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Formation of active state in vanadium–titanium oxide system regarding to reaction of oxidation of β-picoline to nicotinic acid

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Abstract

Binary vanadia–titania catalysts comprising 5–75 wt.% of V_2O_5 and 95–25 wt.% of TiO_2, pretreated at the temperature ranging between 300 and 700°C, were studied as heterogeneous catalysts for oxidation of β-picoline at 250°C, and inlet concentrations of the following components (vol.%): 1% of 3-picoline, 20% of oxygen, 30% of steam. Nicotinic acid, 3-pyridinecarbaldehyde and CO_2 were the reaction products. The most active state for oxidation of 3-picoline into nicotinic acid was shown to result from formation of coherent interface between V_2O_5 and TiO_2 (anatase) crystallites. This state was generated at the temperature particular for each composition and persists below the temperature of the anatase to rutile transition. © 2000 Published by Elsevier Science B.V.

Keywords: Vanadium–titanium oxide system; β-Picoline; Nicotinic acid

1. Introduction

Vanadium–titanium oxide system comprising titanium dioxide of the anatase modification and calcined at 450°C were discovered earlier to be effective, over a wide composition range, for oxidation of β-picoline into nicotinic acid [1].

It is common knowledge that the calcination temperature has a considerable effect on the phase composition of the vanadium–titanium oxide system [2–8]. The phase transition from the anatase modification of titanium dioxide to the rutile one to form a solid solution of V^{4+} ions in rutile is observed at elevated calcination temperatures. The transition temperature decreases as the concentration of vanadium pentoxide increases. Within the temperature range, where the anatase modification of TiO_2 occurs, particular microstructure is characteristic of the binary samples with various component ratios [4–9]. In this case, unit cells of TiO_2 and V_2O_5 contact in such a manner that the [0 0 1] axis is common for both phases [9]. Oxygen positions for both cells fit almost exactly along the [1 0 0] direction to bring the common oxygen row of the different oxides. Appearance of coherent interfacial boundaries is often observed in various oxide materials [10].

It was shown for the catalysts calcined at 450°C that the most active catalyst state for oxidation of 3-picoline into nicotinic acid was achieved upon formation of coherent interface between microcrystals of titanium dioxide and vanadium pentoxide [11].

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The present work is aimed at studies of vanadia–titania catalysts prepared by varying the component concentrations and calcination temperatures over wide ranges in order to determine conditions for generation of the active state and the stability range of it.

2. Experimental

Binary samples comprising 5, 10, 15, 20, 30, 50 and 75 wt.% of vanadium oxide were prepared by spray drying of a mixture of titanium dioxide and solution of vanadyl oxalate. Titanium dioxide of the anatase modification was prepared using the sulfate technology [12], content of sulfate ions was 1.7–1.9 wt.%. The binary samples were calcined at the temperature of 300–700°C in flowing air for 4 h.

XRD studies were conducted using a URD-6 with monochromatic Cu Kα radiation. Electron microscopic spectra were recorded using a JEM-4000FX microscope at the resolution of 1.4 Å and accelerating voltage of 400 kV.

Catalytic properties were studied in a flow-circuit setup equipped with a differential reactor. Experiments were carried out using 0.25–0.50 mm fraction of catalysts at 250°C, contact time of 0.1–5.0 s and the following initial concentrations of the components (vol.%): 1% of 3-picoline, 20% of oxygen, 30% of steam, rest nitrogen. Chromatographic technique was used for analyzing the reaction products.

3. Results

3.1. Catalyst characterization

The specific surface area and phase composition of the catalysts under study as dependent on the chemical composition and the calcination temperature are shown in Table 1.

Elevation of the calcination temperature results in a decrease in the specific surface area of the catalysts. An increase in the proportion of vanadium pentoxide in the samples favors the sintering process.

Either only the anatase or one of the following compositions: anatase+V_2O_5, anatase+V_2O_5+rutile, rutile+V_2O_5 is detected by XRD in the binary samples depending on the proportion of vanadium oxide and the calcination temperature. The higher is the proportion of vanadium pentoxide, the lower is the calcination temperature at which the V_2O_5 phase becomes detectable. The same influence of the vanadium proportion is observed for the transition of anatase into rutile. Three phases are detected in the samples comprising more than 30% of V_2O_5 at the temperature as low as 300°C. The complete transition of anatase into rutile occurs at the range 600–700°C for all the samples.

The catalyst microstructure depends on the composition and the calcination temperature (Table 2). Nothing but highly dispersed (ca. 1 nm in size) V_2O_5 crystallites arranged between crystallites of dispersed anatase particles (3–8 nm), which are aggregated into larger (more than 100 nm) particles, are observed at the proportion of not more than 30% V_2O_5 and the calcination temperature not lower than 300°C. Increase in the content of V_2O_5 and in the calcination temperature results in enlargement of the crystallites of anatase and V_2O_5, their interaction gives rise to coherent interfacial boundaries between crystallites of different phases. The content of V_2O_5 influences the boundary dimension. The anatase crystallites are constant in size (70–90 nm), but the size of vanadium pentoxide crystallites which join anatase depends on the content of V_2O_5. For the sample comprising 5% of vanadium pentoxide, V_2O_5 crystallites (ca. 1.5 nm in size) are attached to the surface of TiO_2 particles to form an interface with the latter. For samples with a high proportion of vanadium oxide, the catalyst morphology transforms: the layers of TiO_2 and V_2O_5 phases interchange with each other in the volume of the single particle 70–90 nm in size. Rutile crystals (ca. 100 nm in size) and V_2O_5 are detected in the binary samples calcined at 600–700°C [4].

3.2. Catalytic properties

Oxidation of 3-picoline produced nicotinic acid, 3-pyridinecarbaldehyde and CO_2 over all the samples under study.

Rates of transformation of 3-picoline and selectivities to the reaction products against conversion of 3-picoline are plotted in Fig. 1 for samples comprising 5 and 20 wt.% of V_2O_5 and calcined at 450°C, and for sample comprising 30 wt.% of V_2O_5 and calcined at 400°C. The rate of 3-picoline transformation is seen to

Table 1

Phase composition and specific surface area of binary vanadia–titania catalysts dependent on calcination temperature[a]

Content (wt.%)	300°C	350°C	400°C	450°C	500°C	550°C	600°C	700°C
5% V_2O_5–95% TiO_2	A (310 m^2/g)	A (310 m^2/g)	A (300 m^2/g)	A (250 m^2/g)	A (146 m^2/g)	A (70 m^2/g)	A (30 m^2/g)	R, A (5 m^2/g)
10% V_2O_5–90% TiO_2	A (300 m^2/g)	A (300 m^2/g)	A (271 m^2/g)	A (250 m^2/g)	A (148 m^2/g)	A, $V_2O_5$17 m^2/g	A, V_2O_5 (6 m^2/g)	R, V_2O_5 (3 m^2/g)
15% V_2O_5–85% TiO_2	A (295 m^2/g)	A (295 m^2/g)	A (205 m^2/g)	A (225 m^2/g)	A, V_2O_5 (30 m^2/g)	A, V_2O_5 (17 m^2/g)	A, V_2O_5 (5 m^2/g)	R, V_2O_5 (1.8 m^2/g)
20% V_2O_5–80% TiO_2	A (240 m^2/g)	A (205 m^2/g)	A (165 m^2/g)	A, V_2O_5 (40 m^2/g)	A, V_2O_5 (27 m^2/g)	A, V_2O_5 (20 m^2/g)	A, V_2O_5 (8 m^2/g)	R, V_2O_5 (0.8 m^2/g)
30% V_2O_5–70% TiO_2	A (185 m^2/g)	A, V_2O_5, R (45 m^2/g)	A, V_2O_5, R (29 m^2/g)	A, V_2O_5, R (28 m^2/g)	A, V_2O_5, R (27 m^2/g)	R, V_2O_5, A (17 m^2/g)	R, V_2O_5, A (5 m^2/g)	R, V_2O_5 (0.8 m^2/g)
50% V_2O_5–50% TiO_2	A, V_2O_5, R (80 m^2/g)	A, V_2O_5, R (42 m^2/g)	A, V_2O_5, R (32 m^2/g)	A, V_2O_5, R (27 m^2/g)	A, V_2O_5, R (27 m^2/g)	R, V_2O_5, A (17 m^2/g)	R, V_2O_5, A (5 m^2/g)	R, V_2O_5 (0.8 m^2/g)
75% V_2O_5–25% TiO_2	A, V_2O_5, R (25 m^2/g)	A, V_2O_5, R (18 m^2/g)	A, V_2O_5, R (17 m^2/g)	A, V_2O_5, R (10 m^2/g)	A, V_2O_5, R 6 m^2/g)	R, V_2O_5, A (2.5 m^2/g)	R, V_2O_5, A (1.5 m^2/g)	R, V_2O_5 (0.6 m^2/g)

[a] A: TiO_2 (anatase); R: TiO_2 (rutile).

Table 2
Microstructure of binary vanadia–titania catalysts dependent on calcination temperature[a]

Content (wt.%)	300°C	350°C	400°C	450°C	500°C	550°C	600°C	700°C
5% V_2O_5–95% TiO_2	X	X	X	X	X	X	**Y**	Z
10% V_2O_5–90% TiO_2	X	X	X	X	X	**Y**	**Y**	Z
15% V_2O_5–85% TiO_2	X	X	X	X	**Y**	**Y**	**Y**	Z
20% V_2O_5–80% TiO_2	X	X	X	**Y**	**Y**	**Y**	**Y**	Z
30% V_2O_5–70% TiO_2	X	**Y**	**Y**	**Y**	**Y**	Z	Z	Z
50% V_2O_5–50% TiO_2	**Y**	**Y**	**Y**	**Y**	**Y**	Z	Z	Z
75% V_2O_5–25% TiO_2	**Y**	**Y**	**Y**	**Y**	**Y**	Z	Z	Z

[a] Area marked as X: highly dispersed crystallites of V_2O_5 (ca. 1 nm in size) arranged between crystallites of TiO_2–anatase (ca. 3–8 nm in size), which are aggregated into larger (more than 100 nm) particles. Area marked as **Y**: existence of the regular coherent interface between crystallites (ca. 70–90 nm in size) of V_2O_5 and TiO_2–anatase. Area marked as Z: TiO_2–rutile crystals (ca. 100 nm in size) and V_2O_5.

change slightly within the conversion range 10–70% but then starts decreasing. As the conversion increases, the selectivity to 3-pyridinecarbaldehyde decreases but the selectivity to nicotinic acid increases that argues the consecutive pathway for formation of the acid. Selectivities to the products of the complete oxidation do not change over a wide range of conversions. These dependencies are typical of all the samples. Variations in the component proportions and in the calcination temperatures affect the activity and contributions of the parallel stages.

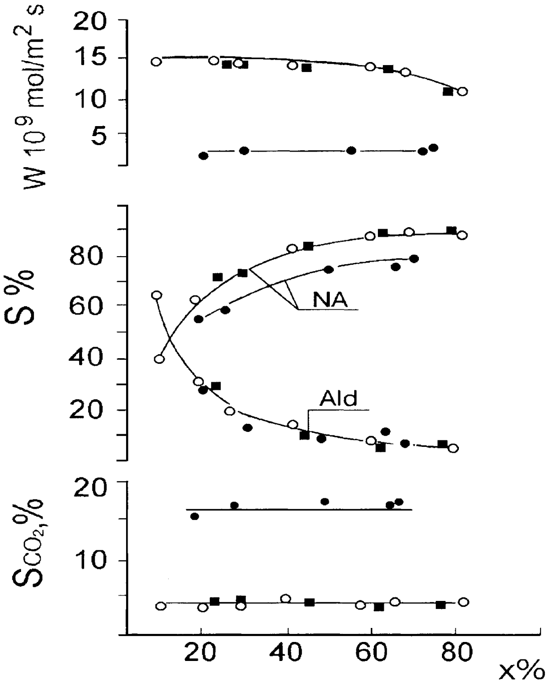

Fig. 1. Rate of conversion of β-picoline and selectivity for reaction products versus conversion of β-picoline for binary vanadia–titania catalysts containing (wt.%): (●) 5% of V_2O_5 (450°C), (○) 20% of V_2O_5 (450°C), (■) 30% of V_2O_5 (400°C).

Catalytic properties of the binary samples are illustrated in Fig. 2. They were compared at the conversion equal to 50%. The dependence of the catalytic properties on the calcination temperature is seen to be determined by the catalyst composition. Activity and selectivity to nicotinic acid increase with temperature over a wide temperature range for the samples containing 5–20 wt.% of V_2O_5 but do not for the samples with a higher vanadium proportion. The maximal level of the activity and selectivity is the same for all the compositions, while the temperature of reaching such a level lowers as the proportion of V_2O_5 increases. The catalyst activity falls off at high calcination temperatures. The higher V_2O_5 proportion in a sample, the lower is the temperature at which the activity starts decreasing, the selectivity to nicotinic acid being at the maximal level.

Hence, the composition and the calcination temperature determine catalytic behavior of the binary vanadium–titanium oxide systems.

4. Discussion

The results of kinetic measurements show that all the binary vanadia–titania catalysts reach their highest activity and selectivity at a particular *threshold* calcination temperature for each composition. The *threshold* temperatures are 590, 550, 530, 450, 350, 300 and 300°C for samples comprising 5, 10, 15, 20, 30, 50

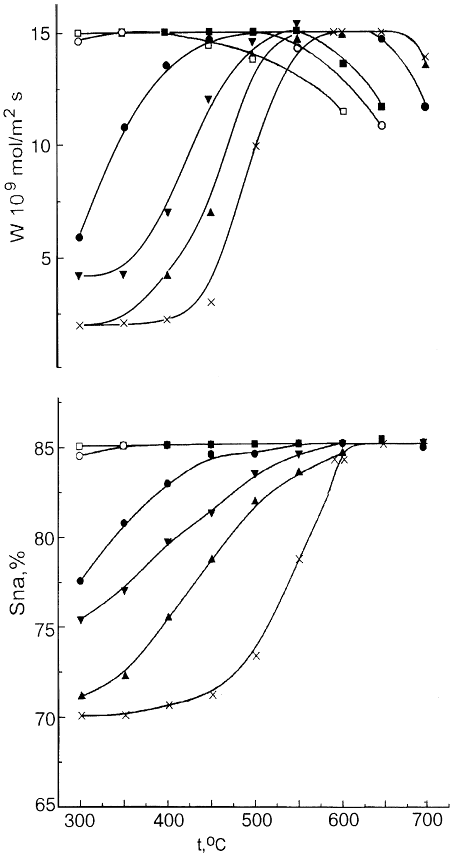

Fig. 2. Rate of conversion of β-picoline and selectivity for nicotinic acid versus heat-treatment temperature for binary vanadia–titania catalysts containing (wt.%): (×) 5% of V_2O_5, (▲) 10% of V_2O_5, (▼) 15% of V_2O_5, (●) 20% of V_2O_5, (■) 30% of V_2O_5, (○) 50% of V_2O_5, (□) 75% of V_2O_5.

and 75 wt.% of vanadium pentoxide, respectively. The high activity and selectivity persist while the treatment temperature raises up to 150–200°C above the *threshold*. The further elevation of the calcination temperature results in a decrease in the activity at retaining high selectivity to nicotinic acid. At below *threshold* temperature, lower values for both activity and selectivity to nicotinic acid are characteristic of the samples.

From the pertinent physicochemical data, variations in the calcination temperature and composition make the samples different in their phase composition and microstructure.

The highest activity and selectivity are observed with the two-phase anatase–vanadium pentoxide or three-phase anatase–vanadium pentoxide–rutile (more than 30 wt.% of V_2O_5) systems characterized by the regular arrangement of crystal lattices of these phases and occurrence of coherent interface (area marked as **Y** in Table 2). The impurity of rutile in such a system does not have any detrimental effect on the catalytic properties. In spite of the dimensions of the coherent interface increases with the increase of the content of V_2O_5, a surface available for reagents do not varies considerably (20–30 m^2/g, Table 1), and the activity of the samples remains almost the same.

Nothing but the anatase phase is detected in the samples calcined at a below *threshold* temperature. Crystallites of vanadium pentoxide, which are not detected by XRD, as well as crystallites of titanium dioxide are highly dispersed and arranged in an irregular manner with respect to one another. These samples reveal lower activity and selectivity to nicotinic acid.

The worst performance is observed with samples which inherit impurities of sulfate ions and water after the initial titanium dioxide [4]. This is true for the samples comprising 5% of V_2O_5, which were calcined at 300–450°C, as well as for the samples comprising 10 and 15% of V_2O_5, which were calcined at 300–350°C. As the calcination temperature raises, the structure of titanium dioxide is ordered upon removal of the impurities of sulfate ions and water, and the coherent interfaces start appearing. These processes are accompanied by increase in the activity and selectivity to nicotinic acid.

The two-phase system (rutile and vanadium pentoxide) is characteristic of the samples calcined at the temperature 150–200°C above the *threshold*. From ESR data [13], a solid solution of V^{4+} ions in rutile is formed in such a system. This catalyst state is less effective for oxidation of 3-picoline. The samples reveal a lower activity but the selectivity is at the same level.

Thus, the most effective transformation of 3-picoline into nicotinic acid proceeds over binary vanadium–titanium catalysts in which TiO_2 and V_2O_5 interact to form coherent interfacial boundaries. This state is generated in the binary systems over a wide range of component ratios at a particular, for each composition, *threshold* temperature and persists below the temperature of the anatase to rutile transition.

The said phase interaction results in formation of –V–O–Ti–bonds [9] to give rise to a new state of oxygen bonded to various cations, which differs from the oxygen state in the individual oxides [14]. The presence of this kind of oxygen in the binary vanadium–titanium system is most likely to favor the effective oxidation of 3-picoline into nicotinic acid.

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