

Preparation of Phthalimide and Kinetics of Vapour Phase Ammoxidation of *o*-Xylene on V-Sb-Bi-Cr/ γ -Al₂O₃ Oxide Catalyst-III

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The conditions for the synthesis of phthalimide by vapour phase ammoxidation of *o*-xylene on V-Sb-Bi-Cr/ γ -Al₂O₃-oxide catalyst were studied. The optimum process conditions to obtain the phthalimide as the main reaction product were determined. It is shown that the problem of difficult separation of crystal mixture of main products in the synthesis of phthalimide, solved with full conversion of *o*-xylene in a single process, using low concentrations of ammonia and water in the initial reaction mixture, which differs from the phthalonitrile obtaining an average from the substrate conversion to oxide catalyst V-Sb-Bi-Zr/ γ -Al₂O₃ by recirculation at high concentrations of ammonia.

Keywords: Catalytic ammoxidation, Kinetics, *o*-Xylene, Partial pressures, Phthalimide.

INTRODUCTION

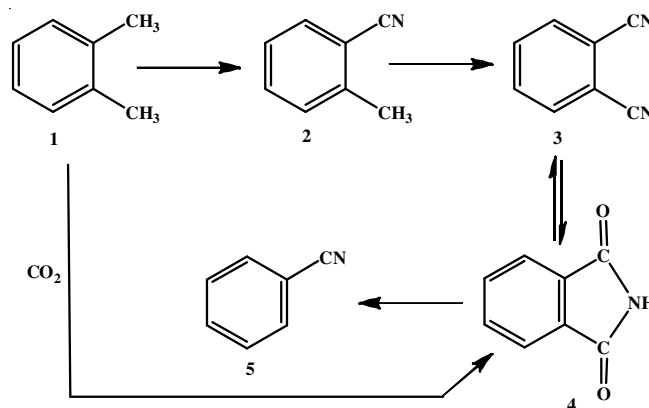
The relevance of the problem is due to the complexity of producing the main products (dinitrile and imide) without difficult separation of crystalline impurity in heterogeneous catalytic ammoxidation of *o*-xylene and the acute need to ensure the optimal conditions of the process towards the formation of each of the target substance. In previous reports [1,2] considered competing path forming phthalimide and phthalonitrile in the vapour phase ammoxidation of *o*-xylene and studied the kinetic regularities of the formation of main product-phthalimide and the byproducts of this reaction on V-Sb-Bi-Cr/ γ -Al₂O₃-oxide catalyst. The vapour phase catalytic oxidative ammonolysis of *o*-xylene allows good yields (90-95 %) to obtain the phthalimide used in the chemical industry as an intermediate in the production of dyes, scorch retarders, stabilizers and flame retardants for plastics, pharmaceuticals [3], plant protection chemicals, lubricant additives and in other areas of organic synthesis [4]. There is a theoretical justification [5] of the formation of a target substance on the basis of structural features of the substrate, discussed the influence of electronic and steric effects in the formation of the main products in the vapour phase catalytic ammoxidation of *o*-xylene and shown that inductive effects of substituents not only cause the formation of a dinitrile as well as contribute to the formation of imide, which is due to rupture of the weakest side of the C-H bonds of the methyl group, located in α -position to the

aromatic nucleus in the primary interaction with the metal oxide catalyst and spatial effects of *ortho*-methyl substituents of the substrate only favour the production of imide through intramolecular cyclization. The formation of the phthalimide is associated with the specific structural features of the substrate, namely locating the methyl groups in *ortho*-position in their molecules, causing the formation of the imide heterocycle resulting from both activation heterolytic breaking C-H bonds with protonation of hydrogen and intramolecular oxidative cyclization of intermediates and thus, under certain conditions, imide becomes main product along with the dinitrile at a one-step gas-phase catalytic ammoxidation of *o*-xylene, which again demonstrates improved thermodynamic stability of the five-membered heterocyclic compounds [6]. It should be added that heterolytic breaking of C-H bonds with hydrogen protonation also relates to the activation of a second methyl group, because under oxidative ammonolysis of *o*-xylene on vanadium catalysts phthalonitrile formed mainly from *o*-tolunitrile [1].

It is known that heterogeneous catalytic oxidative ammonolysis of aromatic compounds having *ortho* methyl groups, affords as the main product as a dinitrile and imide [7], simultaneous presence in the reaction products results in the formation of crystalline hard separable mixture [7,8], while the sphere of consumption impose high requirements for their purity. The problem of separation of a mixture of crystalline products is always present during the reaction with complete conversion of *o*-xylene in a single process to obtain a dinitrile,

which is not typical in the synthesis as imide-based products. The selection of catalysts and reaction conditions for the conversion of substrate to selectively obtain dinitrile of *o*-xylene and its 4-substituted rather complicated due to the fact that being adjacent methyl groups, unlike the corresponding *m*- and *p*-isomers. When ammoxidation on many catalysts along with a dinitrile in an oxidative cyclization always formed imide [7,8]. The possibility of intramolecular interactions at intermediate stages determines the specificity of the kinetic laws. Thus, increasing the concentration of ammonia in initial reaction mixture, usually leads to increased selectivity in dinitrile formation and decreased selectivity in imide formation on some vanadium contacts [7,9-11]. Dinitrile begins to prevail among the reaction products at high partial pressures of ammonia, wherein the formation of an imide directly from *o*-xylene do not happens (Fig. 1). The formation of imide under full conversion of the substrate with high partial pressures of ammonia and long contact occurs through hydrolysis of the dinitrile, due to the water which is the product related reactions, ammoxidation-oxidative dehydrogenation and deep oxidation. However, on the oxide contact V-Sb-Bi-Zr/ γ -Al₂O₃ in the medium conversion imide is hardly generated, therefore, elaborated and offered the option of contacting with an average degree of reaction and recirculation of the remaining substrate and the intermediate corresponding *o*-tolunitrile in the reaction zone [12,13], which prevents the further conversion of the dinitrile to the imide. Therefore, obtaining the dinitrile with recycling does not require separation of a mixture of crystalline products in the absence of an imide. The choice of method depends on the purpose of the reaction, the contact performance at different conversions, the selectivity of the process and, ultimately determined by economic feasibility. It should be noted that the process recycling for imide producing is not acceptable under oxidative ammonolysis, due to the conversion of the intermediate mononitrile to dinitrile only (Fig. 1). Due to formation of imide on V-Sb-Bi-Cr/ γ -Al₂O₃-oxide catalyst without difficult separation of crystalline mixtures of basic products, we can say that at low concentrations of ammonia it is formed not only from *o*-xylene and hydrolysis of the dinitrile (Fig. 1), so that in use the water results in only imides and do not requires separation. Thus, it follows from the foregoing that the problem of hard separable crystalline mixtures of main products solves in the synthesis of phthalonitrile on V-Sb-Bi-Zr/ γ -Al₂O₃-oxide contact by recirculation and in case of phthalimide produce on the oxide catalyst V-Sb-Bi-Cr/ γ -Al₂O₃ with complete conversion of *o*-xylene in a single process using water in the initial reaction mixture. It is interesting to note that the production of pure phthalimide possibly through another main product phthalonitrile in a single process for the ammoxidation of *o*-xylene on V-Sb-Bi-Zr/ γ -Al₂O₃-oxide catalyst at higher concentrations of ammonia and water, but this is impractical in connection with the fact that creates additional difficulties negatively affecting the economy of the process.

The ammoxidation of *o*-xylene at individual vanadium oxide (10 %) applied on calcined at 1673 K alumina oxide, produces a phthalimide with a yield of 72 % at 668 K [14]. In carrying out the reaction in the presence of a catalyst consisting of 30 % tin dioxide and 70 % of vanadium pentoxide at 673 K,



In order to find optimal conditions for the preparation of pure phthalimide results of some of the laws of a single process were discussed. Research conducted in non-gradient reactor with vibro-liquified layer of catalyst in sufficient variation range of parameters [1,2].

RESULTS AND DISCUSSION

Table-1 shows the data obtained at different molar ratios of *o*-xylene–oxygen in the starting reaction mixture. Increasing the amount of oxygen in the mixture greater than a certain minimum value ($(P_{O_2})_{min}$), almost no effect on the conversion (α) of *o*-xylene, leading to a sharp increase in the selectivity of its transformation into phthalimide, the number of intermediate *o*-tolunitrile decreases selectivity as CO_2 increases. As can be seen from Table-1, the temperature raised to 688 K phthalonitrile appears in the reaction products, the quantity of which decreases with increasing oxygen content in the initial reaction mixture. It follows that at the contact time (τ) 0.20 s change of the molar ratio of the starting materials has virtually no effect on the conversion of *o*-xylene, however, significantly affects the selectivity (S_i). It should be noted that increasing the oxygen content in the initial reaction mixture favours the formation of phthalimide and contributes to intensification of reactions of the oxidation of *o*-xylene.

TABLE-1
EFFECT OF OXYGEN CONCENTRATION ON THE
INDICATORS OF AMMOXIDATION OF *o*-XYLENE

Molar ratio I:O ₂ :N ₂ :NH ₃ :H ₂ O	α (%)	S _i (%)			
		2	3	4	CO ₂
648 K					
1:1.5:28.5:12:25	44.0	65.10	31.90	–	3.00
1:3.0:27.0:12:25	44.7	36.19	59.71	–	4.10
1:4.0:26.0:12:25	45.0	24.64	71.10	–	4.26
1:6.3:23.7:12:25	45.2	16.72	78.77	–	4.51
1:8.0:22.0:12:25	45.4	12.12	82.43	–	5.45
1:12.0:18.0:12:25	45.6	7.94	86.51	–	5.55
1:15.0:15.0:12:25	45.8	6.54	87.76	–	5.70
688 K					
1:2:28.0:12:25	73.0	49.85	24.15	22.50	3.50
1:4.0:26.0:12:25	74.1	30.32	48.13	16.67	4.88
1:6.3:23.7:12:25	74.7	17.75	62.93	13.72	5.60
1:8.0:22.0:12:25	75.1	13.50	68.60	11.73	6.17
1:12.0:18.0:12:25	75.4	7.34	77.78	8.30	6.58
1:15.0:15.0:12:25	75.6	5.35	80.92	6.93	6.80

On the composition of the reaction products the ammonia quantity shows substantially affect in initial reaction mixture at a contact time of 0.20 s. With a relatively low molar ratio of NH₃-*o*-xylene phthalimide yield is rather high even at extremely low contact time with the reaction occurs substantially feed-stock deep oxidation (Table-2). With increasing molar ratio NH₃-*o*-xylene yield of *o*-tolunitrile and phthalonitrile increases, but the degree of conversion of *o*-xylene on a V-Sb-Bi-Cr/ γ -Al₂O₃-oxide catalyst is almost independent of the partial pressure of ammonia. As can be seen from Table-2, the temperature is raised to 708 K benzonitrile appears in the reaction products, the number of which increases with increasing ammonia content in the starting reaction mixture. It should be emphasized that the increase in the quantity of ammonia in the initial reaction mixture as opposed to oxygen increases the formation of phthalonitrile.

TABLE-2
INFLUENCE OF AMMONIA CONCENTRATION ON THE
INDICATORS OF AMMOXIDATION OF *o*-XYLENE

Molar ratio I:NH ₃ :O ₂ :N ₂ :H ₂ O	α (%)	S _i (%)				
		2	3	4	5	CO ₂
668 K						
1:3.0:6.3:32.7:25	56.00	2.41	90.13	0.61	–	6.85
1:6.0:6.3:29.7:25	57.12	6.72	84.87	2.01	–	6.40
1:9.0:6.3:26.7:25	59.16	10.20	80.38	3.47	–	5.95
1:12.0:6.3:23.7:25	61.20	13.10	77.65	4.61	–	4.64
1:15.0:6.3:20.7:25	60.71	17.00	71.70	6.00	–	5.30
708 K						
1:3.0:6.3:32.7:25	83.42	4.77	80.00	6.53	0.64	8.06
1:6.0:6.3:29.7:25	83.91	11.93	63.65	15.88	0.84	7.70
1:9.0:6.3:26.7:25	84.40	16.60	52.31	22.47	0.96	7.66
1:12.0:6.3:23.7:25	86.40	18.15	48.99	25.40	1.08	6.38
1:15.0:6.3:20.7:25	85.91	22.10	40.82	29.45	1.19	6.44

Study of the effect of water concentration in the initial reaction mixture was carried out at 688 K and τ 0.20 s (Table-3). From this table it shows that changes in the amount of water in the initial reaction mixture as in the case of ammonia and oxygen does not affect the conversion of *o*-xylene. However, increasing the water content favours the formation of the phthalimide by reducing phthalonitrile. There has been no selectivity relationship of other products from the water.

TABLE-3
EFFECT OF WATER CONCENTRATION ON THE
INDICATORS OF AMMOXIDATION OF *o*-XYLENE

Molar ratio I:H ₂ O:O ₂ :N ₂ :NH ₃	α (%)	S_i (%)			
		2	3	4	CO ₂
1:5:6.3:43.7:12	74.5	17.72	57.10	19.56	5.62
1:15:6.3:33.7:12	74.9	17.69	60.84	15.91	5.56
1:25:6.3:23.7:12	74.7	17.75	62.93	13.72	5.60
1:35:6.3:13.7:12	74.3	17.80	65.39	11.17	5.64
1:45:6.3:3.7:12	75.0	17.61	67.05	9.76	5.58

Effect of contact time on the indicators of the process for the ammoxidation of *o*-xylene was investigated at 668 K, 9.26 kPa, 17.65 kPa, 36.76 kPa (Table-4). With increasing contact time (τ) of phthalimide selectivity increases and the selectivity of *o*-tolunitrile and phthalonitriles reduced. However, for large values of τ benzonitrile appears in the reaction products, the yield of which increases symbatically with contact time.

Fig. 2 shows the dependence of the conversion of *o*-xylene and selectivity of the reaction products on the temperature. It

TABLE-4
INFLUENCE OF THE CONTACT TIME ON THE INDICATORS
OF AMMOXIDATION REACTION OF *o*-XYLENE

τ (s)	α (%)	S_i (%)				
		2	3	4	5	CO ₂
1.87	98.85	1.28	90.37	1.56	2.00	4.79
1.55	98.30	1.80	89.80	1.80	1.84	4.76
1.23	97.50	2.58	89.14	2.16	1.38	4.74
0.91	95.20	4.14	87.30	2.64	1.20	4.72
0.75	93.20	5.45	85.96	2.99	0.90	4.70
0.59	89.80	7.27	83.95	3.41	0.69	4.68
0.27	70.30	11.80	79.20	4.33	–	4.67
0.20	61.50	12.95	77.80	4.59	–	4.66
0.13	47.90	14.10	76.40	4.85	–	4.65

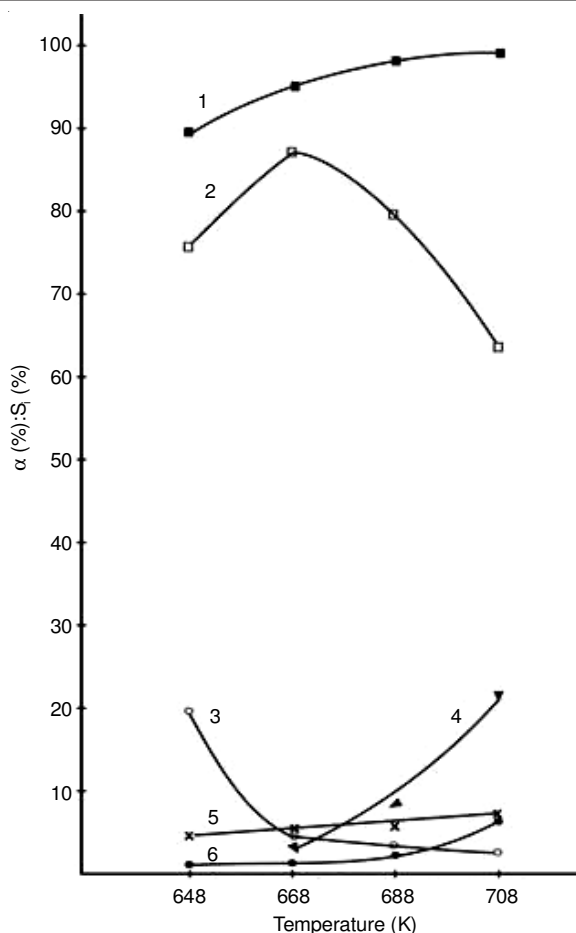


Fig. 2. Dependence of ammoxidation process of *o*-xylene indicators from the temperature at the contact time of 0.91 s, a molar ratio (1) $\text{O}_2\text{--NH}_3\text{--H}_2\text{O}$ 1:6.3: 12: 25. 1– Conversion of the compound (1) (α); 2,6-formation selectivity (S_i) compounds (3), (2), (4), CO_2 and (5) respectively

increases to 668 K results in an increase in the degree of conversion of *o*-xylene and increase the selectivity of phthalimide, which decreases with a further increase in temperature to 708 K. With increasing temperature the selectivity by *o*-tolunitrile decreases and increases by phthalonitriles. At high temperatures the formation reaction of benzonitrile and CO_2 accelerates.

Based on the kinetic regularities determined the optimal conditions of a single process for the ammoxidation of full conversion of *o*-xylene: 668K, τ 1.90 s, the molar ratio of $\text{I-NH}_3\text{--air-H}_2\text{O}$ = 1:12:30:25.

Selection of the optimal mode carried out in a laboratory reactor with a diameter of 40 mm with an organized fluidized bed of catalyst. Process parameters and the results are shown below:

Temperature (K)	658–668
Contact time (s)	1.90–1.95
Molar ratio of <i>o</i> -xylene–air– $\text{NH}_3\text{--H}_2\text{O}$	1:30–60:8–12:25–30
The conversion (<i>o</i> -xylene, %)	~100
Selectivity (%)	
3	93.15
5	2.04
CO_2	4.81

The presented data show that the oxide catalyst V-Sb-Bi-Cr/ $\gamma\text{-Al}_2\text{O}_3$ can be obtained phthalimide with a yield of ~93.15 mol. %, based per taken *o*-xylene. The reaction products do not contain the crystalline phthalonitrile, which is consistent with the earlier work carried out by Bagirzade [7]. Thus, after separation of highly volatile impurities, the problem to receive pure phthalimide without crystalline impurities of phthalonitrile is solved. Quality indicators phthalimide are shown below:

Base substance content, mass (%)	99.76–99.79
Melting point (K)	510.0–511.0
Residue on ignition, mass (%)	0.04–0.05
Humidity, mass (%)	0.17–0.19
The impurity of phthalonitrile	Nil

Conclusion

- Determined the optimal conditions for the ammoxidation of a single process with complete conversion of *o*-xylene on V-Sb-Bi-Cr/ $\gamma\text{-Al}_2\text{O}_3$ -oxide catalyst to produce phthalimide as desired product.

- Selecting the optimum mode was performed in a laboratory setting with the organized fluidized bed of catalyst.

- The proposed V-Sb-Bi-Cr/ $\gamma\text{-Al}_2\text{O}_3$ -oxide catalyst makes it possible to create an effective one-step process for producing the phthalimide by ammoxidation reaction of *o*-xylene without hard separable impurity of crystalline phthalonitrile.

- The foregoing eliminates a stage of separation and purification of main products, simplifies the process technology and makes it more economical.

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