HYDROGENATION OF FURFURAL ON POLYMER-CONTAINING CATALYSTS

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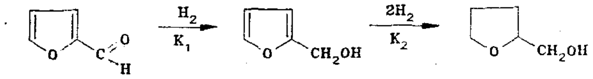
UDC 547.724.1:542.941.7:541.127.1

The catalytic hydrogenation of furfural with molecular hydrogen has been investigated under mild conditions in the presence of metal complex catalysts with a polymeric macroligand. It has been shown that the reaction proceeds according to a consecutive scheme with the formation of furfuryl and tetrahydrofurfuryl alcohols. The kinetics of furfural hydrogenation has been investigated and the order of the reaction established; the rate constants of the first and second stages have been determined. The influence of the solvent and of the metal-to-polymer ratio on the furfural conversion have been investigated.

The hydrogenation of furfural, the main product of the processing of pentosan-containing raw materials, is included in some industrial processes. At present, the development of efficient catalysts which allow the hydrogenation of furfural under mild conditions is of acute interest.

We have reported in [1] on the synthesis of catalysts which are active in the hydrogenation of some aromatic and heterocyclic compounds under mild conditions. In the present work we have investigated the hydrogenation of furfural in the presence of polymer-containing metal complex catalysts at atmospheric pressure and 20-25°C. The catalysts were complexes of Pt, Pd, or Rh with polyacrylic acid (PAA), styrene copolymers with maleic acid (ST-MA), and copolymers of methyl-methacrylate with maleie acid (MA-MMA). The results are presented in Tables 1-4.

In the hydrogenation of furfural the highest activity was shown by the rhodium catalysts. The complexes of Pt and Pd were less active and stable. On rhodium catalysts with macroligands furfural was hydrogenated quantitatively to tetrahydrofurfuryl (THF) alcohol; furfuryl alcohol was formed as an intermediate product of the hydrogenation. The character of the kinetic curves of furfural hydrogenation (Fig. 1) indicates a consecutive character of this reaction:



The high number of conversions N,* reached in the hydrogenation of furfural, must be pointed out. Thus, the number of conversions of the reaction at 25° and a furfural concentration of 0.9 mole/liter was 110. The molar ratio substrate/catalyst was equal to 94 in this case.

We have shown that a significant increase in the furfural concentration leads to a decrease in the number of conversions (Table 1); nevertheless, the catalyst works satisfactorily and the conversion reaches 100%.

The polymer/metal ratio in the complexes also had an effect on the activity and selectivity of the catalyst (Table 2). The data show that a decrease in the metal content of the complex leads to a decrease in the furfural hydrogenation rate. When the metal content of the catalyst is increased (up to 1-2 metal atoms per monomer unit), the conversion as a whole increases, however the amount of pentanediol-1,5 in the reaction products increases sharply (which is a product of furfural ring opening) and the stability of the catalytic system is

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*N was calculated as the number of furfural molecules converted per metal atom in 1 h.

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TABLE 1. Influence of the Catalyst/Substrate Ratio on the Conversion and Number of Conversions in the Hydrogenation of Furfural on an ST—MA—Rh Catalyst (ST—MA 0.26 mmole, $RhCl_3\cdot 4H_2O$ 0.05 mmole, $NaBH_4$ 0.05 mmole, H_2O 3 ml, i-PrOH 3 ml, T = 25°, P = 1 atm)

No.	Furfural concentration, mole/liter	Furfural/$RhCl_3\cdot 4H_2O$ ratio	Conversion in 0.5 h, %	Number of conversions N, h^{-1}
1	0,2	19	94	100
2	0,6	56	87	123
3	0,9	94	52	110
4	1.4	133	66	30

TABLE 2. Influence of Metal Content of Catalyst on the Hydrogenation Rate and Conversion of Furfural (PAA 0.25 mmole, amount of $NaBH_4$ equimolar to $RhCl_3\cdot 4H_2O$; H_2O 3 ml, i-PrOH 3 ml, furfural 6 mole; T = 20°, P = 1 atm, reaction time 2 h)

Number of PAA units per Rh atom	Initial H_2 absorption rate, ml/min	Reaction products, %				Conversion, %
		furfural	furfuryl alcohol	THF alcohol	pentanediol-1,5	
20	12	88	12			12
10	17	83	17			17
5	23	57	43			43
4	24	42	56	1	1	58
2,5	34	45	41	1	13	55
1,5	19	39	56		2	61
1	28		39	41	20	100
0.5	15	4	17	71	6	96

TABLE 3. Influence of Solvent on the Hydrogenation Rate and Conversion of Furfural (PAA 0.25 mmole, $RhCl_3\cdot 4H_2O$ 0.05 mmole, $NaBH_4$ 0.05 mmole, furfural 6 mmole, total solvent volume 6 ml; T = 20°, P = 1 atm, reaction time 1 h)

Solvent	Number of conversions N, h^{-1}	Composition of reaction mixture, %			Coversion, %
		furfural	furfuryl alcohol	THF alcohol	
H_2O—*i*-PrOH (1:1)	44	45	55		45
H_2O—EtOH (1:1)	31	40	59	1	60
H_2O—*i*-AmOH* (1:1)	18	64	36		36
H_2O*	29	44	56		56

*Catalyst partly coagulated.

reduced. This is evidently due to the fact that in the case of a high rhodium content of the catalyst a part of it does not react with the polymer but is present in the reaction medium as black pigment; 5-10 monomer units per rhodium atom can be considered as the optimum polymer/metal ratio.

The reaction order and the effective hydrogenation rate constants K_1 and K_2 were determined for a furfural concentration of 0.2 mmole/liter. It must be pointed out that pentanol-1 was detected in the reaction products at a low furfural concentration. Its amount did not exceed 5%; consequently, this reaction path was neglected in the calculations. The reaction order n and the rate constant of furfural hydrogenation to furfuryl alcohol K_1 were deter-

TABLE 4. Hydrogenation of Furfural and Furfuryl Alcohol at Different Initial Substrate Concentrations (polymers 0.25 mmole, $RhCl_3 \cdot 4H_2O$ 0.05 mmole, $NaBH_4$ 0.05 mmole, H_2O 3 ml, i-PeOH 3 ml, substrate 6 mmole; T = 25°, P = 1 atm)

Catalyst	Time, min	Composition of reaction mixture, %			Catalysts	Time, min	Composition of reaction mixture, %		
		furfural	furfuryl alcohol	THF alcohol			furfural	furfuryl alcohol	THF alcohol
PAA —Rh	0	14	86		MA —MMA—Rh	0	100		
	5	11	89			5	94	6	
	10	6	92	2		10	86	12	2
	15	3	92	5		20	79	19	2
	25	1	90	9		30	61	35	4
	35	1	85	14		42	54	40	6
	50	Traces	73	27		55	46	47	7
PAA —Rh	0	58	42		MA —MMA—Rh	0		100	
	5	56	44			5		87	13
	13	32	66	2		10		78	22
	21	23	74	3		17		61	39
	31	16	81	3		27		51	49
	46	8	87	5		37		39	61
	73	3	90	7		48		22	78
PAA —Rh	0		100		ST—MA —Rh	0		100	
	5		97	3		5		87	13
	10		96	4		10		80	20
	16		92	8		21		65	35
	25		87	13		31		53	47
	36		82	18		41		41	59
PAA-Rh	0	100			ST—MA —Rh	0	100		
	5	97	3			5	86	10	4
	11	93	7			10	77	19	4.
	16	90	10			24	64	32	4
	26	81	17	2		34	53	43	4
	36	78	20	2		44	41	54	5
	46	70	27	3		54	26	68	6

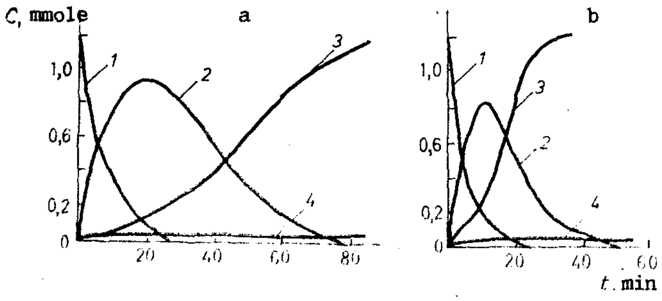

Fig. 1. Kinetic hydrogenation curves of furfural on catalysts: a) PAA-Rh; b) ST-MA-Rh (furfural concentration 0.2 mole/liter, polymer/metal ratio in the catalysts 1:5); 1) furfural; 2) furfuryl alcohol; 3) tetrahydrofurfuryl alcohol; 4) n-amyl alcohol.

mined graphically [2]: n = 1, $K_1 = 0.28\ min^{-1}$ for ST—MA—Rh and $K_2 = 0.22\ min^{-1}$ for PAA—Rh. K_1 was also determined from the half-conversion period of the initial substance: in this case $K_1 = 0.20\ min^{-1}$ for ST—MA—Rh and $K_1 = 0.17\ min^{-1}$ for PAA-Rh.

By assuming that the stage of the hydrogenation of furfuryl alcohol to THF alcohol represents a pseudo-first order reaction according to the equation $K_2 = (2.3/T_{max})$ long (c_0/c_{max}) where c_0 is the initial furfural concentration, c_{max} is the maximum concentration of furfuryl alcohol, and T_{max} is the time in which the maximum concentration is reached, K_2 was determined from the total kinetic curve; it was found to be $0.04\ min^{-1}$ for ST—MA—Rh and $0.01\ min^{-1}$ for PAA—Rh. These constants show that the complex ST—MA—Rh should be used preferably for the production of THF alcohol and PAA—Rh for the production of furfuryl alcohol which is formed on this catalyst with a high selectivity.

The influence of the solvent on the hydrogenation of furfural in the presence of polymer-containing metal complex catalysts has also been studied (Table 3). When the reaction was performed in water, the conversion of furfural in 1 h was the same as that obtained in isopropanol/water and ethanol/water mixtures; however, the stability of the catalysts decreased. When amyl alcohol is added, the conversion decreases, evidently due to disturbance of the homogeneity of the system.

For comparison, the hydrogenation of furfuryl alcohol was investigated under the same conditions. A 100% conversion of the initial substance was also achieved in this case. It was found that the hydrogenation rate of the aldehyde group of furfural and of the heterocycle of furfuryl alcohol were similar on PAA—Rh and ST—MA—Rh, while on MA—MMA—Rh the hydrogenation rate of furfuryl alcohol was higher than the hydrogenation rate of furfural (Table 4). On the other hand, in the hydrogenation of furfural the conversion of the main mass of the furfuryl alcohol started when practically no furfural was left in the reaction mixture (Fig. 1). We have therefore investigated the simultaneous hydrogenation of furfural and furfuryl alcohol at different initial concentrations of both substrates (Table 4). The data show that small amounts of furfural (15%) inhibit the hydrogenation of furfuryl alcohol. At similar quantities of furfural and furfuryl alcohol, furfural is hydrogenated first, practically completely suppressing the hydrogenation of furfuryl alcohol. Such an effect of furfural is evidently due to competing complex formation of furfural and furfuryl alcohol with the catalytic center. It can be postulated that furfural is bonded more strongly to the rhodium ion, primarily through the aldehyde group; in the case of furfuryl alcohol the π-electrons of the heterocycle are the main contributors to the substrate/catalyst interaction. This conclusion is in agreement with data on the homogeneous and heterogeneous H—D exchange of furan compounds in the presence of catalysts based on metals of the VIII group [3, 4].

EXPERIMENTAL

The hydrogenation experiments were carried out in a "duck"-type static system with a thermostated jacket. A weight of the polymer was placed in the reactor and dissolved in distilled water; the solution was then treated with a weight of the metal salt ($RhCl_3 \cdot 4H_2O$, K_2PtCl_4, K_2PdCl_4) and the alcohol component of the solvent. A quantity of sodium borohydride was then added to the solution, equivalent to the amount of metal added. After addition of the substrate the reactor was connected to the thermostat and shaken at a frequency of 400-500 shakes/min. Hydrogen was supplied to the reactor from a gas buret.

The catalyst was separated from the reaction mixture by the addition of K_2CO_3. The reaction products were analyzed by GLC on a Crom-5 chromatograph with flame ionization detector; the column was packed with 10% Carbowax 20 M on Chromosorb W; column length 3.7 m, internal diameter 3 mm. The standard deviation of the GLC results was less than 2%.

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