



Catalytic Properties of V–Ti–O Catalysts in the Oxidation and Ammoxidation of o-xylene, Acenaphthene and β -picoline

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Abstract

Catalytic properties of vanadium–titanium oxide catalysts in the oxidation and ammoxidation of o-xylene, acenaphthene and β -picoline have been studied. Methods of preparation of catalysts with varying amounts contents of V_2O_5 have been described. It has been shown that activity and selectivity in oxidation of organic compounds of different nature depends on the V_2O_5 content and the ratio of the oxides in the solid solution. Maximum selectivity in relation to phthalic and naphthalic anhydrides, naphthalimide and nitrile of nicotinic acid with the maximum conversion is observed with the catalysts having 4–6 wt.% of V_2O_5 . Catalysts with other compositions showed lesser conversion of the initial substance. A catalyst, representing VO_2 – TiO_2 solid solution, exhibits the least activity and selectivity among the tested samples for oxidation of o-xylene and ammoxidation of β -picoline. For oxidation and ammoxidation of acenaphthene, the least activity and selectivity are exhibited by a catalyst, containing alongside with the solid solution no more than 3% by weight of V_2O_5 . Catalysts with an equal V_2O_5 amount, but differing one from the other by a composition of a solid solution, display different catalytic activity in o-xylene oxidation and β -picoline ammoxidation. Enrichment of solid solution with VO_2 or a decrease in the amount of the latter in the content decrease activity and selectivity of a catalyst.

Introduction

Catalysts on the basis of vanadium pentoxide, modified by oxides of transition and other metal oxides, display high activity and selectivity for oxidation and ammoxidation of alkylbenzenes, polycyclic hydrocarbons and pyridine bases [1-4]. It is known [5], that in a series of composition of vanadium–titanium catalysts, two-phase system is formed, consisting of a VO_2 – TiO_2 solid solutions and V_2O_5 . The amount of the latter is determined by the initial composition of the catalyst and preparation conditions employed. The literature data on the effect of the composition of V_2O_5 – TiO_2 catalysts on their catalytic properties in oxidation and ammoxidation of acenaphthene and β -picoline show the main concern on the influence of the ratio of the initial oxides on observed activity and selectivity [3,4]. The absence of information of catalytic properties of VO_2 – TiO_2 solid solution in oxidation reactions [6] and the effect of varying V_2O_5 content on different compositions of

VO_2 – TiO_2 solid solution on oxidation of o-xylene, acenaphthene and β -picoline have motivated an interest to this investigation presented in this paper.

Experimental

Catalysts were prepared from reagent-grade V_2O_5 and TiO_2 . With this purpose the mixtures of oxides of vanadium (V) and titanium (IV) in the molar ratio of 1:16 and 1:32 were thoroughly mixed, formed in tablets, calcined in a continuous air feed furnace zone, then cooled and ground in granules of the dimensions 3–5 mm. The temperature (500–1000°C) and time of calcination (2–10 h) were chosen experimentally, while analyzing them repeatedly for vanadium pentoxide content in the heat treated samples. The preparation methods employed allowed the variation of V_2O_5 content, thus permitting to employ them in catalyst evaluation with definite V_2O_5 content. The V_2O_5 content in the catalyst solid samples was determined by IR-spectroscopy using a SPECORD spectrophotometer in the form of KBr discs [6].

An X-ray phase analysis of the catalysts was car-

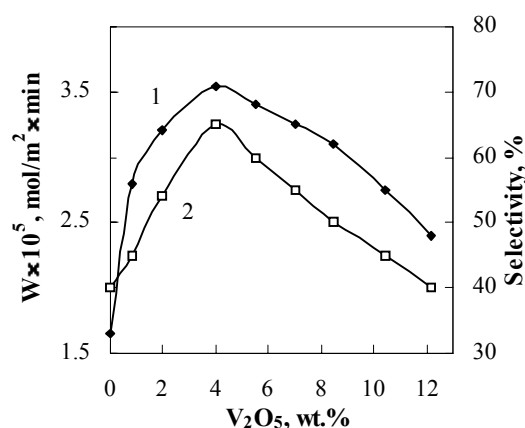
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ried out on a diffractometer "DRON-0.5" with Co K_{α} radiation. The activity was determined in a gradient-free reactor of an ideal shifting [7]. Experiments for the study of oxidation of the initial organic compounds were carried out in a flow-through reactor with a quartz reaction tube with the length of 130 mm and diameter of 20 mm and in a reactor made of stainless steel with the length of 1000 and diameters of 20 mm respectively. The reaction products were analyzed by chromatography with the use of a flame-ionizing detector (FID) and TCD.

Results and discussion

The variation of Catalytic activity of vanadium–titanium catalysts $V_2O_5 \cdot 16TiO_2$ which differ in the stationary state by a vanadium pentoxide content, and therefore by the ratio of V_2O_5 and $VO_2 \cdot TiO_2$, in oxidation of o-xylene is shown in Fig. 1. as a function of V_2O_5 content. The catalyst, representing a solid solution $VO_2 \cdot TiO_2$ possessed the least activity for this reaction. On a vanadium–titanium catalyst, containing apart from a solid solution 0.7–1.0 wt.% of V_2O_5 , o-xylene oxidation rate sharply increased, and was raising smoothly with the further increase of V_2O_5 amount in the catalyst, reaching a maximum value with the V_2O_5 concentration of 4 wt.%, and then was slowly decreasing. The variation of selectivity for phthalic anhydride formation also showed a similar trend. Catalysts with the highest activity, containing 4–5 wt.% of V_2O_5 possessed a maximum selectivity in o-xylene oxidation.

Similar behaviour was also observed on these catalysts for the oxidation of acenaphthene and the



The feed of o-xylene – 188 g, air - 5000 l·l⁻¹ cat·h⁻¹, T – 400°C, contact time – 0.14 s. 1 – The rate of o-xylene oxidation, 2 – selectivity to phthalic anhydride.

Fig. 1. Influence of V_2O_5 content in $V_2O_5 \cdot 16TiO_2$ catalyst on it catalytic activity (W) and selectivity (S) in o-xylene oxidation.

corresponding data are given in Table 1. Vanadium–titanium catalysts, possessing 5.0–6.5 wt.% of V_2O_5 and solid solution, displayed the higher activity and selectivity. The yield of naphthalic anhydride on these catalysts reached 76–78% with the full conversion of initial hydrocarbon. With the content of vanadium oxide (V) in the catalyst up to 1.5–3.0 wt.%, as a result of its reduction to VO_2 and enrichment of the $VO_2 \cdot TiO_2$ solid solution by the latter, a decrease in the acenaphthene conversion was observed as also a sharp decrease in the yield of naphthalic anhydride and acenaphthelene.

Change of the concentration of vanadium oxide (V) in the catalyst $V_2O_5 \cdot 16TiO_2$ influenced its catalytic activity also in acenaphthene ammoxidation. At

Table 1

Oxidation of acenaphthene on the catalyst $V_2O_5 \cdot 16TiO_2$
The feed rate of acenaphthene – 115 g, of air – 2370 liter per 1 liter of catalyst on 1 hour,
contact time – 0.3 s, temperature – 380°C.

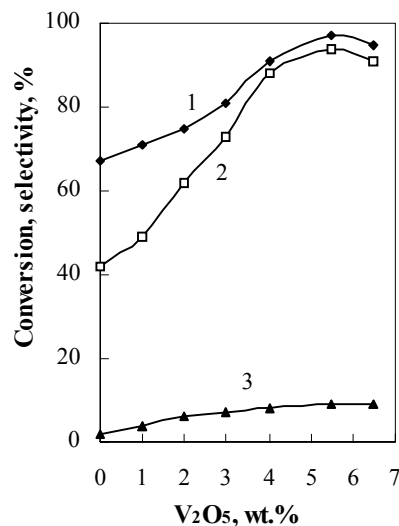
Acenaphthene conversion, %	Yield, %			V_2O_5 , wt.%
	Naphthalic anhydride	Acenaphthylene	CO ₂	
100	76	Absent	22	6.5
100	78	Absent	22	5.7
100	77	Absent	22	5.0
100	71	Absent	27	4.3
84	37	8.6	25	2.8
72	35	10.9	24	1.5

the temperature 365°C, contact time 0.4 s and with molar ratio of acenaphthene:O₂:NH₃:H₂O = 1:32:18:635 vanadium–titanium catalyst, containing 5.3–6.0 wt.% of V₂O₅ and VO₂–TiO₂ solid solution, provided a complete acenaphthene conversion and the yield of naphthalic acid imide of 74%. A decrease of V₂O₅ concentration in the catalyst down to 3.3 wt.% under the same reaction conditions, resulted in a decrease of an initial hydrocarbon conversion down to 83% and that of the naphthalimide yield-down to 48.1%.

Study of ammoxidation reaction of β-picoline under comparable conditions on different samples of vanadium–titanium catalyst, which contained an initial composition 12.4 wt.% of V₂O₅, but differed one from the other in the stationary state by vanadium (V) oxide content and its ratio with a VO₂–TiO₂ solid solution, testified to the fact that activity and selectivity of the samples depended on V₂O₅ amount in the catalyst (Fig. 2). On the VO₂–TiO₂ solid solution, in absence of V₂O₅ in the catalyst, conversion of 3-methylpyridine didn't exceed 65%, with 40% selectivity of the formation of nicotinic acid nitrile. The presence of V₂O₅ and an increase in its concentration resulted in an increase in activity and selectivity, especially noticeable in case of V₂O₅ content more than 4 wt.%. Maximum conversion of β-picoline (95%) and selectivity of nicotinic acid nitrile (93–95%) were observed on catalysts, containing VO₂–TiO₂ solid solution and 5.6–6.0 wt.% of V₂O₅.

It is noteworthy, that vanadium–titanium catalysts are less sensitive to the changes of the reaction conditions employed within certain limits. Thus, for example, durable tests (300 h) of vanadium–titanium catalyst, containing 5.6 wt.% of V₂O₅ ammoxidation of 3-methylpyridine with oxygen excess in the reaction mixture showed that the yield of nicotinic acid nitrile remained practically constant and constituted 91.5 mol.% with 96.2% conversion of β-picoline. The same catalyst with a decrease of oxygen excess due to an increase in the concentration of the initial pyridine base with the molar ratio of β-picoline, oxygen, ammonia and water, equal to 1:35:8:47, provided 3-methylpyridine conversion at the level of 97.7% with the yield of nicotinic acid nitrile, equal to 93–95% from the theoretical one. An analysis of the catalyst showed that in the process of a durable exploitation, V₂O₅ content therein did not change significantly.

X-ray phase analysis of vanadium–titanium cata-



The feed of 3-methylpyridine – 27.5 g, air – 1390 l, NH₃ – 42 g, H₂O – 250 g·l⁻¹ cat.·h⁻¹. T - 380°C, contact time – 0.46 s. 1 – 3-methylpyridine conversion, 2 – selectivity to 3-cyanopyridine, 3 – selectivity to CO₂.

Fig. 2. Variation of ammoxidation of 3-methylpyridine on V₂O₅·16TiO₂ catalyst.

lysts, working in the conditions of oxidation and ammoxidation of o-xylene, acenaphthene and β-picoline, testified to the identity of their compositions. The catalysts represented a two-phase system, containing V₂O₅ and VO₂–TiO₂ solid solution. Reduction of V₂O₅ into VO₂ proceeded both in the process of catalyst preparation under the influence of temperature, and under the conditions of oxidation reaction. The formed VO₂ wasn't determined by X-ray phase analysis in V–Ti–O catalysts, since it was directly included in the catalyst composition, forming with TiO₂ (rutile) a continuous series of solid solution of VO₂–TiO₂. It was proved by the comparison of lattice parameters of vanadium catalysts and specially synthesized solid solutions and the agreement with the known literature data [9]. The presence of V₂O₅ in the catalyst was indicated by the IR-spectral data, possessing an absorption band at 1020 cm⁻¹, which was characteristic for V=O.

From the data presented in this paper it is seen, that the amount of vanadium (V) oxide in the catalyst V₂O₅·16TiO₂ plays a decisive role in the observed activity and selectivity. The composition of a solid solution is also of importance, since a change in V₂O₅ content in the catalyst immediately entails a change therein of not only the ratio between V₂O₅ and VO₂–TiO₂, but also the composition of a solid solution. Enrichment of VO₂ solid solution or a decrease in the amount of the latter in its composition influences

the catalytic activity of the catalyst. This was confirmed by the results of *o*-xylene oxidation and β -picoline ammoxidation on the catalysts $V_2O_5 \cdot 16TiO_2$ and $V_2O_5 \cdot 32TiO_2$, which contained after the preparation an equal V_2O_5 amount (4.2 wt.%), but differed by the composition of a solid solution. Upon the *o*-xylene oxidation on the catalyst $V_2O_5 \cdot 32TiO_2$, in which a solid solution contained more TiO_2 and less VO_2 than the catalyst $V_2O_5 \cdot 16TiO_2$, conversion of the initial substrate and the yield of phthalic anhydride were lower by 10–15% in comparison with the catalyst $V_2O_5 \cdot 16TiO_2$, with an equal V_2O_5 content therein (Table 2). Upon β -picoline ammoxidation on the catalyst $V_2O_5 \cdot 32TiO_2$, alkylpyridine conversion and nicotinonitrile selectivity constituted 78 and 70% respectively, which was by 10% lower than that on the catalyst $V_2O_5 \cdot 16TiO_2$ with the same V_2O_5 amount, but a different composition of a solid solution.

Conclusion

The results obtained show that a change of catalytic properties of vanadium-titanium-oxide catalysts for the oxidation of organic compounds, different by their nature, is connected with a change of V_2O_5 content in the catalysts and the composition of a solid solution VO_2 – TiO_2 formed during the reaction. With an optimal V_2O_5 content (4–6 wt.%) in a stationary catalyst and a corresponding composition of a solid solution, a high selectivity for oxidation and ammoxidation of *o*-xylene, acenaphthene and β -picoline into phthalic and naphthalic anhydrides, naphthalimide and nicotinonitrile is attained.

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Table 2

Oxidation of *o*-xylene on $V_2O_5 \cdot 16TiO_2$ and $V_2O_5 \cdot 32TiO_2$ catalysts, containing 4.2 wt.% of V_2O_5 *.
(Experimental conditions are given in Fig. 1).

T, °C	o-xylene conversion, %	Selectivity, %	
		Phthalic anhydride	CO ₂
360	$\frac{52}{44}$	$\frac{40}{28}$	$\frac{20}{14}$
	$\frac{80}{66}$	$\frac{50}{37}$	$\frac{32}{25}$
400	$\frac{95}{80}$	$\frac{65}{50}$	$\frac{37}{32}$

*Multiplier – catalyst $V_2O_5 \cdot 16TiO_2$, divider – catalyst $V_2O_5 \cdot 32TiO_2$.

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