Kinetics of vapor phase ammoxidation of o-xylene on V-Sb-Bi-Cr / γ-Al$_2$O$_3$ oxide catalyst II. Development of kinetic reaction model

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ABSTRACT

In case when the the partial pressure of oxygen above its minimum value, it is revealed that the consumption rate of o-xylene is represented by the equation half order with respect to the substrate as well as given the kinetic equation for the rate of accumulation of products of the ammoxidation of xylene on V-Sb-Bi-Cr / γ-Al$_2$O$_3$-oxide catalyst. The kinetic model of process describing the rate of reaction products formation and consumption of reaction products is developed as a result. Constants of the model are calculated.

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1.Introduction

Kinetic regularities of formation of the main products in the vapor phase ammoxidation of xylene on V-Sb-Bi-Cr / γ-Al$_2$O$_3$-oxide catalyst depending on the oxygen partial pressure P$_{O2}$, ammonia P$_{NH3}$ and water P$_{H2O}$ were considered in the previous report [1]. It was also revealed that the major reaction products - phthalonitrile and phthalimide are formed in the competing ways, i.e. phthalimide formed directly from o-xylene and o-phthalonitrile through tolunitrile. It is important to add that the ammoxidation of o-xylene on the V-Sb-Bi-Cr / γ-Al$_2$O$_3$-oxide catalyst phthalonitrile and phthalimide are mutually transformed into each other.

The purpose of the current study was discussion of kinetic regularities of formation and consumption of reaction products of the reaction ammoxidation of o-xylene on the V-Sb-Bi-Cr / γ-Al$_2$O$_3$-oxide catalyst, development of kinetic equations for the rates of accumulation.

2. Methods and Apparatus

Kinetic measurements were performed on an installation equipped with flowing non-gradient reactor (20 cm^3) made of "12Kh18N10T " steel with vibroliquified layer of catalyst. The part of the installation was maintained at 500–520 K to avoid the condensation of high-boiling products. Oxygen and nitrogen were purified from traces of organic compounds and dried before use. Ammonia was passed through an oil filter. o-Xylene and phthalimide of chemically pure grade was used. Phthalonitrile, o-tolunitrile and benzonitrile were isolated from the products of o-xylene oxidative ammonolysis and purified by distillation.

Reaction gases were sequentially passed through a trap with 1,4-dioxane to absorb nitriles, phthalimide and o-xylene and with sulfuric acid to absorb ammonia. The analysis of the products absorbed with 1,4-dioxane was carried out on a Chrom-5 chromatograph with flame-ionization detector and the analysis of carbon dioxide was performed on a LKhM-8MD chromatograph [1]. Ammonia concentration at the reactor output was determined by titration results of the unreacted sulfuric acid in the second trap.

3. Experimental

For the development of a kinetic model of reaction ammoxidation of o-xylene on V-Sb-Bi-Cr / γ-Al$_2$O$_3$-oxide catalyst, the effect of the partial pressures of substrate P$_I$ and contact time τ on the process rate in the temperature range 648-708 K was researched. The kinetic measurements were preceded experiments for verification of the reactor in the nongradient mode on concentration and temperature, as well as the lack of impact of the reactor material, mass transfer processes, and homogeneous stages on the observed rates.

It is observed the ammoxidation of o-xylene (I) on V–Sb–Bi–Cr/γ-Al$_2$O$_3$ –oxide catalyst reactions of formation of o-tolunitrile (II), phthalimide (III), phthalonitrile (IV), benzonitrile (V) and CO$_2$ (figure 1). In accordance with figure 1 phthalimide is formed both directly o-xylene, and by the hydrolysis of phthalonitrile; phthalonitrile obtained from o-tolunitrile and ammonolysis phthalimide, benzonitrile was obtained from phthalimide and o-tolunitrile.
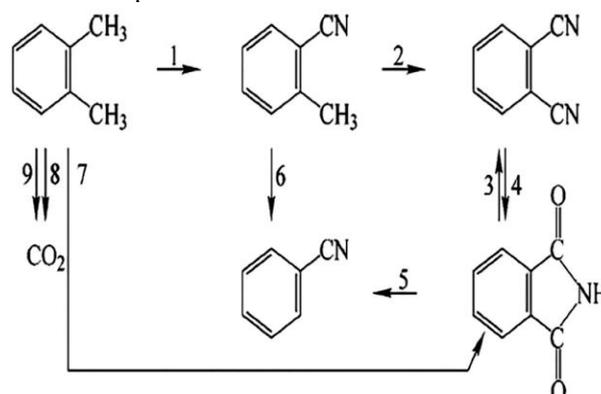
Figure 1. Reaction of ammoxidation of o-xylene on the V–Sb–Bi–Cr/γ-Al$_2$O$_3$ -oxide catalyst.

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4. Results and Discussion

The variation of P_I was by changing its concentration at the reactor inlet P_I^o at τ 0.20 s , 9.26 kPa, 17.65 kPa, 36.76 kPa. The obtained results at temperature 708 K are given in table 1. It was found that the increase of P_I leads to conversion reduction α and increased rate of total hydrocarbon transformation; the selectivity of its transformation in ftalonitril, phthalimide, benzonitril and CO_2 is reduced and the o-tolunitril-increases. Similar regularities were observed at temperatures of 668 and 688K .

The effect of the contact time on the performance of the ammoxidation of o-xylene was investigated at τ 0.20 s, initial partial pressures of P_I^o 1.47 kPa, $P_{NH_3}^o$ 17.65 kPa, $P_{H_2O}^o$ 36.76 kPa, temperatures 648 (table 2) and 688 K (table 3). The variation of τ at low P_{NH3} showed that the formation of the phthalimide occurs over the entire range of the conversion of o-xylene, and this is consistent with the data previously conducted work on the V-Sb-Bi-Zr / γ-Al$_2$O$_3$-oxide catalyst [2]. As can be seen from Table 2 and 3, at all temperatures increase of τ leads to growth of α and to reduction of the total conversion rate of o-xylene; selectivity during its conversion phthalonitrile decreases, and benzonitrile and CO_2 increases. Thus phthalimide selectivity decreases starting from 688 K, and the selectivity of formation of o-tolunitrile reduced at all temperatures, and at the same time, since 688K, phtalonitriles selectivity increases. Similar regularities were observed at temperatures of 668 and 708K.

In figure 2, the dependence of the total conversion rate of o-xylene on its stationary concentration at two different values of the contact time is presented. Independence of the total conversion rate of o-xylene at the same value of its stationary concentration on the contact time indicates the absence of the inhibitory effect of the reaction products on the total conversion rate of o-xylene.

Table 1.Influence of partial pressures of o-xylene on reaction kinetics of ammoxidation of o-xylene.

kPa		α, %	W,	S_i, kPa				
P_1^0	P_I		mmol/g·h	II	III	IV	V	CO_2
0.484	0.028	94.23	1.46	7.80	50.00	32.40	2.81	6.99
0.978	0.109	88.88	2.77	14.90	49.49	27.68	1.44	6.49
1.470	0.200	86.40	4.06	18.15	48.99	25.40	1.08	6.38
1.966	0.352	82.13	5.15	23.16	45.46	24.19	0.85	6.34
2.460	0.528	78.54	6.17	27.64	41.60	23.82	0.64	6.30
2.954	0.694	76.52	7.21	31.90	37.68	23.59	0.57	6.26

P_i, kPa							
II	III	IV	V	CO_2	O_2	NH_3	H_2O
0.036	0.23	0.148	0.01	0.27	7.71	17.07	38.88
0.129	0.43	0.240	0.01	0.46	6.43	16.59	40.64
0.231	0.62	0.323	0.01	0.66	5.19	16.13	42.34
0.374	0.73	0.391	0.01	0.83	4.21	15.74	43.74
0.534	0.80	0.460	0.01	0.99	3.35	15.38	45.00
0.721	0.85	0.533	0.01	1.14	2.50	14.99	46.29

Table 2. Influence of the contact time on the reaction kinetics for the ammoxidation of o-xylene.

τ, s	α, %	W, mmol/g·h	S_i, kPa			
			II	III	V	CO_2
1.87	96.80	0.49	19.51	74.53	1.49	4.47
1.23	93.61	0.72	19.52	75.19	0.85	4.44
0.91	89.66	0.93	19.53	75.40	0.65	4.43
0.75	85.04	1.07	19.54	76.04	–	4.42
0.59	80.20	1.29	19.55	76.04	–	4.41
0.43	71.10	1.56	19.49	76.11	–	4.40
0.27	55.47	1.95	17.50	78.11	–	4.39
0.13	34.20	2.41	16.30	79.32	–	4.38

P_i, kPa							
I	II	III	V	CO_2	O_2	NH_3	H_2O
0.047	0.28	1.06	0.02	0.53	4.93	16.29	42.24
0.094	0.27	1.04	0.01	0.50	5.08	16.33	42.06
0.152	0.26	0.99	0.01	0.48	5.26	16.39	41.84
0.220	0.24	0.95	–	0.44	5.46	16.45	41.58
0.291	0.23	0.90	–	0.42	5.68	16.52	41.30
0.425	0.20	0.80	–	0.37	6.09	16.65	40.79
0.655	0.14	0.64	–	0.29	6.76	16.87	39.92
0.968	0.08	0.40	–	0.18	7.71	17.17	38.72

Table 3. Influence of the contact time on the reaction kinetics for the ammoxidation of o-xylene.

τ, s	α, %	W, mmol/g·h	S_i, kPa				
			II	III	IV	V	CO_2
1.23	98.8	0.76	2.27	81.90	7.23	2.82	5.78
0.91	97.8	1.01	3.75	79.60	8.62	2.28	5.75
0.75	96.9	1.22	5.05	77.50	9.84	1.88	5.73
0.59	95.5	1.53	6.65	76.10	10.25	1.30	5.70
0.27	82.3	2.90	14.99	65.50	13.26	0.59	5.66
0.20	74.9	3.52	17.70	63.00	13.68	–	5.62
0.13	59.2	4.17	21.92	58.73	13.75	–	5.60

P_i, kPa								
I	II	III	IV	V	CO_2	O_2	NH_3	H_2O
0.018	0.033	1.19	0.105	0.04	0.710	4.37	16.17	42.84
0.030	0.050	1.14	0.120	0.03	0.69	4.41	16.17	42.79
0.046	0.072	1.10	0.140	0.03	0.68	4.49	16.16	42.75
0.066	0.090	1.07	0.144	0.02	0.66	4.59	16.18	42.66
0.260	0.180	0.79	0.160	0.01	0.55	5.39	16.34	41.81
0.370	0.195	0.69	0.150	–	0.50	5.79	16.46	41.34
0.600	0.191	0.51	0.120	–	0.39	6.57	16.70	40.34

On the basis of the obtained experimental data showing lack of influence of

products of reaction to the rate of conversion of o-xylene, we analyzed the nature of dependence of the reaction rate from the partial pressure of the substrate (including the dependence of the velocity partial reactions of the partial pressures of oxygen and ammonia, which are the initial components) [1]. Study of the dependence of the total conversion rate of o-xylene on its partial pressure showed that the order of the reaction of the substrate is less than 1 and greater than zero.

Based on a set of experimental data, the rate of formation and consumption of the key components of the oxidative ammonolysis of o-xylene on V-Sb-Bi-Cr / γ-Al$_2$O$_3$-oxide catalyst at partial pressures of oxygen and ammonia in excess of the minimum values can be expressed by the following equations (1-9).

$$W_1 = k_1 P_I^{0.5} b\, P_{NH3} / P_{O2} + b\, P_{NH3} \tag{1}$$

$$W_2 = k_2 P_{II}^{0.5} \tag{2}$$

$$W_3 = k_3 P_{IV}^{0.5} P_{H2O} / P_{NH3} \tag{3}$$

$$W_4 = k_4 P_{III}^{0.5} / P_{H2O} \tag{4}$$

$$W_5 = k_5 \tag{5}$$

$$W_6 = k_6 P_{II}^{0.5} / 1 + a\, P_I \tag{6}$$

$$W_7 = k_1 P_I^{0.5} P_{O2}\, \beta / P_{O2} + b\, P_{NH3} \tag{7}$$

$$W_8 = k_1 P_I^{0.5} P_{O2}\, (1-\beta) / P_{O2} + b P_{NH3} \tag{8}$$

$$W_9 = k_9 P_I^{0.5} \tag{9}$$

Here, k_i -the rate constant of route (see figure 1) ; β- the share of o-xylene, which is directly converted into phthalimide; b- constant reflecting the adsorption equilibrium constant of O$_2$ and NH$_3$.
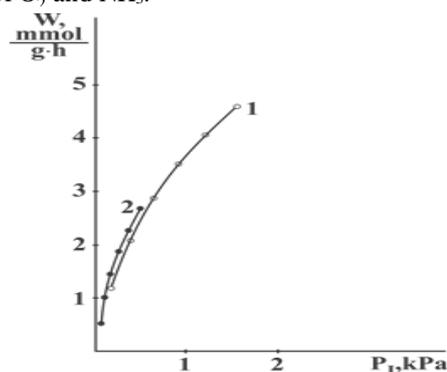
Figure 2. The dependence of the conversion rate of o-xylene on its stationary concentration at 668 K, $P_{O_2}^0$ 9.26 kPa, $P_{NH_3}^0$ 17.65 kPa, $P_{H_2O}^0$ 36.76 kPa: 1– at τ 0.20 s, 2– at τ 0.59 s.

It is worth to note that at low concentrations of ammonia on oxide catalyst V-Sb-Bi-Zr / γ-Al$_2$O$_3$ [2-5], and the V-Sb-Bi-Cr / γ-Al$_2$O$_3$-oxide catalyst in the ammoxidation the total rate of conversion of o-xylene only depends on its partial pressure and is described by following equation (10).

$$W_8 + W_9 = (k_1 + k_9) P_I^{0.5} \tag{10}$$

Table 4. The dependence of rates of accumulation of reaction products and conversion of o-xylene on contact time *.

τ, s	P_i, kPa								
	I	II	III	IV	V	CO_2	O_2	NH_3	H_2O
1.23	0.009	0.0225	0.97	0.260	0.11	0.87	4.20	16.02	43.21
0.91	0.016	0.0390	0.92	0.310	0.09	0.84	4.26	15.98	43.25
0.59	0.037	0.0830	0.83	0.375	0.06	0.80	4.40	15.93	43.26
0.27	0.140	0.1940	0.68	0.354	0.02	0.70	4.93	16.05	42.69
0.13	0.350	0.2430	0.53	0.271	0.01	0.58	5.73	16.33	41.62
0.09	0.507	0.2610	0.44	0.201	–	0.49	6.31	16.54	40.82

τ, s	W_i, mmol/g·h											
	I		II		III		IV		V		CO_2	
	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc
1.23	0.76	0.83	0.012	0.013	0.51	0.56	0.14	0.15	0.057	0.061	0.049	0.050
0.91	1.03	1.11	0.028	0.030	0.65	0.71	0.22	0.24	0.065	0.064	0.066	0.067
0.59	1.56	1.69	0.090	0.090	0.90	1.00	0.41	0.43	0.063	0.063	0.100	0.103
0.27	3.19	3.29	0.470	0.520	1.63	1.59	0.85	0.92	0.045	0.048	0.204	0.204
0.13	5.37	5.20	1.170	1.300	2.53	2.34	1.30	1.19	0.034	0.034	0.342	0.330
0.09	6.64	6.25	1.800	1.710	3.03	2.82	1.39	1.33	–	–	0.420	0.400

Note. *) 708 K, P_1^0 1.47 kPa, $P_{O_2}^0$ 9.26 kPa, $P_{NH_3}^0$ 17.65kPa,

$P_{H_2O}^0$ 36.76 kPa .

In accordance with the figure 1, W is not dependent on the concentrations of O_2 and NH_3 and obeys the equation half order with respect to o-xylene. This dependency suggests dissociative adsorption of o-xylene, which is similar to carrying out this reaction on V-Sb-Bi-Zr / γ-Al_2O_3-oxide catalyst [2]. This relationship is characteristic for oxidative ammonolysis of 4-bromo- and 4-phenyl-o-xylene on V-Sb-Bi-Zr / γ-Al_2O_3-oxide catalyst [6-8].

The constants of the equations (1–9) describing transformation of o-xylene according to the above-stated scheme selected on the personal computer from a condition of minimizing the sum of the squares of relative errors between the experimental and calculated accumulation rates all the products of the reaction [9,10].

It is found that:

$k_1 = 10^{7.26}$ exp (-85772/RT)
$k_2 = 10^{7.37}$ exp (-93303.2/RT)
$k_3 = 10^{-13.83}$ exp (182330/RT)
$k_4 = 10^{-4.77}$ exp (57120/RT)
$k_5 = 10^{4.49}$ exp (-83680/RT)
$k_6 = 10^{11.21}$ exp (-137569.9/RT)
$a = 10^{-8.80}$ exp (156272.4/RT)
$b = 10^{7.38}$ exp (-104600/RT)
$k_9 = 10^{11.78}$ exp (-165268/RT)

The activation energy is given in J / mole. The value of β at all temperatures is 0.95.

Table 4 shows the accumulation rates constants of reaction products and consumption of o-xylene calculated using the equations (1-9). The difference between the experimental and calculated values of W_i does not exceed the accuracy of the experiment. Also from Table. 4 clearly shows that at 708 K are observed similar regularities as at 688 (table 3). It is also important to emphasize that with the help of equation constants (1-9) it is possible to calculate the gap between empirical and estimated values of speeds of reaction products and o-xylene depletion.

5. Conclusions

1) On the basis of the studied kinetic reguliarites data the kinetic model for the ammoxidation reaction of o-xylene is developed..

2) The values of the rates of accumulation of reaction products and consumption of the initial hydrocarbon are calculated.

3) The difference between the experimental and calculated values of the accumulation rates of the reaction products and consumption of o-xylene does not exceed the accuracy of the experiment.

4) It has been determined, that on V-Sb-Bi-Cr / γ-Al_2O_3-oxide catalyst, the feedstock is converted directly into phthalimide, which is as phthalonitrile main product of the ammoxidation of o-xylene.

5) It is specified the absence of the inhibitory influence of the ammoxidation reactions products of o-xylene on the total feedstocks transformation rate.

6) It is determined the dependence of private conversions reaction rate of o-xylene at ammoxidation on the partial pressures of oxygen and ammonia, which relate to the initial components.

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