An ESR Investigation of the Vanadium Pentoxide-Water System Illuminated in the Solar Spectrum Range

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Photoreduction of vanadium (V) ions in aqueous solution is followed by ESR observation of the VO^{2+}_{aq} ions formed. In addition shortlived surface centers are detected at room temperature in illuminated V_2O_5-samples being suspended in water. These centers are tentatively related to the active species in the photoassisted electrolysis of water.

Vanadium (V) oxide glasses, as well as some other semiconducting oxides e.g. ZnO, WO_3, SnO_2, TiO_2 are known to show an anodic photoeffect and are active in the process of the photodecomposition of water upon illumination[1–5]. Different mechanisms for this process were proposed. It is generally agreed that the formation of holes in the valence band of the semiconductor by absorption of light quanta is a controlling factor in the photoassisted electrolysis. Very little spectroscopic information is available on the nature and the chemical behaviour of these photoproduced states which act as reaction centres. The ESR method is hoped to be helpful in providing new insight into these questions as, under suitable conditions, the observation of the paramagnetic species formed upon illumination of the oxides is to be expected. The detection of photoinduced ESR signals in aqueous suspensions of zinc oxide by Cunningham and Corkery[6] seems to be especially interesting. Information concerning the reactions occuring on the solid oxide/electrolyte interface can be obtained this way. In the present contribution the vanadium pentoxide-water system is investigated.

Experimental

Polycrystalline V_2O_5 (Merck, pure) was used for the preparation of the suspensions in neutral buffered and unbuffered distilled water, as well as in 0.01 N HCl and in 0.001 N NaOH respectively. The suspensions were introduced into quartz flat cells of inner dimensions 8 mm × 0.6 mm and placed in a H_{102} resonance cavity of the ESR spectrometer. Illumination of the samples was performed in situ by using of a 500 W xenon lamp. The spectra were recorded at room temperature with an E-12 Varian spectrometer operating in the X-band.

Results and Discussion

1. Initial (dark) Spectrum

Two different signals appear in the ESR spectrum of the unilluminated aqueous V_2O_5 suspensions:

1. a broad line with the g-factor equal to 1.96 and a peak to peak line width ΔH_{pp} of about 70 G (Figure 1 a);
2. a signal with the same g-factor, showing an hyperfine structure composed of eight lines with $\Delta H_{pp} = 10$ G each (Figure 1 b).
   The spectrum shown in Fig. 1 b was observed in the filtrate of the unilluminated suspension.

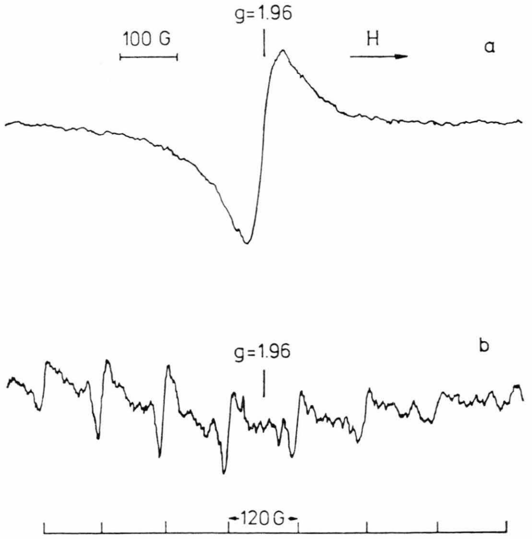

Fig. 1. Dark spectrum of V_2O_5-sample. (a) Spectrum of concentrated V_2O_5 suspension in distilled water; (b) Spectrum of the filtrate obtained from V_2O_5 suspension in 0.01 N HCl.

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The broad signal appears in the ESR spectra of all suspensions regardless of the pH value and does not appear in their filtrates. The intensity of the signal rises with the amount of V_2O_5 present in the suspension. It is the only signal in concentrated suspensions. In diluted suspensions it appears as a background spectrum for the 8-line signal. The parameters of the broad line i.e. its width and g-factor are close to those reported for the V^{4+} ions in the nonstoichiometric V_2O_5 lattice[7].

The hyperfine structure in the spectrum of unilluminated samples is best observed after separating the solution from the solid V_2O_5. The intensity of the 8-line signal is strongly influenced by the pH-value. A signal of very low intensity appears when the suspension was prepared with distilled water. In the acidic medium a stronger spectrum was obtained. The 8-line spectrum was not observed in the basic filtrate.

The shape of the 8-line signal is very similar to that of the VO^{2+} ions spectrum reported by Goodman and Raynor[8]. The change in signal intensity with pH is also in agreement with the interpretation of this signal as corresponding to vanadium (IV) in aqueous solutions of $pH < 7$.

2. Influence of Illumination

The influence of illumination on the ESR spectrum of V_2O_5 suspensions in 0.01 N HCl is shown in Figure 2. A distinct increase in the 8-line signal intensity is observed after exposure of the suspension to xenon lamp irradiation. A small decrease in signal intensity is observed 20 min after ceasing of the illumination. A similar result was obtained in the case of unbuffered V_2O_5 suspensions in water and in the filtrates of both acidic and unbuffered neutral suspensions. Changes in signal intensity as function of irradiation time in different media are summarized in Figure 3. The ESR absorption rises faster in the acidic medium than in the unbuffered suspensions of pH close to 7. In the buffered neutral suspensions the initial intensity of the 8-line signal is negligible and no change in the ESR spectrum is observed during the 60 min illumination.

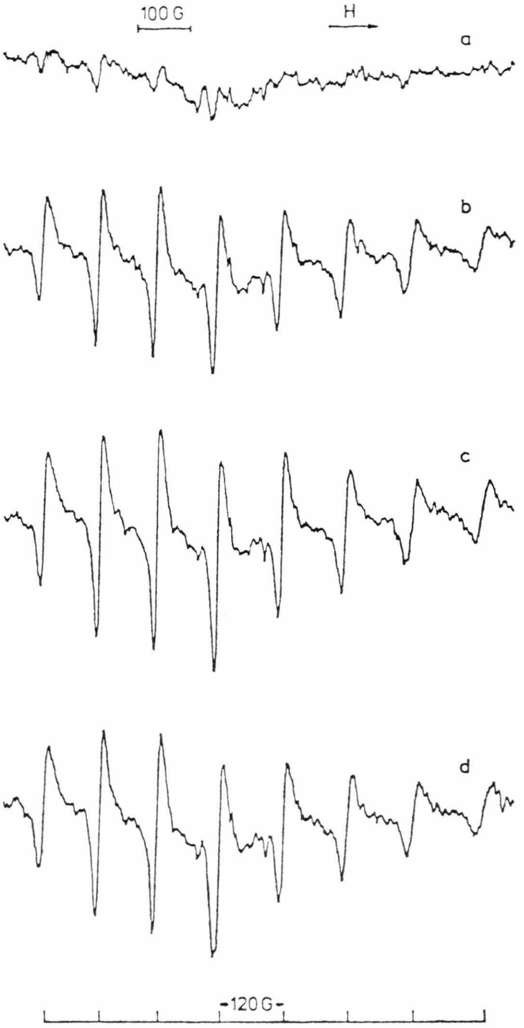

Fig. 2. Influence of illumination on ESR spectrum of V_2O_5 suspension in 0.01 N HCl. (a) before illumination, (b) after 20 min of illumination, (c) after 35 min of illumination, (d) 20 min after ceasing of illumination.

The increase in the 8-line signal intensity indicates, that under the influence of illumination a photoreduction of vanadium (V) takes place leading to a rise in VO^{2+} concentration. The rate of this reaction is strongly influenced by the change in the H^+ ion concentration. The following overall reaction of the photoprocess is proposed:

$$VO^{+}_{2\,\mathrm{aq}} + H^{+} \xrightarrow{h\nu} VO^{2+}_{\mathrm{aq}} + OH^{\cdot} . \qquad (1)$$

The reduction of vanadium (V) is thus accompanied by the formation of $OH^{\cdot}$ radicals which are usually considered as an anodic intermediate in the electrochemical water decomposition.

The radiation chemical and photochemical properties of vanadium (V) compounds in aqueous solutions have been investigated previously by several authors. Investigations on the reduction of VO_2^+

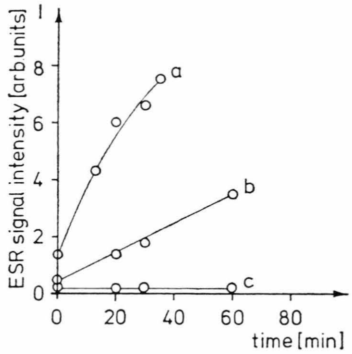

Fig. 3. Dependence of the 8-line signal intensity in V_2O_5 suspensions on the time of illumination. (a) V_2O_5 suspension in 0.01 N HCl, (b) V_2O_5 suspension in unbuffered water, (c) V_2O_5 suspension in buffered water.

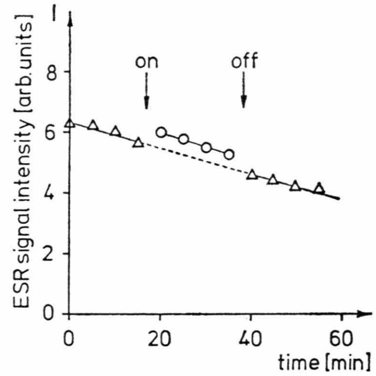

Fig. 4. Influence of illumination on the intensity of the ESR signal attributed to V^{4+} ions in V_2O_5 particles suspended in 0.001 N NaOH.

ions under the influence of γ- and α-irradiation are quoted by Kaindl and Graul [9]. The oxidation of organic compounds in aqueous solutions upon illumination with visible light with the simultaneous reduction of vanadium (V) occurs according to Panwar and Gaur [10]. The photoreduction in the solid phase upon sunlight irradiation was observed in the case of piperidine metavanadate by Baudisch and Gates [11].

To decide whether in the case of the vanadium pentoxide-water system the process of photoreduction is limited to the aqueous solutions, or whether it also occurs in the solid phase, i.e. on the surface of the suspended V_2O_5 crystallites, experiments were performed with dense V_2O_5 suspensions in basic solution. In this case the ESR spectrum consists exclusively of the strong broad signal arrising from vanadium (IV) ions in the bulk and on the surface respectively. It is not overlapped by any signal of vanadium (IV) ions present in the solution.

All experiments in the dense suspensions were hampered by the fact, that changes in signal intensity due to illumination of the probe were superimposed by changes due to sedimentation of V_2O_5 particles during the experiment. As shown in Fig. 4 the latter effect can be taken into account in repetitive experiments with and without illumination. The resulting slope is related to sedimentation of the suspensed particles. As shown in Fig. 4 illumination of the dense V_2O_5 suspensions in 0.001 N NaOH leads to an increase of the broad signal intensity thus indicating, that the photoreduction of vanadium takes place also in the solid phase.

It is assumed that this process is accompanied by the formation of positive holes according to

$$V^{5+}_{(s)} \rightarrow V^{4+}_{(s)} + h^{\cdot} . \qquad (2)$$

The positive holes may then be stabilized on the surface or in the bulk of the crystal lattice in the presence of water. The $V^{4+}_{(s)}$ ions created in process (2) disappear with $\tau_{1/2} < 1$ sec upon shutting off the light source. Apparently the recombination of the positive holes or hole defects with $V^{4+}_{(s)}$ ions is not a fast process under the given conditions.

The process of recombination is more rapid in the absence of water. In "dry" V_2O_5 no change in the $V^{4+}_{(s)}$ ion signal intensity is observed upon illumination at room temperature. It might be argued that the OH^- ions present in water compete with $V^{4+}_{(s)}$ ions as traps for the positive holes thus stabilizing the observed paramagnetic centres.

A number of runs was performed to check whether the signal increase upon illumination can be accounted for, qualitatively at least, on the basis of light intensity available in the experiments. The photoproduced contribution to the ESR absorption is equivalent to roughly 10^{13} spins in the sample as measured against a $CuSO_4$ standard. The lamp output was calibrated using different actinometers [12]. With light being absorbed by the sample at a rate of $\sim 10^{14}$ quanta per sec the observed increase in ESR absorption appears to be reasonable.

The ESR data reported here indicate that upon illumination of V_2O_5 being in contact with an electrolyte two processes are to be expected: reaction at the V_2O_5/electrolyte interface and photoreduction in solution. Provided the solubility of vanadium pentoxide in aqueous electrolytes could be effectively reduced, V_2O_5 might be an attractive anode material for the photoassisted electrolysis of water.

Note added in the proof: Determinations of the weight losses of irradiated V_2O_5 electrodes under anodic bias indicate that under our experimental conditions roughly 10% of the current observed was due to slow dark reactions at the electrolyte-V_2O_5 interface.

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