TRANSFORMATIONS OF METHYL ESTER OF CYCLOHEXANECARBOXYLIC ACID IN THE PRESENCE OF Co-KIESELGUHR CATALYST

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The heterogeneous catalytic transformations of carboxylic acid esters have received comparatively little study. The reaction that has been studied in greatest detail is the decomposition of an ester to the free acid and olefinic hydrocarbon. Even Sabatier [1] found that ethyl benzoate was converted at 400°C and atmospheric pressure, in the presence of ThO₂, to C_6H_5COOH and C_2H_4 . Esters reacted in a similar manner at 300-330° under their own vapor pressure in the absence of a catalyst [2]. The ethyl esters of acetic, propionic, and butyric acids formed over Al_2O_3 , at 400° and atmospheric pressure, symmetrical ketones, CO_2 , C_2H_4 , and H_2O [3]. Under the conditions for the carbonylation of unsaturated hydrocarbons or alcohols with carbon monoxide at 300° under pressure, in the presence of compounds of the group VIII metals (Co, Ni, and Fe) [4], the formed esters also underwent partial decomposition [5]. Ethyl propionate, during its synthesis from C_2H_4 , CO, and C_2H_5OH , in the presence of the halides of CO, Ni, and Fe, began to decompose even at 200°, while at 300° the decomposition went to the extent of 75%, with the formation of C_2H_4 , CO_2 , H_2 , C_2H_6 , and traces of CH₄ and C_2H_5CHO [6]. Methyl propionate reacted in a similar manner [7].

In the present paper are reported some results of studying the transformations of an alicyclic carboxylic acid ester, namely the methyl ester of cyclohexanecarboxylic acid, on a precipitated Co-kiesel-guhr catalyst.

EXPERIMENTAL

The starting methyl ester of cyclohexanecarboxylic acid, bp 181.1-181.3° (760 mm); d_4^{20} 0.9785; n_D^{20} 1.4438, found MR 38.40, calculated 38.50, was synthesized by the hydrocarbalkoxylation of cyclohexene using formic acid in the presence of sulfuric acid, with the subsequent addition of methanol to the reaction mixture [8]. Then the ester was separated from its mixture with the simultaneously formed methyl ester of methylcyclopentanecarboxylic acid by fractional distillation through a column with an efficiency of 40 theoretical plates.

The transformations of the ester were studied in equipment of the flow type, equipped with a quartz tube reactor having an inside diameter of 20 mm, at atmospheric pressure and temperatures of 350, 400, and 450°. The catalyst that was used, having a 1:1 Co – kieselguhr composition, was prepared by the precipitation of Co nitrate solution with sodium carbonate in the presence of kieselguhr (Kisatibi), followed by reduction at 450° and a hydrogen space velocity of 100 h⁻¹ [9]. The liquid catalyzates, collected in a trap at -80° , were analyzed on an LKhM-3 chromatograph (length of column 2 m and diameter 6 mm, liquid phase = poly(ethylene glycol adipate), carrier gas = helium, and detection by the heat conductivity); the gaseous reaction products were analyzed by absorption in solutions and on a KhT-2M chromatograph. The obtained results are given in Table 1.

In each experiment 0.05 mole of the methyl cyclohexanecarboxylate was passed over a freshly reduced catalyst portion, having a volume of either 10 or 40 cm³, with a space velocity of respectively either 0.8-0.9 or $0.2 h^{-1}$. The amount of coke on the catalyst was determined by burning and determination of the CO_2 .

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н Щ о	Space velocity of ester, h ⁻¹	Conversion of ester, %	Yield of liquid catalyzate, wt. %	Yield, moles per mole of reacted ester								
Reaction te perature, °(benzene	toluene	cyclohe- xene	cyclo- hexane	CO2	со	CH4	C ₂ H ₆	H ₂
350 400 450 350 400 450	0,80 0,94 0,83 0,20 0,22 0,20	29,5 59,8 73,5 61,0 91,5 100	87,2 64,0 30,1 63,7 16,7 0,0	32,0 40,0 5,5 21,9 9,9 —	7,7 8,9 1,3 9,9 2,8	1,9 15,9 0,8 11,5 1,7	3,7 4,0 0,3 1,6 0,6	$ \begin{array}{r} 12,3 \\ 36,0 \\ 39,8 \\ \hline 65,4 \\ \\ \\ \end{array} $	20,711,531,7 $-21,2$	35,6 50,4 15 23,0	2, <u>1</u> 1,0	305 254 326 200

 TABLE 1. Catalytic Transformations of Methyl Ester of Cyclohexanecarboxylic Acid

At an ester space velocity of $0.8-0.9 \text{ h}^{-1}$ an increase in the reaction temperature from 350 to 450° caused a decrease in the yield of the liquid catalyzate by a factor of 2.9, and an increase in the ester conversion by a factor of 2.5, while the yield of coke and polymeric formations on the catalyst surface increased from 48 to 69% (when based on the carbon of the reacted ester). The liquid reaction products represented aromatic and alicyclic hydrocarbons containing a six-membered ring: benzene, toluene, cyclohexene and cyclohexane. Their maximum yields were obtained at 400° and space velocity of 0.94 h^{-1} , and respectively were 0.40, 0.09-0.16, and 0.04 mole per mole of reacted ester. The gaseous reaction products contained H₂, CH₄, CO₂, and CO, which were formed in low yields at 450°, and respectively were 3.26, 1.59, 0.40, and 0.32 mole per mole of reacted ester. At an ester space velocity of 0.2 h^{-1} an increase in the reaction temperature from 350 to 450° led to an increase in the ester conversion from 61 to 100%, and a decrease in the yield of liquid catalyzate from 63.7 to 0.0%.

With decrease in the space velocity of the ester from 0.8-0.9 to 0.2 h^{-1} its conversion at 350, 400, and 450° increased by 2.1, 1.5, and 1.3 times, while the yield of liquid catalyzate decreased by 1.3 times at 350°, and by 3.8 times at 400°, while at 450° it dropped from 30% to 0. Simultaneously, the formation of coke and polymeric products on the catalyst surface increased, the yield of which at 400° reached 84% when based on the carbon of the reacted ester. The character of the liquid and gaseous products remained constant, but the yields when based on reacted ester decreased sharply: at 350 and 400° the yields of benzene decreased by 1.5 and 4 times, of toluene by 3.1 times, of cyclohexene by 8.1 times, of cyclohexane by 6.6 times, and of CH₄ by 2.2 times at 400°, while the following yields increased: of toluene by 1.3 times, of cyclohexene by 6.0 times at 350°, and of CO₂ and CO by 1.8 times at 400°.

From the presented data it can be seen that under the studied conditions the methyl ester of cyclohexanecarboxylic acid undergoes a number of transformations, dehydrodecarboxylation with the formation of CO_2 , H_2 , and toluene, with the intermediate formation of methylcyclohexane, demethylation and simultaneous decarboxylation, with the formation of CO_2 , CH_4 , and cyclohexene, which then is dehydrogenated to benzene, and, finally, decarboxylation with the formation of cyclohexene, two molecules of CO and H_2 , in which connection the intermediate formation of methanol is possible [7].

The formation of coke on the catalyst surface is quite intense. These transformations can be depicted by the following scheme:



It could be depicted that CO is also formed according to the reaction: $CO_2 + H_2 \approx CO + H_2O$, but water was not detected in the reaction products.

CONCLUSIONS

The methyl ester of cyclohexanecarboxylic acid in the presence of a precipitated Co-kieselguhr catalyst, at atmospheric pressure and temperatures of $350-450^\circ$, undergoes a number of transformations with the formation of mainly coke, benzene, toluene, cyclohexane, cyclohexane, and the gaseous products: CO₂, CO, CH₄, and H₂.

LITERATURE CITED

- 1. P. Sabatier and A. Mailhe, Compt. Rend., 152, 663 (1911).
- 2. A. Colson, Compt. Rend., 147, 1054 (1908).
- 3. J. B. Sendersens, Bull. Soc. Chim. France [4], 5, 482 (1909).
- 4. Ya. T. Eidus and K. V. Puzitskii, Usp. Khim., 33, 991 (1964).
- 5. S. K. Bhattacharyya and S. K. Palit, J. Appl. Chem. (London), 12, 174 (1962).
- 6. S. K. Bhattacharyya and S. N. Nag, J. Appl. Chem. (London), 12, 182 (1962).
- 7. S. K. Bhattacharyya and S. N. Nag, Brennstoff-Chem., 43, 114 (1962).
- 8. Ya. T. Eidus, M. B. Ordyan, L. I. Shokina, and M. A. Kanevskaya, Zh. Organ. Khim., 2, 266 (1966).
- 9. Ya. T. Eidus, N. I. Ershov, K. V. Puzitskii, and I. V. Guseva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 913 (1960).