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Catalytic conversion of C₁₂–C₁₄ primary alcohols mixture into long-chain ketones

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1. Introduction

Mixtures of ketones have several applications. Ketones and mixtures of ketones are useful organic solvents for painting, agricultural, and other industries as intermediates for the preparation of dyes, crop protection agents and drugs [1–3]. They are found to be a satisfactory drilling fluid dispersant in aqueous drilling fluids [4], reactive solvents to form coatings and foamed plastics [5,6], a stuff for the ammoxidation to a mixture of nitriles [7].

Long-chain ketones can be used for the production of surfactants in detergent compositions [8], particularly gemini surfactants [9–11]. They can be also used as special foam control agents in the paint, paper and food industries and as foam inhibitors in soap-containing detergents [12,13]. It is worth to mention that mixture of long-chain ketones dispersed in fatty alcohols is also of commercial use [14].

Oxidation of hydrocarbons is a well-known method of ketones production. Besides, they can be formed from carboxylic acids [15] and also from alcohols. Liquid-phase oxidation of alcohols has some disadvantages such as costly oxidants, inevitably resulting in the formation of environmentally unfriendly by-products, basic-additives and heavy-metal-solutions [16] or a solvent-dependent over- oxidation [17]. Whereas, it is generally regarded that primary and secondary alcohols are oxidized into corresponding aldehydes and ketones [18], the accomplishment of primary alcohol transformations in vapor-phase conditions over some oxide catalysts also enables to receive ketones. The bimolecular reaction can occur successfully

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ABSTRACT

A charge of raw primary alcohols of high molecular weight from commercial plant was transformed into long-chain ketones fraction of potential commercial use. In this continuous flow method LaMnO₃/La-Al₂O₃ catalyst was used. At 420 °C and a normal pressure mixture of 74.2 wt.% C_{12} and 25.8 wt.% C_{14} primary alcohols and toluene (weight ratio alcohols:toluene = 1:1) was converted into ketones with 73.4% yield in relation to the theoretical value. Ketones were analyzed by TLC, NMR and GC-MSD.

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by selecting proper catalysts. It leads to the symmetric ketones with 2n-1 carbon atoms in relation to initial alcohol [19]. The use of alcohol mixture is an alternative method to obtain required non-symmetric ketones [20]. Esters can be also used as raw materials for such ketonization. One of the directions of use of such transformation may be the synthesis of long-chain ketones [21]. For this purpose, esters possessing high molecular weight, such as these ones originating from the transesterification of fats [22] can be used [23].

Catalysts activity is usually tested with the use of model compounds, reports dealing with catalytic performance for real feed are less common. Despite of practical importance of primary alcohols ketonization there are only few works addressed to conversion of real, commercial feed [19]. Therefore, we assumed that such conversion can be also applied when alcohols of higher molecular weight are use as the raw material. The alcohols fraction—lauryl/myristyl alcohol (*AL C12–C14*) [24,25] produced by the hydrogenation of methyl esters from palm kernel oil (PKO) [26,27] or coconut oil (CNO) [28] are considered as a potential feed for this transformation. Some bases for detergents (sulfated and ethoxylated alcohols for shampoos) are produced from fraction *AL C12–C14* [24,29].

High activity and selectivity of the lanthanum manganite was demonstrated in relation to unconventional conversion of 1-butanol to heptanone-4 [30–32]. It is known that low specific surface area (SSA) is one of the drawbacks of the perovskite-based catalysts. Deposition of perovskites over refractory carrier possessing high SSA is a convenient method for increasing their surface area accessible for reactants and improvement of thermal stability. In this work, LaMnO₃ mixed oxide with perovskite-like structure was supported on alumina precoated with lanthanum oxide and used as a catalyst for primary alcohols transformation.

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Table 1

Results of the ketonization of $\rm C_{12}-C_{14}$ primary alcohol fraction on the $\rm LaMnO_3/La-Al_2O_3$ catalyst.

Reaction temperature [°C]	Conversion [%]	Output of solid product [g/h]	Yield of ketones from the solid product [%]	Selectivity ^a [%]	
380	74	1.45	59.3	61.4	
400	~100	1.92	63.5	87.1	
420	~100	1.70	61.8	75.0	
440	~100	1.50	50.0	53.6	

^a Selectivity = 100 (experimental weight of produced ketones)/(theoretical weight of ketones), see text below.

2. Experimental

Alumina carrier was precoated with lanthanum compound to inhibit the sintering and preventing of the reaction of perovskite components with the support. Procedure of the carrier (La–Al₂O₃) preparation is described elsewhere [31]. Supported LaMnO₃ catalysts were prepared by citrate process according following protocol. At first the citric precursor of LaMnO₃ was prepared by dissolution of La and Mn nitrates in the suitable proportions to give a water solution. Then, metal ions were complexed by the addition 1.2 mol of citric acid per mol of metal to this solution. Powdered carrier was suspended in the solution containing amount of citric precursor of the perovskite necessary to obtain 30 wt.% of LaMnO₃ deposited on La–Al₂O₃. The mixture was evaporated to produce viscous syrup which was carefully decomposed at 350 °C. Produced solid material was grounded and finally calcined for 2 h at 850 (900) °C. Material obtained in this way was pressed, crushed, and screened—particles of 0.6–1.2 mm size were used for catalytic tests.

The total acidity and the acid strength distribution were evaluated by the temperature-programmed desorption of ammonia (TPD NH₃) according to the following procedure. Samples (2 g) were heated to 823 K under argon for 1 h then cooled to 453 K where adsorption of pure ammonia was performed for 0.5 h followed by a purge with argon at 453 K for 1 h in order to remove physically adsorbed NH₃. Finally, TPD NH₃ measurements were started in argon with a heating rate of 10 K/min.

The ketonization of $C_{12}-C_{14}$ primary alcohols fraction was carried out in a fixed bed flow reactor at atmospheric pressure. A quartz tube reactor (10 mm of inner diameter) was loaded with 3 cm³ of the catalyst and placed in a vertical pipe furnace Thermolyne F21100. The outlet of the reactor was additionally heated to avoid the solid products condensation.

Taking into account that 1-butanol ketonization was performed as a model reaction for determination of LaMnO₃/La–Al₂O₃ activity [31], we decided to use the same reaction for controlling the catalyst's activity before and after the reaction. This test was performed two times: once before the experiments with the C_{12} – C_{14} primary alcohol fraction and then after these experiments test was repeated. The



Fig. 1. The ¹³C NMR spectra of the obtained ketone fraction.





second control test was preceded by 7 h regeneration of the catalyst in air at 470 °C in the same reactor. The control trials were made at 3 cm^3 /h flow intensity of liquid 1-butanol (1 h⁻¹ LHSV).

mdc

The C₁₂-C₁₄ primary alcohols fraction from IHOS "Blachownia" industrial plant containing 74.2 wt.% C12 and 25.8 wt.% C14 alcohols was dissolved in toluene (a weight ratio of 1:1; density of the mixture -0.85 g/cm³). Such solution was fed to the top of the reactor and dispersed in pre-heating zone using an infusion pump (Medipan 610-2) with a volume flow of $3.7 \text{ cm}^3/\text{h}$. Due to the additional heating of the receptacle, the obtained solid product was partially deprived of toluene. Product weight gain was monitored. Gaseous by-products (see the transformation scheme below) were not analyzed. Toluene remained in the so obtained samples was removed in a desiccator under pressure of about 15-20 mmHg. Purification of received ketone fractions was performed on a silica gel column [33]. The hexane-ethyl acetate mixture with a volume ratio of 100:5 was used for column elution. Fractions containing ketones were collected and further purified by the column chromatography. The collected fractions from the column were analyzed by thin-layer chromatography using a silica gel coated plates. Ketones were detected on the plates by spraying a solution of 2,4-dinitrophenylhydrazine diluted in H_2SO_4 . This reagent gives a color reaction with aldehydes and ketones. Plates were developed with a mixture of hexane–ethyl acetate.

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4

The final ketone fractions were separated, solvent was removed under vacuum, ketones were dried in a vacuum desiccator and weighed. For analysis of the condensed products a high-resolution time-of-flight (TOF) mass spectrometer (GCT Premier, Waters) with an atmospheric-pressure solids analysis probe (ASAP) was used. NMR spectra were acquired with NMR Bruker DRX 300 (¹H and ¹³C, 300.13 and 75.48 MHz, respectively). X-ray diffraction (XRD) patterns of the catalysts were obtained by a DRON-3 diffractometer operating at 40 kV and 30 mA, using CuK α radiation.

3. Results and discussion

After removing toluene from the reaction products, ketones were separated from the solid by column chromatography. It appeared that ketones were the main component of the solid product. Other

adie 2		
Results of control trials of 1-butanol conversion at 400 $^\circ$	² C before and after experiments with the C_{12} - C_{14}	4 primary alcohol fraction and regeneration.

Test Conversion Selectivity [%]							Yield [%]				
	[%]	Butene	n-Butanal	Dipropyl ketone	Butyl butyrate	Others	Butene	n-Butanal	Dipropyl ketone	Butyl butyrate	Others
Before	53	8	8	73	9	2	4	4	39	5	1
After	56	9	10	70	8	3	5	6	39	4	2

0

3500 before test after test and regeneration LaAIO3 (PDF2: 31-0022) 3000 LaMnO3 (PDF2: 35-1353) AI2O3 (PDF2: 29-0063) 2500 LaMnO3 (PDF2: 33-0713) intensity, a.u. - LaMnO 2000 1500 1000 500 0 20 40 60 80 2_O dea

Fig. 3. XRD patterns of LaMnO₃ perovskite supported on stabilized alumina before and after test and regeneration.

compounds were present in minor trace amounts, as it was confirmed by thin-layer chromatography. The best results of tests performed at 400 and 420 °C are shown in Table 1. It was found that at lower or higher reaction temperatures, conversion or selectivity is lower than these ones obtained at 400–420 °C. The semi-product, resulting from the reaction at 380 °C contained over 25% of unreacted alcohols. After the test at 420 °C, at the full conversion, the ketones efficiency dropped to 53.6%. The brownish product contained 46.4% of hydrocarbons and other unidentified compounds resulting from the cracking and the other side transformations [19,21,23].

The transformation follows the general reaction scheme [19,21]:

Thus, this transformation causes the loss of one carbon atom in relation to two molecules of alcohols, regardless of the length of the chain. Therefore, the atom economy of this method increases with increasing alcohol's carbon chain length. This difference in the carbon balance has been taken into account in the calculations below.

Since, during ketonization of equimolar mixture of primary alcohols RCH₂OH and R'CH₂OH, three ketones are produced in the quantitative relations resulting from the probability:

RCOR : RCOR' : R'COR' = 1/4 : 1/2 : 1/4 [21].

In this event, the average molecular weight of the mixture of ketones $C_{11}COC_{11}$, $C_{11}COC_{13}$ and $C_{11}COC_{13}$ is equal to 366 Da.

As the molar ratio of alcohols C_{12} : C_{14} in the raw material was = 3:1, one can assume that the probability of quantitative relations of received ketones will be close to:

RCOR : RCOR' : R'COR' = 5/8 : 1/4 : 1/8.

The expected average molecular weight of the mixture of so obtained ketones is 352 Da.

If we assume full conversion and selectivity only to ketones, the 3.14 g/h of raw material (including 1.57 g/h of alcohol fraction and

Acid	strength	distribution	determined	by	TPD	NH ₃	

Table 3

Sample	Concen	Concentration of acid centers with equal strength, %						
	473-	523-	573-	623-	673-	723-	773-	
	523 K	573	623	673	723	773	823	
La-Al ₂ O ₃	4.0	9.1	18.5	20.4	20.1	15.3	12.6	
$LaNinO_3/La-Al_2O_3$	5.2	14.9	20.9	20.9	17.2	13.5	7.3	

1.57 g/h of toluene) should yield 2.97 g/h of product containing 1.43 g/h of ketone fraction and 1.57 g/h of toluene. Since, at 400 °C the solid product was produced at 1.92 g/h, the difference 1.08 g/h can be related to evaporated toluene and unidentified by-products of the reaction. Solid product separated in this way still contained toluene. Drying in a desiccator resulted in a 36.5% weight loss. Thus, 1.22 g/h of ketone fraction was obtained at 400 °C. This represents an efficiency of 85.3% as compared to the theoretical value. Similarly, 1.70 g/h solid product was obtained at 420 °C. The greater difference (1.3 g/h) indicates a higher degree of toluene evaporation and a larger share of side destruction reactions and/or secondary condensations. Drying of such samples in a desiccator resulted in 38.1% weight loss. Thus, at 420 °C the ketone fraction was obtained with the efficiency 1.05 g/h, i.e. 73.4% yield in relation to the theoretical value.

Obtained fraction of ketones was characterized by means of GC– MS and NMR. The ¹³C NMR spectra (Fig. 1) revealed the 210 ppm signal of C-carbonyl group. Other signals should be assigned in descending order, starting from the CO group: 31.95 ppm—second carbon in chain, 29.65 ppm—third methylene carbon, etc. The last signal—22.73 ppm is assigned to methyl carbons. The ¹H NMR spectra (Fig. 2) show a triplet at 0.88 ppm (CH₃ group) and a large multiplet 1.25 ppm (CH₂ groups). These alpha and beta groups are shifted 2.38 ppm and 1.55 ppm, respectively. Additional signal at beta CH₂ (probably due to H₂O, shift 1.56) increases the integration by 2.

Results of GC–MS measurements have confirmed that material labeled as "ketone fraction" contains the expected ketones of high molar mass.

It was found that the catalyst's activity was stable during the run, exhibiting low tendency to formation of carbon deposits of resin and tar type accumulating on it. After the test catalyst remained in the reactor and was regenerated by heating at 470 °C for 4 h under air flow. Model test with the use of 1-butanol (Table 2) showed that both the fresh and the regenerated catalysts exhibit the same activity and selectivity for 1-butanol conversion. Also the XRD patterns of the LaMnO₃/La–Al₂O₃ material before and after catalytic test do not show noticeable differences (Fig. 3). LaMnO₃ is very well dispersed on the surface of La-stabilized alumina and only weak signals of lanthanum manganite are visible on the XRD pattern of both fresh and used material.

Properties of the LaMnO₃/La-Al₂O₃ catalyst are presented and discussed elsewhere [31]. Here it is worth to remind that this material possesses relatively high specific surface area (46.0 m²/g), concentration of basic and acidic sites 0.22 and 0.55 mmol/m², respectively. Results of cyclohexanol decomposition on this material show that dehydrogenation of cyclohexanol to cyclohexanone proceeds in higher extent than dehydration to cyclohexene (CHON/CHEN selectivity ratio 3.1) which suggests that basic sites are more reactive than acidic ones. This has significant implications for dehydrogenation. Nevertheless, the acid centers also play an important role in relation to the secondary conversion of aldehydes to ketones [30]. From TPD NH₃ analyses, we found that the total acidity of LaMnO₃/La-Al₂O₃ was as high as 0.284 mmol NH₃/g. For comparison the total acidity of Ladoped alumina carrier was measured and the value of 0.362 mmol NH_3/g was found. Higher acidity of carrier alone than catalyst supported on this material results from participation of acidic sites of alumina. These sites are then covered by less acidic mixed oxide deposited on the carrier's surface. It is worth to note that concentration of acidic sites determined for LaMnO₃/La-Al₂O₃ by TPD NH₃ method is lower than concentration determined previously by titration method. This difference is related with peculiar character of each procedure. Nevertheless, acidic sites are more abundant than basic ones.

The share of acid strength distribution is shown in Table 3. It can be clearly observed that deposition of 30 wt.% of LaMnO₃ develops mainly weak and medium acid sites (desorption temperature $T_d = 473-673$ K) at the charge of strong acid sites (T_d >773 K).

4. Conclusion

It was found that by using elaborated catalyst, one can transform the industrial fraction of primary alcohols of high molecular weight into fraction containing long-chain ketones. The high efficiency of ketones to the relatively large load of catalyst (1/2 of 3.7 cm³/h in relation to $3 \text{ cm}^3 = 0.62 \text{ h}^{-1}$) draws attention.

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