

Application of Zr-Mg-Y-O Catalyst for Ketonization of Ester and Alcohol Type Industrial Wastes

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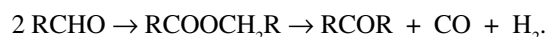
Abstract

Aldehydes and their derivatives – primary alcohols and esters undergo ketonization in the gas phase in the range of 350-450 °C over multicomponental oxide catalyst – Zr-Mg-Y-O. This method is appropriate for processing mixtures of components. An experimental study was performed on ketonization of methyl esters fractions of waste fats and residuary alcohol fractions originating from industrial installations. In both cases mainly ketone fractions were obtained. During transformation of methyl esters and alcohols total yields of ketones amounted to over 60% and about 75%, respectively. Also, other catalytic systems (i.e. Fe-Si-Cr-K-O and Sn-Ce-Rh-O) can be used for ketonization of both raw materials.

Keywords: waste technical alcohols, waste technical esters, catalytic ketonization, ketones.

Introduction

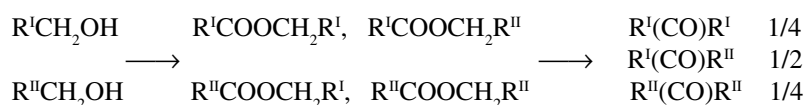
Over some oxide systems applied as heterogeneous catalysts, aldehydes undergo condensation of the Tishchenko type [1] to esters, or the conversion goes on to ketones:



Thus, the material for obtaining ketones in this way can be esters and primary alcohols, provided they are dehydrogenated in reaction conditions. The possibility of primary alcohol dehydrogenation with their subsequent ketonization has been documented [2-4].

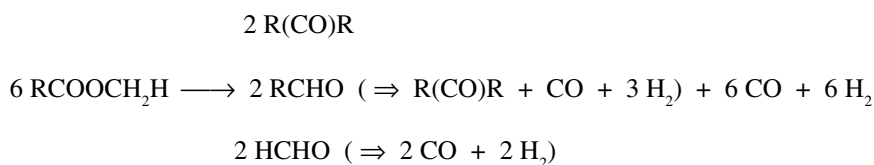
When the material is ester of different carbon chain lengths, or a mixture of alcohols and/or esters, a mixture of symmetrical and non-symmetrical ketones is obtained.

SCHEME 1



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SCHEME 2



Scheme 1 illustrates the process of ketonization of two different primary alcohols and ester ketonization. A particular case are methyl esters (RCOOCH_3) because, according to the general model of transformation, only one ketone R(CO)R is formed (Scheme 2).

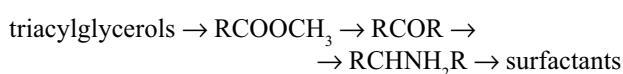
The method proposed (including the choice of catalysts) of primary alcohols and ester transformation to ketones can be applied for processing of some waste materials containing the above-mentioned compounds. Preliminary experiments with ketonization of waste materials have been carried out for:

- materials of fat origin (a mixture of methyl esters of fatty acids)
- post-production mixture of alcohols and their derivatives from cyclohexanone production.

Ketones are intermediates applied to a large extent in organic synthesis. They are characterized by high polarity and relatively low vapor pressure. The compounds undergo intermolecular condensation and that is why they are characterized by higher boiling points than non-polar compounds of similar molecular mass. Moreover, they are easily mixed with both polar and non-polar substances. The major applications include: deodorants, pharmacological substances, synthetic resins, plasticizers of cellulose products, dryers of nitrocellulosic layers, stabilizing agents, greasing, adhesive and extractive factors, antioxidants, waxes, varnishes, baking enamels, organosoles, and plant protective agents [5].

There are no reasons restricting the application of mixtures of ketones obtained from mixtures of methyl esters of fatty acids or primary alcohols and their derivatives, for example as surfactants. Also ketones separated from the mixture can be used for obtaining other small-tonnage products.

The increasing importance of environmental issues has resulted in the search for natural resources and biodegrading products. This concerns the utilization of harmful, extensive and renewable raw material resource, e. g. waste technical fats [6]. The proposed conversion from triacylglycerols to amines with two long chains proceeds according to the scheme:



Stages of fat conversion (esterification of fatty acids and transesterification of triacylglycerols) [7, 8] and reductive amination of ketones [9] have already been technologically mastered. The resultant amines can provide

a raw material basis for the production of surfactants of gemini type [10, 11]. The synthesis of these surfactants with the participation of carbohydrates is the subject of intense research. The gemini type surfactants are nonionic, biodegrading and efficient, and thus less harmful to the natural environment [12].

Experiments carried out by the authors provide the complementing element of the above sequence – they concern the ketonization of fatty acid esters.

Another example of the possibility of these catalysts' application is utilization of waste alcohol fractions by ketonization. The aim of this research was to work out the method of utilizing alcohol fractions containing mainly primary alcohols and aldehydes being waste products in the process of manufacturing cyclohexanone from benzene (Cyclopol Process) in the Nitric Plant "Tarnów" (ZAT). A similar fraction is obtained in the Nitric Plant "Puławy". The waste fraction, which is formed at the stage of cyclohexane oxidation to cyclohexanone, is not utilized but burnt [13].

Material and Methods

The reactions were carried out by a conventional flow method. All runs were performed at atmospheric pressure without added carrier gas. There was used a vertical quartz reactor of 10 mm inner diameter with a fixed bed containing 2 and 4 cm³ of catalyst of 0.6-1.2 mm particle size. The substrates were supplied through the top of the reactor using a metering pump at an appropriate flow rate. In the case of methyl esters methanol was used as a diluent. Continuous monitoring of bed temperature was achieved by a thermocouple placed inside the catalyst bed. The ketonization reactions were started at 350°C and studied as a function of increasing temperature up to 450°C. The products were collected and analyzed by gas chromatography and mass spectroscopy.

For ketonization of long-chain esters and waste alcohols, a fraction of the catalyst Zr-Mg-Y-O active in ketonization of primary alcohols was applied [14]. Zr-Mg-Y-O catalyst contained 90mol.% of ZrO_2 , 9mol.% of MgO and 1mol.% of yttrium(III) oxide. It was synthesized using the low-temperature method [15]. In the first step zirconyl hydroxyoxide was precipitated from the water solution of zirconium(IV) chloride and next hydroxides of magnesium and yttrium were co-precipitated from aqueous solution containing ions of Mg^{2+} and Y^{3+} . The obtained precipitate was water washed by decantation, dried at 50°C and calcined at 650 °C/6h. X-ray analysis of the catalyst,

performed with the use of a Philips diffractometer, indicated that it is one-phase material and magnesium and yttrium oxides as single phase were not detected. Information about the surface area and porosity was obtained by the evaluation of nitrogen, carbon monoxide and benzene adsorption-desorption data with a Micrometrics ASAP 2010. The BET specific surface area determined on the basis of the measurements for Zr-Mg-Y-O composition was equal to about 78 m²/g and the average pore radius 101.3 Å. The SEM studies of the catalyst investigated, performed using a JSM 5800 LV scanning microscope, indicated that the material obtained exhibited polycrystalline structure with an crystallite average size of 60 µm.

Also, other catalysts active in ketonization of primary alcohols i.e. Fe-Si-Cr-K-O [16] and Sn-Ce-Rh-O [17] can be used for transformations of both raw materials. Details of catalyst preparation and their properties were published earlier – for iron catalyst in [18] and for tin catalyst in [4].

Results and Discussion

Since 12-tricosanone was obtained as a result of methyl *n*-dodecylate transformation in the presence of Fe-Si-Cr-K-O catalyst at temperature 395°C and load of 1.5 h⁻¹, with a yield 58.3% (at 93% conversion) [19] and because ketonization of long-chain esters also occurs over Sn-Ce-Rh-O catalyst with similar yield [20], it was possible to use mixtures of fatty acid esters from technical wastes as raw materials and their transformations to ketones in the presence of all catalysts studied.

A mixture of methyl esters of fatty acids obtained by transesterification of nonerucic rapeseed oil was ketonized. The starting material, diluted with methanol, was converted at atmospheric pressure over Zr-Mg-Y-O catalyst. At 395°C the mixture of ketones was obtained with a total yield of 61% with 96% conversion (Table 1). During the reaction of ester ketonization no harmful by-products are formed.

The results of the ketonization of fatty acid ester fractions of waste origin over iron and tin catalysts were published earlier (i.e. for Fe-Si-Cr-K-O [21-23], and for Sn-Ce-Rh-O [24, 25]).

As mentioned above, all the catalysts obtained were tested in the gas phase reactions of primary alcohols. These catalysts dehydrogenate primary alcohols into aldehydes and at higher temperatures, as a result of bimolecular condensation, ketones were the main products of the reaction. For example, *n*-butanol reacts to dipropyl ketone in the presence of Sn-Ce-Rh-O catalyst with an 80% yield at 360°C and at load of 1.0 h⁻¹. In these conditions conversion of *n*-butanol was 91% [4]. In the case of mixtures of alcohols used as substrates, the mixture of symmetrical and non-symmetrical ketones was obtained (Scheme 1). On the basis of the results it was possible to utilize waste fractions containing mixtures of alcohols.

In the gas phase, in the temperature range of 350-450°C, over Zr-Mg-Y-O catalyst after processing the initial waste fraction (mainly composed of *n*-pentanol and isopentanol),

a ketone fraction containing a mixture of symmetrical and non-symmetrical ketones (mainly nonanone-5) was produced with about 75% yield and 80% selectivity. Table 2 presents exemplary results of the studies [26-28].

The results are similar to those obtained over tin catalysts [29].

Table 1. Results of methyl esters fraction ketonization.

Catalyst: Zr-Mg-Y-O (100 : 10 : 1)	2.0 cm ³
Content of C ₁₈ ester in methyl esters fraction (C ₁₂ to C ₂₂)	87%
Fraction/methanol (1 : 1)	3.0 cm ³ /h
Temperature	395°C
Conversion	96%
Total yield of ketones	61%
Pentatriacontanone-18 (C ₁₇ H ₃₅ CO C ₁₇ H ₃₅)	45%
Hentriacontanone-16 (C ₁₅ H ₃₁ CO C ₁₅ H ₃₁)	3%
C ₁₇ and C ₁₅ methyl ketones	6%
Others ketones	7%
Hydrocarbons (mainly C ₁₈ and C ₁₈₌)	15%
Other collected	5%
Gases	15%

Table 2. Results of waste alcohols fraction (ZAT) ketonization [27].

Catalyst: Zr-Mg-Y-O (100 : 10 : 1)	4.0 cm ³
Raw material waste alcohols fraction (ZAT) contents:	
<i>n</i> -pentanol	54%
cyclohexanone	11%
<i>n</i> -butanol	11%
cyclopentanol	8%
others	16%
Feed rate	4 cm ³ liquid/h
Temperature	420°C
Conversion	93%
Total content of ketones in reaction products	58%
where 75% of ketones yield from <i>n</i> -pentanol:	
nonanone-5	32%
octanone-4	6%
decanone-5	2%
and:	
cyclohexanone	12%
heptanone-4	6%
heptanone-4	35%

Conclusions

The adaptation of Zr-Mg-Y-O as well as Fe-Si-Cr-K-O and Sn-Ce-Rh-O catalysts, previously applied for primary alcohol transformations, resulted in the possibility of processing waste esters or alcohol fractions. Tests of the ketonization of methyl ester fractions of fat origin and alcohol fractions derived from industrial installations have been performed. In both cases mainly ketone fractions were obtained.

This method enables rational waste management, and the obtained fraction – composed mainly of ketones – opens possibilities for broadening the spectrum of ketone applications. From a technological point of view the method proposed of conversion of primary alcohol and aldehydes contained in waste alcohols fractions or esters in methyl esters fractions of waste fats origin is very simple. The conversion proceeds in a continuous manner with the use of a given material without any additional substances. In the case of long-chain methyl esters fraction a diluent is recommended. It is consistent with trends set in the modern chemical industry of the maximization of the number of atoms coming from the material to the final products. From technological and economical perspectives this method meets both modern process demands and the assumptions of eco-development strategy.

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