TRANSFORMATIONS OF HETEROCYCLIC COMPOUNDS
ON MEMBRANE CATALYSTS

I. HYDROGENATION OF FURAN COMPOUNDS ON A Pd—Ni ALLOY

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The transformations of furan, α-methylfuran, furfural, and 2,3-dihydrofuran on a palladium—nickel membrane catalyst at 50-300°C under conditions of diffusion of hydrogen through the catalyst were investigated. Under these conditions furan is hydrogenated to tetrahydrofuran in quantitative yield. Considerable amounts of furan, the hydrogenation of which in the presence of the above-named derivatives is inhibited, are detected in the catalyzate along with hydrogenation products in the transformations of α-methylfuran, furfural, and 2,3-dihydrofuran.

Membrane catalysts have been found to be effective for the realization of a number of transformations of aromatic and aliphatic compounds that occur with the participation of hydrogen [1]. An assumption regarding the promising character of the utilization of the principle of interlinked reactions on membrane catalysts in the catalytic transformations of heterocyclic compounds has been expressed. The present paper is devoted to a study of the transformations of furan compounds on a palladium—nickel membrane catalyst. The transformations of furan and its closest homologs on ordinary palladium catalysts under conditions of vapor-phase hydrogenation have been studied by a number of authors, and it has been shown that furan and 2-methyl-, 2-ethyl-, and 2-propylfurans are hydrogenated to the corresponding tetrahydro derivatives in 70-100% yields on palladium-coated asbestos or carbon at 150-170°C. At higher temperatures (275°) on palladium applied to carbon, α-methylfuran undergoes partial hydrogenolysis to give 2-pentanone in yields up to 30%, whereas under pulse-operation conditions 2-pentanone is obtained in 60-70% yield [3, 4].

The hydrogenation of furan on a palladium—nickel membrane catalyst takes place to a considerable degree even at 75°, whereas the yield of tetrahydrofuran (THF) reaches 100% at 120-150° (Fig. 1). At higher temperatures (200°) the furan molecule undergoes disintegration to give volatile hydrocarbons. α-Methylfuran, like furan itself, is completely hydrogenated to α-methyltetrahydrofuran at 150°. As the temperature is raised, hydrogenation of the double bonds is accompanied by demethylation of α-methylfuran, as a consequence of which furan is detected in the catalyzate (Fig. 2). This phenomenon is observed only on

TABLE 1. Results of Experiments on the Hydrogenation of 2,3-Dihydrofuran (DHF) on a Membrane Catalyst in Excess Hydrogen

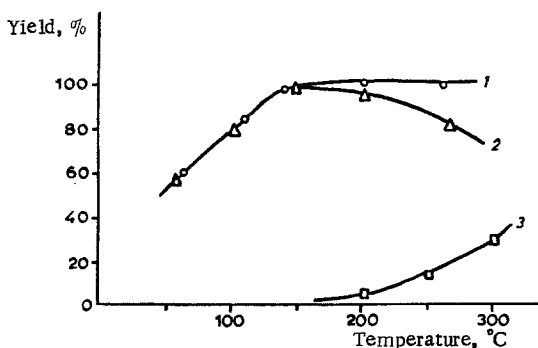| Temp., °C	Conversion of DHF, %	Yield, %		Selectivity, %	
		furan	THF	for furan	for THF
100	44	25	14	57	32
150	62	40	16	64	26
200	85	45	28	53	33

Fig. 1. Conversion of furan (1) and yields of products of hydrogenation of furans — THF (2) and volatile hydrocarbons (3) — as a function of the temperature.
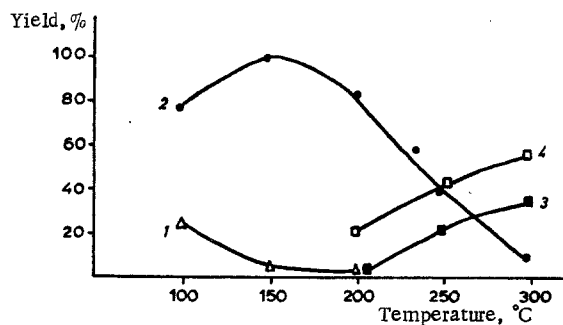
Fig. 2. Dependence of the compositions of the catalyzates from the hydrogenation of α-methylfuran on the temperature: 1) α-methylfuran; 2) α-methyltetrahydrofuran; 3) furan; 4) light hydrocarbons.

a membrane catalyst, inasmuch as the furan ring undergoes hydrogenolysis with primary cleavage of one of the carbon—oxygen bonds on palladium on supports at high temperatures (275°), and this leads to the formation of the corresponding ketones. However, their development should not be considered to be the result of isomerization of α-methyltetrahydrofuran; thus in special experiments we showed that both THF and α-methyl-THF are stable at 100-300° on a membrane palladium—nickel catalyst. We found that the conversion of furan to THF is suppressed considerably in the presence of dihydrofuran (DHF), and its degree of conversion at 200° does not reach 50%. It was shown by chromatography that the redistribution of hydrogen in 2,3-dihydrofuran, which is known to take place on ordinary applied palladium catalysts, does not occur on the palladium—nickel membrane in the absence of hydrogen, whereas THF is formed in considerably smaller amounts than furan (Table 1) in excess hydrogen; this is possibly due to blocking of the surface of the membrane by the products of polycondensation of dihydrofuran. The results of experiments with furfural, which causes an accelerated decrease in the activity of the membrane catalyst, also constitutes evidence for the occurrence of parasitic processes involving resinification of the membrane catalyst. Hydrogenation of the carbonyl group to give furfuryl alcohol occurs primarily in the presence of excess hydrogen at 100-150°, and the carbonyl group is eliminated (to give furan) as the temperature is raised to 200-300°. Thus the experiments on the conversion of α-methyl-THF, DHF, and furfural constitute evidence for competition for the active centers of the membrane catalyst and for the ability of the cited derivatives to deactivate the catalyst with respect to the hydrogenation of furan.

EXPERIMENTAL METHOD

The experiments were carried out at atmospheric pressure under pulse nonchromatographic conditions with a catalytic apparatus connected directly to a gas chromatograph; a seamless tube made from a Pd alloy with 5.5%Ni [5] was used as the membrane catalyst. Hydrogen or a mixture of hydrogen with a carrier gas was fed into the inner circuit of the reactor, and the carrier gas (argon), in the stream of which pulses (10^{-5}-10^{-6} mole) of the investigated substances were introduced through a special injection device, flowed within the palladium—nickel tube. Inasmuch as the inner and outer circuits are not in communication with one another, the diffusion of hydrogen from the inner circuit of the glass reactor within the palladium tube was followed with a catharometer. The carrier gas, hydrogen, and air were purified by the method in [6]. Prior to each series of experiments, the reactor was heated in a stream of the carrier gas to the necessary temperature, after which hydrogen was fed into the outer contour of the reactor by means of a fine-regulation stopcock. The catalyst was regenerated in a stream of air for 1 h at 400°, and the catalyst was activated with hydrogen for 2-4 h after purging with the carrier gas.

The starting compounds and the reaction products were analyzed with the flame-ionization detector of a Khrom-3 chromatograph. The analytical conditions were as follows: 6 mm by 2.0 m steel column, Celite-545 (60-80 mesh) support, 30%Se-30 liquid phase, column temperatures 90 and 160°, and argon flow rate 60 ml/min. The starting compounds were fractionated twice with a rectification column prior to introduction into the reactor.

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