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CATALYTIC ACTIVITY OF VANADIUM OXIDE CATALYSTS MODIFIED BY Ti, Sn, Zr OXIDES IN THE PARTIAL OXIDATION OF 4-METHYLPYRIDINE

Abstract. The results of catalytic activity of $V_2O_5 \cdot MeO_2$ (Me = Ti, Sn, Zr) binary catalysts in the partial oxidation of 4-methylpyridine are discussed. It was found that the binary vanadium zirconium oxide catalyst showed the greatest activity in this process. Isonicotinic acid is obtained with the highest yield (57%) at 270 °C and a molar ratio of 4-methylpyridine:O_2:H_2O=1:14:110.

Keywords: oxidation, 4-methylpyridine, isonicotinic acid, catalysts.

Pyridinecarboxylic acids have a high biological activity and serve as drugs or precursors of drugs. Nicotinic acid is an active substance in niacin (vitamin B3).

The global demand for nicotinic acid and its derivatives tends to increase and, according to forecasts for 2020, will reach 100,000 tons [1]. Isonicotinic acid is used in the synthesis of a number of anti-TB drugs of the isonicotinic acid hydrazide group (isoniazid, phtivazide, metazide, etc.) [2], antidepressants (iproniazide, nialamide), quinuclidic drugs (phencarol, oxylidine, aceclidine) [3] and is used in production of herbicides.

The coordination compounds of metals with isonicotinic acid are intensively studied in connection with the variety of properties they exhibit: catalytic, luminescent, magnetic, thermochromic, and are also used as precursors for the synthesis of nanosized metal oxides and nanocomposites during their thermal decomposition. Compounds based on isonicotinic acid are of interest due to the fact that isonicotinic acid as a ditope ligand (the functional group – COOH and a nitrogen heteroatom in the para position of the pyridine ring) cannot simultaneously form bonds with one metal ion and therefore is prone to the formation of polymers by intermolecular interaction with the formation of a hydrogen bond [4-7].

The vapor-phase oxidation of 4methylpyridine by air oxygen in the presence of oxide catalysts is the most rational method for the preparation of isonicotinic acids. Partial oxidation catalysts usually contain transition metal oxides, such as Ti, V, Cr, Mo, W [8].

At Bekturov Institute of Chemical Sciences JSC the research is being conducted for searching development of new catalysts for this process, since the latter are widely used in the manufacture of drugs. The purpose of this work is the research of catalytic properties of V-Ti-O, V-Sn-O, V-Zr-O binary catalysts in the vapor-phase oxidation of 4-methylpyridine.

EXPERIMENTAL PART

In this work, dried and distilled 4-methylpyridine with boiling point of 141°/695 mm, d_4^{20}=0.9547, n_D^{20}=1.5053 was used. These characteristics corresponded to the reference data.

As initial components of the catalysts, we used vanadium pentoxide, titanium, tin, zirconium dioxides of analytical grade. The initial oxides in a molar ratio of 1:4 were ground in a porcelain mortar to form a homogeneous batch, which then was compressed into tablets of 15 mm in diameter and 3-4 mm in thickness and calcined at 640 °C for 4 hours. After cooling, the tablets were crushed into grains of 3-5 mm in size.

The specific surface area of the synthesized catalysts were determined by low-temperature nitrogen desorption method on the NOVA 1000e gas sorption analyzer from Quantachrome (USA).

The oxidation of 4-methylpyridine was carried out in a continuous installation of reaction tube made of stainless steel with a diameter of 20 mm and a length of 150 mm into which 10 ml of a granular catalyst was loaded.

The unreacted 4-methylpyridine and reaction products were trapped in air-lift type scrubbers filled with water and analyzed by gas-liquid chromatography. Isonicotinic acid was titrated with 0,035 N alkali using phenolphthalein.

The deep oxidation products were analyzed by LXM-8MD chromatograph with a thermal conductivity detector. The stainless steel columns had a length of 3,5 m and an inner diameter of 3 mm. The adsorbent for CO detection was an AG-5 activated carbon (0,25-0,50 mm), for CO_2 – polysorbent-1 (0,16-0,20 mm). The temperature of the thermostat was 40 °C.

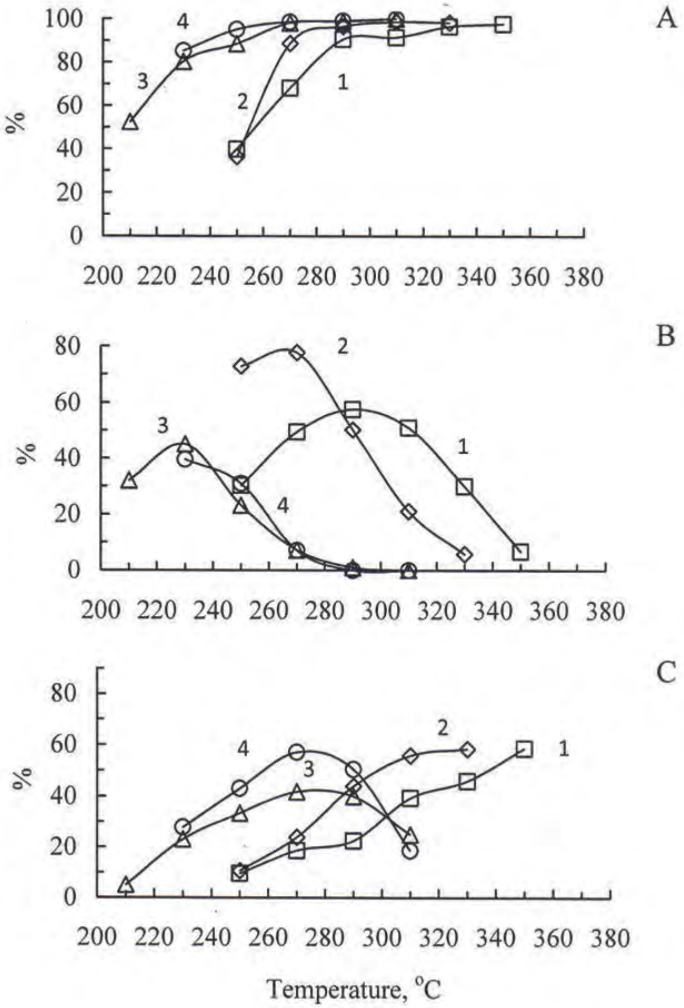
The B3LYP exchange-correlation density functional method and the Lanl2DZ two-exponential basis set with an effective core potential [9] was used for optimization of the geometry and calculation of total energy of the clusters modeling the active centers of the catalysts. Calculations were carried out in the Born-Oppenheimer approximation using the GAUSSIAN 09W program, version D.01.

RESULTS AND DISCUSSION

Binary catalysts of the composition V-Ti-O, V-Sn-O and V-Zr-O were prepared and tested for the purpose to search new active and selective catalysts for the vapor-phase oxidation of 4-methylpyridine.

The main oxidation products of 4-methylpyridine on these catalysts are pyridin-4-aldehyde and isonicotinic acid. The general laws of the reaction, in particular, the effect of temperature, the amount of oxygen (air) supplied to the reaction zone and water vapor on the yield of the main products of the reaction were investigated.

Figure 1 shows the results showing the change in the conversion of 4-methylpyridine and the yield of pyridin-4-aldehyde and isonicotinic acid on binary vanadium oxide catalysts depending on temperature.



The molar ratio of 4-methylpyridine:O_2:H_2O = 1:14:110,0.
Catalysts: 1 - V_2O_5, 2 - $V_2O_5 \cdot 4SnO_2$, 3 - $V_2O_5 \cdot 4TiO_2$, 4 - $V_2O_5 \cdot 4ZrO_2$.

Figure 1 – The effect of temperature on the oxidation of 4-methylpyridine on binary catalysts of various compositions: A - conversion of 4-methylpyridine, B - the yield of pyridin-4-aldehyde, C - the yield of isonicotinic acid

For comparison, the results of the initial unmodified vanadium oxide catalyst are also given. It is seen from the presented data that binary catalysts incorporated with titanium, tin, and zirconium oxides in their activity are superior to vanadium pentoxide. The binary oxide vanadium-zirconium contact showed the greatest activity in this process. When the initial components were fed with a molar ratio of 4-methylpyridine:O_2:H_2O = 1:14:110.0 on this catalyst, the conversion of the initial substance even at a temperature of 230 °C reached 85%. According to the degree of 4-methylpyridine conversion, the tested catalysts are arranged in the following order: $V_2O_5 < V_2O_5 \cdot 4SnO_2 < V_2O_5 \cdot 4TiO_2 < V_2O_5 \cdot 4ZrO_2$.

The yield of pyridin-4-aldehyde on a vanadium oxide catalyst under the studied conditions is 57,6 %. The highest selectivity in the formation of pyridine-4-aldehyde was shown by vanadium-tin contact (77,7% at a temperature of 270 °C).

Another oxidation product of 4-methylpyridine - isonicotinic acid - is formed on vanadium pentoxide with a yield of 58.6% at a relatively high temperature (350 °C). Isonicotinic acid is formed with a yield of 55,8-58,4% in the temperature range of 310-330 °C on the binary vanadium-tin catalyst. On the most active of the studied - vanadium zirconium oxide catalysts, the acid yield was 57 % at 270 °C.

It is known that the catalytic properties of multicomponent oxide systems are affected not only by their chemical composition, but also by the specific surface area and porous structure.

The specific surface area of the synthesized binary catalysts was determined by nitrogen adsorption method on the NOVA 1000e analyzer (Quantachrome, USA). The obtained results showed that the specific surface area of the vanadium-titanium catalyst is 0.31 m^2/g, the vanadium-tin catalyst is 0.64 m^2/g, and the specific surface area of the vanadium-zirconium catalyst is 10 times higher than the initial vanadium pentoxide (0.31 m^2/g) and reaches 3.55 m^2/g, which, obviously, led to an increase in its catalytic activity.

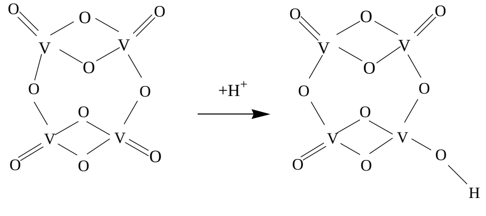
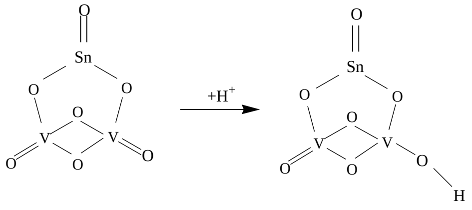
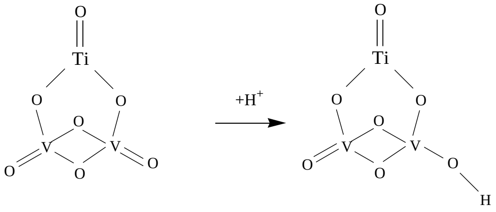
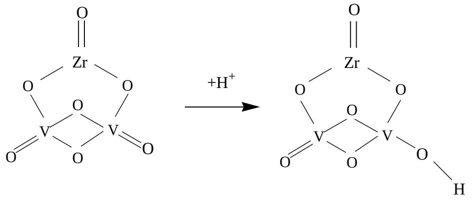
For interpretation of the experimental data on the relative catalytic activity of the studied compositions in the gas-phase oxidation of 4-methylpyridine, we carried out quantum-chemical calculations of the proton affinity of vanadyl oxygen [10], which is involved in the separation of proton from the oxidizing methyl substituent at the initial stages of 4-methylpyridine oxidation.

The active catalysts sites were modeled by clusters containing V_2O_5, SnO_2, TiO_2, and ZrO_2 fragments. The proton affinity (nucleophilicity) of vanadyl oxygen was calculated as the difference in the total energies (E_{total}) of the initial and protonated clusters with optimized geometry. Thus, the proton affinity is equal to the energy released as a result of the proton addition detached from the methyl group to vanadyl oxygen.

A comparison of the experimental results (figure 1) and calculations (table 1) indicates that the catalytic activity of the studied compositions, estimated by the conversion of 4-methylpyridine and the yield of desired products, increases in the same series as the calculated proton affinity for vanadyl oxygen ($PA_{V=O}$, $kJ \cdot mol^{-1}$) contact surfaces: V_2O_5 (756,9) < $V_2O_5 \cdot 4SnO_2$ (773,7) < $V_2O_5 \cdot 4TiO_2$ (801,6) < $V_2O_5 \cdot 4ZrO_2$ (827,9).

Figure 2 clearly demonstrates the obtained regularity.

Table 1 – Total energies of vanadium-containing clusters and their protonated forms (E_{total}), proton affinity of oxygen bound to a vanadium ion ($PA_{V=O}$) calculated by the DFT method (B3LYP / LanL2DZ)

Reaction	$-E_{total}$, a. u.		$PA_{V=O}{}^{1}$, kJ·mol^{-1}
	Initial state	Final state	
 q=0, m=1 q=1, m=1	1038.1701915	1038.4584905	756.9
 q=0, m=1 q=1, m=1	672.9076577	673.2023395	773.7
 q=0, m=1 q=1, m=1	727.7636779	728.0689935	801.6
 q=0, m=1 q=1, m=1	716.2660144	716.5813479	827.9

Примечание. ^{1} – PA = ($E_{initial}$ – E_{final}) · 2625.46.

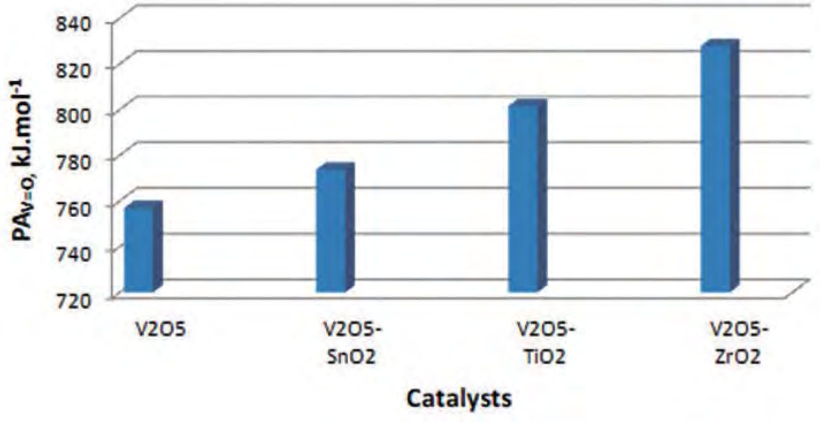


Figure 2 – The effect of modifiers on the proton affinity of vanadyl oxygen

Thus, as it is seen on the basis of the research, modification of vanadium pentoxide by the addition of tin, titanium, and zirconium increases oxygen nucleophilicity associated with vanadium, which entails an increase in the catalytic activity of the contacts during the oxidation of 4-methylpyridine.

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Резюме

Т. П. Михайловская, П. Б. Воробьев, Қ. А. Кадирбеков, Р. Курмақызы

4-МЕТИЛПИРИДИННІҢ ПАРЦИАЛДЫ ТОТЫҒУЫНДАҒЫ ОКСИДВАНАДИЛДІ КАТАЛИЗАТОРЛАРЫМЕН Ti, Sn, Zn ТҮРЛЕНДІРІЛГЕН ОКСИДТЕРІНІҢ КАТАЛИТКАЛЫҚ БЕЛСЕНДІЛІГІ

4-Метилпиридиннің парциалды тотығуында $V_2O_5 \cdot MeO_2$ (Me = Ti, Sn, Zr) бинарлы катализаторлардың каталитикалық белсенділігін зерттеу нәтижелері талқыланады. Бинарлы оксидті ванадий цирконий катализаторы осы процесте белсенділік танытқаны анықталды. 4-Метилпиридин:O_2:H_2O молдік қатынасы 1:14:110 тең болғанда және 270 °С температурада изоникотин қышқылы үлкен шығымымен (57 %) алынды.

Түйін сөздер: парциалды тотығу, 4-метилпиридин, изоникотин қышқылы, катализаторлар.

Резюме

Т. П. Михайловская, П. Б. Воробьев, К. А. Кадирбеков, Р. Курмакызы

КАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ МОДИФИЦИРОВАННЫХ ОКСИДАМИ Ti, Sn, Zr ОКСИДНОВАНАДИЕВЫХ КАТАЛИЗАТОРОВ В ПАРЦИАЛЬНОМ ОКИСЛЕНИИ 4-МЕТИЛПИРИДИНА

Обсуждаются результаты исследования каталитической активности бинарных катализаторов $V_2O_5 \cdot MeO_2$ (Me = Ti, Sn, Zr) в парциальном окислении 4-метилпиридина. Установлено, что бинарный оксидный ванадийциркониевый катализатор проявил наибольшую активность в данном процессе. Изоникотиновая кислота с наибольшим выходом (57 %) получена при температуре 270 °С и мольном соотношении 4-метилпиридин:O_2:H_2O=1:14:110.

Ключевые слова: окисление, 4-метилпиридин, изоникотиновая кислота, катализаторы.