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Vapor-Phase Ketonization of Aliphatic Acids on a Chromite Catalyst

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Abstract—The catalytic conversion of acetic, propionic, and butyric acid in the presence of water vapor on oxide chromium–zinc–manganese catalyst promoted by potassium carbonate in the temperature range 300–400°C was studied. The main products of the acids conversion were found to be symmetrical ketones, water, and carbon dioxide. The optimum yield of ketones is achieved at 325°C. The yields were as follows: up to 96 mol % of acetone, 95 mol % of diethyl ketone, and 92 mol % of dipropyl ketone. A side reaction is the decarboxylation of acids, the contribution of which increases with increasing temperature. Under these conditions a clevage of molecules with the formation of lower ketones, hydrogen, methane, and carbon monoxide. Yield of symmetrical ketones from aliphatic acids is much higher than from the corresponding aldehydes and alcohols, and the maximum yield is obtained at a lower temperature. By the example of ketonization of the acetic acid it was found that the reaction proceeds quite successfully at reducing the water concentration in the reaction mixture. This enabled us to improve the performance of the process of ketones production.

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The ketonization of aliphatic acids is `assumed to proceed through intermediate formation of acyl radicals and carboxylate structures adsorbed on the catalyst surface, which in the presence of water vapor form ketones. The molecules of acid and water on the catalyst surface undergo fragmentation and association of the formed fragments to afford the reaction products. Such assumption on the reaction mechanism of ketonization of acids is confirmed by quantum-chemical calculations by AM1 method of the reaction of the acetic acid ketonization on the silicon oxide, as well as by considering the properties of oxide catalytic systems with the existing view on the course of the surface conversion of the reacting molecules.

Ketones are highly reactive compounds, widely used in the synthesis of polymers, pesticides, stabilizers, photographic materials, fragrances, solvents, extractants, and medicines [1, 2]. There are many ways of obtaining ketones. For example, more than 30 methods for their synthesis is described in [3], but they are associated with the use of large quantities of various reagents and, consequently, to increased cost of the product and the formation of significant quantities of waste. More promising are the methods of catalytic synthesis of ketones from alcohols [4], aldehydes [5], acids [6–9] and esters [10] which we have developed. These methods are characterized by high selectivity, simplicity of design and low cost of the process. A mixture of the corresponding parent compound and water is passed through a chromite catalyst at a temperature of 325–350°C, liquid and gaseous products are separated and analyzed chromatographically. The reaction products can be recycled.

Current studies of the ketonization of aliphatic acids on oxide catalysts are carried out mainly using the dioxides of cerium, zirconium, or titanium [11–14], but the yield of ketones seldom exceed 50–60%. Synthesis of dipropylketone from butanol we developed by us [15] and implemented at the pilot plant of the Institute of Organic Synthesis of the Latvian SSR and the Reagents Plant in Kiev. The comparison of ketonization of butyric acid, butanol, and butyraldehyde shows a clear advantage of the acid in the synthesis of dipropylketone (Table 1). While conversions of acid and alcohol are quite comparable, the yield of the dipropylketone from the acid is by 20%

Table 1. Comparison of processes of ketonization of butyric acid, butanol [4], and butyric aledehyde [5]

Temperature, °C	Conversion, %			Selectivity of dipropyl ketone formation, mol %		
	acid	alcohol	aldehyde	acid	alcohol	aldehyde
300	19.8	22.8	39.6	87.8	19.0	25.8
325	40.2	54.6	68.5	92.3	49.4	53.7
350	91.5	86.2	97.5	90.3	72.2	80.4
375	99.0	99.5	100	67.8	75.6	67.7
400	99.0	100	100	25.6	22.2	23.0

Table 2. Effect of temperature on the conversion of acetic acid

Temperature, °C	Acid conversion, %	Acetone yield, mol %	Yield of gaseous products, mol per 1 mol of reacted acid	Composition of gaseous products, %			
				CO_2	CH_4	H_2	CO
300	95.1	93.3	0.46	97.5	1.4	1.1	0
325	98.8	96.1	0.48	96.1	2.8	1.1	0
350	100	93.9	0.55	88.3	5.0	6.6	0.1
375	100	90.3	0.71	75.7	8.1	14.9	0.4
400	100	84.2	0.98	66.5	13.5	18.7	1.3

higher and is achieved at lower temperature (by 25°C lower).

The ketonization of acetic acid (Table 2) was also found to occur with high activity and selectivity. The yield of acetone reaches maximum (96.1 mol %) at 325°C with the acid conversion 98.8%. Yield of acetone is sufficiently high (above 90%) in a wide range of temperatures (300–375°C):

$$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O.$$

The contribution of the side reaction, the acetic acid decarboxylation, increases with increasing temperature and reaches ~7% at 400°C:

$$CH_3COOH \rightarrow CH_4 + CO_2.$$

The share of the catalytic oxidation of acetic acid in the presence of water vapor at 400°C does not exceed 5%:

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2.$$

At the ketonization of propionic acid (Table 3) the maximum yield of diethyl ketone is 95 mol %, which is also achieved at 325°C. Yield of diethyl ketone is by 1% lower than that of acetone from acetic acid, and the conversion of propionic acid is by 8% lower than that of acetic acid. In addition to the above-mentioned side reactions (decarboxylation and oxidation), the increase in temperature to 400°C enhances the side reaction of methyl ethyl ketone formation to 12%, and decarboxylation–dehydrogenation, to 3%:

$$2C_2H_5COOH + H_2O \rightarrow CH_3COC_2H_5 + 2CO_2 + 3H_2,$$

$$C_2H_5COOH \rightarrow C_2H_4 + CO_2 + H_2.$$

At the ketonization of butyric acid (Table 4) the maximum yield of dipropylketone (92.3 mol %) also is achieved at 325°C, but the conversion of butyric acid is significantly lower (40%) than that of propionic acid. With increasing the reaction temperature the yield of dipropyl ketone falls more sharply, and increases the yield of the side products, methyl propyl ketone and acetone. The selectivity of the decarboxylation reaction is low, but significantly increases the contribution of the reactions of the cleavage of the molecules and oxidation of the formed fragments. As a result, the yield of gaseous products increases and also the content of methane and hydrogen in them. Nevertheless, the yield of dipropyl ketone from butyric acid considerably exceeds that in the known hitherto process of the butanol ketonization. Besides, there is a possibility to improve its yield by reducing the concentration of water in the reaction mixture.

Table 3. Effect of temperature on the conversion of propionic acid

Temperature, °C	Acid conversion, %	Yield, mol %		Yield of gaseous products, mol per 1 mol of reacting acid	Composition of gaseous products, vol %					
		methyl ethyl ketone	diethyl ketone		CO_2	C_2H_6	C_2H_4	CH_4	H_2	CO
300	48.4	0.6	89.7	0.35	99.2	0.2	0.1	0.0	0.5	0.0
325	90.2	0.7	95.0	0.38	96.5	0.3	0.1	0.0	3.1	0.0
350	99.8	2.7	93.1	0.44	93.5	0.5	0.2	0.1	5.6	0.1
375	100	6.5	84.9	0.65	86.0	1.6	0.9	1.3	9.9	0.3
400	100	12.3	62.1	1.12	60.5	3.5	3.0	5.7	25.9	1.4

Table 4. Effect of temperature on the conversion of butyric acid

Temperature, °C	Acid conversion, %	Yield, mol %			Yield of gaseous products, mol per 1 mol of reacting acid	Composition of gaseous products, vol %					
		acetone	methyl propyl ketone	dipropyl ketone		CO_2	C_3H_8	C_3H_6	CH_4	H_2	CO
300	19.8	0	3.4	87.8	0.30	98.8	0	0	0	1.2	0
325	40.2	0	2.6	92.3	0.40	96.2	0.2	0.2	0	3.4	0
350	91.5	0.1	4.2	90.3	0.61	92.9	0.4	0.4	0.1	6.1	0.1
375	99.0	2.3	17.0	67.8	0.99	84.4	1.0	1.2	3.0	10.0	0.4
400	99.0	7.8	21.8	25.6	1.80	51.1	1.6	2.9	15.8	27.2	1.4

Table 5. Effect of water concentration on the ketonization of acetic acid at 350°C and feeding with a solution of acetic acid of 500 g h^{-1} per 1 l of catalyst

Acid : water ratio, mol/mol	Acid concentration, %	Acid conversion, %	Selectivity with respect to acetone, mol %	Acetone output, g h^{-1} per 1 l of catalyst
1:3	52.6	21.6	90.8	32
1:2	62.5	27.3	94.9	47
1:1	76.9	38.9	95.1	82
1:0.5	87.0	47.5	95.8	115
1:0.1	97.1	80.9	96.5	220
1:0	100.0	92.9	97.2	262

By the example of ketonization of aldehydes and alcohols [4, 5] an improvement of the process was shown to occur at the dilution of the initial compounds with water. The reaction of ketonization of acids was studied previously under similar conditiuons. However, the ketonization of acids is accompanied by the release of water in the reaction, while alcohols react with water consumption. Therefore, by the example of ketonization of acetic acid (Table 5) we checked the influence of water concentration in the reaction mixture on the process performance. By reducing the water content in the reaction mixture, we were able to improve dramatically the dipropyl ketone yield. Even at the concentration of water equal to 0.5 mole per 1 mole of acid (Table 6) excellent results were achieved at a high acid load at 350°C and 375°C. The output of acetone exceeded 200 g per hour per 1 l of catalyst.

The sample of the chromium–zinc–manganese (6:5:1 at %) oxide catalyst used in the research heated at 400°C contains only one crystal phase, the spinel, identical to zinc chromite, with a very disordered lattice. We suggest that at the introduction of

Table 6. Effect of temperature on ketonization of acetic acid at the acetic acid: water mol. ratio 1:0.5 and feed of acetic acid solution of 500 g h^{-1} per 1 l of catalyst

Reaction temperature, °C	Acid conversion, %	Selectivity in respect of acetone, mol %	Acetone output, g h^{-1} per 1 l of catalyst
300	24.7	93.5	58
325	38.8	94.8	93
350	94.1	98.0	233
375	100.0	98.0	247

manganese into the zinc chromite spinel structure results in the substitution of chromium and dissolution of zinc oxide in the spinel.

The reaction mechanism of the aliphatic acids ketonization is easier to understand considering jointly the ketonization reactions of aldehydes, alcohols, and acids. All these reactions have much in common. Comparing the reactivity and the selectivity of the conversion of aldehydes, alcohols, and acids, we concluded that the conversion of these compounds occurs on the same active centers on the surface of the oxide catalyst with the formation of the similar intermediate: acyl radicals adsorbed on the catalyst surface:

$$\text{R–CO–X} \rightarrow \text{R–CO}^{\bullet} + \text{X}^{\bullet},$$
$$\text{X} = \text{H, OH, R'}.$$

The formation of acyl radicals from the alcohol proceeds through the dehydrogenation of the surface alcoholate [16].

This hypothesis is supported by the fact of high selectivity of ketonization of the studied compounds. Moreover, the formation of acyl radical as an intermediate is likely in the conversion of acids, since the C–OH bond in molecules of aliphatic acids is weaker than C–C bond, and the structure of the acyl radical adsorbed on the catalyst surface corresponds to the structure of the surface carboxylate described in literature. The formation of the latter was found by many researchers in the reactions of aldehydes, alcohols, acids, and ketones with the surface of oxide catalysts [17]. It is also known that the adsorbed carboxylate structure disappears from the surface of the catalyst in contact with water, indicating that it is an intermediate structure in the ketonization reaction [18]. The acyl radical is formed apparently in the reaction of functional groups of the adsorbed compound with the bridging structures of the surface and the coordinationally unsaturated metal atoms of the catalyst [19].

An important role in the process of transformation of aldehydes, alcohols, and acids on the oxide catalysts play the surface hydroxy groups and water involved in the reaction. It is known that on the surface of oxide catalysts water dissociates into hydrogen and hydroxy group, which can interact with the surface of the catalyst and react with the compounds to be converted [20, 21]. Further dissociation of acyl radical and other complex species is also possible.

A high mobility of the hydrogen of the hydroxy groups on the surface, of the oxygen of the lattice, as well as free electrons and vacancies of the crystal lattice is typical for oxide catalyst systems. The chemisorption of organic molecules on the catalyst may be accompanied by a rupture of existing and formation of new covalent bonds, that is, by the occurrence of catalytic reactions [22–24]. The formation of by-products is easily understood by the interaction between the radicals adsorbed on the catalyst surface or with active hydrogen or hydroxy groups formed at the dissociation of water. Hydroxy groups cause the oxidation of CO to CO_2 [4], and the desorption regenerates the active center of the catalyst.

This suggestion is well confirmed by the theoretical study of the mechanism of such reactions, using semiempirical quantum-chemical method AM1, which was carried out earlier by the example of ketonization of acetic acid in the presence of SiO_2 [25].

It was shown that the synergism of conjugate acid–base pairs of active centers formed at high temperatures causes the dissociative adsorption of acid with the subsequent formation of surface carboxylate particles. Newly added acetic acid interacts with the active particles in the gaseous phase, transforming into the acyl cation and water. The subsequent interaction between active particles, the carboxylate anion and acyl cation, occurs spontaneously and through the bimolecular electrophilic substitution reaction leads to the formation of carbon dioxide and the target product, the molecule of acetone.

EXPERIMENTAL

The chromite catalysts was precipitated from saturated aqueous solutions of nitrates of zinc and manganese by adding a saturated solution of ammonium chromate and ammonia. The precipitate was filtered off, dried at 110–120°C, slowly heated to 400°C, graphite was added thereto, it was moisturized and pressed [17, 26]. The specific surface of the catalyst was determined chromatographically by thermal desorption of argon.

Radiographs of the catalyst samples were obtained with a X-ray powder diffractometer Ultima IV (Rigaku).

The ketonization reactions of aliphatic acids in the presence of water vapor were studied using a steel tube with 40 ml of catalyst at 300–400°C. The acid was fed at 100 g h^{-1} per one liter of the catalyst, The ratio acid: water = 1:2 mol. The influence of water on the process of the acid ketonization was studied by the example of acetic acid using 2 g of the catalyst and the acid feed at 500 g h^{-1} per one liter of the catalyst.

The derivatograms were obtained on a derivatograph OD-102 (MOM). The rate of heating was 5°C min^{-1}. Samples were mixed in 1:1 ratio with α-Al_2O_3 calcined up to 1500°C [17].

The liquid reaction products were analyzed on a Varian Aerograph gas–liquid chromatograph on Porapak Q in the programmed temperature regime (70–240°C), [3]. Gaseous products were analyzed on a modified gas–liquid chromatograph with two chromatographic column (gas–liquid and gaz adsorbtion) at room temperature [27].

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