

## Catalysts for Alkylbenzene and Alkylpyridine Ammoxidation

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### Abstract

An increase of effectivity of binary and ternary vanadium containing oxide catalysts can be achieved by a regulation of chemical and phase catalyst composition during their preparation. Activity and selectivity of V-Ti catalysts depend on the ratio of  $V_2O_5$  to  $VO_2$  in the succession of substitutional solid solutions  $VO_2$ - $TiO_2$ , as well as on the crystal modification of  $TiO_2$ . It was investigated the influence of vanadium oxides over the rate of the polymorphous conversion from anatase to rutile and the kind of  $TiO_2$  crystal modification over  $V_2O_5$  reduction degree during the thermal treatment of V-Ti catalysts. The synthesized catalysts offered producing nicotinonitrile from 3-methylpyridine with 93-95% mol. yield. Modifying of V-Ti catalysts by  $SnO_2$  increased their activity. The reason is V=O bond weakening under the influence of  $SnO_2$ . That was verified by increasing of  $V_2O_5$  dissociation rate almost by an order in comparison with V-Ti catalysts.  $SnO_2$  in the ternary catalysts exists as individual phase and acts as a donor of oxygen for the lower vanadium oxides. It provides the high stability of V-Ti-Sn catalysts and possibility of obtaining isonicotinonitrile with 95-97% mol. yield from 4-methylpyridine. The investigation of the mutual influence of starting components in the ternary V-Ti-Zr catalysts showed that  $ZrO_2$  prevented the polymorphous transformation from anatase into rutile. In its turn, anatase stabilized baddeleyite, which has a higher catalytic activity than ruffite. Taking into account the mutual influence of the components, it was able to prepare the selective V-Ti-Zr catalyst. It offered obtaining nicotinonitrile from 3-methylpyridine with 92-96% mol. yield.

### Introduction

One of the steady tendencies in catalysis consists in discovering of ways for the selection of the effective catalysts for oxidation and ammoxidation of benzene and pyridine derivatives to nitriles, imides and anhydrides of carbon acids, which are the important products of organic synthesis.

The vanadium containing oxide catalysts, which are widely used in the oxidative reactions, were investigated by many researchers [1,2]. However, it is necessary to continue this work, because there is a deficiency of information about phase and chemical composition of such catalysts. Especially it refers to the multicomponent catalysts. There is little information about them, or there is nothing at all.

The aim of the present work was to find a possibility to increase the effectivity of binary and ternary vanadium containing oxide catalysts in alkylbenzene and alkylpyridine ammoxidation during their prepara-

tion. The chemical and phase catalysts changes have been studied under various preparation conditions. At the same time the prepared catalysts were tested in the oxidative reactions. The following catalysts V-Ti, V-Sn, V-Zr, V-Ti-Sn and V-Ti-Zr were chosen as the investigation objects.

The results of our work gave us a possibility to synthesize the active and selective catalysts for alkylbenzene and alkylpyridine ammoxidation.

### Experimental

Vanadium-titanium, vanadium-titanium-zirconium and vanadium-titanium-tin catalysts were prepared from  $V_2O_5$  of «chem. Pure» mark,  $TiO_2$  of «pure» mark,  $ZrO_2$  of «pure» mark and  $SnO_2$  of «pure» mark by mixing of oxides followed by pressing of the charge into pills. The formed samples were dried at 120°C and heated at 620°C in the air atmosphere.

The phase and chemical contents of the catalysts were studied by recording of sample diffractograms on X-Ray diffractometer.

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Experiments of oxidation and oxammonolysis of *o*-xylol, 3-methylpyridine and 2-methyl-5-ethylpyridine were conducted on a running plant with a reaction tube made of stainless steel, of 1100 mm of length and 20 mm in diameter.

Analysis of the catalyst content was done by the method of chromatography. Chromaton N-AW-DMCS, impregnated with 15% of silicon DC-550 was used as a sorbent for separation of the reaction products.

Catalytic activity of the catalysts was studied in a gradient-free glass reactor with a mixing device.

## Results and discussion

It is known [3,4], that the activity of anatase containing V-Ti catalysts is higher than that of rutile. The activity of anatase itself is two times as much than rutiles one. Thus, the anatase activity in 2-methyl-5-ethylpyridine oxidation is two times as much than that of rutile [5]. We have studied a polymorphous transformation of TiO<sub>2</sub> from anatase to rutile under the action of vanadium oxides, which can be present in V-Ti catalysts. It was determined, that this transformation is promoted by the all studied vanadium oxides, namely V<sub>2</sub>O<sub>5</sub>, VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>. As Fig. 1 shows, the rate of polymorphous conversion depends on the oxidation degree of vanadium. The severity of exposure of vanadium oxides increases in the following row: VO<sub>2</sub> < V<sub>2</sub>O<sub>5</sub> < V<sub>2</sub>O<sub>3</sub>.

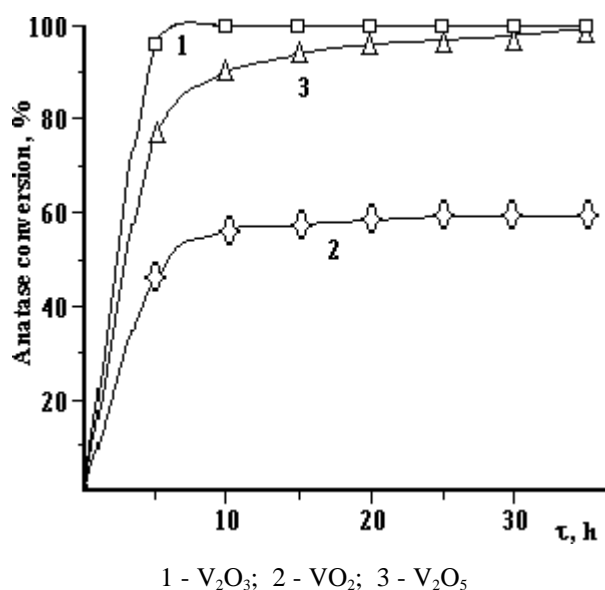


Fig. 1. Transformation of anatase into rutile in the presence of V<sub>x</sub>O<sub>y</sub> (10% wt.) at 700°C.

On the other hand, the kind of TiO<sub>2</sub> crystal modification influences on the reduction degree of V<sub>2</sub>O<sub>5</sub> upon the heat treatment of V-Ti catalysts. It is known [6], that the thermal dissociation of V<sub>2</sub>O<sub>5</sub> with the formation of VO<sub>2</sub> takes place during the heating of such catalysts. The reduction rate of V<sub>2</sub>O<sub>5</sub> into VO<sub>2</sub> increases with the rise of a treatment temperature. As Fig. 2 shows, V<sub>2</sub>O<sub>5</sub> concentration decreases with the rising of temperature. The reduction of V<sub>2</sub>O<sub>5</sub> is higher in the presence of anatase, than that in the presence of rutile. Forming VO<sub>2</sub> interacts with the rutile phase. The result is the formation of the succession of substitutional solid solutions of VO<sub>2</sub>-TiO<sub>2</sub>. They themselves have rather low activity in the oxidative reactions. However, it is possible to receive the high-active and selective catalyst by the choice of a necessary ratio of V<sub>2</sub>O<sub>5</sub>/solid solution.

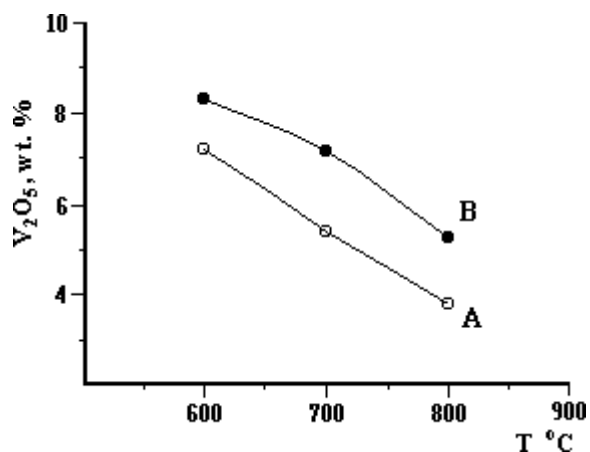


Fig. 2. V<sub>2</sub>O<sub>5</sub> content as a function of temperature upon thermal treatment of V-Ti-catalysts ( the atomic ratio of V : Ti = 1:8). A - in the presence of anatase; B - in the presence of rutile.

Taking into account the formation peculiarities of chemical and phase composition of V-Ti catalysts, it is possible to obtain the effective catalysts for the ammoxidation of *o*-xylene to phtalimid (85% yield) and 3-methylpyridine to nicotinonitrile (92-95% yield).

Modifying of V-Ti catalysts by SnO<sub>2</sub> results in a rise of their activity. The ternary catalysts have a specific catalytical activity almost two times higher, than the binary catalysts have in 4-methylpyridine ammoxidation. We supposed that the cause of it is an increase of V<sub>2</sub>O<sub>5</sub> reaction capability due to V=O bonds weakening under the action of SnO<sub>2</sub>. It is verified by the significant increase of V<sub>2</sub>O<sub>5</sub> dissociation rate in the presence of SnO<sub>2</sub> in comparison with TiO<sub>2</sub>. Fig. 3

shows the kinetic curves of the oxygen emission at  $V_2O_5$  thermal dissociation in the presence of  $TiO_2$  and  $SnO_2$ .

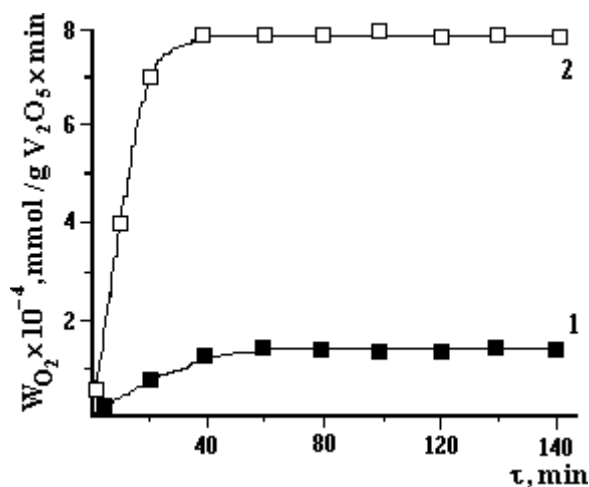


Fig. 3. The rate of oxygen emission at  $V_2O_5$  thermal dissociation at 660 °C for the following compositions: 1 -  $V_2O_5 : TiO_2 = 1:16$  (mol.); 2 -  $V_2O_5 : SnO_2 = 1:16$  (mol.).

Unlike  $TiO_2$ ,  $SnO_2$  does not form the solid solutions with  $VO_2$ . It was determined by X-ray diffraction method, that only  $V_2O_5$ ,  $VO_2$  and  $SnO_2$  phases are present in V-Sn catalysts. In the ternary V-Ti-Sn catalysts  $V_2O_5$ ,  $SnO_2$  and  $VO_2$ - $TiO_2$  solid solutions have been found.  $SnO_2$  exists as an individual phase. Both in the ternary catalysts and in V-Ti ones  $V_2O_5$  reduction degree depends on the calcination temperature, as well as on  $SnO_2$  concentration.  $V_2O_5$  reduction rate, as it is shown on the Fig. 4, increases with the decrease of  $TiO_2/SnO_2$  ratio from infinity to zero.

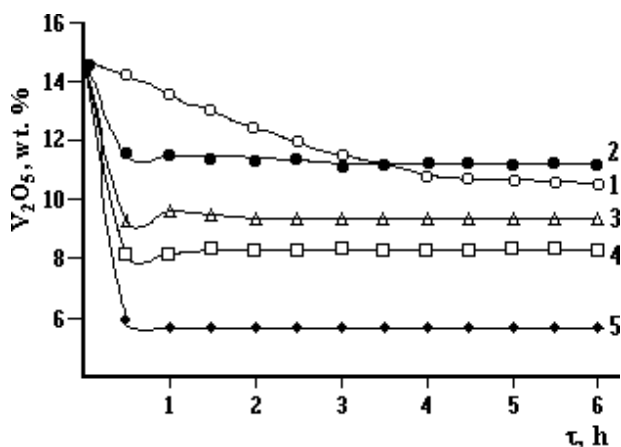


Fig. 4.  $V_2O_5$  concentration change during the thermal treatment at 700°C for V-Ti-Sn catalysts of various compositions. The molecular ratio  $TiO_2/SnO_2$  is equal to: 1 -  $\infty$ ; 2- 10; 3 - 1; 4- 0,2; 5 - 0.

The ternary V-Ti-Sn catalysts differ from V-Ti ones by high stability. They hold their activity and selectivity for a long time. Our experiments have shown that  $SnO_2$  is able to oxidize  $VO_2$  with the formation of  $V_2O_5$ , as a final product. In the same time  $SnO_2$  itself is reduced to  $SnO$ . Then  $SnO$  is easy reoxidized by oxygen from gas phase and can serve again as a donor of oxygen for the low vanadium oxides. Therefore,  $SnO_2$  is able to stabilize the chemical composition of V-Ti-Sn catalysts, facilitating their reoxidation by the gas phase oxygen. Such catalyst worked on 4-methylpyridine ammoxidation a long time. It had high selectivity of isonicotinitrile - up to 98%. The yield of nitrile was 95-98% mol., upon a loading to 300 g. of 4-methylpyridine on 1 l cat. per 1 h.

V-Zr binary catalysts can include either  $ZrV_2O_7$  compound and  $V_2O_5$ , or  $ZrV_2O_7$  and  $ZrO_2$ , according to the ratio of the starting components.  $V_2O_5$  in V-Zr catalysts is not subjected to thermal dissociation.  $VO_2$  is not determined. It seems that  $ZrO_2$  and  $ZrV_2O_7$  stabilize  $V_2O_5$ . The catalysts, containing  $ZrV_2O_7$  and  $ZrO_2$ , have the highest activity and selectivity. Such catalysts don't require activation and don't suffer the changes during ammoxidation. They have high stability and can work upon a high loading - up to 300 g of o-xylene per 1 l of cat. for 1 hour. The formation of  $ZrV_2O_7$  compound proceeds rather fast and finishes in 8-9 hours upon the thermal treatment of the starting oxide mixture at 600°C (Fig. 5).

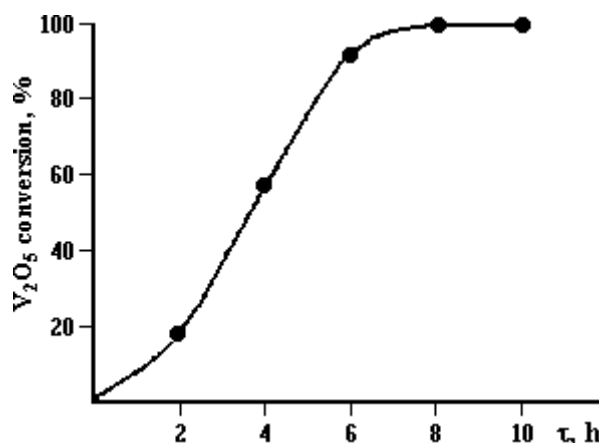


Fig. 5.  $ZrV_2O_7$  formation rate for  $V_2O_5$ - $ZrO_2$  catalyst (the molecular ratio is 1:1) at 600°C.

The catalytic properties of V-Zr catalysts largely depend on  $ZrO_2$  crystal modification. The specific catalytic activity and selectivity of o-tolunitrile formation on baddeleyite, which is a monoclinic crystal

modification of  $ZrO_2$ , is higher by an order in o-xylene ammoxidation, than that is on ruffite (tetrahedral structure). However, a selectivity of phtalimide formation on ruffite is more than that is on baddeleyite.

The ternary V-Ti-Zr catalysts can consist of following phases:  $V_2O_5$ ,  $TiO_2$ ,  $ZrO_2$ ,  $ZrV_2O_7$ , solid solutions  $VO_2$ - $TiO_2$ , limited solid solution  $ZrTiO_4$ . The finished catalyst composition depends on a ratio of the starting components and preparation conditions, as well as on mutual influence of catalyst's components. As we noted,  $V_2O_5$  increases the transformation of anatase into rutile. On the other hand anatase promotes  $V_2O_5$  dissociation and  $VO_2$  formation. Then, the interaction between rutile and  $VO_2$  gives solid solutions  $VO_2$ - $TiO_2$ , which have a low catalytic activity. It would be desirable to prevent their formation. The study of the mutual influence of anatase and baddeleyite showed, that baddeleyite inhibited the polymorphous transformation of anatase into rutile.  $ZrV_2O_7$  compound prevents this process too. The solid solutions  $VO_2$ - $TiO_2$  were not found in the presence of baddeleyite and  $ZrV_2O_7$ . Anatase, in its turn, prevents the phase transition of baddeleyite into ruffite. Thus, the catalysts, containing the excess of  $ZrO_2$ , consist of the following phases:  $ZrV_2O_7$ , anatase, baddeleyite and limited solid solution  $ZrTiO_4$ . The mutual stabilization of anatase and baddeleyite causes the raised activity and selectivity of the ternary catalysts. For example, the yield of nitrile is 93-95% on 3-methylpyridine ammoxidation.

Anatase partially transforms into rutile in the presence of chemical compound upon the rising of a calcination temperature up to 800°C. It is explained by a decomposition of the chemical compound into

$V_2O_5$  and  $ZrO_2$  at such a temperature.  $V_2O_5$  is the strong rutilisator. Its action exceeds a retarding action of  $ZrO_2$ . In consequence of it, the solid solutions are formed and catalyst activity decreases.

## Conclusions

Thus, the investigations made have shown a possibility to regulate valent state of vanadium, its reaction capacity, the formation of crystal phases and chemical compounds on the studied catalysts. This work became a basis for a synthesis of the active and selective catalysts for ammoxidation of benzene and pyridine derivatives.

## References

1. In M.V.Shimanskaya (ed.), Vanadium Catalysts for the Oxidation of Heteroatomic Compounds, "Zinatne", Riga, 1990.
2. Alkhazov, T.G., and Margolis, L.Y., High-selective Catalysts for Oxidation of Hydrocarbons, Moscow, 1988.
3. Mori K., Miyamoto A., and Murakami Y., Ztschr. Phys. Chem., Bd.131, S.251-254 (1982).
4. Volta J.C. Adsorption and Catalysis on Oxide Surfaces. Amsterdam etc.: Elsevier, 1985, pp. 331-344.
5. Yugay, O.K., and Sembaev D.Kh., Izvestiya MON RK, ser.chem., 4:9 (1998).
6. Sembaev D.Kh., Suvorov B.V., Saurambaeva L.I., and Suleimanov H.T., Kinetika i Kataliz XX:3:750 (1979)

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