

Article

Synthesis of Vanadium-Containing Catalytically Active Phases for Exhaust Gas Neutralizers of Motor Vehicles and Industrial Enterprises

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Abstract: The catalytically active vanadium-containing system of γ -Al₂O₃ was studied using a wide range of physical and chemical methods, depending on the synthesis conditions. It is shown that the vanadium-containing system includes several complexes with different thermal stabilities and catalytic activities. Low-active complexes are destroyed with the formation of more active ones based on V₂O₅ oxide, as the temperature of heat treatment increases. It can be assumed that V₂O₅ oxide has the decisive role in its catalytic activity. It was concluded that the vanadium-containing catalytic system on aluminium oxide, in the studied temperature range, is thermally stable and shows high activity not only in the reduction of nitrogen oxides but also in the oxidation of hydrocarbons (even of the most difficult ones, such as oxidizable methane). These properties of the system make it quite promising in the field of application for the purification of the exhaust gases of motor transport and industrial enterprises with environmentally harmful components, as well as for understanding the mechanism of the action of the catalysts in these processes, which is very important for solving the problems of decarbonization and achieving carbon neutrality.

Keywords: neutralizers; catalysts; vanadyl sulfate; aluminium oxide; oxidation of saturated hydrocarbons



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1. Introduction

Environmental protection is one of the most pressing problems. One of the main factors that has a negative impact on the environment are the exhaust gases of industrial enterprises and vehicles, as a variety of gases enter the atmosphere as a result of their functioning. Harmful toxic emissions include unreacted fuel hydrocarbons, CO, NO_x, sulphur-containing compounds, soot, etc. Catalytic purification can be one of the most effective and rational ways to neutralize as well as recycle components of harmful emissions, in particular, the complete catalytic oxidation of organic substances to carbon dioxide and water and sulphur dioxide and the reduction of nitrogen oxides.

Often, catalytic systems of aluminium–cobalt, aluminium–cobalt–magnesium and systems using 4 and 5d transition metals of the VIII group are the basis for catalytic converters of toxic exhaust-gas components from motor vehicles and industrial plants [1–22]. As a rule, the latter show the best results and are the most effective.

Vanadium containing an oxide catalytically active phases were synthesized to replace expensive components in neutralizers and to approximate the efficiency of such systems to that of systems based on noble metals. The choice of vanadium oxides is due to the

fact that catalytic systems based on vanadium (V) oxide such as [23] and supported on various supports with a high specific surface area, for example, oxides of aluminium, silicon, titanium, etc., are known [24–30], which can be used as oxidation catalysts, in particular, nitrogen oxides, as well as in the selective purification of exhaust gases from internal combustion engines [31–37].

The emission of incompletely burned and unreacted hydrocarbons into the atmosphere is one of the main and intractable problems in relation to non-stationary consumers of hydrocarbon fuel (internal combustion engines of vehicles, mobile power generators, heat guns, etc.). This is due to the frequent switching of the engine-operation mode, causing changes in the conditions of hydrocarbon fuel combustion [38].

In this regard, vanadium containing an oxide's catalytically active phases that exhibit activity in redox reactions was synthesized, as specified above. The physical and chemical properties and catalytic activity in the oxidation of saturated hydrocarbons using the example of methane, as the most difficult object to be oxidized, were studied by a wide range of physicochemical methods.

Testing the activity of catalysts in redox processes in the presence of and, most importantly, after the destruction of the sulfo group in vanadyl sulfate was the goal of studying the catalytic characteristics.

2. Results and Discussion

The elemental composition of powdered samples of catalytically active phase 10% V/ γ -Al₂O₃ was investigated after its calcination by energy dispersive X-ray fluorescence spectroscopy. The results are shown in Table 1.

Table 1. Elemental content of the 10% V/ γ -Al₂O₃ catalyst calcined in air at different temperatures.

T (°C)	Elements (wt%)					Total
	O	Al	Si	S	V	
25 (initial)	45.07	40.60	0.42	5.19	8.72	100
300 °C	44.79	41.62	0.11	5.11	8.37	100
400 °C	45.28	41.30	0.07	4.95	8.40	100
500 °C	47.23	41.16	0.09	4.04	7.49	100
600 °C	45.69	44.14	0.10	3.21	6.86	100
700 °C	37.92	50.99	0.08	0.00	11.01	100
800 °C	40.42	48.78	0.08	0.00	10.72	100

As follows from Table 1, an increase in the calcination temperature above 600 °C results in the disappearance of sulphur. This is due to the formation of vanadium oxide from VOSO₄·3H₂O, the decomposition of aluminium sulfate and the transition of sulphur to the gas phase. The increase in vanadium content occurs as a result.

Powdered samples of the initial substance VOSO₄·3H₂O and the catalytically active phase of 10% V/ γ -Al₂O₃ under different temperature conditions were studied using the electron paramagnetic resonance (EPR) method. The samples were calcined for 1 h in air at varying temperatures. The EPR spectra were recorded at room temperature in air in the registration mode: microwave power –2 mW, modulation amplitude 20 gauss, time constant 0.1 s, magnetic field 3300 ± 2500 gauss and field sweep time 2.5 min.

Figure 1 shows the EPR spectra of the 10% V/ γ -Al₂O₃ catalyst. Table 1 shows the results of their processing. The ⁵¹V isotope is the only stable isotope with a nucleus spin of 7/2. Therefore, its EPR signal should have eight superfine splitting components with slightly different g-factors. Thus, the recorded total spectrum was the sum of all signal components. Indeed, at least eight strongly broadened hyperfine structure components are observed in the EPR spectra of the samples (Figure 1).

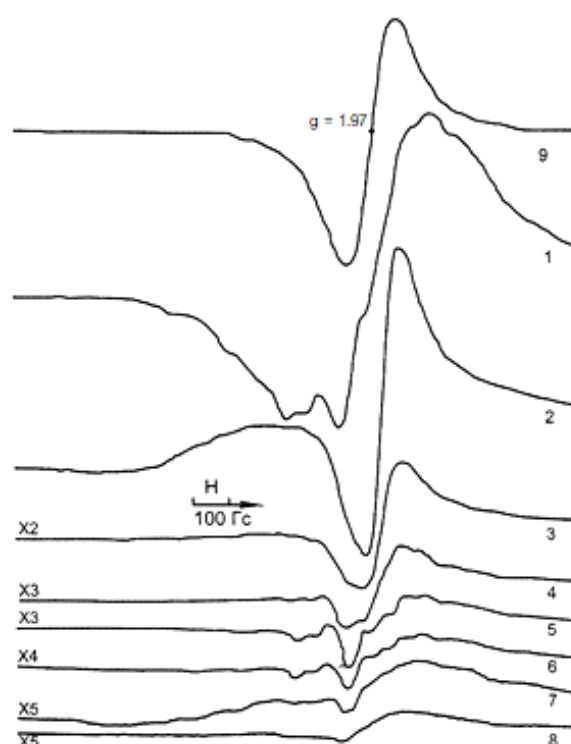


Figure 1. EPR spectra of 10% V/ γ -Al₂O₃. 1—initial catalyst after heating in air for 1 h at temperatures: 2—300 °C; 3—400 °C; 4—500 °C; 5—600 °C; 6—700 °C; 7—800 °C; 8—900 °C; 9—initial VOSO₄·3H₂O.

The EPR spectra have ΔH width (116–483 gauss) and a g -factor ≈ 1.97 . The spectra intensity decreases with an increase in the sample calcination temperature. The EPR signal is associated with V⁴⁺ ions, which are part of the vanadyl ion of the original VOSO₄·3H₂O that undergoes destruction when deposited on a carrier, due to the interaction of aluminium oxide with the sulfo group of vanadyl sulfate. The resulting free vanadyl transforms into diamagnetic vanadium oxide V₂O₅, which does not give an EPR signal, upon deposition and drying at room temperature. This process intensifies with increasing temperature (Table 2).

Table 2. Results of EPR spectra of vanadium-containing phases at various heating temperatures.

Sample	Intensity, Amplitude (a.u.)	g -Factor	ΔH (gauss)
Initial 10% V/ γ -Al ₂ O ₃	120	1.99	270
300 °C	116	1.97	261
400 °C	24	1.97	116
500 °C	13	1.97	155
600 °C	11	1.97	193
700 °C	6.5	1.97	213
800 °C	1.3	1.97	213
900 °C	1.5	1.97	174
VOSO ₄ ·3H ₂ O	2250	1.97	126

Since vanadium is present in all samples, regardless of the calcination temperature (Table 1), therefore, in this case, the EPR method can serve as an “ideal indicator” of vanadium oxidation states, which means determining the presence or absence of vanadyl or V₂O₅ oxide by the signal intensity.

Since 10% vanadium in terms of metal is present on the carrier, the signal-amplitude intensity for all supported samples (Table 2) should be increased 10-fold, and it will increase from 2250 to 9570 a.u. for VOSO₄·3H₂O in terms of metallic vanadium.

Consequently, even a simple impregnation of γ - Al_2O_3 with an aqueous solution of vanadyl sulfate and drying at room temperature results in a decrease in the signal amplitude from V^{4+} ions from 9570 to 1200 a.u., or almost eight times, which can be associated with the formation of diamagnetic phase of the V_2O_5 .

X-ray diffraction patterns of 10% $\text{V}/\text{Al}_2\text{O}_3$ catalysts under different heat treatment regimes are shown in Figure 2. Three main maxima corresponding to V_2O_5 (4.37; 3.40; 2.87; ASTM 9-387) are present against the background of broad maxima of γ - Al_2O_3 (2.28; 1.97; 1.52; 1.395 Å-ASTM 10-425) on the diffraction pattern of the original sample dried in air at room temperature (Figure 2a). The same pattern persists after heating the samples up to 400 °C (Figure 2b).

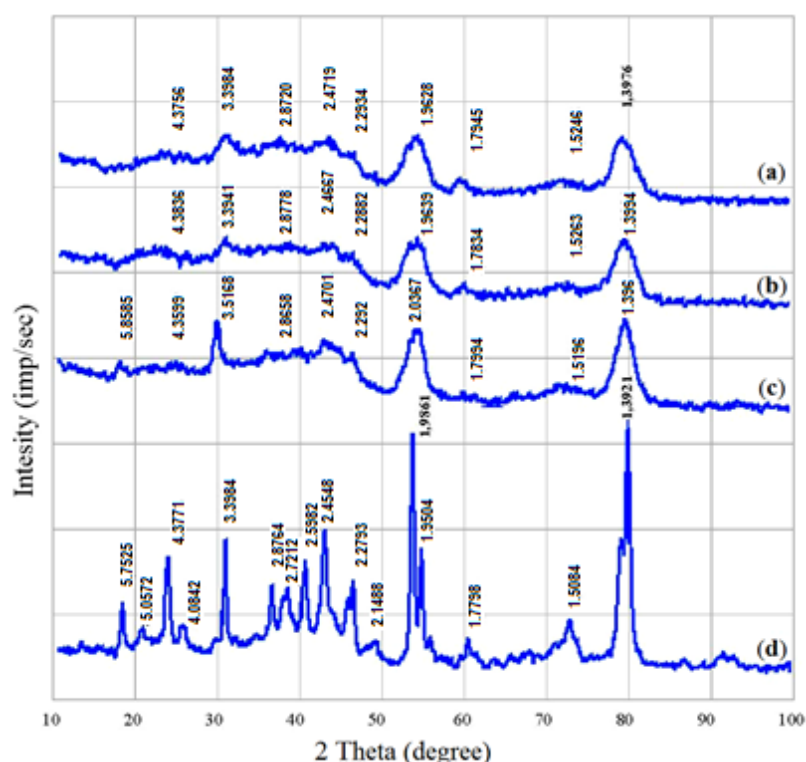


Figure 2. X-ray diffraction patterns of 10% $\text{V}/\text{Al}_2\text{O}_3$ catalyst under different heat-treatment modes: (a) initial system; (b) heating at 400 °C; (c) heating at 600 °C; (d) heating at 700 °C.

Diffraction maxima from $\text{Al}_2(\text{SO}_4)_3$ (5.86; 3.51–3.52; 2.03; ASTM 30-43) appear additionally in the samples heated at temperatures above 400 °C (Figure 2c). The diffraction maxima from aluminium sulfate disappear, and the intensity of the V_2O_5 maxima increases at heating temperatures of 700 °C and above (Figure 2d).

The narrowing of the diffraction peaks and an increase in their intensity is associated with a better crystallization of the sample, as evidenced by a decrease in the X-ray amorphous component. The formation of more ordered structures can be associated with the melting of the V_2O_5 phase at 700 °C and its subsequent crystallization after cooling.

The data obtained using scanning electron microscopy also indicate a change in the surface morphology of 10% $\text{V}/\text{Al}_2\text{O}_3$ catalysts during the transition from 500 to 700 °C (Figure 3). It is clearly seen that the particles have more clearly defined contours after heating at 700 °C at all magnifications, and this is in good agreement with the X-ray diffraction data. It can be assumed that the vanadium oxide phase on the surface of aluminium oxide is in a weakly crystallized state, up to the melting point. After melting upon cooling, the phase has a clearer crystalline structure. The decrease in the width of the diffraction peaks and the increase in their intensity are associated precisely with this effect. It should be noted that in this case there is no significant change in particle size.

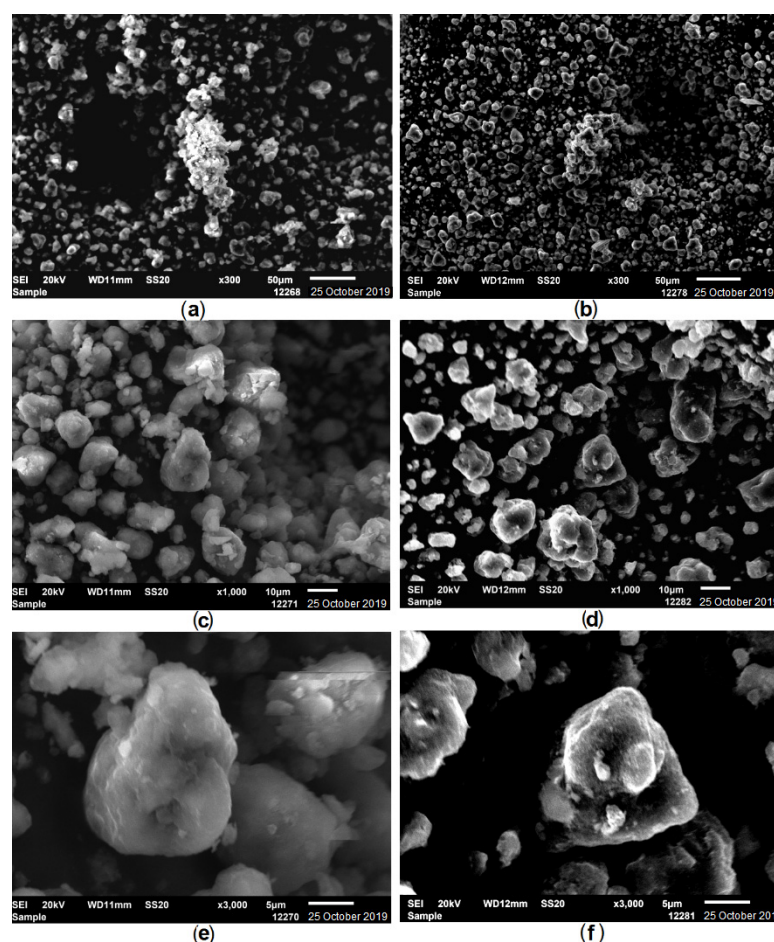


Figure 3. Micrographs of the 10% V/Al₂O₃ system at different magnifications and heat treatment modes: (a) magnification by 300 times, 500 °C; (b) magnification by 300 times, 700 °C; (c) magnification by 1000 times, 500 °C; (d) magnification by 1000 times, 700 °C; (e) magnification by 3000 times, 500 °C; (f) magnification by 3000 times, 700 °C.

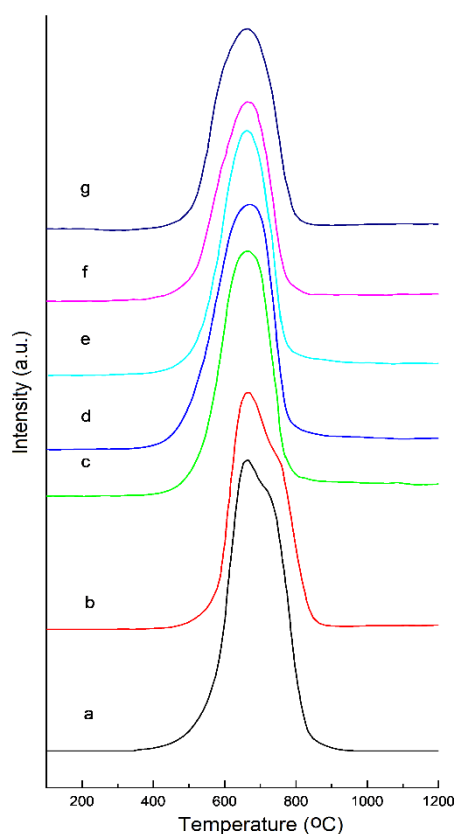
The specific surface area (*S*) of samples of aluminium–vanadium phases at different temperatures were determined by the BET method by low-temperature nitrogen adsorption, (Table 3). The use of this method is due to the fact that the value of the specific surface area can serve as a criterion for the uniformity and degree of filling of the carrier surface with a vanadium-containing phase. It follows from the obtained data that the specific surface area of the samples was in the range of 172–195 m²/g, in the temperature range of 25–600 °C. Per the literature data, V₂O₅ melts at 670–690 °C [39,40]. After the melting of vanadium oxides at 700 °C, the surface of the catalyst decreases by about 6.5 times compared with the surface of the sample heated at 600 °C, from 174 to 27 m²/g. At the same time, in the same temperature range, the surface of aluminium oxide without supported vanadium oxide practically does not change.

A sharp decrease in the specific surface area (for the 10% V/γ-Al₂O₃ catalyst) indicates a change in the surface morphology, which also confirms the conclusions made on the basis of X-ray diffractometry and electron microscopy data. Comparison of specific surface data of the 10% V/γ-Al₂O₃ catalyst, γ-Al₂O₃ carrier at various temperatures and vanadyl sulfate indicates that during the melting process, vanadium oxide is more evenly distributed over the surface of carrier than it was in the initial state, thereby reducing its specific size. Therefore, it can be argued that vanadium is retained on the surface of aluminium oxide even after the melting of V₂O₅ (at temperatures above 600 °C). Moreover, its relative content increases as a result of the decomposition of aluminium and vanadium sulfates (Table 3).

Table 3. Specific surface area of the aluminium–vanadium phases after calcination in air at different temperatures.

Sample	S (m ² /g)
VOSO ₄ ·3H ₂ O vanadyl sulfate	23
10% V/γ-Al ₂ O ₃ , initial	192
10% V/γ-Al ₂ O ₃ , calcination for 1 h, 300 °C, air	184
10% V/γ-Al ₂ O ₃ , calcination for 1 h, 400 °C, air	195
10% V/γ-Al ₂ O ₃ , calcination for 1 h, 500 °C, air	172
10% V/γ-Al ₂ O ₃ , calcination for 1 h, 600 °C, air	174
10% V/γ-Al ₂ O ₃ , calcination for 1 h, 700 °C, air	27
10% V/γ-Al ₂ O ₃ , calcination for 1 h, 800 °C, air	10
γ-Al ₂ O ₃ after calcination in air at 600 °C, 1 h	195
γ-Al ₂ O ₃ after calcination in air at 700 °C, 1 h	189

The H₂-TPR method was used to reduce the 10% V/γ-Al₂O₃ catalyst by varying the preheating temperature in air. H₂-TPR spectra are shown in Figure 4, and their results are given in Table 4.

**Figure 4.** Reduction of the 10% V/γ-Al₂O₃ catalyst by H₂-TPR method at varying the preheating temperature in air. (a) 25 °C; (b) 300 °C; (c) 400 °C; (d) 500 °C; (e) 600 °C; (f) 700 °C; (g) 800 °C.

As follows from Figure 4 and Table 4, two peaks at 640 and 670 °C are observed in the initial sample (25 °C). It can be assumed that they are associated with the interaction of hydrogen with oxygen of vanadium oxide and oxygen of vanadyl sulfate. Based on the EPR data (Table 2), the more intense peak at 640 °C belongs to vanadium oxide. The relatively high temperatures of the TPR peaks, in contrast to the data of [29] for aluminium–vanadium catalysts, may be associated with a higher content of vanadium on the carrier, as well as another initial vanadium compound used to prepare the catalyst.

Table 4. Results of the study of 10% V/ γ -Al₂O₃ catalyst using H₂-TPR.

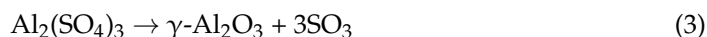
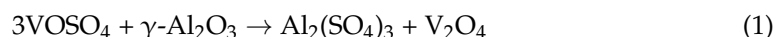
Temperature of Heating in Air (°C)	Total Area of Peaks (a.u.)	Temperature of the Peaks (°C)
25	14,407,832	640,670
300	11,858,380	640,670
400	11,382,953	640
500	11,110,654	650
600	11,063,026	635
700	7,920,939	645
800	8,052,778	645

The same situation persists for 300 °C. At the same time, there is a decrease in the total area of the peaks (Table 4), probably due to a decrease in the amount of vanadyl sulfate.

Starting from 400 °C, the spectra contain only one peak corresponding to the oxygen of vanadium oxide. The identical positions of the peaks and their area in the range of 400–600 °C should be noted. This indicates the completion of the formation of 10% V/ γ -Al₂O₃ catalyst after 300 °C.

The decrease in the peak area at 700 °C and above is associated with the melting of vanadium oxide (BET method, Table 3).

Thus, the data obtained in the study of physical and chemical properties of the 10% V/ γ -Al₂O₃ catalyst in the process of its preparation allow to describe the processes according to the following scheme:



Therefore, the thermal decomposition of vanadyl sulfate should not lead to side effects (formation of additional phases), since this process results in the formation of the γ -Al₂O₃ phase, which is similar to the initial carrier.

The S-shaped curves shown in Figure 5 were obtained from testing the activity of the vanadium-containing catalysts.

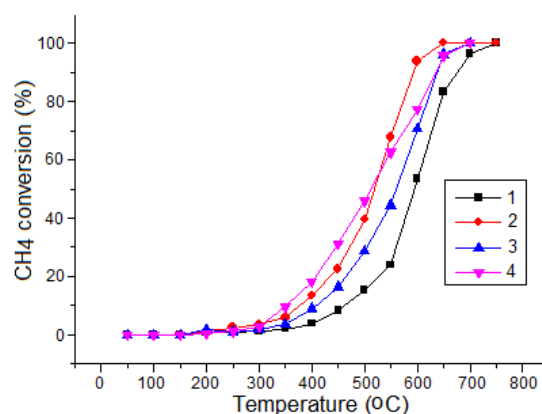


Figure 5. The relative content of methane in the methane–air mixture after reaction on the 10% V/Al₂O₃ catalyst at different temperatures: 1—heating of the catalyst in air for 1 h at 300 °C; 2—at 600 °C for 1 h; 3—at 700 °C for 1 h; 4—sample additionally heated at 600 °C for 1 h after all measurements.

The catalyst showed the lowest activity at a heating temperature of 300 °C (Figure 5, curve 1). Apparently, the presence of the product of interaction between the carrier and vanadyl sulfate on the surface reduces its catalytic activity. The presence of strong interac-

tion of vanadyl sulfate with aluminium oxide is evidenced by the EPR data (Table 2). The catalyst activity increases (Figure 5, curve 4), and the sample itself turns from dark green at 300 °C (almost black) to an orange colour at 600 °C, when the same catalyst is reheated at 600 °C in air during 1 h in order to decompose this complex. It may indicate the presence of an inactive complex of vanadyl sulfate with aluminium oxide at 300 °C and its destruction as the temperature increases, with the formation of a more active complex with V_2O_5 .

The specific surface area of catalyst sharply decreases from 174 to 27 m²/g, due to the melting of vanadium oxide at the increase in heating temperature in the air from 600 to 700 °C (Table 3). The catalyst activity in methane oxidation at these temperatures was determined. The data are shown in Figure 5, curves 2 and 3. Activity of the catalyst heated at 700 °C is somewhat lower than the activity of the catalyst heated at 600 °C. Despite the fact that the specific surface area decreases by more than six times, the catalytic activity does not drop so significantly, so its activity is higher than when heated at 300 °C (Figure 5, curves 3, 4).

3. Materials and Methods

The catalytically active phase was prepared by impregnation of γ - Al_2O_3 with a 30% $VOSO_4$ solution, followed by drying at room temperature. The content of vanadium in terms of metal was 10% for all samples. This sample was the zero-reference point for all subsequent catalyst treatments. Sometimes the starting substance $VOSO_4 \cdot 3H_2O$ was used to compare changes when supporting vanadyl sulfate to the carrier. Vanadyl sulfate was chosen as initial compound due to the possibility to obtain aqueous solutions of high concentration and low decomposition temperature (lower than the melting point of vanadium (V) oxide).

The dependence of the catalytic properties of the vanadium-containing phase on the preheating temperature in air was evaluated. For this purpose, 10% V/ Al_2O_3 catalysts (per metallic vanadium) were prepared on metallic blocks (neutralizer body) from X15U5 Fechral.

The simplest hydrocarbon methane was used to simulate the interaction of the saturated hydrocarbons with the neutralizers.

Activity tests were performed in a flow-through apparatus at atmospheric pressure with chromatographic control of methane concentration in the gas mixture (1% methane in argon–air) before and after the catalyst. The ratio of methane to oxygen in the mixture before reaction was 1/15 at space velocity of 25,000 h^{−1}. The initial catalyst with a secondary carrier from alumina was preliminarily impregnated with an aqueous salt solution of $VOSO_4 \cdot 3H_2O$ according to its moisture capacity and dried at room temperature. Then, the catalyst was heated in air at a given temperature for 1 h and placed in a quartz reactor. Methane content before and after passage through the catalyst was measured at different temperatures of the gas mixture (methane–argon–air) on a gas chromatograph with a flame ionization detector.

Electron paramagnetic resonance (EPR) studies were performed at room temperature with a JES ME ESR spectrometer, JEOL, in the 3 cm range.

A surface analyser, an AccuSorb gas adsorption porosimeter by Micromeritics, was used in the BET method for low-temperature nitrogen adsorption.

Microphotographs were taken with a JSM 6610 LV scanning electron microscope, JEOL, at different magnifications. The accelerating voltage was 20 kV, imaging mode was SEL.

The elemental composition was determined using an INCA Energy 450 energy dispersive microanalysis system mounted on a JSM 6610 LV scanning electron microscope, JEOL.

X-ray diffractometry was performed on DRON-4M X-ray diffractometer. A tube with a cobalt cathode was used. Imaging conditions were tube voltage 30 kV, current 20 mA, and sweep rate 2 °C/min.

Thermo-programmed hydrogen reduction (H_2 -TPR) of the 10% V/ γ - Al_2O_3 system was performed between 25 and 1100 °C in linear mode, with the 5% mixture of hydrogen and argon at a temperature change rate of 5 °C/min. The gas flow rate was 30 mL/min.

Signals were recorded using a thermal conductivity detector on the Crystal 5000 “Chromatec” chromatograph.

4. Conclusions

As a result of this research, it was possible to show that the catalytically active vanadium-containing system includes several complexes with different thermal stability and catalytic activity. The presence of thermal stable, but inactive spinel complexes with aluminium oxide, which are quite easily formed from low-valent s- and d-elements and aluminium oxide, was not detected in the system at moderate heating [22,37].

As the temperature of the heat treatment increases, the low-active vanadyl sulfate complexes decompose with the formation of more active ones based on V_2O_5 oxide. It can be assumed that V_2O_5 plays the determining role in the catalytic activity of the system.

Since the decomposition temperature of aluminium sulfate is lower than the melting point of vanadium oxide, it was possible to obtain an aluminium–vanadium catalyst with a well-developed surface, high activity and low sulphur content.

Thus, the 10% V/ Al_2O_3 catalyst in the studied temperature range is thermally stable and exhibits high activity not only in the reduction of nitrogen oxides [31–37] but also in the oxidation of hydrocarbons (even the most difficult oxidizable methane). These properties of the system make it quite promising in the field of the application for the purification of the exhaust gases of motor vehicles and industrial enterprises with environmentally harmful components as well as for understanding the mechanism of the action of the catalysts in these processes, which is very important for solving the problems of decarbonization and achieving carbon neutrality.

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References

1. Garbowski, E.; Guenin, M.; Marion, M.; Primet, M. Catalytic properties and surface states of cobalt-containing oxidation catalysts. *Appl. Catal.* **1990**, *64*, 209–224. [\[CrossRef\]](#)
2. Zeng, H.; Ji, L.; Lin, J. Metal–support interactions in Co/ Al_2O_3 catalysts. A comparative study on reactivity of support. *Phys. Chem.* **2000**, *104*, 1783–1790.
3. Thormählen, P.; Skoglundh, M.; Fridell, E.; Andersson, B. Low-temperature CO oxidation over platinum and cobalt oxide catalysts. *J. Catal.* **1999**, *188*, 300–310. [\[CrossRef\]](#)
4. Avgouropoulos, G.; Ioannides, T.; Papadopolou, C.; Batista, J.; Hocevar, S.; Matralis, H.K. A Comparative study of Pt/ $\gamma-Al_2O_3$, Au/ $\alpha-Fe_2O_3$ and CuO–CeO₂ catalysts for the selective oxidation of carbon monoxide in excess hydrogen. *Catal. Today* **2002**, *75*, 157–167. [\[CrossRef\]](#)
5. Jansson, J. Low-temperature CO oxidation over Co₃O₄/ Al_2O_3 . *J. Catal.* **2000**, *194*, 55–60. [\[CrossRef\]](#)
6. Ma, W.; Jacobs, G.; Keogh, R.A.; Bukur, D.B.; Davis, B.H. Fischer-Tropsch synthesis: Effect of Pd, Pt, Re, and Ru noble metal promoters on the activity and selectivity of a 25% Co/ Al_2O_3 catalyst. *Appl. Catal. A Gen.* **2012**, *437*, 1–9. [\[CrossRef\]](#)
7. Rattan, G.; Kumar, M. Carbon monoxide oxidation using cobalt catalysts. *Chem. Chem. Technol.* **2014**, *8*, 249–260. [\[CrossRef\]](#)

8. Zavyalova, U.F.; Tretyakov, V.F.; Burdeinaya, T.N.; Lunin, V.V.; Titkov, A.I.; Salanov, A.N.; Ryzhova, N.D.; Tsyrlunikov, P.G. Oxidation of CO, deep oxidation of CH₄ and reduction of NO_x by propane on CuCo₂O₄ and Pd-CeO₂ catalysts supported on tape carriers. *Pet. Chem.* **2005**, *45*, 281–286. (In Russian)
9. Zavyalova, U.F.; Petrov, V.F.; Burdeinaya, T.N.; Tsyrlunikov, T.N. Block catalysts for neutralization of exhaust gases synthesized by the combustion method. *Chem. Sustain. Dev.* **2005**, *13*, 751–755. (In Russian)
10. Noskov, A.S.; Pai, Z.P. *Technological Methods for Protecting the Atmosphere from Harmful Emissions at Energy Enterprises*; SB RAS: Novosibirsk, Russia, 1996; p. 156. (In Russian)
11. Popova, N.M. *Catalysts for the Purification of Gas Emissions from Industrial Production*; Nauka: Alma-Ata, Kazakh SSR, 1991; p. 176. (In Russian)
12. Borshch, V.N.; Pugacheva, E.V.; Zhuk, S.Y.; Andreev, D.E.; Sanin, V.N.; Yuxhvid, V.I. Multicomponent metal catalysts for deep oxidation of carbon monoxide and hydrocarbons. *Proc. Acad. Sci.* **2008**, *419*, 775–777. (In Russian) [[CrossRef](#)]
13. Vaneman, G.L. Comparison of metal foil and ceramic monolith automotive catalytic converters. *Catal. Automot. Pollut. Control II* **1991**, *71*, 537–555.
14. Anders, J.J.; Palmqvist, E.C.; Fridell, E.; Skoglundh, M.; Österlund, L.; Thormählen, P.; Langer, V. On the catalytic activity of Co₃O₄ in low-temperature CO oxidation. *J. Catal.* **2002**, *211*, 387–397.
15. Wang, H.F.; Kavanagh, R.; Guo, Y.L.; Guo, Y.; Hu, P. Synthesis-structure-activity relationships in Co₃O₄ catalyzed CO oxidation. *J. Catal.* **2012**, *296*, 110–119. [[CrossRef](#)]
16. Ozkara, S.; Akin, A.N.; Misirli, Z.; Aksoylu, A.E. The effect of metal loading on structural characteristics and low temperature CO oxidation activity of coprecipitated Co/Al₂O₃. *Turk. J. Chem.* **2005**, *29*, 219–224.
17. Oliveira, H.A.; Franceschini, D.F.; Passos, F.B. Cobalt catalyst characterization for methane decomposition and carbon nanotube growth. *J. Brazil. Chem. Soc.* **2014**, *25*, 53–65. [[CrossRef](#)]
18. Vosoughi, V.; Dalai, A.K.; Abatzoglou, N.; Hu, Y. Performances of promoted cobalt catalysts supported on mesoporous alumina for Fischer-Tropsch synthesis. *Appl. Catal. A Gen* **2017**, *547*, 155–163. [[CrossRef](#)]
19. Kurzina, I.A. Deep oxidation of methane on platinum and palladium catalysts supported on silicon nitride. *Bull. Tomsk. Polytech. Univ.* **2005**, *308*, 104–109.
20. Ivanova, N.D.; Ivanov, S.V.; Boldyrev, E.I.; Sokolsky, G.V.; Makeeva, I.S. Highly efficient manganese oxide catalysts for the CO oxidation reaction. *J. Appl. Chem.* **2002**, *75*, 1452–1455.
21. Olsson, L.; Fridell, H.; Skoglundh, M.; Andersson, B. A kinetic study of NO oxidation and NO_x storage on Pt/Al₂O₃ and Pt/BaO/Al₂O₃. *J. Phys. Chem. B* **2001**, *105*, 6895–6906. [[CrossRef](#)]
22. Massenova, A.; Kalykberdiyev, M.; Ussenov, A.; Sass, A.; Kenzin, N.; Kanatbayev, E.; Baiken, A. Catalytic technologies for the production of eco-friendly gasolines and reducing the toxicity of vehicle exhaust gases. *Orient. J. Chem.* **2019**, *35*, 351–357. [[CrossRef](#)]
23. Gruber, M.; Hermann, K. Elementary steps of the catalytic NO_x reduction with NH₃: Cluster studies on reaction paths and energetics at vanadium oxide substrate. *J. Chem. Phys.* **2013**, *139*, 244701–244708. [[CrossRef](#)] [[PubMed](#)]
24. Kalinkin, P.; Kovalenko, O.; Lapina, O.; Khabibulin, D.; Kundo, N. Kinetic peculiarities in the low-temperature oxidation of H₂S over vanadium catalysts. *J. Mol. Catal. A Chem.* **2002**, *178*, 173–180. [[CrossRef](#)]
25. León, M.; Jiménez-Jiménez, J.; Jiménez-López, A.; Rodríguez-Castellón, E.; Soriano, D.; Nieto, J.M.L. Vanadium oxide-porous phosphate heterostructure catalysts for the selective oxidation of H₂S to sulphur. *Solid State Sci.* **2010**, *12*, 996–1001. [[CrossRef](#)]
26. Barba, D.; Palma, V.; Ciambelli, P. Screening of catalysts for H₂S abatement from biogas to feed molten carbonate fuel cell. *Int. J. Hydrogen Energy* **2013**, *38*, 328–335. [[CrossRef](#)]
27. Soriano, M.D.; Nieto, J.M.L.; Ivars, F.; Concepcion, P.; Rodriguez-Castellon, E. Alkali-promoted V₂O₅ catalysts for the partial oxidation of H₂S to sulphur. *Catal. Today* **2012**, *192*, 28–35. [[CrossRef](#)]
28. Amiridis, M.D.; Solar, J.P. Selective catalytic reduction of nitric oxide by ammonia over V₂O₅/TiO₂, V₂O₅/TiO₂/SiO₂, and V₂O₅–WO₃/TiO₂ catalysts: Effect of vanadia content on the activation energy. *Ind. Eng. Chem. Res.* **1996**, *35*, 978–981. [[CrossRef](#)]
29. Garbarino, G.; Kowalik, P.; Riani, P.; Antoniuk-Jurak, K.; Pieta, P.; Lewalska-Graczyk, A.; Lisowski, W.; Nowakowski, R.; Busca, G.; Pieta, I. Improvement of Ni/Al₂O₃ catalysts for low-temperature CO₂ methanation by vanadium and calcium oxide addition. *Ind. Eng. Chem. Res.* **2021**, *60*, 6554–6564. [[CrossRef](#)]
30. Wachs, I.E. Catalysis science of supported vanadium oxide catalysts. *Dalton Trans.* **2013**, *42*, 11762–11769. [[CrossRef](#)]
31. Koebel, M.; Elsener, M.; Kleemann, M. Urea-SCR: A promising technique to reduce NO_x emissions from automotive diesel engines. *Catal. Today* **2000**, *59*, 335–345. [[CrossRef](#)]
32. Forzatti, P. Present status and perspectives in de-NO_x SCR catalysis. *Appl. Catal. A Gen* **2001**, *222*, 221–236. [[CrossRef](#)]
33. Borovkov, V.Y.; Mikheeva, E.P.; Zhidomirov, G.M.; Lapina, O.B. Theoretical and experimental studies of the nature of the catalytic activity of VO_x/TiO₂ systems. *Kinet. Catal.* **2003**, *44*, 710–717. [[CrossRef](#)]
34. Wu, M.; Ung, K.C.; Dai, Q.; Wang, X. Catalytic combustion of chlorinated VOCs over VO_x/TiO₂ catalysts. *Catal. Commun.* **2012**, *18*, 72–75. [[CrossRef](#)]
35. Inomata, Y.; Hata, S.; Mino, M.; Kiyonaga, E.; Morita, K.; Hikino, K.; Yoshida, K.; Kubota, H.; Toyao, T.; Shimizu, K.; et al. Bulk vanadium oxide versus conventional V₂O₅/TiO₂: NH₃-SCR catalysts working at a low temperature below 150 °C. *ACS Catal.* **2019**, *9*, 9327–9331. [[CrossRef](#)]

36. Marberger, A.; Elsener, M.; Ferri, D.; Kröcher, O. VO_x surface coverage optimization of V₂O₅/WO₃-TiO₂ SCR catalysts by variation of the V loading and by aging. *Catalysts* **2015**, *5*, 1704–1720. [[CrossRef](#)]
37. Massenova, A.; Kalykberdiyev, M.; Sass, A.; Kenzin, N.; Ussenov, A.; Baiken, A.; Rakhmetova, K. Catalytic technologies for solving environmental problems in the production of fuels and motor transport in Kazakhstan. *Catalysts* **2020**, *10*, 1197. [[CrossRef](#)]
38. Rovenskikh, A.S.; Kariychina, A.E.; Iguminova, V.A. Automobile emission effect on the environment. Investigations of young scientists. In Proceedings of the XV International Scientific Conference, Kazan, Russia, 24 December 2020; pp. 15–18. (In Russian).
39. Zeidel, A.N.; Prokofiev, V.K.; Raysky, S.M.; Slavny, V.A.; Schrader, E.Y. *Tables of Spectral Lines. Directory*; Nauka: Moscow, Russia, 1977; p. 800. (In Russian)
40. Kalinkin, I.P.; Mosichev, V.I. *New Handbook of Chemist and Technologist. Analytical Chemistry*; Peace and Family: St. Petersburg, Russia, 2003; p. 984. (In Russian)