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Structure Peculiarities of Reduced Vanadium–Titanium Oxide Catalysts

G. A. Zenkovets, G. N. Kryukova, S. V. Tsybulya, V. F. Anufrienko, and V. Yu. Gavrilov
Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—The properties of vanadium–titanium oxide catalysts, which contain coherent phase boundaries formed by V_2O_5 and TiO_2 crystallites during reduction by hydrogen at 150–500°C, are examined. The phase boundary is preserved over the entire examined temperature range regardless of the structure of vanadium oxide, which is formed. The state of vanadium ions at the phase boundary is determined. The presence of a phase boundary in the catalyst is responsible for the $V_2O_5 \longrightarrow V_2O_3$ transition without the formation of intermediate structures.

INTRODUCTION

Earlier [1–3], the formation and structure of new nanostructured vanadium–titanium catalysts containing coherent interfaces of V_2O_5 and TiO_2 crystallites were examined. These catalysts are highly active and selective in a number of important partial oxidation reactions, such as the oxidation of β-picoline to nicotinic acid [4], *ortho*-xylene to phthalic anhydride [5], and formaldehyde to formic acid [6]. The catalyst may undergo reduction in a reaction medium; therefore, the stability of phase boundaries and the states of vanadium ions in oxidizing and reducing media are important for both fundamental studies of this oxide system and practical applications of the catalysts.

Vanadium–titanium catalysts with coherent interfaces remain stable after thermal treatment in an oxidizing atmosphere up to the melting temperature of V_2O_5, after which anatase transforms into rutile with the formation of a substitutional solid solution of V^{4+} ions in TiO_2 (rutile) [3, 7]. However, the stability of coherent interfaces in a reducing atmosphere was not studied before.

In this work, we consider the structure of vanadium–titanium oxide catalysts with coherent interfaces in the course of the reduction by hydrogen over a wide range of temperatures.

EXPERIMENTAL

A vanadium–titanium oxide catalyst containing 20 wt % V_2O_5 and 80 wt % TiO_2 was prepared by the spray drying of finely divided anatase and a vanadyl oxalate solution followed by thermal treatment in an air flow at 500°C according to the procedure described in [1–3].

The catalyst was reduced in a flow reactor by first heating in a helium flow to a preset temperature of 150–500°C and reducing in a hydrogen flow at a flow rate of 80 cm^3/min for 2 h, and finally cooling to room temperature in a helium flow. In a number of cases, the catalyst was purged with helium after reduction, heated to a given temperature, and then oxidized by controlled O_2 pulses until complete saturation.

For some experiments, the reduced samples were washed with 10% nitric acid to remove the vanadium oxide phase according to the procedure described in [3].

X-ray diffraction analysis was performed on a URD-63 diffractometer equipped with a graphite monochromator using CuK_α radiation. The amounts of V_2O_5 and rutile phases were determined from their corundum numbers.

Electron-microscopic studies were performed on a JEM-2010 instrument with a resolution of 0.14 nm and an accelerating voltage of 200 kV.

Electronic diffuse-reflectance spectra were measured on a Specord M-40 spectrometer. The spectra were recalculated by the Kubelka–Munk formula.

RESULTS AND DISCUSSION

The results of X-ray diffraction phase analysis presented in Fig. 1 indicate that the initial oxidized vanadium–titanium catalyst is a mixture of well-crystallized anatase and V_2O_5 phases. According to electron microscopic data, TiO_2 (anatase) and V_2O_5 particles coalesced in strictly specified crystallographic directions are present in these catalysts; these particles are separated by a well-defined coherent interface (Fig. 2a) [2, 3]. In the above sample, V^{4+} ion associates were also detected in the region of phase boundary using EPR spectroscopy; these ion associates were stabilized at the sites of substitution for Ti^{4+} ions in the anatase lattice [8].

Figure 3 demonstrates electronic diffuse-reflectance spectra for the initial vanadium–titanium catalyst and a catalyst from which a vanadium phase was removed by

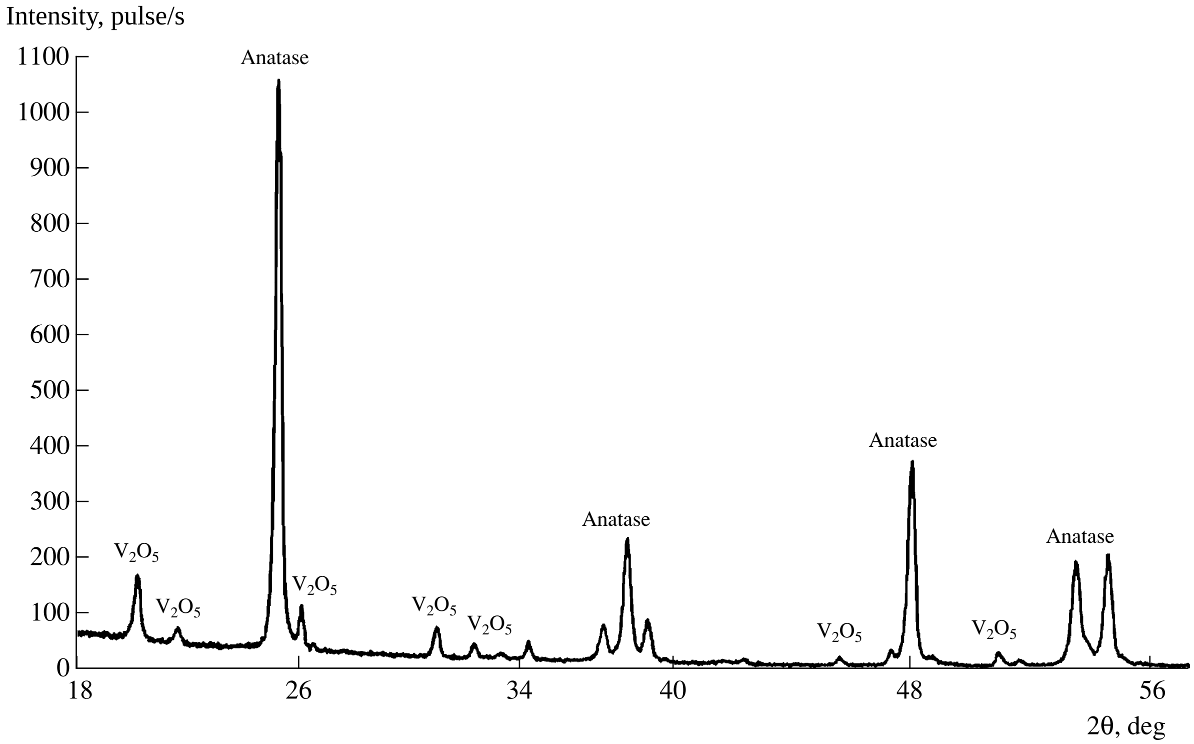

Fig. 1. X-ray diffraction pattern of the initial vanadium–titanium catalyst.

washing with nitric acid. Only an absorption edge at 27000–28000 cm^{-1}, which is typical of TiO_2 [9], was detected for the initial sample. In the washed sample, the absorption edge of TiO_2 exhibits a very typical dissolve, which makes it possible to distinguish a band at 25000 cm^{-1}. According to published data [9], the *d–d* transition bands, which are observed in the electronic diffuse-reflectance spectra of vanadium–titanium samples at 20000 cm^{-1}, are due to isolated V^{4+} ions in the octahedral substitutional positions of rutile. It is certain that the band energy at 25000 cm^{-1} is not associated with the *d–d* transitions of isolated V^{4+} ions because the structure of rutile or anatase is free from positions at which the crystal field strength (in terms of *Dq*) is greater than that at the substitutional positions of rutile [9]. This fact suggests that this band is due to the intervalence charge transfer of V^{4+}–O–V^{5+} ions in intercrystalline positions where the V–O–V bond is more covalent than that in V_2O_5 [10]. Such a state of vanadium ions can be typical of surface or intercrystalline layer structures. These results in combination with electron microscopic data and with the evidence for the absence of surface vanadium structures [3] allowed us to suggest with reasonable confidence that vanadium ions in the above states belong to the interface.

The table summarizes the chemical composition of catalysts calculated from the data on the limiting amounts of oxygen absorbed under reoxidation conditions at 450°C. This calculation is correct because it was found [10] that titanium dioxide is not reduced under these conditions. The table demonstrates that, after reduction at 250°C, the vanadium oxide composition differed only slightly from the composition of parent vanadium pentoxide. However, a further increase in the temperature resulted in strong reduction. After treatment at 450°C, the vanadium phase was similar to vanadium trioxide.

Figure 4 shows that, after the reduction of the catalyst at 300°C, the peak intensity corresponding to a V_2O_5 phase in the X-ray diffraction pattern dramatically decreased, and this peak completely disappeared at 400°C. This behavior indicates that the amount of the crystalline vanadium pentoxide phase decreased and then this phase underwent full amorphization. After reduction at a temperature higher than 450°C, the peak of a V_2O_3 phase appeared in the X-ray diffraction pattern. The table summarizes X-ray diffraction data on the concentrations of the crystalline vanadium pentoxide phase in samples reduced at different temperatures. The amount of the V_2O_5 phase remained almost unchanged up to 250°C and then dramatically decreased. The rutile phase fraction remained almost constant over the entire range of temperatures.

A small peak corresponding to the rutile phase appeared in the X-ray diffraction pattern upon catalyst reduction even at 150°C. As the temperature increased to 500°C, this peak somewhat broadened and shifted; however, its intensity remained almost unchanged. This is likely due to the presence of trace impurities in the

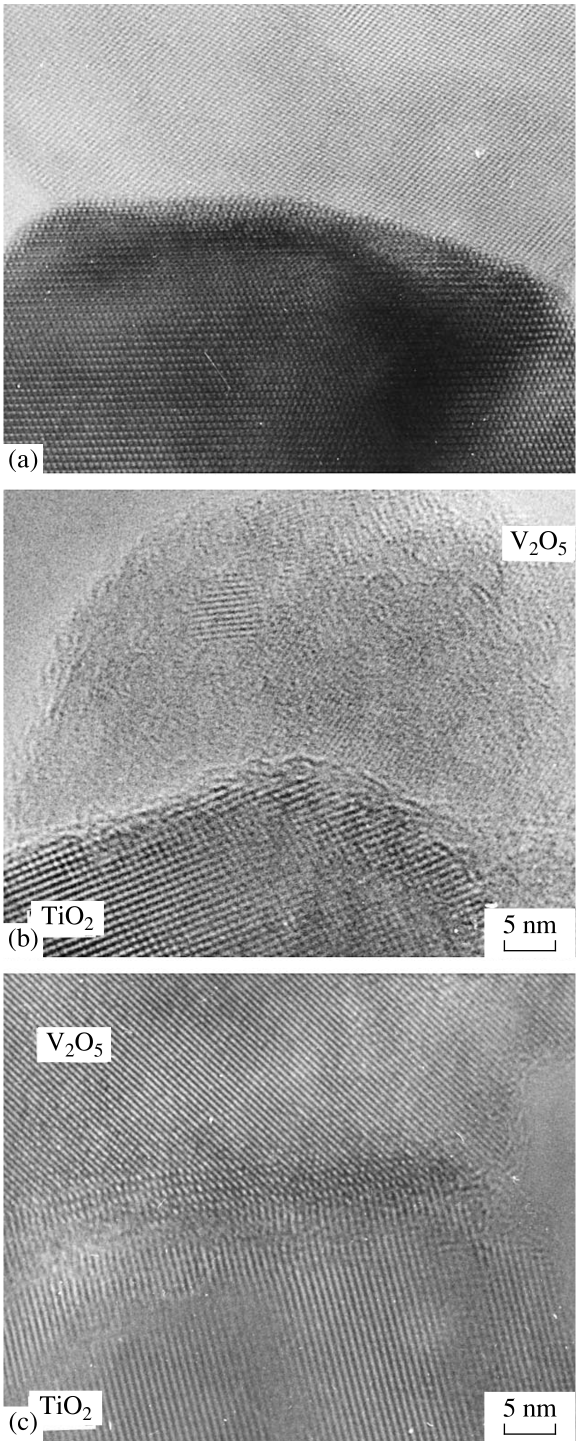

Fig. 2. Electron micrographs of (a) the initial vanadium–titanium catalyst and the samples reduced by hydrogen at (b) 300 and (c) 500°C.

initial sample of titanium dioxide. In the course of reduction, these impurities form a compound with a rutile structure, and the concentration of this compound, which was formed even at the initial stage of reduction, did not increase with temperature.

According to electron microscopic data, the catalyst microstructure remained unchanged upon reduction below 250°C. Disorder in the blocks of the V_2O_5 phase and the gradual amorphization of these blocks were observed in the sample reduced at 300–450°C; however, V_2O_5 particles did not disintegrate into smaller amorphous blocks (Fig. 2b). The structure disorder of V_2O_5 under the conditions of reduction at temperatures higher than 250°C due to the formation of $(V{=}O)^{2+}$ complexes, which are typical of nonstoichiometric compounds like V_2O_{5-x} (where $x < 1$), was confirmed by the shape of the EPR spectra of vanadyl ions [11]. At the same time, the microstructure arrangement of the interface was retained.

Electron micrographs of samples reduced at 500°C clearly indicate well-crystallized V_2O_3 oxide particles coalesced with TiO_2 particles; the interface between them was retained. Moreover, in the sample reduced at 500°C, crystallographic shift structures began to form in TiO_2 (rutile); evidently, this results in the broadening and shifting of the rutile diffraction peak (Fig. 2c).

It follows from Fig. 3 that the electronic diffuse-reflectance spectrum of the sample reduced at 250°C remains almost identical to the spectrum of the oxidized sample; only the TiO_2 adsorption edge is observed in the region 25000–27000 cm^{-1}. In the spectrum of the sample that was reduced at 450°C and washed to remove the vanadium oxide phase, the intervalence charge-transfer band with a maximum at 18000 cm^{-1} and the absorption edge of TiO_2 at 28000 cm^{-1} were detected. The assignment of the intervalence charge transfer to the *d*–*d* transition of V^{4+} ions in anatase seems improbable [9] because it is beyond reason to expect that the energy of this transition will noticeably differ from the energy of T_{2g}–E_{2g} transitions for V^{4+} ions that replace titanium ions in the rutile structure, where this transition is characterized by a band at 20000 cm^{-1}. It is most likely that this transition is due to the V^{4+}–O–V^{3+} intervalence charge transfer [10].

Another special feature of the synthesized vanadium–titanium catalysts is the absence of intermediate reduced phases of vanadium oxides. It is well known [12] that these phases appear after the reduction of a free V_2O_5 phase. For comparison, we reduced pure V_2O_5 (which was prepared by drying a vanadyl oxalate solution followed by thermal treatment at 500°C in an air flow for 4 h) and its mixture with anatase (in the ratio that corresponds to the catalyst composition) under identical conditions. The following homologous series of reduced vanadium oxides was detected, which was identical in pure V_2O_5 and in the mixture with titanium dioxide:

$$V_2O_5 \longrightarrow V_nO_{2n+1} \longrightarrow VO_2 \longrightarrow V_nO_{2n-1} \longrightarrow V_2O_3.$$

This homologous series was not observed upon the reduction of a vanadium–titanium catalyst [13]:

$$V_2O_5 \longrightarrow \text{X-ray amorphous phase} \longrightarrow V_2O_3.$$

Evidently, differences observed upon the reduction of a pure V_2O_5 phase or its mixture with TiO_2 and a vanadium–titanium catalyst resulted from the formation of a coherent interface between V_2O_5 and TiO_2 particles and from the state of vanadium ions at this interface.

Catalysts reduced at 150–500°C were readily reoxidized after calcination in air, and the interface was retained in them. Thus, TiO_2 and V_2O_5 phases and an impurity phase of rutile (in an amount of 4 to 5%) were detected by X-ray diffraction analysis in the sample reduced at 500°C and then reoxidized by oxygen at this temperature until complete saturation. It follows from the electron microscopic data that the reoxidized sample structurally corresponds to the initial oxidized sample that was not subjected to reduction; in both cases, well-defined interfaces were observed. According to EPR data, the state of tetravalent vanadium ions was restored after reoxidation: only associated V^{4+} ions were detected at the sites of substitution for Ti^{4+} ions in the anatase structure, and their concentration was approximately equal to that in the initial sample. Consequently, the reoxidation of a catalyst that was subjected to severe oxidation by hydrogen at 500°C resulted in the restoration of the microstructure and the initial state of vanadium ions.

It is likely that trace impurities in the starting commercial titanium dioxide were responsible for the presence of a minor impurity of rutile in the reoxidized sample. These trace impurities formed a stable phase with the rutile structure in the course of reduction [10]; this phase appeared at the initial stage of reduction, and its concentration did not increase afterwards.

Thus, during the reduction of a vanadium–titanium oxide catalyst over the temperature range 150–500°C, a coherent boundary between the crystallites of vanadium oxide and anatase was retained regardless of the structure of the vanadium oxide. This coherent boundary also remained unchanged upon the reoxidation of the reduced sample. In connection with this, it was of interest to trace the state of the coherent interface under the conditions of repeated reduction and reoxidation of a sample in the course of a catalytic process. For this purpose, the catalyst was successively reduced and then reoxidized by oxygen at 450°C seven times. The electron micrograph of the sample treated in this manner indicates that the coherent boundary became even somewhat more ordered; it is likely that the interaction became deeper. That is, the coherent boundary was not broken in the cyclic process of reduction and reoxidation of the catalyst.

Thus, the reduced vanadium–titanium oxide catalyst with coherent interfaces is essentially different from the reduced mixture of vanadium oxide and titanium dioxide in physicochemical properties. It is likely that under reductive conditions the presence of a coherent interface and the state of vanadium ions at this interface significantly affect the crystal structure of the particles of the vanadium oxide phase involved in the formation of this interface.

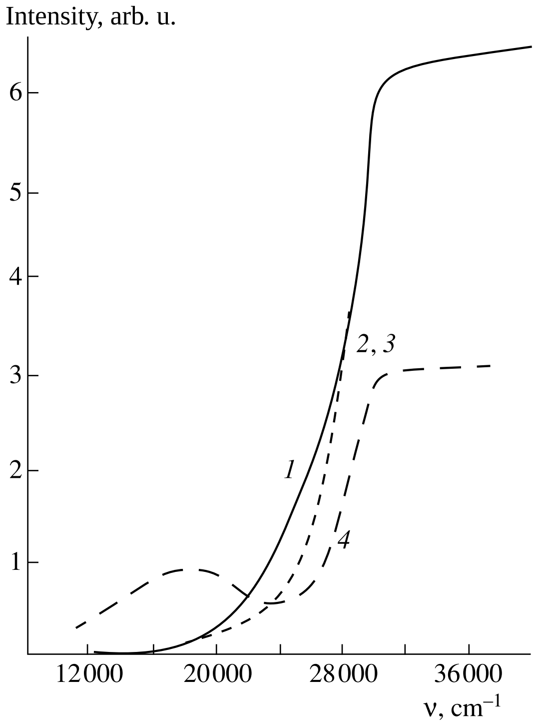

Fig. 3. Electronic diffuse-reflectance spectra of (*1*) the initial vanadium–titanium catalyst, (*2*) the above catalyst after the removal of a V_2O_5 phase, (*3*) the catalyst after reduction at 250°C followed by washing for the removal of a vanadium oxide phase, and (*4*) the catalyst after reduction at 450°C followed by washing for the removal of a vanadium oxide phase.

It follows from the experimental results and published data [11] that, at a reduction temperature of 150–250°C (when the degree of reduction of vanadium

Effect of the temperature of catalyst reduction on the degree of oxidation of vanadium oxide and on the concentration of a crystalline V_2O_5 phase

Reduction temperature, °C	Catalyst composition, wt %	Fraction of a crystalline V_2O_5 phase, wt %
150	$20\%V_2O_5 + 80\%TiO_2$	20
250	$20\%V_2O_{5-x} + 80\%TiO_2$ ($x = 0.14$)	20
300	$20\%V_2O_{5-x} + 80\%TiO_2$ ($x = 0.75$)	6.5
350	$20\%V_2O_{4-x} + 80\%TiO_2$ ($x = 0.16$)	0
450	$20\%V_2O_{4-x} + 80\%TiO_2$ ($x = 0.8$)	0
500	$20\%V_2O_3 + 80\%TiO_2$	0

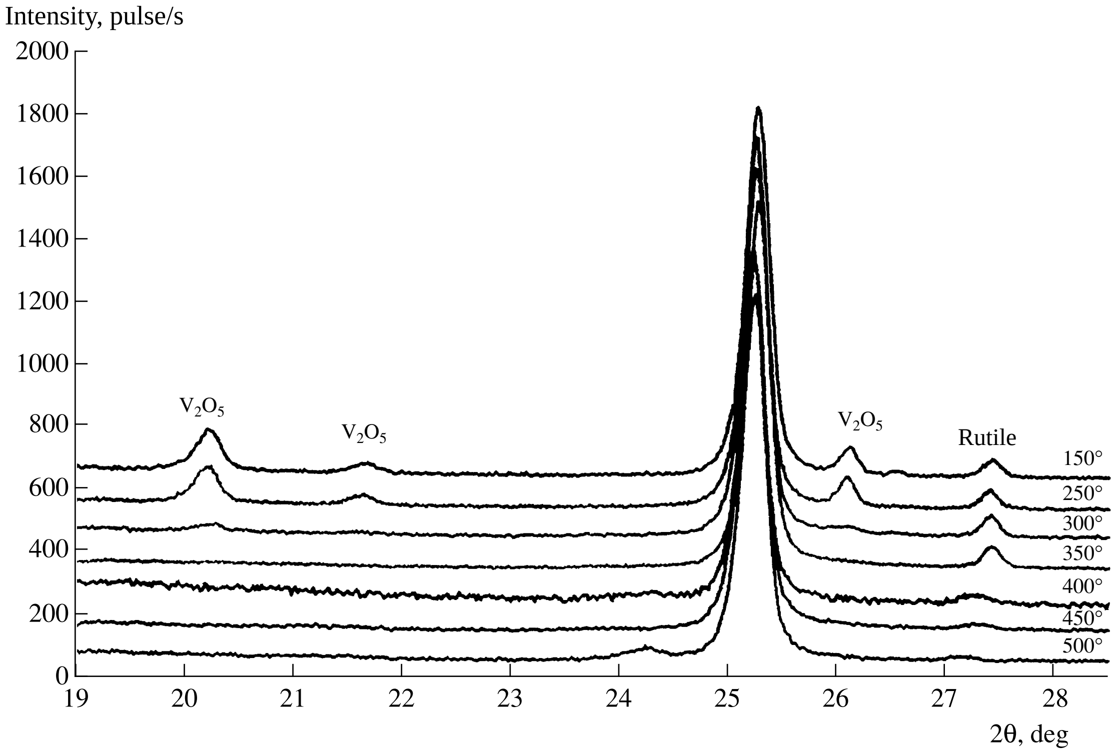

Fig. 4. X-ray diffraction patterns of the vanadium–titanium catalysts reduced by hydrogen at different temperatures (figures at the diffraction patterns indicate the reduction temperatures, °C).

oxide is low and vanadium ions at the interface appear as V^{4+} ion associates and V^{4+}–O–V^{5+}; moreover, the concentration of V^{4+} ions is not too high), the catalyst structure did not undergo considerable changes: the crystal structures of V_2O_5 particles and anatase were retained. At reduction temperatures from 250 to 450°C, the concentration of tetravalent vanadium increased further, and the VO_2 oxide fragments were formed at the interface. This resulted in disordering in the blocks of the crystalline V_2O_5 phase and in gradual amorphization of this phase. In this case, vanadium oxide with the V_2O_4 structure was not formed. According to published data [14], V^{4+} ions in the V_2O_4 structure strongly correlate with each other (long-range ordering), and the dielectric → metal Mott transition results from this correlation. It is likely that the long-range ordering between the state of V^{4+} ions at the interface and the state of these ions in reduced vanadium oxide (this long-range ordering is typical of the V_2O_4 oxide) did not occur in the catalysts reduced at 250–450°C. Therefore, the crystalline phase of V_2O_4 was not formed. A further increase in the reduction temperature resulted in the formation of V^{4+}–O–V^{3+} fragments, which contain vanadium(III) ions, at the interface. Therefore, it is highly probable that the correspondence between the state of V^{3+} ions and their coordination environments at the interface and in the structure of the V_2O_3 oxide is attained at a considerable concentration of the above fragments.

Thus, the coherent interface between titanium dioxide and vanadium oxide particles was retained upon the reduction of vanadium–titanium oxide catalysts in the temperature range 150–500°C. The occurrence of this interface is responsible for the formation of the vanadium oxide structure on reduction. A correlation between the state of vanadium ions at the interface and the structure formed during the reduction of vanadium oxide was observed.

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