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Effect of Reaction Medium on V-Ti Oxide Catalyst Composition in 2-Methyl-5-Ethylpyridine Ammoxidation

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Abstract

A chemical composition of V-Ti oxide catalyst changes in accordance with the reaction medium composition in a process of 2-methyl-5-ethylpyrydine ammoxidation into nicotinonitrile in an integral reactor. The presence of alkylpyridine concentration gradient along the catalyst bed leads to the appearance of V_2O_5 content gradient in the catalyst. V_2O_5 concentration increases in the conditions of alkylpyridine completed conversion in consequence of oxidative decomposition of VO_2-TiO_2 solid solution under the influence of N_2O nitrogen oxide, which is formed upon the NH_3 oxidation. An increase of V_2O_5 contents over 5 wt% causes rising of the share of the 2-methyl-5-ethylpyridine and nicotinonitrile destructive oxidation. An introduction of small amounts of alkylpyridine directly into the catalyst bed permits to create the definite alkylpyridine concentration gradient, which the optimal content of V_2O_5 is corresponding to, for any given conditions of oxidative reaction. The catalysts containing 1-5 wt% of V_2O_5 and solid solution of VO_2-TiO_2 possess of the highest selectivity to nicotinonitrile.

Introduction

V_2O_5-TiO_2 system is well known as a catalyst for partial oxidation and ammoxidation of aromatic and heterocyclic substances. Thus, it is successfully used in 3-methylpyridine ammoxidation into 3-cyanopyridine [1], in 3-methylpyridine oxidation into nicotinic acid [2], o-xylene into phtalic anhydride [3]; acenaphthene into naphtalic anhydride [4]. It is shown [5] that during the preparation of such catalysts thermal dissociation of V_2O_5 into VO_2 and formation of the succession of $VO_2 – TiO_2$ substitutional solid solutions, which become the basic component of the present system, take place.

Vanadium oxide V_2O_5 is the second component. Activity and selectivity of V-Ti catalysts depend on the ratio of $V_2O_5/VO_2 – TiO_2$, as well as on the composition of solid solution itself [5]. The final formation of the catalyst chemical composition occurs under the reaction medium influence during the catalytic reaction [6].

As a result of chemical interaction between the catalyst and reagents, its composition can undergo the considerable changes. There are the concentration gradients of the initial matter and the products of its conversion. In consequence of it, the contents of the catalyst and its catalytic effect are different along the length of the bed. Therefore, in order to get the objective data about activity and selectivity of catalyst, it is necessary to take into consideration the special features of the reaction medium action on a catalyst, especially in the complex, multicomponent reaction like ammoxidation. It is important for selection of efficient catalyst, as one can obtain incorrect information of the catalyst properties because of unsuccessful choice of the reaction conditions.

The present work is devoted to the investigation of the influence of reaction medium on V-Ti oxide catalyst in the condition of 2-methyl-5-ethylpyridine ammoxidation into 3-cyanopyridine in an integral reactor.

Experimental

V-Ti catalyst was prepared by the method [7] of mixing the vanadia V_2O_5 (Chem. Purum) and rutile TiO_2 (Purum) powders (mole ratio 1/16; V/Ti atomic ratio is 1/8). The mixture was pressed into the tablets 4 mm in diameter and in thickness, which were sin-

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*corresponding authors. E-mail: pochtennaya@yahoo.com tered in a muffle furnace at 700°C for 2 h in air. V_2O_5 contents in the finished catalyst was 4 wt%. The rest (96 wt%) was the solid solution of $VO_2 – TiO_2$.

The flow reactor with a fixed catalyst bed was used for conducting of 2-methyl-5-ethylpyridine ammoxidation. The reactor's design provided to take the samples of catalysate at 5 points along the catalyst bed 1 meter in length.

The starting components – alkylpyridine, air, ammonia and water – were fed into the reactor in the form of a vaporous mixture of the following composition: alkylpyridine – 0.1; O_2 – 9.1; NH_3 – 2.7 and H_2O – 53.9 vol%; the rest was N_2. A reaction temperature was 360-380°C. The reaction products were collected in the scrubber, sprayed with water, and analyzed by the gas chromatograph with a flame ionization detector.

For experiments on 3-cyanopyridine oxidative ammonolysis, the samples of V-Ti catalyst with the various contents of V_2O_5 in a range from 1 to 7.5 wt% were prepared. It was achieved by varying of the heat treatment temperature and activation conditions of the catalyst during the oxidative reaction.

For the experiments on investigation of the influence of N_2O on catalyst, three samples of V-Ti catalyst were used: 1 – the fresh sample sintered at 800°C for 2 h, containing 2.5 wt% of V_2O_5 both in a surface layer and in bulk; 2 - the fresh sample sintered at 700°C for 2h, containing 4.1 wt% of V_2O_5 both in a surface layer and in bulk; 3 – the sample number 2, which had worked in 2-methyl-5-ethylpyridine ammoxidation in the next conditions: alkylpyridine loading – 4.2 g/h; composition of reaction mixture: alkylpyridine – 0.4; O_2 – 14.0; NH_3 – 5.3 and H_2O – 27.6 vol%; the rest is N_2. The used catalyst contained 5.7 wt% of V_2O_5 in a surface layer and 4.6 wt% of V_2O_5 in bulk.

The influence of reactants on the catalysts was studied using an electric heated quartz microreactor with the fixed catalyst bed. For each experiment, 5 g of fresh catalyst sample, or one worked at the conditions described above, were taken.

Atmospheric air, distilled water, commercial N_2O and NH_3 were used for experiments. Nicotinonitrile has been obtained by 3-methylpyridine ammoxidation and purified by recrystallization from hexane, following distillation at barometric pressure (B.p. – 201°C at 689 mm Hg).

V_2O_5 content in the catalysts was analyzed by IR spectroscopy method [8] on UR-20 spectrophotometer; the phase composition was determined by X-ray powder method, using DRON-0.5 equipment.

Results and discussion

The rate of V-Ti catalysts analysis change depends on the process conditions and has the highest value in the beginning of catalyst running [9]. In 20-30 hours after starting of 2-methyl-5-ethylpyridine ammoxidation, V-Ti oxide catalyst (atomic ratio of V/Ti is 1/8) reaches the steady state, what manifests itself in constancy of the catalysate's contents. The analysis of the catalyst in the steady state along the length of the bed demonstrates that the V_2O_5 distribution through the bed depends on the concentration of starting alkylpyridine there (Fig. 1). In the catalyst layers, which are in the beginning of the bed, where the alkylpyridine concentration is maximal, V_2O_5 content decreases to 0.8-1.0 wt%. The original contact contains 4 wt% of V_2O_5. As the alkylpyridine concentration decreases along the catalyst bed, vanadium oxide (V) is reduced less and less, and in the end of the bed, where the amount of starting material is only a few percent of the initial one (Fig. 1, curve 1), V_2O_5 content in the catalyst is equal to the original (Fig. 1, cur. 3). The concentration of forming 3-cyanopyridine increases gradually through the bed and has a maximum at the outlet from the bed (Fig. 1, cur. 2).

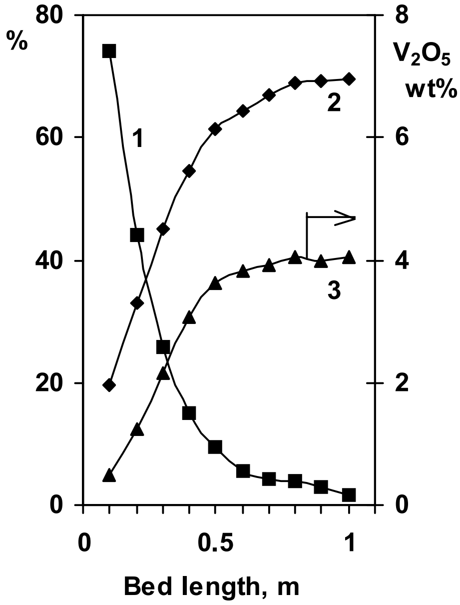

Fig. 1. 2-Methyl-5-ethylpyridine (MEP) ammoxidation on V-Ti catalyst. T - 360-380°C, MEP loading - 6.5 g/h. Composition of the starting reaction mixture: MEP – 0.15; O_2 – 9.1; NH_3 – 2.7; H_2O – 53.6 vol%; the rest - N_2. V_2O_5 content in the fresh catalyst – 4.0 wt%. 1 –unreacted MEP; 2 – 3-cyanopyridine yield; 3 – V_2O_5 content.

When alkylpyridine concentration in the starting reaction mixture was made lower than that in the previous case it was an unexpected result of dropping of the 3-cyanopyridine yield from 68 to 38%. From Figure 2, where the plots of the original 2-methyl-5-ethylpyridine conversion and 3-cyanopyridine yield against the catalyst bed length during the ammoxidation process are presented (curves 1 and 2), one can see that the full conversion of alkylpyridine in such conditions is reached approximately in the middle of the catalyst bed. The sharp drop of the nitrile yield occurs in those catalyst layers, where alkylpyridine is already absent. As it follows from the same figure, the running (more than 100 h) catalyst undergoes substantial changes. Comparison of V_2O_5 and alkylpyridine distribution curves (Fig. 2, cur. 1 and 3) along the catalyst bed length shows that an increase of V_2O_5 percentage takes place at full alkylpyridine conversion. In the bed's end the amount of V_2O_5 goes up to 7.5 wt%, *i.e.* almost two times exceeds the starting quantity (4 wt%).

The established steady catalyst composition along the bed length displays the different selectivity to 3-cyanopyridine. As Fig. 2, cur. 2 shows, the nitrile forming, when it falls within the bed zone having the increased V_2O_5 content, is subjected to the oxidative conversion, what is indicated by the corresponding increase of CO_2 yield (Fig. 2, cur. 4). Comparing the plots of nitrile yield and V_2O_5 content along the catalyst bed in Fig. 1 and Fig. 2, one can notice that the decrease of nitrile yield is not observed, if the V_2O_5 percentage in the catalyst layer is not more than that in the original contact (4 wt%). Therefore, we supposed that just an increase of vanadia contents in the catalyst above 4 wt% causes the decrease of its selectivity to cyanopyridine.

The special study of 3-cyanopyridine behavior in ammoxidation conditions confirms this supposition and shows that a decrease of the nitrile yield is an outcome of its oxidative decomposition. The experiments were carried out with some samples of V-Ti oxide catalyst (V/Ti atomic ratio is 1/8) containing different amounts of V_2O_5, in a range from 1 to 7.5 wt%. The data in Table 1 show that in the ammoxidation conditions, as the V_2O_5 content in the catalyst is increasing, the nitrile conversion degree rises. On the catalysts containing 1-5 wt% of V_2O_5, the nitrile conversion even at 400°C does not exceed 11%. When increasing of V_2O_5 content in the catalyst above 5 wt%, the sharp rise of its activity is observed. The nitrile conversion with the catalyst containing 7.5 wt% of V_2O_5 reaches 85% at 400°C.

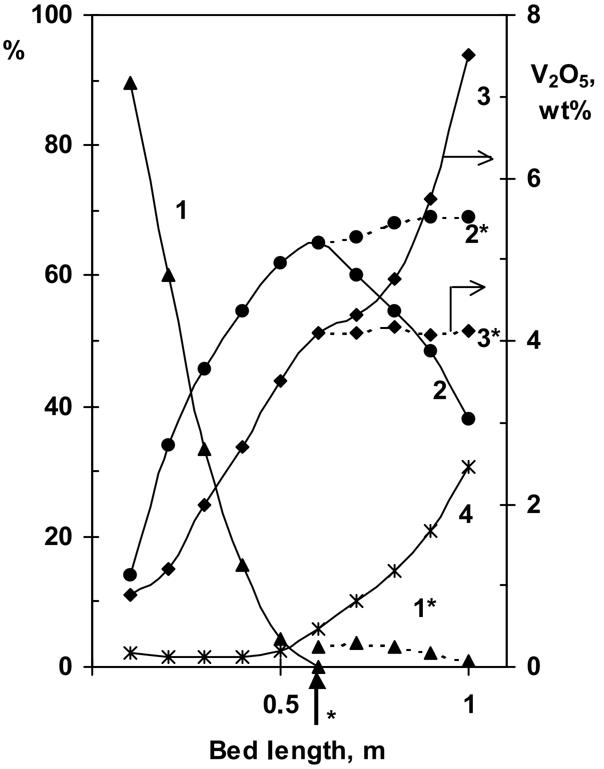

Fig. 2. 2-Methyl-5-ethylpyridine (MEP) ammoxidation on V-Ti catalyst. T - 360-380°C, MEP loading – 4.2 g/h. Composition of the starting reaction mixture: MEP – 0.1; O_2 – 9.1; NH_3 – 2.7; H_2O – 53.9 vol%; the rest - N_2. Additional MEP feed – 0.168 g/h, the place of extra injection is indicated by the arrow. V_2O_5 content in the fresh catalyst – 4.0 wt%. 1,1* – unreacted MEP; 2,2* – 3-cyanopyridine yield; 3,3* – V_2O_5 content; 4 – CO_2 yield. Solid lines – in the steady conditions; dotted lines – with the extra feeding of MEP.

A decrease of nitrile yield due to its oxidative de-

Table 1

Influence of V_2O_5 content in V-Ti catalyst on 3-cyanopyridine conversion. (contact time – 0.2 s, molar ratio: 3-cyanopyridine: O_2:NH_3:H_2O = 1:250:20:135)

V_2O_5 content, wt%	Conversion, %		
	340°C	360°C	400°C
1.0	3	3	4
2.2	5	6	7
3.8	8	9	10
5.0	9	10	11
5.6	19	28	36
6.7	32	45	60
7.5	45	61	85

composition is possible to prevent by making an optimal concentration profile of V_2O_5 in the catalyst through its bed length. It may be attained by an injection directly into the layers containing more than 5 wt% of V_2O_5 in the steady conditions of a small extra amount (4% from the total loading) of starting alkylpyridine which easily reduces the catalyst and makes it an optimal one for the given conditions. The place of the injection of the additional amount of alkylpyridine is marked by the arrow in Fig. 2. As a result of such operation, V_2O_5 concentration gradient along the bed decreases and becomes like in conditions with higher alkylpyridine concentration in the starting reaction mixture (compare Fig. 1, cur. 3 and Fig. 2, cur. 3*). A decrease of 3-cyanopyridine yield is not observed in these conditions (Fig. 2, cur. 2*).

An increase of V_2O_5 content in V-Ti catalyst under the conditions of 2-methy-5-ethylpyridine ammoxidation, what was detected by us, is very curious. The catalyst is a system consisting of V_2O_5 and VO_2-TiO_2 solid solution. Because of that the only possible way to form vanadium oxide (V) is the oxidative decomposition of VO_2-TiO_2 solid solution with the release of V_2O_5 phase under the effect of reaction medium. As far as we know from the literature, it has been noted that solid solutions have a high stability in the oxidizing and reducing conditions, as well they further for the stabilization of all established catalytic system on the whole [5,10].

Among the components of the reaction mixture molecular oxygen and, potentially, some of nitrogen oxides forming at NH_3 oxidation [11] are the oxidizers.

According to the literature data [5,12], the oxygen does not exert an effect on the composition of V-Ti catalysts. Nitrogen oxide (I) N_2O is used as an oxidant instead of oxygen in the processes of catalytic oxidation, for example, of benzene into phenol [13]. It is noted that the reduced V-containing catalysts may be oxidized under N_2O effect [13]. The small quantities of N_2O are often present in the mixture of ammoxidation gas products. For that matter, an investigation of N_2O effect on a row of the V-Ti catalyst samples at the catalysis temperature in order to find out the N_2O oxidizing ability has been carried out.

The experiment has shown that the treatment of the catalyst by N_2O causes a slow increase of V_2O_5 content there. The data on N_2O influence on the chemical composition of three samples of V–Ti catalyst, having similar atomic ratio of V/Ti (1/8) but different V_2O_5 content, are presented in Fig 3. The samples 1 and 2 (both fresh) had the homogeneous composition in depth of grain and contained 2.5 and 4.0 wt% of V_2O_5, correspondingly. The sample 3 has previously been subjected to the action of reaction medium in 2-methyl-5-ethylpyridine ammoxidation and had 5.7 wt% of V_2O_5 in surface layer and 4.6 wt% in bulk. It has been found that V_2O_5 content gradually increases in all samples under N_2O effect, and the relative change of V_2O_5 content in the surface layers has been more than that in bulk (Table 2). The sample having the least V_2O_5 amount before the treatment by N_2O (#1) suffers the greatest change, and vice versa, the sample containing the highest quantity of V_2O_5 undergoes the least change. As all three samples have the same atomic ratio of V/Ti and are the systems of $V_2O_5/VO_2–TiO_2$ (solid solution), it is clear that the less is V_2O_5 content in the catalyst the higher is VO_2 quantity in the solid solution. Hence, the more is VO_2 content in $VO_2–TiO_2$ solid solution the higher is the value of V_2O_5 concentration change in the sample.

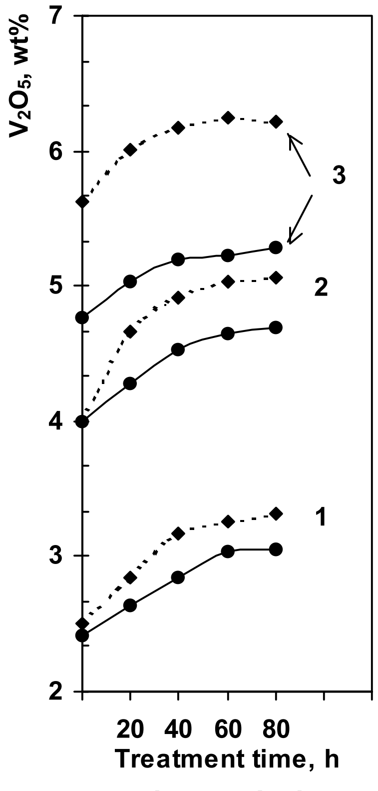

Fig. 3. V_2O_5 content change under the N2O effect on three samples of V–Ti catalyst at 275°C. V_2O_5 initial concentration: sample 1 – in the surface layers and bulk – 2.5 wt%; 2 – in the surface layers and bulk – 4.0 wt%; 3 – in the surface layers – 5.76; in bulk – 4.6 wt%. N_2O content in the air mixture – 35 vol%; volumetric flow rate V_{vol} – 8000 h^{-1}. Solid lines – in bulk; dotted lines – in the surface layers.

Table 2

Change of V-Ti oxide catalyst composition under N_2O effect. (T - 275°C, treatment duration 80 h).

#	Catalyst samples (atomic ratio of V/Ti = 1/8)	V_2O_5 content, wt%	Absolute concentration of V_2O_5 after the treatment, wt%		Relative change of V_2O_5 concentration after the treatment, rel%	
			Surface layer	Bulk	Surface layer	Bulk
1	Tsint. - 800°C,fresh	2.50	3.30	3.10	32.0	24.0
2	Tsint. - 700°C, fresh	4.00	5.10	4.72	27.5	18.0
3	Tsint. - 700°C, used in 2-methyl-5-ethylpyridine ammoxidation	4.60 - in bulk	-	5.30	-	15.2
		5.76 - in a surface layer	6.82	-	18.4	-

In the catalysis conditions, N_2O can interact with V^{4+} ions in $VO_2 – TiO_2$ solid solution, oxidizing them to V^{5+}. In the presence of alkylpyridine, the forming V^{5+} ions are reduced back to V^{4+}. Thus, in the steady conditions and with the presence of alkylpyridine in the reaction mixture, the definite ratio of V^{5+}/V^{4+} is formed in the catalyst. Such catalyst possesses of the high selectivity to 3-cyanopyridine. However, in the tail of the catalyst bed, in the absence of the reductant - alkylpyridine, the oxidation of catalyst by N_2O is observed. A result from it is the oxidative decomposition of VO_2-TiO_2 solid solution with formation of vanadium oxide (V). The optimal ratio of $V_2O_5/VO_2 – TiO_2$ is shifted to increasing of V_2O_5 content, which is unfavorable for the catalyst selectivity.

As the oxidative decomposition of the solid solution is a very slow process, the change of the catalyst effect is displayed only after the definite amount of V_2O_5 (5 wt% or more) is accumulated in the catalyst, and it manifests itself in intensification of the destructive oxidative processes leading to a sharp decrease of 3-cyanopyridine yield.

Conclusions

The reaction medium can have a considerable influence on the V–Ti catalyst composition and consequently on its selectivity. The creation of a definite gradient of the alkylpyridine concentration along the bed allows one to change the catalyst steady composition directionally. The catalysts containing 1-5 wt% of V_2O_5 and $VO_2 – TiO_2$ solid solution possess the highest selectivity in 2-methyl-5-ethylpyridine ammoxidation to 3-cyanopyridine. N_2O forming at NH_3 oxidation during the ammoxidation process can interact with VO_2-TiO_2 solid solution, causing its oxidative decomposition with V_2O_5 formation.

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