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Catalytically Active Complexes and Influence of SiO_2 on the Catalytic Properties of the Active Component of Vanadium Catalysts for SO_2 Oxidation

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The complexes present in the active form of vanadium catalysts for SO_2 oxidation have been studied with use of ^{51}V, ^{17}O, and ^{23}Na NMR at room temperature and at 500°C in reaction mixture media. In the V_2O_5–$K_2S_2O_7$ melt the coordination of vanadium(V) with 2 or 3 pyrosulfate anions takes place. At vanadium concentrations above 1.5 mol/liter associated complexes are formed. These species are most active in the oxidation of SO_2. This conclusion follows from measurements of the catalytic activity of V_2O_5–$K_2S_2O_7$ supported on Pyrex tubes. ^{51}V NMR shows that the interaction of vanadium with SO_2 results in the formation of tetracoordinated surface complexes. These tetracoordinated vanadium complexes which are catalytically inactive form active species upon interaction with monomeric vanadium–pyrosulfate complexes in the melt.

INTRODUCTION

The active component of vanadium catalysts for sulfur dioxide oxidation is known to be formed directly in the course of the catalytic reaction (*1*). Concepts on the reaction mechanism are based mainly on kinetic data (*2, 3*) and only poor information on the nature of the catalytically active complexes is available. This situation arises due to the experimental difficulties of investigating catalysts at high temperatures and in the reaction medium atmosphere. However, knowledge of the nature of the catalytically active complexes is crucial for establishing the reaction mechanism.

Spectrophotometric, potentiometric, and cryoscopic studies of V_2O_5–$K_2S_2O_7$ melts carried out at 410–450°C, in air, at vanadium concentration 0.005–0.04 mol/liter, reveal under these conditions the presence of monomeric oxosulfatevanadate complexes (V) (*4*). Based on kinetic data for catalysts with a considerably higher vanadium content (2–4 mol/liter) in the active component melt, it is concluded (*2*) that dimeric vanadium complexes are active in the reaction.

Another important problem concerns the role of the support in a catalytic reaction. The question is whether it serves only to create high specific surface area and optimal porous structure or whether it may also interact with the active component of the catalyst. Previous studies revealed (*5*) that in the model systems V_2O_5–SiO_2, KVO_3–SiO_2, and K_2O–V_2O_5–SiO_2 surface vanadium compounds with SiO_2 are formed. This follows from the appearance in ^{51}V NMR spectra of a nearly isotropic line with a chemical shift of −540 ppm (with respect to $VOCl_3$), corresponding to a nearly regular tetrahedral vanadium environment. The active component of vanadium catalysts for SO_2 oxidation differs from model systems by an extra content of SO_3, which forms compounds of oxosulfatevanadate type with potassium and vanadium under the conditions of the catalytic reaction (400–500°C) (*6*). Numerous suggestions have been made concerning the effect of silica on the catalytic properties of the active com-

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ponent (7–9), yet the chemical nature of this phenomenon is still obscure. Using ^{51}V NMR, we have found the formation of surface vanadium–silica complexes also for vanadium catalysts (5).

In the present work, V_2O_5–$K_2S_2O_7$ melts have been examined in a wide range of vanadium concentrations using ^{17}O and ^{51}V NMR. We have also measured ^{23}Na NMR spectra for the V_2O_5–$Na_2S_2O_7$ system. These data have been compared with the catalytic activity of V_2O_5–$K_2S_2O_7$ melts. In addition, the effect of surface compounds on the catalytic activity has been considered for catalysts with various vanadium contents and with varying SiO_2 specific areas.

EXPERIMENTAL

Samples modeling the active component ($M_2S_2O_7$–V_2O_5) were prepared by melting a mixture of V_2O_5 and $M_2S_2O_7$, obtained by decomposition of $M_2S_2O_8$ (M = K, Na) at 500°C. To label the samples with ^{17}O, $K_2S_2O_7$ was treated with $H_2\,^{17}O$. The resulting $KHSO_4$ was employed for the active component synthesis. The enrichment of pyrosulfate by ^{17}O isotope was ~1%. The concentration of vanadium (C_V) in the $K_2S_2O_7$ melt varied in the 0–3.5 mol/liter range. The melts were treated with SO_3 by prolonged exposure (80 h in SO_3 atmosphere at 500°C and 400 Torr). SO_3 was produced by decomposition of potassium pyrosulfate.

For catalyst preparation two methods were involved. The first one consisted in sintering V_2O_5 and $KHSO_4$ at 500°C, after which the solid was thoroughly ground with silica powder and sintered again in air at 500°C for 2 h. The second method, involving mixing, was similar to that used for the preparation of real catalysts. The mixture of $K_4V_2O_7$ and KOH solutions in a given ratio was acidified by sulfuric acid to pH = 0.5, then powdered SiO_2 was added, dried, and calcined in air at 500°C for 2 h. The vanadium content in the samples was varied from 1.7 to 9.5%, and the K/V molar ratio from 3 to 14. For convenience, samples were arranged in four series (Table 2) differing in preparation technique, V_2O_5 content and K/V ratio. The samples of each series were obtained on three types of silica with surface areas 55, 155, and 300 m^2/g, respectively. In the last series, the V_2O_5 content and K/V ratio were varied at the same silica surface area and preparation technique.

The catalysts were treated with reaction mixture in a flow-circulation reactor at 485°C; the initial mixture composition was 7.5% SO_2, 10% O_2, 82.5% N_2, conversion of SO_2 to SO_3, $x = 70\%$. Grain size was 0.5–1 mm. The catalytic activity was evaluated by the reaction rate constant, k, ml/g · s · atm, calculated using the Boreskov–Ivanov equation (*10*).

After catalytic experiments the catalysts were cooled for vanadium NMR measurements and the samples were placed in Teflon sample tubes. The fraction of blocked (inaccessible) vanadium α was determined as V/V_0, where V_0 and V are the vanadium contents in the catalyst before and after extraction of vanadium by 10% solution of H_2SO_4, respectively (*11*).

NMR experiments were performed using a Bruker CXP-300 spectrometer (7.04 T for ^{51}V NMR, 20°C, 2.14 T for ^{17}O, ^{23}Na NMR, 500°C). ^{51}V spectra were recorded at 78.86 MHz in the frequency range 250 kHz with a 1 μs radio frequency pulse and with a pulse repetition frequency of 10 Hz. The scan accumulation number used was from 10^3 to 10^5. The chemical shift in the ^{51}V spectra was measured relative to the $VOCl_3$ signal. The measurement at 500°C of ^{17}O and ^{23}Na NMR spectra were performed in 10-mm-outer-diameter Pyrex sample tubes using the high temperature probe head cooled with flowing water. For such experiments a BE-45 Bruker magnet with a 40-mm pole gap and with ^{19}F field stabilization was used. The ^{17}O NMR spectra were taken at 12.21 MHz in the frequency range of 30 kHz. Pulse duration was 30 μs, and pulse repetition frequency was 50 Hz. The signal

TABLE 1

Catalytic Activity of $K_2S_2O_7$–V_2O_5 Melts as a Function of Vanadium Concentration

K/V	$C_V \times 10^3$ (mol/l)	$P_{SO_2} \times 10^3$ (atm)	$P_{O_2} \times 10^3$ (atm)	$P_{SO_3} \times 10^2$ (atm)	$X_{dif.}$ (%)	$W \times 10^7$ ($mol_{SO_2}/cm^3 \cdot s$)	$k_3 \times 10^{-3}$ (cm^3/mol_{O_2})
5	3.2	4.3	3.3	3.2	10	31.0	4.0
6.7	2.4	5.6	3.2	3.8	8	11.6	1.3
10	1.7	5.2	4.4	3.8	2	4.0	0.5
20	0.9	4.6	3.7	3.5	10	0.95	0.4
50	0.38	7.7	3.3	4.0	1	0.097	0.08

Note. K/V—mole ratio of potassium to vanadium in the melt; C_V—vanadium concentration (mol/l) in the melt; P_{SO_2}, P_{O_2}, P_{SO_3}—the partial pressures of sulfur dioxide, oxygen and sulfur trioxide in the gas mixture used for the catalytic activity measurements, respectively; $X_{dif.}$—the sulfur dioxide to sulfur trioxide conversion in differential reactor, %; W—the reaction rate, calculated by the kinetic equation (*2*), see text; k_3—reaction rate constant for interaction of binuclear vanadium complexes with O_2.

from H_2O at room temperature was used as a reference for chemical shift measurements. From 5×10^4 to 10^5 scans were usually used for signal accumulation. The ^{23}Na NMR spectra were registered at 23.8 MHz in the frequency range of 20 kHz. Pulse duration was 5 μs, pulse repetition time 10 Hz. The ^{23}Na chemical shifts were measured from solid Na_2SO_4 (whose linewidth at 500°C is less than 100 Hz). Before NMR measurements at 500°C the $K_2S_2O_7$–V_2O_5 or $Na_2S_2O_7$–V_2O_5 melts in 10-mm NMR tubes were contacted with SO_3 or SO_2 gases for 70–80 h at 500°C, and were then sealed off with the gas media. These sealed sample tubes were used for the measurements of high temperature ^{17}O and ^{23}Na NMR spectra.

The catalytic activity of melts was estimated using a flow reactor. The internal surface of Pyrex tubes of 7 mm diameter and 200 mm length was covered with a thin layer of V_2O_5–$K_2S_2O_7$ melts (3×10^4 Å) with different K/V molar ratios (Table 1). Tubes with melts were placed in a glass cylinder, to which the reaction mixture SO_2+SO_3+O_2+He, corresponding to ~85% conversion degree, was supplied. The number of such tubes and the volume rate of reagents were chosen so that conversion in the reactor did not exceed 10%, and hence it could be considered as a differential reactor. The steady state reaction rate was measured at 500°C. The reaction mixture composition and the reaction rates in the forward direction are shown in Table 1. The reaction rate constant was estimated by the equation

$$W = k_3 \cdot P_{O_2} \frac{K_2 \cdot P_{SO_2}}{1 + K_2 \cdot P_{SO_2}} \left[1 - \frac{P^2_{SO_3}}{P^2_{SO_2} \cdot P_{O_2} \cdot K_p}\right]$$

which follows from the reaction mechanism proposed in Ref. (*2*). Here W is the reaction rate, k_3 the reaction rate constant for interaction of binuclear vanadium complexes with O_2, K_2 the equilibrium constant for interaction of binuclear vanadium complexes with SO_2, K the equilibrium constant of the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$, and P_{O_2}, P_{SO_2}, P_{SO_3} are the O_2, SO_2, and SO_3 partial pressures, respectively.

RESULTS AND DISCUSSION

Figure 1 shows ^{17}O NMR spectra for $K_2S_2O_7$ and for V_2O_5–$K_2S_2O_7$ melts at various K/V ratios, taken after exposure in SO_3 atmosphere at 500°C. Also the dependence of the chemical shift and linewidth on vanadium content is shown. The $K_2S_2O_7$ spectrum is a singlet line, ca. 100 Hz wide, with

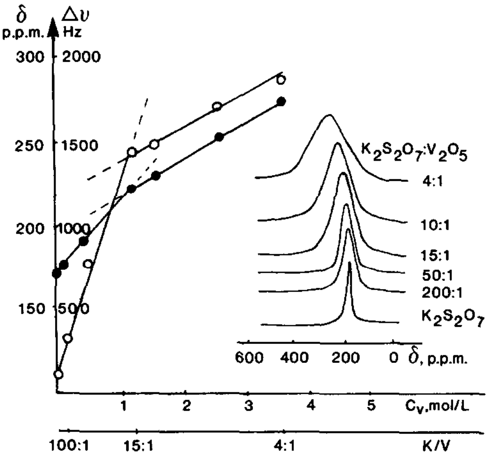

FIG. 1. ^{17}O NMR spectra of V_2O_5–$K_2S_2O_7$ melts (measured at 500°C, frequency 12.2 MHz, pulse duration 30 μs, relaxation delay 0.02 s) and dependence of ^{17}O chemical shift (●), and linewidth (○) on vanadium concentration (reference H_2O).

a chemical shift of 170 ppm. The $S_2O_7^{2-}$ anion is made up of two tetrahedra having a common oxygen atom, so the ^{17}O spectrum should comprise two lines with the intensity ratio of 6 : 1. The presence of one line indicates a rapid exchange between the bridge and terminal oxygen atoms, which seems to occur due to the reaction $S_2O_7^{2-} \rightleftarrows SO_4^{2-} + SO_3$. With addition of V_2O_5 to potassium pyrosulfate, a shift and a broadening of the ^{17}O line are observed. As the vanadium concentration (C_V) increases, two regions can be seen with an approximately linear dependence of chemical shift and linewidth on C_V (Fig. 1). This dependence indicates that sulfate-type ions ($S_2O_7^{2-}$ or SO_4^{2-} anions) enter into the inner coordination sphere of vanadium and that there is rapid exchange between sulfate-ion oxygen bound with vanadium and sulfate-ion oxygen in a "free" state in the melt. In this case for the chemical shift δ' it is possible to use a formula similar to that used for fast exchange of ligands between the coordination of metal complexes and solution (*12*)

$$\delta' = \delta_k \cdot K \cdot n \cdot C_V/(1 + K \cdot P),$$

where $\delta' = \delta - \delta_{K_2S_2O_7}$, δ_k is the shift of oxygen atoms coördinated with vanadium relative to $\delta_{K_2S_2O_7}$, C_V is the vanadium concentration in the melt, n the number of coordination sites for vanadium, P the pyrosulfate concentration in the melt, and K is the complex formation constant. This equation is valid for a large excess of ligand (pyrosulfate in our case) and if the formation of a complex of one type takes place. At $K \cdot P > 1$ the equation can be simplified to $\delta' = \delta_k \cdot n \cdot C_V/P$ which is linear relative to vanadium concentration, C_V. A similar expression is valid for the linewidth. The above expression suggests that the dependence of δ' on vanadium concentration should be linear. In the experiments two approximately linear sections are observed. This indicates a changing of the complex composition at $C_V > 1.5$ mol/liter. With known δ_k one may find n, the number of coordination sites for vanadium by sulfate-ion oxygen. There is a lack of literature data on chemical shifts of sulfate and pyrosulfate oxygen bound with vanadium, but there is information concerning related systems. The chemical shift is −568 ppm for VO_4^{3-} and 700 ppm for $V_2O_7^{4-}$ (*13*). For vanadium–molybdenum heteropolyanions chemical shifts of oxygen bound with vanadium are 1200 and 620 ppm for terminal and bridged Mo–O–V atoms, respectively. It is likely that chemical shifts of sulfate-ion oxygen bound with vanadium are in the range −550 to −750 ppm. This leads to a value of n from 6.5 to 4.3, respectively.

Usually the sulfate ion is bonded with metal cations by two oxygens (bidentate coordination) (*4*). This leads to the conclusion that with one vanadium cation are bonded two or three sulfate anions according to the scheme

$$VO^{3+} + 3SO_4^{2-} \rightleftarrows VO(SO_4)_3^{3-} \quad (1)$$

Complexes of this type were proposed in Ref. (*4*) on the basis of spectrophotometric and potentiometric data. Usually vanadium forms distorted octahedral (or tetrahedral) complexes. On this basis it is reasonable to assume that a complex of this type appears to be a distorted octahedron with one short V–O bond, two sulfate ions, bidentately coordinated in an equatorial plane, and, probably, one sulfate ion, monodentately coordinated in the position opposite to the short V–O bond. One may assume that the short V–O bond oxygen, tightly bound with vanadium, originates from vanadium pentoxide oxygen and does not exchange with sulfate-ion oxygen.

The change of the slope in the dependence of the chemical shift and linewidth at vanadium concentration above 1.5 mol/liter is evidence for a variation in the complex structure and seems to be accounted for by association of the complexes in the melt. As seen from spectrophotometric and potentiometric data there are monomeric vanadium complexes within the concentration range 0.005–0.7 mol/liter (*4*). One may assume that dimerization or polymerization of vanadium complexes takes place at vanadium concentrations above 1.5 mol/liter.

Attempts to measure ^{51}V NMR spectra for melts met with no success because of a large linewidth. The large linewidth indicates a rather long correlation time of vanadium complex rotation in the melt, apparently due to its large size. By estimating the hydrodynamic radius using the formula for the quadrupole relaxation (*14*) the value of $r > 16$ Å was found (*15*).

Processes taking place under variations of vanadium concentrations in the melt are also seen in ^{23}Na NMR spectra for the V_2O_5–$Na_2S_2O_7$ system. Figure 2 presents the dependence of the ^{23}Na NMR chemical shift on vanadium concentration. Here two regions of variation of chemical shift may be seen. The ^{23}Na chemical shift varies slightly up to 3 mol/liter, the dependence becoming more sharp at higher vanadium concentrations. This suggests the existence in the melt of at least two types of vanadium complexes interacting with sodium. The rather narrow (100 Hz) ^{23}Na linewidth in the NMR spectra, and its independence of vanadium concentration, permits one to assume that sodium bound with the complex rapidly exchanges with that in the melt and that its lifetime in the coordination sphere is considerably less than the correlation time of complex rotation. The complexes of vanadium with sulfate ions are negatively charged (see Eq. (1)), and their association leads to the increasing of the net negative charge which must be compensated by the positive charge of alkali cations. Therefore, interaction of Na^+ with vanadium may be considered as an ionic interaction between two charged particles, and the sharp increase in the ^{23}Na chemical shift with growing C_V may be accounted for by the increased charge of the anion.

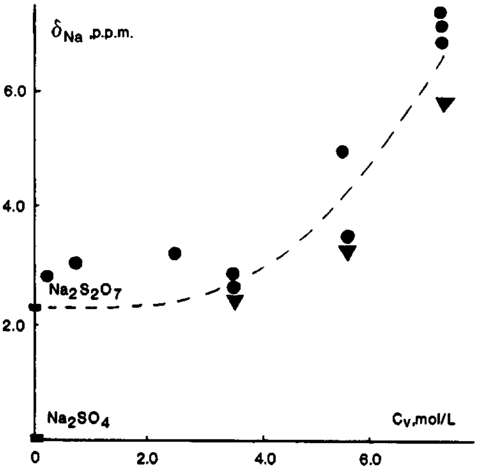

FIG. 2. Dependence of ^{23}Na chemical shift on vanadium concentration (T = 500°C, frequency 23.8 MHz, pulse duration 5 μs, relaxation delay 0.1 s): (●) in V_2O_5–$Na_2S_2O_7$ melts, (▼) in catalysts (reference Na_2SO_4, measured at 500°C).

Hence, it may be concluded that vanadium, under conditions of the catalytic reaction, is coordinated by sulfate ions taking part in the rapid exchange with sulfate ions in the melt. From this viewpoint the complexes in the melt and oxosulfatevanadates isolated from the melt in Ref. (*16*) are of similar nature. At low concentrations (not over 1.5 mol/liter) vanadium complexes in the melt represent monomer particles.

As revealed by measurements of the catalytic activity of melts (Table 1 and Fig. 3), the activity per mole of vanadium is not

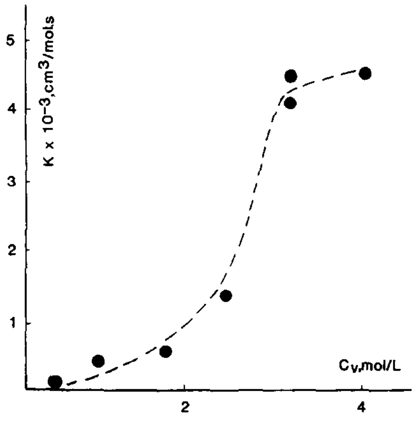

FIG. 3. Dependence of catalytic activity of V_2O_5–$K_2S_2O_7$ melts (per mole of vanadium) on vanadium concentration in melt (reaction rate constant was measured using the equation of Balzhinimaev *et al.* (*2*) at 500°C).

constant, but drastically increases at concentrations above 2 mol C_V/l. Since the dependence of ^{17}O and ^{23}Na chemical shifts is of the same type, it is possible to suppose that associated complexes formed at high vanadium concentrations are more active than monomeric complexes. Note that binuclear vanadium complexes were previously stated to be active in the reaction on the basis of kinetic data (*2*). Dimerization of monomeric complexes alone fails to account for the dramatic change in the catalytic activity, and in ^{17}O and ^{23}Na NMR spectra parameters. This process of complex rearrangements seems to be also accompanied by a considerable variation in the vanadium ligand environment.

In accordance with Ref. (*4*) monomeric vanadium(V) complexes are assumed to be in equilibrium:

$$VO_2(SO_4)_2^{3-} + S_2O_7^{2-} \rightleftarrows VO(SO_4)_3^{3-} + SO_4^{2-} \quad (2)$$

With excess $S_2O_7^{2-}$ (which corresponds to low vanadium concentrations or to a high content of gaseous SO_3) equilibrium (2) shifts toward formation of $VO(SO_4)_3^{3-}$, which seems to be more prone to dimerization than $VO_2(SO_4)_2^{3-}$ complexes. Further formation of binuclear complexes may be presented, for example, as

$$2VO(SO_4)_3^{3-} + nS_2O_7^{2-} \rightleftarrows V_2O_2(SO_4)_{6-n}(S_2O_7)_n^{6-} + nSO_4^{2-} \quad (3)$$

where $n = 1$ or 2 is the number of bridged pyrosulfate ligands. As seen from Eqs. (2) and (3), the equilibrium concentration of binuclear complexes should be quadratic in C_V at large excess of SO_4^{2-} anions. However, the latter enter the coordination sphere of the complex and the concentration of SO_4^{2-} anions becomes comparable with C_V (8.3 mol/liter in the $K_2S_2O_7$ melt) at large C_V. This leads to a sharper than quadratic dependence of the dimeric complexes concentration (and, hence, the catalytic activity) on C_V.

The regions of C_V where the sharp changes in dependences of δ' and K on C_V take place somewhat differ. Thus the chemical shift dependence changes its slope at lower vanadium concentrations ($C_V \sim 1.5$ mol/liter). This can be explained by the fact that the measurements of δ' were performed on thick films (~1 cm) which resulted in a nonequilibrium composition of the melt with respect to the gas phase, because the equilibrium between the gas and liquid phases is determined by diffusion in the liquid of soluble particles. The $S_2O_7^{2-}$ concentrations can considerably exceed the equilibrium value and the formation of associated complexes begins at lower C_V. In thin films (3×10^{-4} cm), under steady state conditions the SO_3 content in the melt corresponds to that of the gas. It is expected that on increasing the partial pressure of SO_3 and, consequently, of the $S_2O_7^{2-}$ concentration, a sharp rise of activity will occur at lower vanadium concentrations.

Thus, the results obtained reveal that associated vanadium complexes are active in the catalytic reaction. Their detailed structure calls for further investigation.

The second part of this work deals with the effect of the silica support on the catalytic activity. There are two viewpoints concerning this problem. One considers the

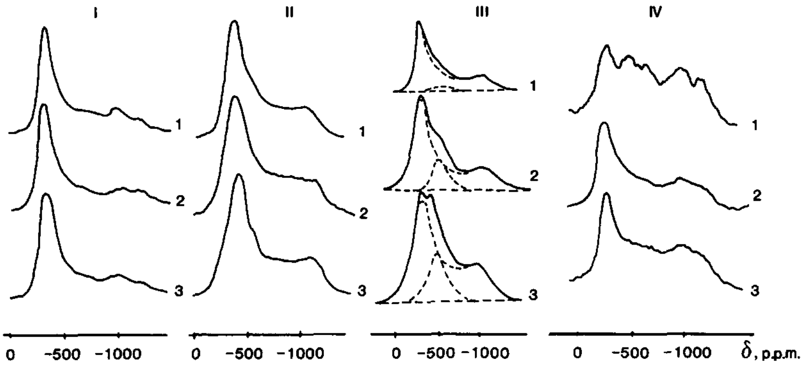

FIG. 4. ^{51}V NMR spectra (frequency 78.86 MHz, pulse duration 2 μs, relaxation delay 0.1 s, reference $VOCl_3$) for catalysts with characteristics listed in Table 2 (series and sample number correspond to spectra number).

support just as an inert material used to create a high surface and an optimal porous structure. The other proposes the interaction of SiO_2 with the active component leading to an increase of activity. However, neither of these suppositions has been so far proved.

We have investigated this problem by the ^{51}V NMR method in combination with catalytic activity measurements.

Figure 4 shows ^{51}V NMR spectra for catalysts of series I–IV. Spectra of series I samples, obtained by sintering and containing 7.7–9% V_2O_5, have lines typical for vanadium in oxosulfatevanadates with the composition of $K_3VO_2(SO_4)_2$ ($\sigma_{\parallel}$ = 1040 ppm, $\sigma_{\perp}$ = 320 ppm) and $K_3VO_2SO_4S_2O_7$ ($\sigma_{\parallel}$ = 1260 ppm, $\sigma_{\perp}$ = 320 ppm) (*17*). The line at −540 ppm is practically not observable for the samples of this series.

Series II, similar to series I in composition but prepared by mixing, has in its spectra an anisotropic line characteristic of $K_3VO_2(SO_4)_2$ oxosulfatevanadate. The line with the chemical shift of −540 ppm is observed at specific surface area SiO_2 = 155 m^2/g, its intensity growing with increase of SiO_2 surface (Fig. 4-II, curves 1–3).

Note that the method of catalyst preparation also affects the type of vanadium complexes. Samples prepared by sintering produce spectra of two oxosulfatevanadates(V), and those, prepared by mixing, only one type of oxosulfatevanadate (V). A higher intensity of the line with the chemical shift of −540 ppm is observed for samples prepared by mixing. This fact corresponds to a more homogeneous distribution of the melt over the support surface for the samples prepared by mixing. The relative intensity of this line increases with decreasing content of vanadium. Thus, in series III (~4% V_2O_5) the line with the chemical shift of −540 ppm appears even at the specific surface area of 55 m^2/g and is pronounced at S_{sp} = 155–300 m^2/g (Fig. 4-III, curves 1–3). Thus, catalysts based on a silica support contain along with oxosulfatevanadates(V), having vanadium in an octahedral oxygen environment, also tetrahedrally coordinated vanadium characterized by the ^{51}V line with the chemical shift of −540 ppm in NMR spectra. The intensity of the line grows with increasing specific surface area of SiO_2 and decreasing V_2O_5 concentration. This indicates that surface compounds of vanadium with silica are formed also in these catalysts.

To estimate the effect of surface compounds on catalytic properties the catalytic activity was measured in oxidation of SO_2 (Table 2).

As is known, the active component may be blocked by the support under thermal treatment (*11*). Owing to intensive agglomeration a part of the melt localized in thin

TABLE 2

Effect of Silica Specific Area and Catalyst Composition on Vanadium Catalyst Properties

Series	Sample	S_{sp} (m^2/g)	V_2O_5 (wt%)	K/V	Amount of melt (wt%)	α	S^*_{sp} (m^2/g)	k_V, 485°C, $x = 70\%$ ($cm^3/g \cdot s \cdot atm$)
I	1	55	9.0	3	40	0.03	12	130
	2	155	7.7	3	40	0.09	47	100
	3	300	8.1	3	40	0.06	—	130
II	1	55	7.0	3	40	0.08	12	160
	2	155	6.5	3	40	0.14	18	150
	3	300	7.4	3	40	0.06	95	130
III	1	55	4.4	3	20	0.10	25	120
	2	155	4.5	3	20	0.15	60	120
	3	300	3.9	3	20	0.12	200	95
IV	1	55	1.9	3	10	0.21	220	13
	2	155	3.8	6.5	40	0.10	220	90
	3	300	2.2	14	40	0.04	100	60

Note. Series I is prepared by sintering, Series II–IV by mixing. S_{sp}—the SiO_2 specific area; α—the portion of blocked vanadium; S^*_{sp}—the catalyst specific area after extraction of vanadium with 10% sulfuric acid; k_V—the sulfur dioxide oxidation reaction rate constant, calculated by the Boreskov–Ivanov equation (*10*).

pores is blocked by silica in thin pores. Table 2 presents the portions of the active component α (with respect to V_2O_5) blocked in this way in the catalysts studied. As seen, there is no correlation between the intensity of the line with the chemical shift of −540 ppm and the portion of vanadium blocked. This serves as evidence that the vanadium in the blocked active component and vanadium forming surface compounds with silica are not identical. The reaction rate constants given in Table 2 refer only to catalytically active unblocked vanadium (k_V).

Comparison of these rate constants reveals that in series I, obtained by sintering and containing 7.7–9% V_2O_5, the catalytic activity is practically independent of the specific surface area of the support. The content of tetrahedrally coordinated vanadium is also small, as evidenced from the ^{51}V NMR spectra (Fig. 4-I). Series II, prepared by mixing, is characterized by some increase of activity. Since for this series the line at the chemical shift of −540 ppm is not intense we ascribe the rise of activity to the peculiarities of the method of catalyst preparation. The ^{51}V NMR spectra show that the preparation by mixing has achieved a more uniform distribution of the melt on the surface. Further on we shall compare the activities of catalysts prepared by mixing. Another peculiarity of series II is some decrease of activity with increase of silica specific surface up to 300 m^2/g. This corresponds to the increase in intensity of the line with the chemical shift of −540 ppm in the ^{51}V NMR spectra. The NMR data show that the line with the chemical shift of −540 ppm increases its intensity with decreasing the total amount of vanadium and with increasing the support specific surface. According to Table 2, both factors lead to decrease of activity. For series III samples (with a rather pronounced line from surface-bound vanadium) lines from vanadium were separated into those in octahedral and tetrahedral environment (Fig. 4-III). As found, in catalysts based on silica with S_{sp} = 55 m^2/g the amount of tetrahedrally coor-

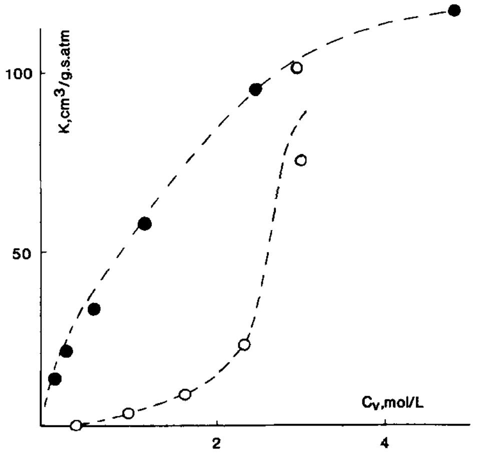

FIG. 5. Catalytic activity of V_2O_5–$K_2S_2O_7$ melts versus vanadium concentration. (○) Present data for melts supported on Pyrex glass tubes; (●) literature data (*18*) for melts supported on silica surface with S_{sp} = 200 m^2/g (reaction rate constant was measured in both cases using the Boreskov–Ivanov equation (*10*) at 500°C).

dinated vanadium is about 0.3% and grows to 1.1% at S_{sp} = 300 m^2/g. Such amounts appear to slightly affect the activity of highly concentrated samples (7–9%). However, for less concentrated samples (series III and IV particularly), increase of the relative portion of surface vanadium compounds involves considerable drop of activity. For example, at a vanadium content of 1.9% V_2O_5, the reaction rate constant decreases by almost one order of magnitude. This indicates that surface vanadium compounds are not more active than the main part of the active component, as was previously assumed (*7–9*), but they appear to be inactive or less active in SO_2 oxidation. However, it has been shown (*8, 18*) that the activity of catalysts based on silica is higher than that of samples on other supports. These data seem to contradict the low activity of surface vanadium compounds. Therefore, to clear up this problem we measured the catalytic activity of melts supported on Pyrex glass tubes (the effect of the very low Pyrex surface area on the active component may be ignored) and compared it with the activity of the same melts on SiO_2 (*18*). The measurements of catalytic activity are shown in Fig. 5. In both cases the activity per gram of vanadium increases with increasing content of vanadium (Fig. 5). This provides the conclusion that the dimeric and polymeric vanadium complexes are the most active in SO_2 oxidation. It is worth emphasizing that the dependence on vanadium content in the melt is of a different character. For silica the activity is always higher compared with other supports and is described by a second order equation with respect to vanadium, whereas for the melt it is very low at low concentrations of vanadium and rises considerably with increase of the latter.

The high activity of the melt on SiO_2 seems to contradict the conclusion about low activity of surface complexes. However, one will give up this idea when assuming that vanadium compounds, being not active themselves, interact with inactive monomer vanadium complexes in the melt to form active (associated) complexes. This interaction involves a change in coordination of tetrahedral surface vanadium turning it into octahedral coordination. The capability of tetrahedral vanadium to rearrange its coordination sphere with H_2O and SO_2 to an octahedral one for tetravalent (*19*) and for pentavalent vanadium is well known (*5*). This is also evidenced by the increased activity of series IV samples compared to melts of the same composition (Table 2). Thus, samples with the ratio K/V = 14 are highly active, whereas melts are practically inactive at the same ratios. At the same time, the spectra of these samples reveal that for the sample with K/V = 14 surface vanadium changes its tetrahedral coordination to an octahedral one. Based on the results reported, we propose the following scheme illustrating the influence of the interaction of vanadium with SiO_2 on the catalytic properties:

monomeric octahedral vanadium in the melt —(inactive)(I)	$\rightleftarrows$	dimeric or polymeric vanadium in the melt —(active)(II)

$$\begin{array}{ccc} \text{surface vanadium} & & \text{complexes between} \\ \text{in tetrahedral environment} & \rightarrow & \text{I and III} \\ \text{—(inactive)(III)} & & \text{—(active)} \end{array}$$

Vanadium forms on the SiO_2 surface tetrahedral compounds that are inactive or have low activity in catalytic reactions. Nevertheless, these compounds form the much more active associated complexes, thereby giving rise to an increase of the overall activity of catalysts compared to melts without SiO_2.

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