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RESEARCH ARTICLE

KINETICS OF VAPOR PHASE AMMOXIDATION OF O-XYLENE ON V-SB-BI-ZR/γ-AL_2O_3 OXIDE CATALYST I. ABOUT THE COMPETING WAYS OF FORMATION OF THE MAIN PRODUCTS

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ABSTRACT

Kinetic regularities of vapor ammoxidation of xylene on the V-Sb-Bi-Cr / γ-Al_2O_3-oxide catalyst in the temperature range 648-708K are studied. It is shown that the formation of the phthalimide occurs both directly from o-xylene and in parallel through tolunitrile phthalonitrile. It is determined that the carbon dioxide formed by oxidation of o-xylene and decarboxylation of phthalimide, and benzonitrile from o-tolunitrile, and phthalimide.

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INTRODUCTION

It is known that heterogeneous catalytic oxidative ammonolysis of aromatic compounds having methyl groups in ortho - situation, leads to obtaining as the main product both a dinitrile and imide (Bagirzade *et al.*, 2015; Bagirzade *et al.*, 2014; Bagirzade *et al.*, 2014; Bagirzade and Tagiyev, 2014), the simultaneous presence in the reaction products results in the formation hard-to separable crystal mixture and all areas of consumption make high demands on the purity of the desired products. It is important to note that for the ammoxidation of o-xylene (CCCR 1728240, 1990) on the base V-Sb-Bi /γ -Al_2O_3-oxide catalyst phthalimide obtained directly from the substrate and by the hydrolysis of phthalonitrile. Previously we (Rizayev *et al.*, 1985; Rizayev *et al.*, 1986) studied kinetic regularities of vapor phase catalytic ammoxidation of xylene-on V-Sb-Bi-Zr / γ-Al_2O_3-oxide catalyst at higher concentrations of ammonia and water in the absence of the initial reaction mixture in order to obtain phthalonitrile. However, in the presence of water was observed formation of the phthalimide (Fig. 1.) through mono-dinitrile at the initial molar ratios of o-xylene: air: NH_3: H_2O, equal to 1: 30: 50: 100-120 . As you can see, obtaining successively phthalimide only through phthalonitrile requires the use of high concentrations of ammonia and water, which creates additional difficulties and shortcomings, negatively affecting the economic performance of the process. Rather at high concentrations of ammonia and water is necessary to increase the volume of the reaction zone and therefore the amount of the catalyst to maintain optimum contact time, as well as in connection with regeneration and ammonia using a large amount of water increases overhead capital and energy costs . As for the ammoxidation of xylene on V-Sb-Bi-Zr / γ-Al_2O_3-oxide catalyst, at low ammonia concentrations yield of phthalimide low due to the additional CO_2 formation in a large amount (route 8, Fig.1) (Bagirzade and Tagiyev, 2012).

The aim of this work was to study the kinetic regularities of the ammoxidation of xylene on V-Sb-Bi-Cr / γ-Al_2O_3-oxide catalyst at low concentrations of ammonia in the presence of water in the initial reaction mixture to obtain the phthalimide.

METHODS AND APPARATUS

Kinetic measurements conversion of o-xylene and chromatographic separation of components catalysate and the quantitative calculation of their contents was performed according to previously established procedures (Rizayev *et al.*, 1985). However, unlike these kinetic reactor made of steel 12X18H10T and analyzes were carried out on Chrome-5 chromatograph with a flame ionization detector. As a stationary phase, which filled the column length of 1.2 m was used as a

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mixture (Rizayev *et al.*, 1985), and only polisorb-1 (0.25-0.5 mm). Carbon dioxide was determined on an LKhM-8MD chromatograph with triethylene glycol butyrate supported on INZ- 600 (calcined diatomaceous earth) as the stationary phase. Separation of O_2 and N_2 was carried out on the same chromatoraph using a parallel column packed with NaX.

Experimental

In the products of the reaction of ammoxidation of o-xylene (I) on the V-Sb-Bi-Cr / γ-Al2O3-oxide catalyst o-tolunitrile (II), pthalimide (III), phthalonitrile (IV), benzonitrile (V), carbon dioxide, unreact- ed I, oxygen and the diluent gas nitrogen were determined by gas chromatography. The reaction gases were successively passed through a 1.4-dioxane-filled trap for absorption of nitriles, and III and a sulfuric acid-filled trap for absorption of ammonia. The concentration of ammonia at the reactor outlet was determined, by titration of unreacted sulfuric acid from the second trap.

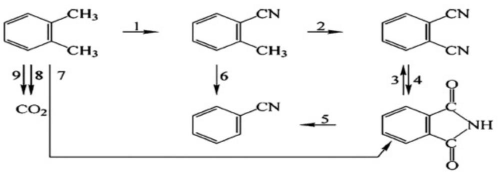

Figure 1. Reaction of ammoxidation of o-xylene on the V-Sb-Bi-Cr/γ-Al_2O_3-oxide catalyst

RESULTS AND DISCUSSION

To clarify the nature of the kinetic dependence of ammoxidation reaction of o-xylene on the V-Sb-Bi-Cr / γ-Al_2O_3-oxide catalyst studied the effect of the partial pressures of oxygen PO_2, ammonia PNH_3, P_I substrate and water PH_2O, and the contact time τ in the process speed in the temperature range 648-708 K. In this report discussed the results of the impact of PO_2, PNH_3 PH2O on process indicators and it is shown that competing ways of formation of the main products depends on the ratio of the partial pressures of components (PO_2 / PNH_3 and PH_2O / PNH_3). Influence of oxygen concentration on the process performance of the ammoxidation of o-xylene was investigated at τ 0.20 s and initial partial pressures of 1.47 kPa, 17.65 kPa, 36.76 kPa. At temperatures of 668 (Table 1) and 708 K (Table 2) in the investigated range of variation PO_2 conversion ratio α and the total conversion rate of o-xylene W is independent of oxygen partial pressure.

Table 1. Effect of oxygen partial pressure on the reaction kinetics of oxidative ammonolysis of o-xylene

kPa		α, %	W, mmol/g·h	S_i, kPa			
$P^0_{O_2}$	P_{O_2}			II	III	IV	CO_2
2.21	0.21	59.61	2.80	59.22	28.53	10.00	2.25
4.41	1.94	60.15	2.83	32.15	56.90	7.20	3.75
5.88	3.25	60.50	2.84	23.89	65.64	6.27	4.20
9.26	6.43	61.20	2.87	13.10	77.65	4.61	4.64
11.76	8.78	61.70	2.90	8.85	81.76	3.79	5.60
17.65	14.60	61.50	2.89	5.20	85.83	2.94	6.03
22.06	18.97	61.40	2.88	3.55	87.65	2.45	6.35

However, the selectivity of product formation (S_i) strongly depends on PO_2 and temperature. Similar patterns were observed at temperatures of 648 and 688 K.

Study of the effect PNH_3 at τ 0.20 s, 1.47 kPa, 9.26 kPa, 36.76 kPa, temperature 688 K (Table 3) on α has demonstrated that the conversion of o-xylene is independent of the ammonia concentration in the range of 3.86-21.44. At the same time there is the dependence of the S_i on PNH_3 and temperature as in the case of the influence of PO_2. Similar patterns were observed at temperatures of 648, 668 and 708K.

Table 2. Effect of oxygen partial pressure on the reaction kinetics of oxidative ammonolysis of o-xylene

kPa		α, %	W, mmol/g·h	S_i, kPa				
$P^0_{O_2}$	P_{O_2}			II	III	IV	V	CO_2
4.41	0.81	85.7	4.03	34.74	22.58	36.23	1.38	5.07
7.35	3.46	86.2	4.05	23.46	38.53	31.10	1.31	5.60
9.26	5.19	86.4	4.06	18.15	48.99	25.40	1.08	6.38
11.76	7.57	86.7	4.07	13.76	57.04	21.62	0.98	6.60
17.65	13.28	86.5	4.06	8.20	65.37	18.30	0.74	7.39
22.06	17.59	86.9	4.08	6.13	69.24	16.10	0.73	7.80

Increasing the concentration of O_2 in the initial reaction mixture increases the selectivity of phthalimide and decrease selectivity phthalonitriles (Table 1 and Table 2), and increasing the partial pressure of NH_3 is valid vice versa (Table 3). As you can see the relative increase in the concentration of ammonia and the reduction of oxygen in the gas contact it favors the formation of phthalonitrile, which is consistent with the previously conducted studies (Kolodina and Suvorov, 1962; CCCR 691447, 1979).

Table 3. Effect of the partial pressure of ammonia at the reaction kinetics for the ammoxidation of o-xylene

kPa		α, %	W, mmol/g·h	S_i, kPa			
$P^0_{NH_3}$	P_{NH_3}			II	III	IV	CO_2
4.41	3.42	71.70	3.37	3.70	86.22	2.30	7.78
8.82	7.77	72.17	3.39	10.10	75.77	6.80	7.33
13.24	12.13	72.66	3.41	14.85	68.00	10.27	6.88
17.65	16.46	74.70	3.51	17.75	62.93	13.72	5.60
22.06	20.86	74.21	3.49	21.65	57.29	15.25	5.81

This indicates an important role of oxidative steps in the proses of forming the imide heterocycle, since phthalimide unlike phthalonitrile contains in functional groups not only a nitrogen atom but also an oxygen atom. Therefore, for the ammoxidation of xylene, changing the ratio of O_2 and NH_3 on the used catalyst, it can be adjusted advantageously selectivity not only nitrogen - but also oxygen-containing derivatives of o-phthalic acid. Indeed, the modification of basic V-Sb-Bi / γ-Al_2O_3 oxide catalyst an additive of Cr_2O_3 increases the number of strongly acidic centers on the surface of the contact, which consequently causes the formation of the phthalimide directly from o-xylene (Bagirzade and Tagiev, 2014). In case of modification of ZrO_2 additive, the concentration of weakly acidic centers that favor phthalonitrile (Bagirzade and Tagiev, 2013) increases in the surface. As seen from the Tables 1-3, the distribution of products is observed to be dependent on the concentration ratio as the O_2 and NH_3, and H_2O and NH_3. Taking into consideration the similar kinetic laws of ammoxidation of xylene, and 4-bromo- and 4-phenyl-o-xylene (Bagirzade and Tagiev, 2014), we can say that if adsorbed fragment of the corresponding substrate as a common activated complex interacts with $ZrNH_3$, then a mononitrile is formed, which in turn, converted to dinitrile and in the case of interaction with ZrO_2, - imide, or CO_2 and H_2O on routes 7 and 8 (Fig.1) (Bagirzade, 2014). This suggests that the rate of competing reactions of equations (routes 1, 7 and 8, fig.1) to obtain-tolunitrile, phthalimide and CO_2 must be present partial pressures of O_2 and NH_3, which are consistent with those of the ammoxidation of o-xylene to V- Sb-Bi-Zr / γ-Al_2O_3-oxide catalyst at low ammonia concentrations (8,10). As for the two pathways of CO_2, it should be noted that one of these ways does not depend on the concentration of NH_3 (route 9, Fig.1) whereas the other-dependent (route 8, Fig.1). This is consistent with the results of previously conducted our work (Kolodina and Suvorov, 1962). It is important to add that the formation of CO_2 from 8 accompanied with obtaining phthalimide directly from o-xylene on route 7.

Study of the effect of water concentration in the feed was carried out at τ 0.20 s, 1.47 kPa, 9.26 kPa, 17.65 kPa and 668 K (Table 4). As seen in Table 4, which studied the range of variation PH_2O conversion and the total conversion rate of o-xylene are not dependent on the partial pressure of water. Moreover, PH_2O increase does not affect the selectivity formation of o-tolunitrile, benzonitrile and CO_2, but phthalimide selectivity is observed to grow as a result of reduction in the formation of phthalonitrile. Similar patterns were observed at temperatures of 688 and 708 K.

Table 4. The effect of partial pressure of water in the reaction kinetics of oxidative ammonoliz o-xylene

kPa				S_i, kPa			
$P^0_{H_2O}$	P_{H_2O}	α, %	W, mmol/g·h	II	III	IV	CO_2
7.35	11.03	61.00	2.87	13.20	72.67	9.41	4.72
22.06	25.67	60.80	2.86	13.30	75.56	6.40	4.74
36.76	40.37	61.20	2.87	13.10	77.65	4.61	4.64
51.47	55.07	61.40	2.88	12.97	78.77	3.57	4.69
66.18	69.77	61.30	2.88	12.92	79.38	3.00	4.70

Given the above, it is fair to say that carrying out the process for the ammoxidation of xylene in low concentrations of ammonia in the presence of water causes the formation of the corresponding imide, as it increases the proportion of reaction on routes 7 and 3 (Fig.1) and dinitrile disappears. However, by increasing ammonia feed to the initial total yield of the mixture of oxygen-containing compounds is reduced amid spontaneous increase of the amount of mono- and dinitriles on routes 1 and 2. Thus, the formation of staple associated with the competition of ammonia with oxygen and water for space on the surface of the V-Sb-Bi-Cr / γ-Al_2O_3-oxide catalyst at vapor phase ammoxidation of o-xylene.

The results of the effect of the partial pressure of the substrate and the impact of the contact time to the pace of the process, as well as the kinetic equations route scheme will be presented in the next report.

Conclusion

1) Kinetic regularities of ammoxidation on V-Sb-Bi- Cr / γ-Al_2O_3 oxide catalyst in the temperature interval 648-708K have been studied.
2) Presence of competitive adsorption of ammonia with oxygen and water as an example of ammoxidation of xylene-oxide catalyst V-Sb-Bi-Cr / γ-Al_2O_3 indicates that competing processes that form basic products occur on the surface of this contact
3) It is demonstrated that this phthalimide could be obtained both directly from the substrate, and hydrolysis of phthalonitrile.

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