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Obtaining cyclopentanone in the presence of metal oxides

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Abstract

The possibility of obtaining cyclopentanone by pyrolysis of calcium adipate at different temperatures was considered. The pyrolysis proceeded with the formation of cyclopentanone and cyclopentene. The use of metal salts and metal oxide catalysts for the dehydrogenation of lower alkanes makes it possible to increase the yields of the target products. The best results were achieved in the presence of a «K-16u» catalyst.

Keywords

adipic acid
pyrolysis
cyclopentanone
cyclopentene
catalysts
metal oxides

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1. Introduction

In the period of development of the chemical and petrochemical industry, the main tasks are deep conversion, maximum use of feedstocks, and waste disposal. The problem of the impact of the chemical industry byproducts on the environment is being solved by the development of new technologies and advanced waste processing.

Water-acid effluents are formed in the process of obtaining caprolactam after isolation of the target product by washing the reaction mixture with water. Generally, incineration is used for the disposal of these effluents. However, they contain large amounts of oxygen-containing by-products. One of these compounds is adipic acid – a promising raw material for the production of cyclopentanone and other valuable monomers [1]. The content of adipic acid in water-acid effluents is significant. Theoretically, with a capacity of 100 thousand tons per year, 200–300 tons of adipic acid can be obtained.

Earlier, the possibility of obtaining cyclopentanone from byproducts of caprolactam production by pyrolysis of calcium salts of adipic acid was shown. The thermal stability study of calcium adipate using a Shimadzu DTG-60/60H derivatograph was carried out. Its decomposition temperature was 400 °C [2].

In this work, we study the thermal decomposition of adipic acid salts in the presence of metal oxides. The raw material is adipic acid, isolated from the water-acid effluent of the caprolactam production.

This work is aimed at improving the method for cyclopentanone production on the basis of water-acid effluents, studying the dependence of the yield of cyclopentanone on the process conditions, and investigating the possibility of using metal oxides as process catalysts.

2. Experimental

The pyrolysis was carried out in an electric furnace using a quartz reactor at different temperatures (from 400 to 600 °C) and a contact time of 2 hours. The masses calcium adipate samples were from 1.5 to 3.0 g. A refrigerator was attached to a quartz test tube, distillation adapter. A conical flask was used to collect the resulting product. Over time, a liquid product with a characteristic odor formed in the flask; the color of the liquid changed from light yellow to light brown, depending on the pyrolysis temperature.

The analysis of the obtained liquids composition was carried out using a Kristallux 4000M chromatograph with a flame ionization detector (capillary column, helium carrier gas, quartz, DB-WAX (PEG), 30 m/0.32 mm/0.5 μm).

Calcium adipate pyrolysis can proceed in two directions – with the formation of cyclopentanone and cyclopentene (Fig. 1). The composition of the resulting product included these compounds [3].

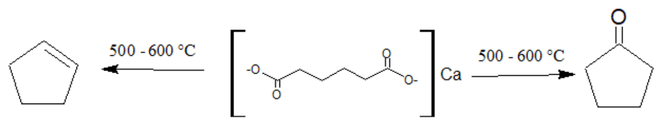

Fig. 1 Two directions of pyrolysis of calcium adipate

For the identification of retention times, pure substances were introduced into the chromatograph.

Cyclopentene was synthesized by acid dehydration of cyclopentanol. Cyclopentanol was obtained by reduction of cyclopentanone with sodium borohydride (Fig. 2) [4].

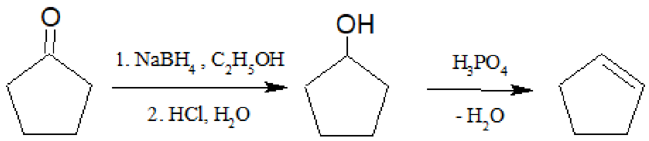

Fig. 2 Cyclopentene synthesis

The quantitative chemical analysis of calcium adipate was carried out using an EDX-8000 energy dispersive X-ray fluorescence spectrometer (X-ray tube – Rh anode, silicon drift detector); the results are presented in Table 1.

Table 1 The results of X-ray fluorescence analysis of calcium adipate

Analyte	Ca	Na	Mg	K	S	Zn	Cu	Cl
Result, wt.%	46.60	8.10	0.20	0.10	0.10	0.05	0.02	<0.01

3. Results and discussion

The chromatograms of the samples obtained at 500 and 600 °C are shown in Fig. 3. The chromatograms of cyclopentanone and cyclopentene are shown in Fig. 4. The difference between the retention times of pure substances and the obtained samples is due to the presence of impurities in the technical products.

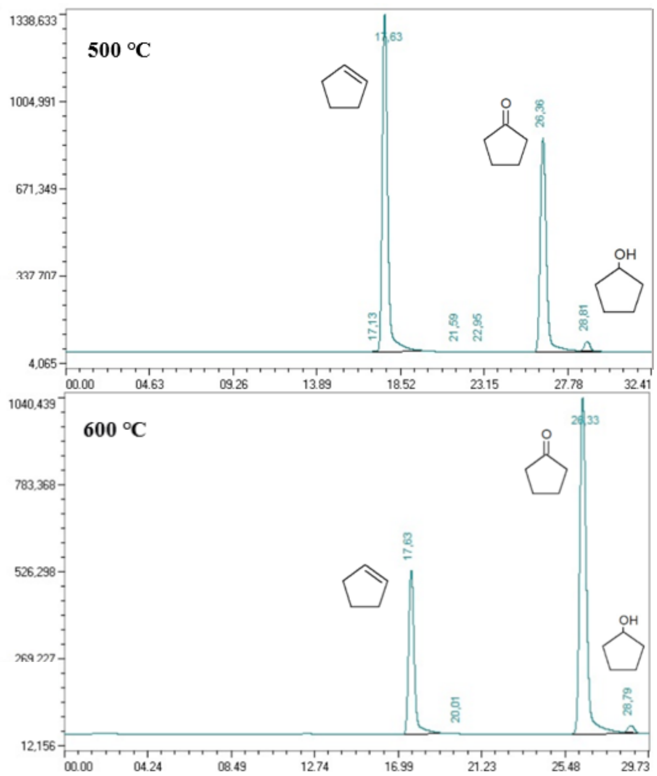

Fig. 3 Chromatograms of a liquid product obtained at 500 and 600 °C

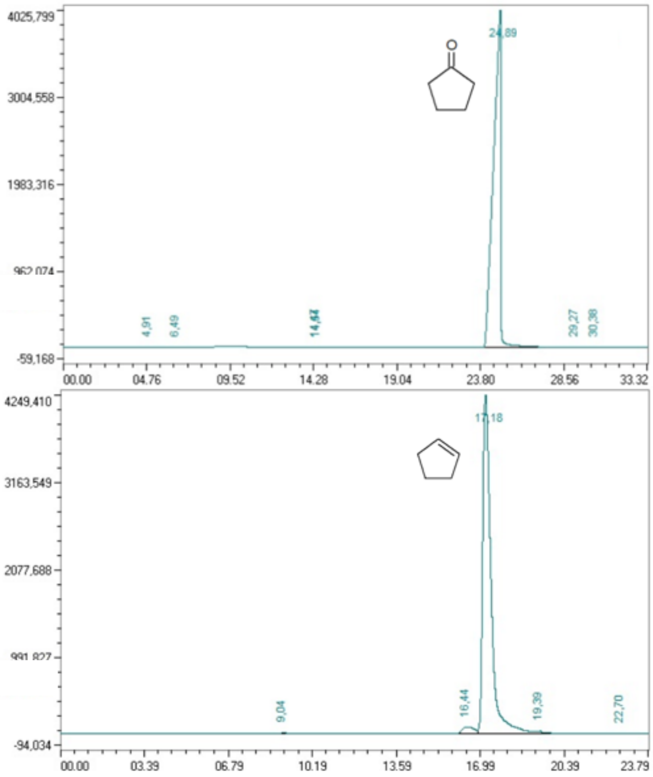

Fig. 4 Chromatograms of pure cyclopentanone and cyclopentene

Based on the results of X-ray fluorescence analysis, calcium phosphate and zinc chloride were chosen to study the possibility of using metal salts as catalysts for the process. The chromatograms of the products obtained during pyrolysis are shown in Fig. 5 and Fig. 6.

The results obtained in the presence of zinc chloride suggest that it is possible to use dehydrogenation catalysts (two- and three-component mixtures of metal oxides). The «K-16u» and «IM-2201» catalysts were tested.

The «K-16u» catalyst can be represented by the formula $Fe_2O_3 \cdot Cr_2O_3 \cdot ZnO_2$. It is used in the dehydrogenation of butylenes and isoamylenes [5].

The chromatograms of liquid products obtained using the «K-16u» catalyst at temperatures of 500 and 600 °C are shown in Fig. 7.

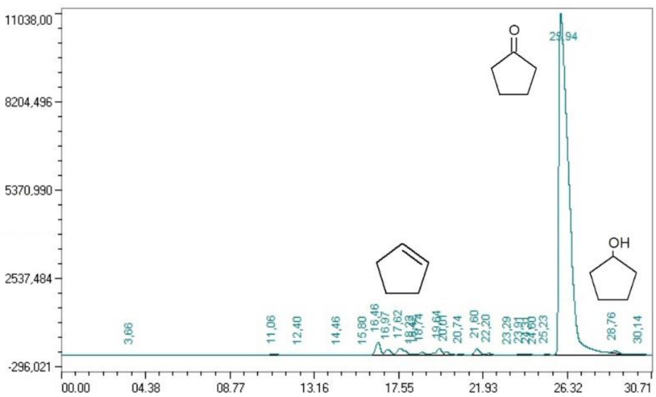

Fig. 5 Chromatogram of the product obtained at 500 °C in the presence of calcium phosphate

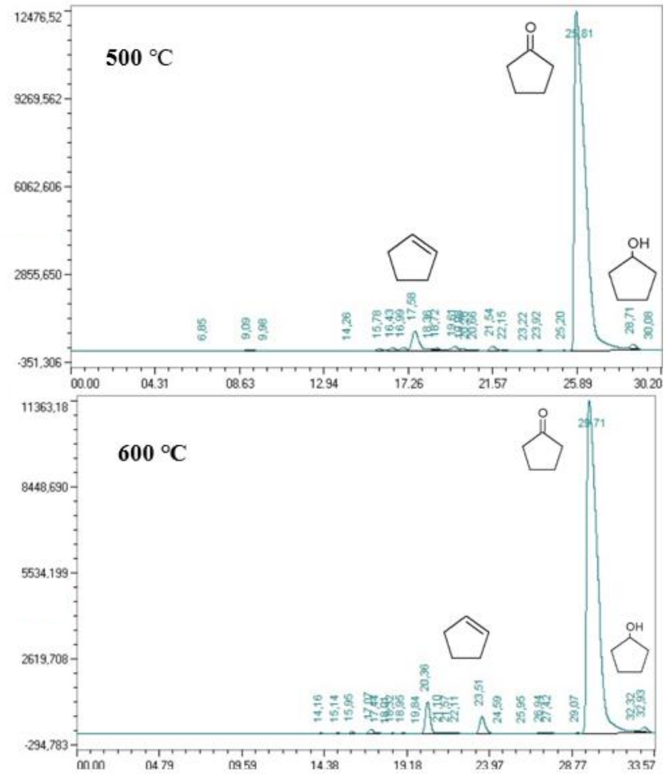

Fig. 6 Chromatograms of the product obtained at 500 and 600 °C in the presence of zinc chloride

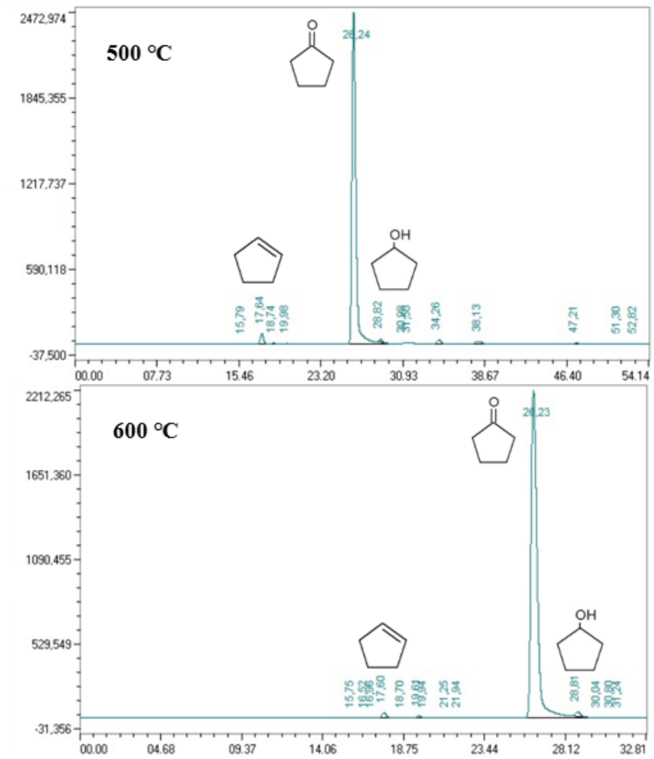

Fig. 7 Chromatograms of the product obtained at 500 and 600 °C in the presence of «K-16u» catalyst

The «IM-2201» catalyst is a chromium-alumina catalyst (Al_2O_3·Cr_2O_3), using for the dehydrogenation of butane, isopentane and isobutane. The chromatograms of liquid products obtained using the «IM-2201» catalyst at temperatures of 500 and 600 °C are shown in Fig. 8.

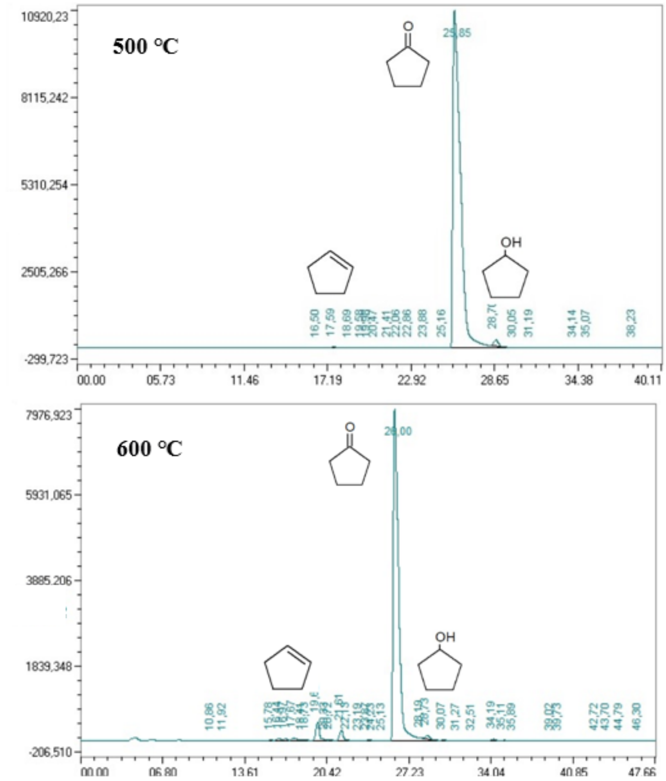

Fig. 8 Chromatograms of the product obtained at 500 and 600 °C in the presence of the «IM-2201» catalyst

A comparison of the results of pyrolysis of calcium adipate in the presence of catalysts is shown in Table 2. The dependence of the cyclopentanone yield on the catalyst is shown in Fig. 9.

Table 2 Comparison of the results of pyrolysis of calcium adipate in the presence of catalysts

Catalyst	№	Process conditions		Cyclopentanone yield, wt.%
		t, h	*T*, °C	
Without catalyst	1	2	600	16.81
«K-16u» (Fe_2O_3·Cr_2O_3·ZnO_2)	2	2	500	34.14
	3	2	600	51.62
	4	2	700	42.05
$ZnCl_2$	5	2	500	23.70
	6	2	600	29.27
«IM-2201» (Al_2O_3·Cr_2O_3)	7	2	500	4.99
	8	2	600	24.56
$Ca_3(PO_4)_2$	9	2	500	17.88

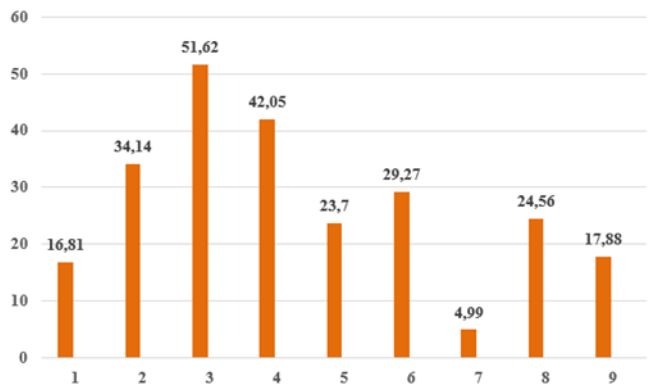

Fig. 9 The dependence of the cyclopentanone yield on the catalyst see Table 2

4. Conclusion

According to the results of pyrolysis of calcium adipate in the presence of oxides and metal salts, it was found that the highest product yield is achieved using the «K-16u» catalyst for the dehydrogenation process. In addition to cyclopentanone, cyclopentene is formed. Its maximum yield is reached at 500 °C. The developed method of pyrolysis of calcium adipate can be used to obtain valuable substances for organic synthesis – cyclopentanone and cyclopentene.

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