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# DEACTIVATION OF VANADIUM SULFURIC ACID CATALYSTS ON DIATOMITE

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***Abstract.*** *The vanadium oxide-based systems on various carriers are of great interest for the obtaining of catalysts for natural gas processing and organic synthesis. An important stage in the development of sulfuric acid catalysis was obtaining of sulfovanadium catalysts based on diatomite. The catalyst is easy to manufacture, sufficiently durable, and has a relatively long service life. It is necessary to process deactivated vanadium contact masses due to the high hazard of spent vanadium catalysts to humans and the environment, as well as the scarcity and high cost of vanadium compounds. In this regard, there is a need to determine the causes of deactivation of sulfuric acid vanadium catalysts of the SVD brand after their operation. All studied samples have low specific surface area and porosity, indicating the destruction of the support. X-ray spectral analysis indicates a low content of* $V_2O_5$*. This is due to the presence of impurities in the diatomite. Aluminum and iron oxides interact with potassium pyrosulfovanadate. As a result of this reaction, there is a formation of aluminum-potassium and iron-potassium alums. Consequently, is causes the release of* $V_2O_5$ *crystalline phase. This leads to a sharp change in the composition and properties of the active component and decreasing of activity. The results of X-ray diffraction studies show that all studied samples contain crystalline forms of diatomite, predominantly in its high-temperature modification – cristobalite. A significant amount of cristobalite leads to a disruption in the mechanical strength of the granules and a low specific surface area.*

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## Introduction

A distinctive feature of the modern development of the chemical industry is the widespread use of catalysts. They increase labor productivity, improve product quality, and

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significantly reduce production costs. However, their use is accompanied by catalysts deactivation during the reaction. This is due to operating conditions, the quality of the raw materials, and the physicochemical properties of the catalysts themselves.

Vanadium oxide-based catalysts are widely used in the production of important industrial products (sulfuric acid, phthalic anhydride) and for the purification of industrial gas emissions from nitrogen oxides. Analysis of modern research has shown that vanadium oxide-based systems on various supports are of great interest for preparing catalysts for natural gas processing and organic synthesis. They are used for the selective oxidation of methanol and methane to formaldehyde, olefin polymerization, direct conversion of methane into aromatic compounds, etc. [1, 2]. Vanadium catalysts for sulfur dioxide oxidation have been used in the chemical industry since the early 1930s [3]. Nowadays, the several types of vanadium catalysts have been developed and implemented [4-6]. An important stage in the development of sulfuric acid catalysis was the creation of saturated catalysts. One of the first catalysts of this type was SVD (sulfovanadium on diatomite). SVD is easy to manufacture, sufficiently durable, and has low production costs. The main disadvantages include the dependence of its properties on the raw materials used [7].

Compared to other catalysts, vanadium catalysts have a relatively long service life. The catalysts are sieved annually, with the top layer and one of the subsequent layers removed in turn. Losses are replenished with fresh catalyst. Typically, every 5–10 years, the catalyst is completely replaced. Improper storage and use of the catalyst can significantly reduce its service life. During storage, moisture is the most hazardous [7], as free $SO_3$ can be hydrated to form sulfuric acid. This leads to reddish spots on the catalyst surface, resulting in loss of strength and catalyst degradation.

The increasing production of sulfuric acid is followed by the growing of industry's demand for vanadium catalysts. At the same time, an equivalent amount of spent catalyst accumulates at industrial plants. It is necessary to process deactivated vanadium contact masses due to the high hazard of spent vanadium catalysts to humans and the environment, as well as the scarcity and high cost of vanadium compounds.

The purpose of this work is to investigate the causes of deactivation of sulfuric acid vanadium catalysts of the SVD brand.

## Experimental part

The synthesis of catalytic compositions and their effective application as industrial catalysts results from the specific interaction between the support and the active component and requires in-depth knowledge of solution chemistry, solid-state chemistry, and inorganic chemistry. The understanding of methods for preparing long-lasting catalysts demands research into the active component's structure at the molecular level, not only during synthesis but also under prolonged operating conditions [6].

The authors used a spent vanadium catalyst of the SVD brand from sulfuric acid production. Samples were collected from different layers of the contact apparatus. We selected a catalyst of the SVD brand from BASF CE as a reference for comparison, with a specific surface area of 10–15 $m^2/g$ and an activity of at least 40% at 420 °C and at least 90% at 485 °C.

We determined the specific surface area of the studied catalysts using the low-temperature nitrogen adsorption-desorption method on a Sorbi-MS instrument. We calculated the surface area using the BET equation [8]. We measured the total pore volume of the samples on a Quantachrome Poremaster 33 mercury porosimeter. We calculated the pore size distribution using the Barrett-Joyner-Halenda (BJH) model.

We obtained images of the catalyst surfaces and information about the chemical composition of the near-surface layers using a Vega 3 SBH scanning electron microscope (TESCAN, Czech Republic).

We performed X-ray diffraction analysis on a hardware-software complex based on the POWDIX-600 multifunctional X-ray diffractometer (Belarus). The authors used crystallographic databases [9, 10] to identify the diffraction patterns.

We employed the catalytic activity determination method according to TU 48-0323-6-90 with modifications.

## Discussion of the results of the study

The initial stage involved studying the catalysts' appearance. The analysis revealed approximately 30% of damaged granules in each sample. We polished 10-20 defect-free granules to achieve parallel end faces. The prepared granules were tested on a hydraulic press by applying axial load until complete destruction. We calculated the data according to the rules for handling equally precise group measurements using the confidence interval method. The formula for calculating granule mechanical strength is:

$$Str = \frac{P \cdot D^2}{d^2};\ \text{MPa},$$

where P is the hydraulic system fluid pressure (MPa); D is the piston diameter (mm); d is the catalyst pellet size (mm).

The measurements of granule mechanical strength by axial crushing showed satisfactory strength values. Table 1 and Figure 1 present the summary data of specific surface area and porosity of the samples.

**Table 1.** Specific surface area and porosity values of the investigated catalysts

| Name of sample | BET surface area ($m^2/g$) | Porosity, % | Characteristic pore sizes, µm |
|---|---|---|---|
| VKT-1 | 2.2 ± 0.6 | 61.87 | 0.3 – 2 |
| VKT-2 | 1.3 ± 0.1 | 57.06 | 1 – 4.<br>250 – 1000 |
| VKT-3 | 3.3 ± 0.2 | 59.73 | 0.3 – 3 |
| VKT-4 | 3.5 ± 0.1 | 61.55 | 0.7 – 5<br>250 – 1000 |
| VKT-5 | 3.1 ± 0.0 | 60.12 | 0.3 – 4 |
| VKT-6 | 2.0 ± 0.0 | 54.14 | 0.3 – 4 |

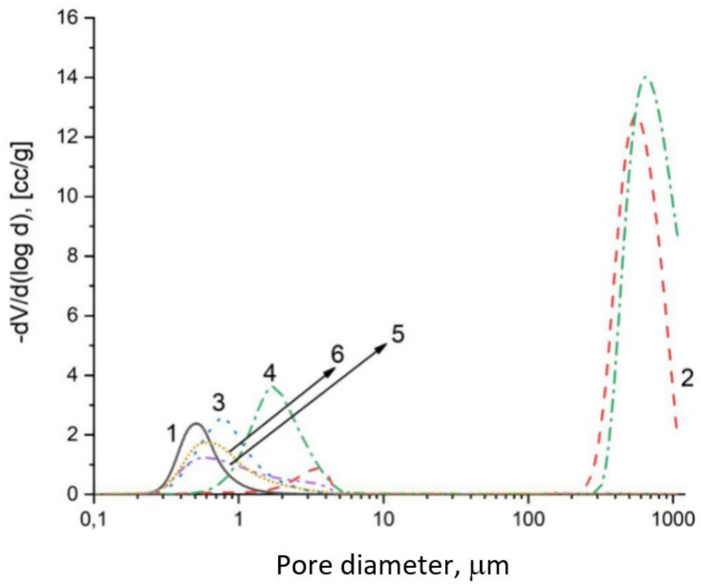

**Fig. 1.** Pore diameter distribution: **1** – VKT-1; **2** – VKT-2; **3** – VKT-3; **4** – VKT-4; **5** – VKT-5; **6** – VKT-6

The obtained data indicate that all catalysts have a low specific surface area of less than 3.5 m$^2$/g.

Analysis of porosity and pore characteristics reveals lower porosity in VKT-2 and VKT-6 compared to other samples (Table 1). The pore diameter distribution suggests significant support degradation in VKT-2 and VKT-4 samples, indicative of mechanical deactivation.

For quantitative assessment of the surface layer composition, X-ray spectral (energy-dispersive) analysis was implemented. Theoretical diffraction patterns were calculated and modeled as references, resulting in a synthesized composite pattern. It shows high agreement with experimental data. Table 2 presents the X-ray spectral analysis results in terms of the elemental composition of catalyst samples (recalculated as oxides)

**Table 2.** The elemental composition of catalyst samples recalculated as oxides

| Sample | Oxide content, wt% | | | | | | | | | | Amount, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $SO_3$ | $K_2O$ | $V_2O_5$ | $Fe_2O_3$ | $Cs_2O$ | $Cr_2O_3$ | |
| TU 48-0323-6-90 | 2.2-3.3 | | | | | 9.5-12 | 7.5-8.5 | | | | |
| VKT-1 | 4.72 | – | – | 60.5 | 20.3 | 8.9 | 5.2 | 0.24 | – | 0.20 | 100 |
| VKT-2 | 3.62 | – | – | 51.5 | 25.9 | 10.2 | 6.7 | 0.41 | – | – | 98.52 |
| VKT-3 | 2.37 | – | 1.41 | 55.8 | 23.9 | 9.6 | 6.3 | 0.58 | – | – | 100 |
| VKT-4 | 1.95 | – | – | 58.9 | 21.9 | 8.9 | 6.3 | 0.66 | – | – | 98.62 |
| VKT-5 | 0.59 | – | 1.14 | 61.9 | 17.2 | 7.1 | 5.3 | 0.32 | 6.5 | – | 100 |
| VKT-6 | 3.57 | 2.11 | 0.71 | 44.9 | 31.2 | 10.4 | 5.5 | 1.49 | – | – | 100 |

Analysis results demonstrate decreased vanadium pentoxide ($V_2O_5$) concentrations in samples VKT-1, VKT-5, and VKT-6.

The analysis revealed the presence of contaminant compounds including:

- MgO и $Al_2O_3$ – in samples VKT-3, VKT-5, VKT-6;
- $Cr_2O_3$ – in the sample VKT-1;
- $Fe_2O_3$ was found in all samples; particularly high concentrations was in VKT-6.

The VKT-6 sample also shows the increased sulfur content.

The findings indicate significant reduction in catalytic activity due to contaminants such as aluminum and iron oxides, which negatively affect catalyst performance. These impurities react with potassium pyrosulfovanadate, forming aluminum-potassium and iron-potassium alums. This process subsequently releases crystalline $V_2O_5$ phase, drastically altering the active component's composition, and properties, ultimately decreasing activity [7, 11-13, 14].

X-ray phase analysis enables qualitative and quantitative identification of the catalyst support's crystalline phase, typically a tridymite-cristobalite mixture. X-ray diffraction results demonstrate that all studied catalyst samples contain diatomite crystalline forms, predominantly as high-temperature cristobalite modification - with a 4.1 Å peak (Fig. 2, Table 3).

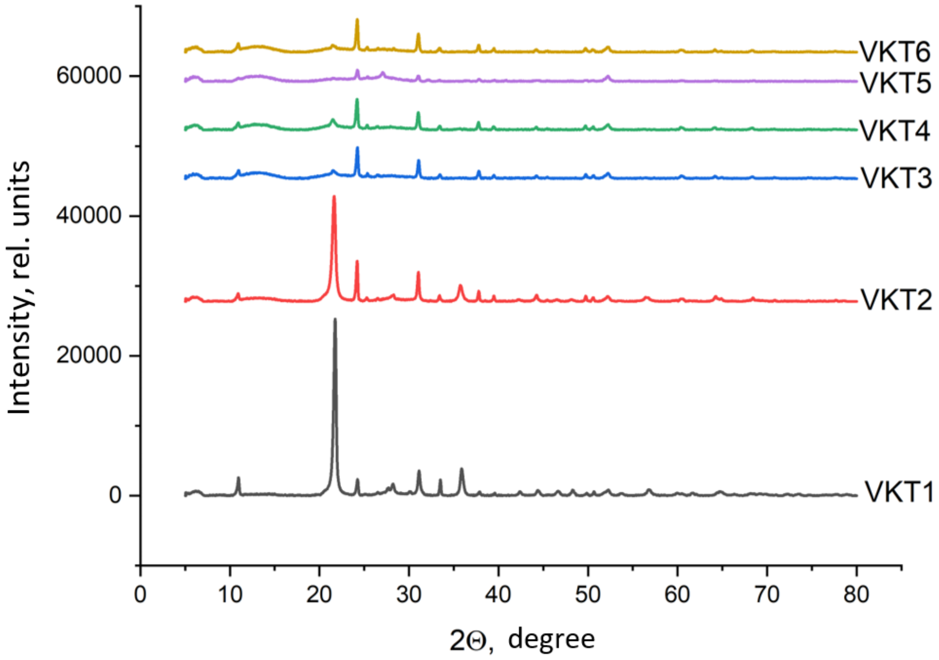

**Fig. 2**. X-ray diffraction patterns of the studied samples CuK α-radiation

**Table 3.** X-ray phase analysis of catalysts. Crystalline phase content in diatomite

| Sample | 2Θ, grade | $d_{hkl}$, Å | FWHM, grade | $S_{of\ peak}$ | Cristobalite phase content, % | Tridymite phase content, % |
|---|---|---|---|---|---|---|
| VKT1 | 21.73 | 4.086 | 0.356 | 8829 | 79.57 | 5.05 |
| VKT2 | 21.61 | 4.109 | 0.463 | 6716 | 36.63 | 46.99 |
| VKT3 | 21.57 | 4.116 | 0.673 | 422 | 15.69 | 18.63 |
| VKT4 | 21.50 | 4.129 | 0.605 | 580 | 67.94 | – |
| VKT5 | – | – | – | – | – | 55.24 |
| VKT6 | 21.59 | 4.112 | 0.683 | 356 | 56.91 | 11.82 |

The VKT-1 and VKT-2 samples demonstrate 15-20 times higher cristobalite phase content compared to other samples. The VKT-5 sample contains crystalline $SiO_2$ exclusively in tridymite form. The VKT-1, VKT-2, VKT-3, and VKT-6 samples show ongoing transition from medium-temperature (tridymite) to high-temperature (cristobalite) $SiO_2$ modification, while this process is complete in VKT-4. The significant cristobalite content reduces granule mechanical strength and catalyst specific surface area.

Silica properties are well studied [15, 16]. The crystallization of silica yields in cristobalite, tridymite, or quartz depending on temperature, pressure, and environment. Each polymorph exists in high-temperature (α) and low-temperature (β/γ) forms. Alkali metal pyrosulfates present in the catalyst react with the silica support at higher temperatures, forming low-activity vanadium pentoxide phase.

Alkali metal vanadates in vanadium catalysts also induce silica polymorphic transformations, contributing to catalytic activity loss. Mineralizers accelerate phase transitions and decrease their temperature thresholds. These polymorphic transitions cause quartz volume changes, leading to catalyst attrition and surface area reduction due to bed movement in reactors during SiO2 modification shifts. The chemical reactivity of silica increases from quartz to cristobalite, then to tridymite, and finally to amorphous silica (most reactive).

Catalytic activity was determined per TU 48-0323-6-90. Table 4 presents $SO_2$-to-$SO_3$ oxidation activity data for spent catalysts.

**Table 4.** Catalytic activity of spent vanadium catalysts in $SO_2$ to $SO_3$ oxidation

| Catalytic activity according TU 48-0323-6-90 | Degree of $SO_2$ oxidation to $SO_3$, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | SVD | VKT-1 | VKT-2 | VKT-3 | VKT-4 | VKT-5 | VKT-6 |
| 485 °C | 88 | 43.99 | 43.4 | 45.99 | 43.99 | 44.01 | 46.96 |
| | 90 | 43.5 | 43.9 | 44.5 | 43.3 | 42.8 | 46.84 |
| | 88 | 44.1 | 43.03 | 44.1 | 44.1 | 43.6 | 45.94 |
| | 90 | 44.1 | 42.6 | 44.1 | 44.1 | 41.9 | 44.82 |
| av. value | 89 | 43.92 | 43.23 | 44.67 | 43.87 | 43.08 | 46.14 |
| 420 °C | 40 | 19.4 | 26.03 | 19.4 | 19.4 | 34.4 | 30.94 |
| | 42 | 20.6 | 20.6 | 20.6 | 20.6 | 36.1 | 34.6 |
| | 41 | 14.7 | 21.7 | 14.7 | 14.7 | 36 | 34.07 |
| | 40 | 18.3 | 21.9 | 18.3 | 18.3 | 35.7 | 34.02 |
| av. value | 40 | 18.25 | 22.56 | 18.25 | 18.25 | 35.55 | 33.4075 |

The activity of the studied samples is significantly below the permissible limit.

## Conclusions

A study was conducted to determine the causes of sulfuric acid vanadium catalysts deactivation. The degree of deactivation depends on the catalyst type, chemical composition of the raw material, volume of the active component, porous structure of the support, etc. According to the research, the activity reduction is caused by the presence of impurities and processes of diatomite structure destruction, leading to surface loss and changes in the catalyst's porous structure. The reason is also the transition of low-temperature modifications of diatomite to high-temperature ones.

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