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CATALYTIC HYDROGENATION OF THIOPHENE TO THIOLANE IN THE GAS PHASE

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The hydrogenation of thiophene in the gas phase in the presence of palladium-sulfide catalyst leads to the production of thiolane and hydrogenolysis products (butane and hydrogen sulfide), which are formed during the decomposition of the thiophene and thiolane. The hydrogenation rate of thiophene increases with increase of its content in the reaction mixture and also with increase of the hydrogen pressure and is reduced by thiolane. The yield of thiolane calculated on the reacted thiophene is 70-90% with 30-60% conversion of the thiophene.

Keywords: thiophene, catalytic hydrogenation.

The selective catalytic reduction of thiophenes to the practically useful thiolanes has been investigated quite thoroughly in the liquid phase. The most active, selective, and stable catalysts of this process are the sulfides of metals of group 8 and rhenium [1-3]. In the liquid-phase hydrogenation of thiophene there are hindrances related to the separation of catalyst and products from the reaction mixture. It was therefore interesting to develop a method free from this disadvantage for the hydrogenation of thiophenes in the gas phase.

Most publications on the gas-phase hydrogenation of thiophenes as model compounds in the hydropurification of petroleum products at Mo, W, Ni, and Co catalysts indicate that hydrogenolysis mostly occurs during the hydrogenation of thiophene with the release of hydrocarbons and hydrogen sulfide and that thiolane is only formed in small amounts under certain conditions [1, 2, 4, 5]. Nickel-zeolite catalysts are more active in the production of thiolane, but they are quickly deactivated in the hydrogenation process [6, 7].

In the present work we investigated the relationships governing the hydrogenation of thiophene in the gas phase in the presence of palladium-sulfide catalyst.

Experiments on the effect of the conditions on the direction of transformation of thiophene and the hydrogenation rate were conducted at 200-260°C, hydrogen pressure 0.2-3.1 MPa, initial thiophene concentrations (C_0) 0.9-4.9 vol. %, and various contact times (τ). In addition to unreacted thiophene, the reaction products contained thiolane, hydrogen sulfide, and butane. Some of the results are presented in Table 1. As seen, at constant temperature, hydrogen pressure, and initial thiophene concentration the conversion of the thiophene (X) and yield (Y) of the hydrogenolysis product H_2S* increase with increase in the contact time, while the yield of thiolane calculated on the initial thiophene increases up to a certain limit and then decreases. The catalyst does not change its initial activity for at least 70 h. (Longer experiments were not undertaken.)

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* Here and subsequently the yield of one of the hydrogenolysis products H_2S is given, since in all the experiments the yields of H_2S and butane coincided within the experimental accuracy limits.

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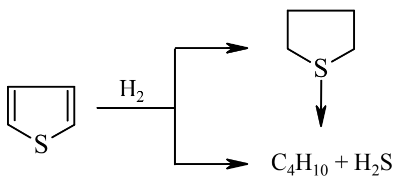
TABLE 1. Hydrogenation of Thiophene in the Presence of Palladium-Sulfide Catalyst ($C_0 = 1 \pm 0.1$ vol. %)

Contact time, τ, sec	Conversion, X, %	Yield, Y, mole %		Selectivity in thiolane, S, %	Contact time, τ, sec	Conversion, X, %	Yield, Y, mole %		Selectivity in thiolane, S, %
		thiolane	H_2S				thiolane	H_2S	
240°C, $P = 0.2$ MPa					240°C, $P = 3.1$ MPa				
0.3	35	22	12	63	2.1	43	35	6	81
0.6	40	26	15	65	2.4	33	27	7	82
0.9	50	28	21	56	4.5	71	45	24	63
2.0	64	19	43	30	7.8	81	42	38	52
240°C, $P = 0.5$ MPa					200°C, $P = 2.1$ MPa				
0.6	40	24	14	60	7.0	20	18	2	90
1.3	51	29	20	57	11.2	33	30	3	91
2.9	65	24	41	37	21.2	46	34	11	74
4.6	69	21	46	30	23.0	60	30	28	50
240°C, $P = 1.4$ MPa					220°C, $P = 2.1$ MPa				
0.8	36	24	10	67	5.9	31	26	3	84
1.9	52	35	16	67	8.3	44	37	7	84
5.9	61	37	24	61	10.7	58	38	18	66
9.9	67	37	31	55	22.6	67	32	34	48
240°C, $P = 1.0$ MPa					240°C, $P = 2.1$ MPa				
0.6	28	20	6	71	0.4	23	20	3	87
1.3	44	30	15	68	0.9	31	26	4	84
2.0	50	35	16	70	3.0	58	43	14	74
2.9	62	40	20	64	8.0	75	36	40	48
4.4	68	33	34	49	18.0	78	25	52	32
6.9	74	30	32	41	7.5[d]	59	44	14	75
8.3	8.0	22	57	28	1.0[e]	52	40	12	76
240°C, $P = 1.0$ MPa, $C_0 = 2.8$-4.9 vol. %					260°C, $P = 2.1$ MPa				
*8.0[a]	56	36	18	65	0.6	28	20	6	71
2.0[b]	27	20	8	74	1.0	40	27	12	68
9.1[b]	46	35	10	76	1.3	65	31	32	48
6.3[c]	47	33	12	70	3.5	89	21	66	24

The selectivity in relation to the thiolane (S) and hydrogen sulfide does not change with increase in the conversion of the thiophene up to a certain limit; the selectivity in the thiolane then decreases, while that in hydrogen sulfide increases (Table 1). These results make it possible to conclude that hydrogenation under the investigated conditions takes place in a parallel–consecutive scheme:



The degree of conversion of thiophene at which the selectivity among the products remains constant depends on the reaction conditions. For example, at 240°C and C_0 ~1 vol. % constancy in the selectivity is observed up to $X = 40$-50%, and in this range it increases with increase in the hydrogen pressure:

P, MPa	0.2	0.5	1.0	1.4	2.1	3.1
S, %	64	66	72	74	82	84

At various temperatures with $P = 2.1$ MPa and $C_0 = 1$ vol. % the selectivity remains constant up to $X = 30$-45%, and in this range it decreases with increase in the hydrogenation temperature:

T, °C	200	220	240	260
S ,%	94	90	82	70

If the initial concentration of thiophene is increased its conversion and the yields of the reaction products are reduced (see the experiments at 240°C and $P = 1.0$ and 2.1 MPa in Table 1). In order to determine the reaction orders experiments were carried out with various contact times and with the other conditions constant. From the kinetic curves we determined the contact time at which $X = 50\%$ and calculated the average rate of hydrogenation of thiophene and the average values of the variable parameters. It was found that at 240°C and $P = 1$ MPa the rate of the overall transformation of thiophene (W), referred to its current concentration (C), decreases with increase in the current concentration of thiolane ([TAN]):

[TAN], vol. %	0.16	0.20	0.31	0.44	0.62	0.70
W/C, mmol/g·h (vol. %)$^{-1}$	6.3	4.6	2.93	2.3	1.5	1.0

Under the same conditions the rate of the overall transformation of thiophene (with due regard to the concentration of thiolane) increases with increase in the current concentration of thiophene:

C, vol. %	0.6	0.8	1.0	2.0	2.4	3.2	4.0
W[TAN], mmol/h·g, vol. %	0.5	0.6	0.81	1.6	2.1	2.4	3.2

Increase of the hydrogen pressure in the system helps to increase the rate of the overall transformation of thiophene, referred to the value of $C[\text{TAN}]^{-1}$; here the selectivity in the thiolane also increases:

P, MPa	0.2	0.5	1.0	1.4	2.1	3.1
$W/C[\text{TAN}]^{-1}$, mmol/g·h	0.26	0.42	0.61	0.81	1.22	1.65
S, %	56	58	66	68	80	82

From the logarithmic dependence of the reaction rates of the partial pressures of the components or the overall pressure of hydrogen it was established that the hydrogenation of thiophene has first and minus first order with respect to thiophene and thiolane respectively; the order in hydrogen is 0.7.

Increase in the temperature leads to an increase in the reaction rate and a decrease in the selectivity with respect to thiolane. Thus, at $P = 2.1$ MPa, $C_0 = 1$ vol. %, and $X = 50\%$ the following results were obtained:

T, °C	200	220	240	260
$W/C[\text{TAN}]^{-1}$	0.14	0.33	0.78	1.62
S, %	80	76	66	62

The apparent activation energy of the hydrogenation of thiophene is 83±5 kJ/mole.

Thus, it was established that the selective hydrogenation of thiophene to thiolane in the gas phase can be realized by the action of a palladium-sulfide catalyst. At 200-260°C with $P = 2.1$-3.1 MPa and with 30-40% conversion of the thiophene the yield of thiolane calculated on the reacted thiophene amounts to 80-90% while at $X = 50$-60% it is reduced to 70-75%.

EXPERIMENTAL

The thiophene and thiolane were of 99% pure reagent grade. The catalyst was prepared by impregnating the support (amorphous aluminosilicate containing 10 wt. % of Al, S_{sp} = 360 m^2/g) with an aqueous hydrochloric acid solution of palladium chloride, drying at 110°C for 5 h, and treatment with hydrogen sulfide at 150°C for 1 h. The catalyst with a particle size of 0.25-0.5 mm secured reaction under kinetic control.

Catalytic Hydrogenation of Thiophene in the Gas Phase (General Procedure). The hydrogenation of thiophene was carried out at increased hydrogen pressure in flow-type apparatus connected to a chromatograph. Hydrogen from a bottle was delivered to a thermostated saturator and then to a reactor with the catalyst, heated by an inertialess furnace. Samples were taken periodically for chromatographic analysis (Tsvet-500 chromatograph with a katharometer, 2 m × 3 mm column, filled with Porapak Q+R, 1:1). The ratio of the volume of catalyst (cm^3) to the velocity of the gas (cm^3/sec) at the working temperature and pressure was used for the contact time τ. The degree of conversion of the thiophene, the yields of the reaction products calculated on the initial thiophene, the selectivity with respect to the thiolane, and the average transformation rate of the thiophene, calculated for 1 g of catalyst, were calculated from the results.

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