. By using the above catalyst fraction (10–70 µm) and at an intensity of stirring of 1 000 revs/min, the reactions under study proceeded in the kinetic region⁸. The activity of poisoned catalysts in the aldol condensation of cyclohexanone was measured at 210 ± 0.5°C and that in the retroaldolisation reaction at 20°C and 100 ± 0.2°C. Catalytic poisons were injected onto the isothermal, stainless steel micro-reactor¹⁹ before adding the reactant; the catalysts placed in the reactor were poisoned by injecting benzoic acid or pyridine in an amount corresponding to a 2.5-fold basicity of the catalysts.

Parallel informative experiments of the homogeneous catalytic decomposition of the aldol (0.2 g in 10 ml of methanol) in basic and acidic medium were conducted in the presence of potassium hydroxide (0.1 g) and sulphuric acid (0.1 g), respectively, at 65°C; methanol was evaporated under reduced pressure, the residue was extracted with decalin, the extract was filtered and the filtrate was analysed by liquid or gas chromatography. After 15 min, the product of the base catalysed aldol decomposition contained about 90% of cyclohexanone, about 10% of the aldol and only traces of 2-(1-cyclohexen-1-yl)cyclohexanone. The acid catalysed reaction (5 min) produced more than 90% of 2-(1-cyclohexen-1-yl)cyclohexanone and less than 10% of the aldol; the decomposition of the aldol (0.2 g) in decalin (10 ml) at 65°C (5 min) catalysed by aluminium trichloride (0.1 g) gave a product having the same composition.

Analytical methods. The composition of reaction mixtures resulting from the condensation of cyclohexanone was determined by gas chromatographic analysis on the Chrom-3 instrument equipped with a flame-ionisation detector and a stainless steel column (2 m × 3 mm), which was packed with 7% Silicone OV-17 on Gas Chrom Q (80–100 mesh); the column temperature was 164°C. The internal standard was n-octadecane. The structure of several compounds present in trace amounts in addition to 2-cyclohexylidenecyclohexanone and 2-(1-cyclohexen-1-yl)cyclohexanone was not investigated in detail. The reaction mixtures from the aldol retroaldolisation were analysed by means of high-performance liquid chromatography using a stainless steel column (25 cm × 2 mm) which was packed with spherical silica gel (10 µm) and connected to a differential refractometer RD 1 (Development Workshops, Prague) as the detector. Cyclohexane containing 15% (v/v) of diethyl ether was used as the mobile phase at a flow rate of 2.5 ml min⁻¹.

RESULTS AND DISCUSSION

The time changes in the composition of product mixtures from the aldol condensation of cyclohexanone in decalin over aluminium oxide or ferric oxide at 210°C are consistent with a reaction sequence suggested in Scheme 1.



SCHEME 1

The absence of 2-(1-hydroxycyclohexyl)cyclohexanone (*I*) can be explained by its extremely low equilibrium concentration in the reaction mixture at 210°C. 2-Cyclohexylidenecyclohexanone (*II*) formed in a small amount is evidently the primary product of dehydration of the aldol *I*. The major products of the condensation

TABLE I

Surface area (s), radius of the most frequent pores (r), basicity (c_B) and acidity (c_A) of Al_2O_3 and Fe_2O_3 catalysts

Catalyst ^a	s $\text{m}^2 \text{g}^{-1}$	r nm	c_B $\mu \text{mol g}^{-1}$	c_A $\mu \text{mol g}^{-1}$
Al_2O_3 -110	101	—	78	1.8
450	259	3.5	245	1.3
520	285 ^b	3.8 ^c	326	2.1
580	171	4.0	156	1.5
710	138	—	107	0.6
850	122	—	84	0.7
Fe_2O_3 -110	137	2.0	228	6.0
230	88	2.9	148	9.2
300	52	7.3	85	2.0
340	41	9.0	66	2.1
450	28	—	35	0.9
510	12	—	10	0.9

^a The numbers refer to the calcination temperature; ^b the value calculated from the pore distribution corresponds to $183 \text{ m}^2 \text{ g}^{-1}$; ^c the radius of micropores is equal to 1.6 nm.

of cyclohexanone are 2-(1-cyclohexen-1-yl)cyclohexanone (*III*) and water. The liquid-phase condensation of cyclohexanone catalysed by aluminium oxide or ferric oxide (Table I) affords therefore the same products as the homogeneous catalytic reaction; in consequence of the high basicity of alkali metal hydroxides used as homogeneous catalysts, the latter reaction is, however, less selective and produces significant amounts of highly condensed compounds²⁰.

The kinetics of the liquid-phase condensation were measured at cyclohexanone concentrations varying between 0.4 and 4 mol l⁻¹, with use of the method of initial reaction rates. The initial rates of condensation r_k^0 were calculated according to Eq. (1),

$$r_k^0 = c_c^0 V dx / W dt, \quad (1)$$

where c_c^0 denotes the initial cyclohexanone concentration in decalin, V the volume of the reaction mixture, W the weighed amount of the catalyst and dx/dt the slope of the time dependence of cyclohexanone conversions. The reaction mixtures changed their density during heating to the reaction temperature; the concentrations of cyclohexanone and the volumes of reaction mixtures were therefore corrected, according to the reaction conditions (210°C, 0.6 MPa), by means of the Gunn-Yamada method²¹. The slopes dx/dt were obtained by least-squares analysis of the linear course of ketone conversions ($x \leq 8\%$) with time.

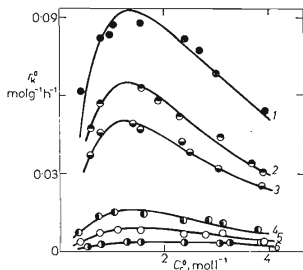


FIG. 1

The initial rate of formation of the ketone *III* (r_k^0) in decalin catalysed by aluminium oxide as a function of the initial concentration of cyclohexanone (c_c^0). 1 Al₂O₃-450, 2 Al₂O₃-520, 3 Al₂O₃-580, 4 Al₂O₃-710, 5 Al₂O₃-110, 6 Al₂O₃-850; 210°C; pressure 0.6 MPa

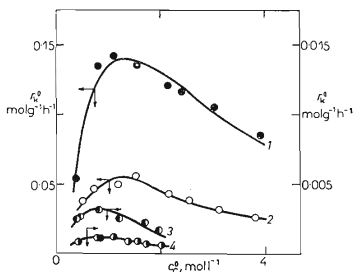


FIG. 2

The initial rate of formation of the ketone *III* (r_k^0) in decalin catalysed by ferric oxide as a function of the initial concentration of cyclohexanone (c_c^0). 1 Fe₂O₃-110, 2 Fe₂O₃-230, 3 Fe₂O₃-300, 4 Fe₂O₃-340; 210°C; pressure 0.6 MPa.

The experimental dependences of the initial reaction rate upon the concentration of cyclohexanone are given in Figs 1 and 2. These dependences exhibit a maximum for all catalyst samples. For aluminium oxide, the position of the maximum does not depend on the calcination temperature; on the other hand, starting with a sample of ferric oxide calcined at 300°C, the maximum for this type of catalysts is shifted to the lower initial cyclohexanone concentrations and this shift is accompanied by a significant decrease in the reaction rate. Both these changes are evidently in close relation with the composition of the ferric oxide catalysts; this conclusion is corroborated by a previous finding that the catalysts obtained by calcination at $\geq 300^\circ\text{C}$ reveal a marked change in the radius of pores (Table I) and pore distribution and that the latter is characteristic for the conversion of iron hydroxides to the α modification of ferric oxide^{22,23}. For samples $\text{Fe}_2\text{O}_3\text{-450}$ and $\text{Fe}_2\text{O}_3\text{-510}$ (Table I), which showed very low condensation activities, the values of r_k^0 were determined only at a concentration of cyclohexanone corresponding to $c_C^0 \sim 0.8 \text{ mol l}^{-1}$.

The above dependences were modeled by applying the Langmuir-Hinshelwood kinetics. In an effort to find the most adequate kinetic model and taking into account the known mechanism of the homogeneous catalytic aldol condensation, we have derived equations for different cases of the rate determining step. Since all the experimental kinetic dependences exhibit a maximum, the equations have to fulfil the condition that $dr_k^0/dc_C^0 = 0$. Most of the derived expressions could thus be rejected already in the initial stage of considerations giving a more narrow group of equations (2)–(5).

$$r_k^0 = k_{\text{exp}} K_C c_C^0 / (1 + K_C c_C^0 + K_D c_D^0)^2 \quad (2)$$

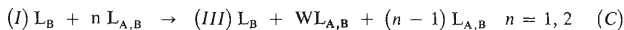
$$r_k^0 = k_{\text{exp}} K_C c_C^0 / (1 + K_C c_C^0 + K_D c_D^0)^2 \quad (3)$$

$$r_k^0 = k_{\text{exp}} K_C K_A c_C^0 / (1 + K_C c_C^0 + K_C K_A c_C^0 + K_D c_D^0)^2 \quad (4)$$

$$r_k^0 = k_{\text{exp}} K_C K_A c_C^0 / (1 + K_C c_C^0 + K_C K_A c_C^0 + K_D c_D^0)^3 \quad (5)$$

The experimentally determined rate constant k_{exp} involves the rate constant of the slowest step, the concentration of basic or acid sites and a factor depending on the mutual distribution of catalytic sites²⁴; K_C and K_D are adsorption coefficients of cyclohexanone and decalin, respectively, and K_A is the equilibrium constant for the formation of aldol I. The validity of Eqs (2)–(5) was tested also by means of the „likelihood ratio approach”²⁵. Large standard deviations between the experimental and calculated values of r_k^0 make the Eqs (2) and (3) unsuitable for reproducing the experimental results. We find that the experimental data are best reproduced by Eqs (4) and (5), which are kinetically indistinguishable. With use of Eq. (4), the standard deviation between the values of r_k^0 determined experimentally and those calculated

by non-linear regression (Marquardt method)²⁶ corresponds to about 6%. Equations (4) and (5) have been derived on the basis of a model suggested by analogy to the mechanism of the homogeneous catalytic aldol condensation of cyclohexanone and by anticipating that the rate determining step is the dehydration of aldol *I*; at the same time, it has been supposed that according to Eq. (4), there are two sites L_B and according to Eq. (5) three sites L_B participating in the rate determining step. The model is described by Eqs (A)–(E).



In the first step (Eq. (A)), which is analogous with the formation of a carbanion in the homogeneous catalytic reaction, cyclohexanone (*K*) is adsorbed on a basic site to form a transient complex. This complex reacts in the next step (Eq. (B)), which is analogous to the addition of a carbanion to a carbonyl group, with a cyclohexanone molecule to yield the aldol *I*. The dehydration of aldol *I* (Eq. (C)), in which further free sites $L_{A,B}$ are participating, is followed by desorption of the ketone *III* (Eq. (D)) and water (*W*) (Eq. (E)) as products from the catalyst surface. One can therefore arrive at Eqs (4) and (5) also in cases involving participation of an acid site L_A in the dehydration of aldol *I* (Eq. (C)); this involvement of an acid site in Eq. (C) does not affect the form of the kinetic equation for the initial rate of formation of the ketone *III* (r_k^0).

In order to provide evidence that the rate determining step is really the dehydration of aldol *I*, we have attempted to determine the rate of this reaction. Unfortunately, the retroaldolisation of aldol *I* predominating strongly on both types of catalysts at 20–210°C eliminated the possibility of determining the rate of the aldol dehydration with an acceptable accuracy. Aldol *I* behaved therefore on both solid catalysts similarly as in the presence of a homogeneous basic catalyst. We have proved that in a strongly basic solution (potassium hydroxide) the aldol *I* undergoes easily retroaldolisation and that it is relatively stable toward dehydration; on the other hand, a rapid dehydration of aldol *I* predominates in an acid solution (sulphuric acid or aluminium trichloride). The behavior of the aldol *I* on aluminium oxide and ferric oxide is therefore in agreement with their relatively high surface basicity¹⁸ and low acidity¹⁷. The predominately basic properties of both types of solid catalysts and the fact that in the homogeneous catalytic condensation of cyclohexanone the aldol

dehydration is the slowest step support the proposal that the latter reaction is the rate determining step also in the Langmuir-Hinshelwood kinetics. In harmony with this kinetics, this step (Eq. (C)) is irreversible⁸; no cyclohexanone was formed by heating the ketone *III* with water over Al_2O_3 and Fe_2O_3 catalysts at 100–210°C.

TABLE II

The effect of the catalyst poisoning on the relative activity of catalysts (A_{rel}) in the formation of ketone *III* at 210°C

Catalytic poison	A_{rel}^a	
	Al_2O_3 -450	Fe_2O_3 -230
0	1	1
Benzoic acid	0.02	0
Pyridine	0.67	0.50

^a Calculated from the ratio of slopes for the time dependence of conversion of cyclohexanone over the poisoned and non-poisoned catalyst.

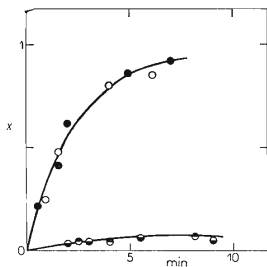


FIG. 3

The formation of cyclohexanone (x) as a function of time in the retroaldolisation of aldol *I* in decalin at 100°C over Al_2O_3 -450 (●), Al_2O_3 -450 poisoned by pyridine (○), Al_2O_3 -450 poisoned by benzoic acid (◐) and in the thermal retroaldolisation (◑)

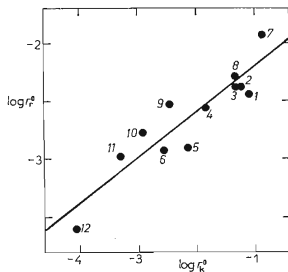


FIG. 4

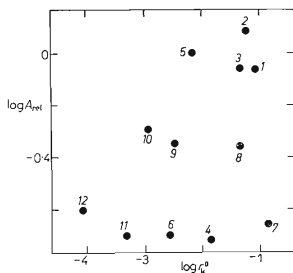
Linear correlation between the initial rates of formation of the ketone *III* ($\log r_k^0$) in decalin at 210°C and the initial rates of retroaldolisation of the aldol *I* ($\log r_I^0$) in decalin at 20°C over Al_2O_3 and Fe_2O_3 catalysts. $[\text{Cyclohexanone}]_0 = 0.8 \text{ mol l}^{-1}$; the numbering of Al_2O_3 catalysts (1–6) is the same as that in Fig. 1; 7 Fe_2O_3 -110, 8 Fe_2O_3 -230, 9 Fe_2O_3 -300, 10 Fe_2O_3 -340, 11 Fe_2O_3 -450, 12 Fe_2O_3 -510

Aimed at confirming the participation of basic or acid sites in the dehydration and retroaldolisation of aldol *I*, we have examined the course of these reactions in the presence of catalytic poisons. The effect of catalyst poisoning upon the formation of ketone *III* is evident from Table II. The effect of benzoic acid and pyridine as catalytic poisons on the initial rate of retroaldolisation of aldol *I* follows from the time dependence of conversions of aldol *I* over the non-poisoned and poisoned catalyst Al_2O_3 -450 (Fig. 3). Analogous dependences were obtained for the catalyst Fe_2O_3 -230. The poisoning by pyridine does not affect the activity of catalysts in the retroaldolisation reaction and this result provides evidence that only the basic sites participate in the formation of aldol *I*. Contrastingly, the dehydration of aldol *I* proceeds with participation of basic and acid sites as well. The decrease in the activity of catalysts poisoned by pyridine shows (Table II) that the acid sites on Al_2O_3 -450 contribute by 33% and those on Fe_2O_3 -230 by 50% to the acid-base catalysed dehydration of aldol *I*. The overall activity of aluminium oxide and ferric oxide in the formation of ketone *III* is therefore a complex function of the concentration and strength of both types of catalytic sites. The results of these experiments are entirely consistent with the model described by Eqs (A)–(E).

Based on the linear free energy relationships (LFER)²⁷, an attempt was made to correlate the initial rates of formation of the ketone *III* (r_k^0) with the initial rates of a typically base catalysed reaction, *i.e.* the retroaldolisation of aldol *I* (r_r^0). The linear correlation shown in Fig. 4 (correlation coefficient $r = 0.9074$) provides an additional evidence that the rate determining step (Eq. (C)) in the formation of the ketone *III* is affected by basicity rather than by acidity of the solid catalysts. This is in agreement with an unsuccessful attempt to correlate r_k^0 with the relative reactivities (A_{rel}) of catalysts in the acid catalysed dehydration of tert-butyl alcohol^{8,17} (Fig. 5) ($r = 0.4035$). Let us now compare the dependences given in Figs 4 and 5; whereas

FIG. 5

Attempted correlation of the initial rates of formation of the ketone *III* ($\log r_k^0$) in decalin at 210°C over Al_2O_3 and Fe_2O_3 with the relative reactivities of these catalysts ($\log A_{rel}$) in the liquid phase dehydration of tert-butyl alcohol at 170°C. The numbering of Al_2O_3 and Fe_2O_3 catalysts is the same as that in Fig. 1 and Fig. 4, respectively



in the dehydration of tert-butyl alcohol the catalysts Fe_2O_3 -510, Fe_2O_3 -450, Al_2O_3 -850, Al_2O_3 -710 and Fe_2O_3 -110 exhibit nearly the same activity, in the formation of the ketone *III* the activity increases in the stated order of catalysts and the difference between the first (Fe_2O_3 -510) and the last member (Fe_2O_3 -110) of the series attains more than three orders of magnitude. Since all these catalysts have a comparable acidity, the overall activity of catalysts in the formation of ketone *III* should increase in the stated order parallelly with their increasing surface basicity c_B . Such a dependence does exist and is documented satisfactorily by an increase in the initial rate of retroaldolisation (Fig. 4) with increasing basicity of catalysts in the order: Fe_2O_3 -510 < Fe_2O_3 -450 < Al_2O_3 -850 < Al_2O_3 -710 < Fe_2O_3 -110 (Table I).

All the above results show that particularly the basicity of solid catalysts (Table I) is significantly influenced by the calcination temperature. The samples of aluminium oxide prepared by calcination at temperatures ranging from 110 to 850°C differ in the catalytic activity enhancing the formation of ketone *III* by about two orders of magnitude; the activity of samples of ferric oxide obtained by calcination at 110 to 510°C varies within three orders of magnitude. It is worthy of note that the most active catalyst in the aldol condensation of cyclohexanone is ferric oxide calcined at temperatures up to 230°C. A decrease in the activity of ferric oxide catalysts prepared by calcination at higher temperatures is evidently due to the transformation into the α - Fe_2O_3 modification.

The results of the kinetic measurements, catalyst poisoning and LFER correlations lead to the following conclusions. The liquid-phase aldol condensation of cyclohexanone on aluminium oxide and ferric oxide catalysts is a typical acid-base catalysed reaction. Similarly as in the homogeneous catalytic condensation, the first step, *i.e.* the formation of the aldol *I*, is a base catalysed reaction. Basic as well as acid sites participate in the second step, *i.e.* the dehydration of the aldol *I*. Parallel base and acid catalysed dehydration of the aldol *I* represents therefore the major difference between the liquid-phase aldol condensation on solid catalysts and in the homogeneous catalytic reaction.

REFERENCES

1. Frost A. A., Pearson R. G.: *Kinetics and Mechanism*, p. 335. Wiley, New York 1961.
2. Plešek J., Zobáčová A.: *Preparativní reakce v organické chemii*, Vol. V, p. 117. Academia, Prague 1960.
3. Malinowski S., Basinski S.: *J. Catal.* 2, 203 (1963).
4. Malinowski S., Jedrzejewska H., Basinski S., Lipski Z., Moszczenska J.: *Rocz. Chem.* 30, 1129 (1956).
5. Malinowski S., Basinski S., Czczepanska S., Kiewlicz W.: *Bull. Acad. Pol. Sci., Ser. Sci. Chim* 12, 149 (1964).
6. Scheidt F. M.: *J. Catal.* 3, 372 (1964).
7. Ganguly P.: *Proc. Indian Acad. Sci.* 86A, 65 (1977).
8. Vit Z.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1980.

9. Watanabe Y., Okada M., Izumy Y., Mizutani Y.: *Bull. Chem. Soc. Jap.* **50**, 1539 (1977).
10. Nondek L., Málek J.: *This Journal* **45**, 1812 (1980).
11. Nondek L., Málek J.: *This Journal* **44**, 2383 (1979).
12. Johansen A. V., Kurchi G. A., Bayeva V. P., Rasskazova Z. N., Salamatina G. A.: *Zh. Org. Khim.* **7**, 2509 (1971).
13. Wallach O.: *Ber. Deut. Chem. Ges.* **40**, 70 (1907).
14. Reese J.: *Ber. Deut. Chem. Ges.* **75**, 384 (1942).
15. Wenkert E., Bhattacharya S. K., Wilson E. M.: *J. Chem. Soc.* **1964**, 5617.
16. Nondek L., Vít Z., Málek J.: *React. Kinet. Catal. Lett.* **10**, 7 (1979).
17. Vít Z., Nondek L., Málek J.: *React. Kinet. Catal. Lett.* **14**, 459 (1980).
18. Vít Z., Nondek L., Málek J.: *Appl. Catal.* **2**, 107 (1982).
19. Nondek L., Vít Z., Málek J.: *Chem. Listy* **74**, 428 (1980).
20. Plešek J.: *Chem. Listy* **50**, 252 (1956).
21. Reid R. C., Prausnitz J. M., Sherwood Z. K.: *The Properties of Gases and Liquids*, p. 61, 74. McGraw Hill, New York 1977.
22. Kölbel H., Leuteritz G.: *Z. Elektrochem.* **64**, 437 (1960).
23. Kölbel H., Schöttle E.: *Z. Elektrochem.* **65**, 91 (1961).
24. Kraus M., Schneider P., Beránek L.: *Chemická kinetika pro inženýry*, p. 161. Published by SNTL, Prague 1979.
25. Rao R. S., Hudgins R. R., Reily P. M., Silveston P. L.: *Can. J. Chem. Eng.* **49**, 354 (1971).
26. Marquardt D. W.: *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).
27. Kraus M.: *Advan. Catal.* **29**, 151 (1981).

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