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CATALYTIC HYDROGENOLYSIS OF ALKYLFURANS

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The vapor-phase conversion of α-methylfuran and α-methyltetrahydrofuran on a sodium- and potassium-activated palladium catalyst in a stream of hydrogen at atmospheric pressure at 200-450°C was investigated. Hydrogenolysis of α-methylfuran and isomerization of α-methyltetrahydrofuran to give 2-pentanone in both cases occur at 300° with identical selectivities. It is assumed that aliphatic ketones are formed from the alkylfurans on this catalyst via a parallel-consecutive scheme through direct hydrogenolysis of the alkylfurans and isomerization of their tetrahydro derivatives, which are formed as intermediates.

A considerable number of studies have been devoted to the problem of the vapor-phase hydrogenolysis of alkylfurans (for example, see [1, 2]). Metals on carbon, Raney nickel catalysts, nickel on metal oxides, etc. have been tested as catalysts. All of them, except for palladium, are typical catalysts for the hydrogenolysis of the furan ring. Palladium is distinguished by a clearly expressed capacity for hydrogenation of the double bonds of the furan ring over a broad range of temperatures, and its tendency to bring about hydrogenolysis is manifested to only a slight degree.

We have shown that, depending on the conditions used to carry out the catalytic process, activated palladium changes its selectivity and acts as a catalyst for hydrogenation of hydrogenolysis of the furan ring. The vapor-phase conversion of α-methylfuran in a stream of hydrogen at atmospheric pressure on sodium- and potassium-activated palladium catalysts at 200-450° was investigated. The selectivity of this catalyst depends on the temperature at which the catalytic reaction is carried out (Fig. 1).

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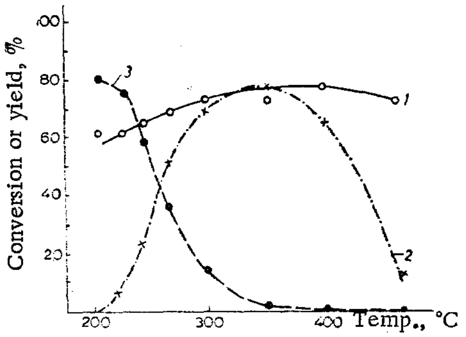


Fig. 1. Effect of the temperature on the activity and selectivity of an activated palladium catalyst (reaction of α-methylfuran): 1) conversion of α-methylfuran; 2) yield of 2-pentanone; 3) yield of α-methyltetrahydrofuran (based on the converted α-methylfuran).

TABLE 1. Effect of the Temperature on the Composition of the Contact Gases Formed during the Vapor-Phase Reactions of α-Methylfuran and α-Methyltetrahydrofuran on an Activated Palladium Catalyst

Starting compound	Temp., °C	Composition of the contact gases, vol. %				
		H_2	CO_2	CO	C_nH_{2n}	C_nH_{2n+2}
α-Methylfuran	200	99,5	0	0,5	0	0
	350	92,7	1,4	1,6	0,3	4,0
	450	64,1	5.6	10,6	2,5	17,2
α-Methyltetrahydrofuran	200	97,8	0,9	1,0	0	0,3
	350	76,5	6,5	7,5	1,5	8,0
	450	65,2	4,2	13,6	3,7	13,3

Below 200° it is a typical catalyst for the hydrogenation of the double bonds of α-methylfuran, and this is in agreement with the literature data; above this temperature (up to 350°) it takes on the character of a catalyst for hydrogenolysis of the furan ring at the C–O bond that is not adjacent to the methyl group, and this leads to 2-pentanone. Cracking processes increase during catalysis at temperatures above 350°, as attested to by the decrease in the yield of the liquid catalyzate and the change in the composition of the contact gases (Table 1).

According to one point of view, the formation of aliphatic ketones from alkylfurans is the result of direct hydrogenolysis of alkylfurans; according to another point of view, it is the result of isomerization of the intermediate alkyltetrahydrofurans.

The higher stability of the tetrahydrofuran ring as compared with the furan ring over certain catalysts (nickel, platinum, and copper chromite) [1] is a confirmation of the first point of view. However, one cannot exclude the possibility that the picture may change to the other point of view over other catalysts, including palladium. To clarify this problem we also investigated the conversion of α-methyltetrahydrofuran, which is assumed to be the intermediate in the formation of 2-pentanone, over a potassium- and sodium-activated palladium catalyst under similar conditions.

The experimental results (Fig. 2) showed that α-methyltetrahydrofuran undergoes conversion via three pathways – isomerization, dealkylation, and dehydrogenation – to give 2-pentanone, tetrahydrofuran, and α-methylfuran, respectively. Cracking processes increase at temperatures above 300° (Table 1).

Thus, 2-pentanone is formed from both α-methylfuran and from α-methyltetrahydrofuran with identical and quite high selectivities on the tested catalyst under identical conditions. It may be assumed that the formation of 2-pentanone from α-methylfuran on the palladium catalyst may be realized simultaneously both by direct hydrogenolysis and as a result of isomerization of the intermediate α-methyltetrahydrofuran.

On the basis of the results of our study it may be assumed that, depending on the conditions under which the catalytic reaction is carried out and the nature of the catalysts, the vapor-phase conversion of alkylfurans is realized via different mechanisms. Whereas aliphatic ketones are formed from alkylfurans on catalysts that are incapable of bringing

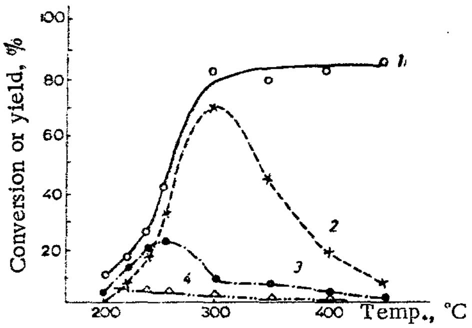
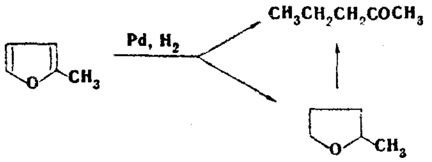


Fig. 2. Effect of temperature on the activity and selectivity of an activated palladium catalyst (reaction of α-methyltetrahydrofuran): 1) conversion of α-methyltetrahydrofuran: 2) yield of 2-pentanone; 3) yield of α-methylfuran; 4) yield of tetrahydrofuran (based on the converted tetrahydrofuran).

about izomerization of the tetrahydrofuran ring by direct hydrogenolysis, the formation of ketones may be the result of two parallel reactions — hydrogenolysis of the alkylfurans and isomerization of the resulting intermediates of their tetrahydro derivatives — on catalysts that have this capacity. The formation of 2-pentanone may be represented by the following scheme on an activated palladium catalyst that is effective both in the hydrogenolysis of α-methylfuran and in the isomerization of α-methyltetrahydrofuran:



EXPERIMENTAL

The vapor-phase catalytic reactions of α-methylfuran and α-methyltetrahydrofuran were carried out at atmospheric pressure in a stream of hydrogen in a flow apparatus. An industrial palladium catalyst on activated charcoal (1.8% Pd) activated by potassium and sodium carbonates was used as the catalyst. The catalyzer (38 ml) prior to the start of the experiments in the contract tube was treated with hydrogen at 180° for 3 h and for another 2 h at 240°. The experiments were carred out at 200-450° at an α-methylfuran feed rate of 13 g/h (the α-methyltetrahydrofuran feed rate was 13.5 g/h); the hydrogen feed rate in both cases was 3.8 liters/h, and the experimental time was 1 h. The composition of the liquid catalyzate was determined by gas—liquid chromatography with a Tsvet-1 chromatograph with a thermal-conductivity detector. The chromatographic conditions were as follows: the column dimensions were 2 mm by 2 m, the stationary liquid phase was dinonyl phthalate (30%) on Chromosorb W, the temperature was 74°, and the carrier gas (hydrogen) feed rate was 10 ml/min. The contact gases were analyzed with a VTI-2 gas analyzer.

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