Redox transformations of vanadium species at the rutile surface

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Redox transformations of vanadium species, deposited on the surface of a rutile monocrystal by annealing rutile with V_2O_5 were investigated by cyclic voltammetry. Two different vanadium species were observed at the surface: first, present in the crystal lattice of rutile, which undergoes the redox transformation V^{4+}/V^{3+} only, and the second, present at the surface, which undergoes both the V^{5+}/V^{4+} and V^{4+}/V^{3+} redox transformations. The latter appears only when the subsurface layer becomes saturated with the former.

Keywords: vanadium oxide/rutile catalyst; monolayers of vanadium species; redox transformations of vanadium species; voltammetry of vanadium species

1. Introduction

Most of the published papers concerning titania supported vanadium oxide catalysts treat the structural properties of the vanadium species present at the surface [1–4]. Much less attention was paid to the redox properties of the system [5,6], although they may play a decisive role in determining the catalytic properties. Electrochemistry offers great possibilities of studying the redox behavior of surface species. So, we have undertaken the electrochemical investigations of the redox reactions of vanadium species present at the ⟨110⟩ crystal plane of rutile.

2. Experimental

The synthetic rutile monocrystal was obtained by the Vernouil method [7] from high purity TiO_2. It was next X-ray oriented and cut to expose the ⟨110⟩ surface. To increase the conductivity the crystal was reduced by heating in hydrogen for 3 h at the temperature of 1000 K. The concentration of free charge carriers in such prepared rutile crystal was estimated, from the slope of the Mott–Schottky plot [8], to be $\sim 8 \times 10^{24}$ m^{-3}. Assuming that each oxygen vacancy introduces two free charge carriers (electrons) one may estimate the deviation from stoichiometry (oxygen deficit) to be of the order of 0.01 at%, which is well below the nonstoichiometry range in rutile [9]. Taking into account the uniform distribution of vacancies in the lattice, their concentration at the surface was negligible in comparison with the surface concentration of vanadium, which was of the order of one monolayer, and could not influence the process of incorporation of vanadium atoms into the lattice. Before the experiments the surface was polished on 1 μm diamond paste and washed carefully with water, acetone and ethyl alcohol.

Vanadium pentoxide was obtained by thermal decomposition of ammonium metavanadate or by precipitation from aqueous solution. The latter method consisted of dissolving ammonium metavanadate in 0.1 mol/dm^3 NaOH solution and precipitation of hydrated vanadium pentoxide by acidifying with sulfuric acid to pH of 3. The fine orange precipitate was washed three times with water and decanted.

The surface of the rutile monocrystal was covered by a suspension of V_2O_5 in water and after evaporation of water the crystal was annealed during 1 h in air at a temperature of 750 K, to form vanadium oxide monolayer by thermal spreading [10,11]. After cooling V_2O_5 was removed from the surface by polishing on filter paper and the crystal was next washed during 1 h in 0.5 mol/dm^3 H_2SO_4 to remove the weakly bound vanadium species.

The electrochemical measurements were conducted using the digital potentiostat ECI 1286 (Schlumberger-Solartron) and the one-compartment cell similar to that usually used in electrochemical measurements on semiconductor electrodes [8]. A saturated calomel electrode (SCE) was used as a reference electrode: all potentials are given versus that electrode. All measurements were performed in the dark, in a constant temperature (25°C) box, which served at the same time as a Faraday cage. In the electrochemical measurements a Na_2SO_4 solution (0.5 mol/dm^3) of $pH = 4.0 \pm 0.1$ was used. Doubly distilled water and analytical grade reagents were used to prepare the solutions. Oxygen was removed from the solution by passing high purity argon (below 1 ppm of O_2) through it.

3. Results and discussion

For a semiconductor electrode the exchange of electrons between the electrode and a redox couple in solution is possible only if the redox potential of this couple is located at a favorable position versus the band edges [8]. The standard electrode potential for the redox couple V^{5+}/V^{4+} at pH of 3–3.5 is +0.48 V versus SCE and the corresponding value for the V^{4+}/V^{3+} couple is +0.24 V [12]. In real systems, due to the solvation and differences in activity coefficients, the measured potentials may differ significantly from calculated ones. From the data of Filipovic et al. [13] the potential of 0.29 V may be estimated for the redox couple V^{5+}/V^{4+} at pH 4. Ducret [14] measured in equimolar solution of pentavalent and tetravalent vanadium at pH 4 the redox potential of 0.13 V. In line with these values we have measured in the equimolar solution of ammonium metavanadate and vanadyl sulfate (concentration 5×10^{-3} mol/dm^3, pH = 4) the redox potential of 0.229 V. The cyclic voltammetry curve, performed on an Au electrode in this solution is shown in fig. 1. A pair of peaks A2/C2 is observed with the anodic peak at ~ 24 V and cathodic one at −0.10 V. Thus, assuming that these peaks represent the redox couple V^{5+}/V^{4+}, the mid-peak position at 0.07 V is significantly shifted in the cathodic direction in comparison with the measured rest-potential of 0.229 V in that solution; however, the overpotential for the cathodic and anodic processes may differ significantly. Note, that the separation of the anodic and cathodic peaks was 0.34 V, which should be compared with the 0.06 V expected for a one-electron reversible process. Another pair of peaks (A1/C1), much less distinctive, with the mid-peak position at −0.14 V was also visible. It might be ascribed to the redox couple V^{4+}/V^{3+}.

The system behaves in a different way when rutile is used as the electrode. Fig. 2 shows the cyclic voltammetry curve for a rutile electrode in 5×10^{-2} mol/dm^3 NH_4VO_3 solution. It may be seen, that no current flowed in the anodic part of the sweep, despite the fact that a significant concentration of vanadium in the lower oxidation state must have been accumulated during the preceding cathodic sweep. Note also that the cathodic process required a much higher overpotential than in the case of the gold electrode. The described behavior is consistent with the theory of electrode processes on semiconductor electrodes: the redox potential V^{5+}/V^{4+} of 0.229 V is situated in the region of the band gap of rutile, about 0.6 V below the conduction band edge [8], thus no oxidation reaction is possible for this system on the rutile electrode. The absence of V^{4+} oxidation was confirmed in a similar experiment in which a solution of V^{4+} ions ($VOSO_4$) was used.

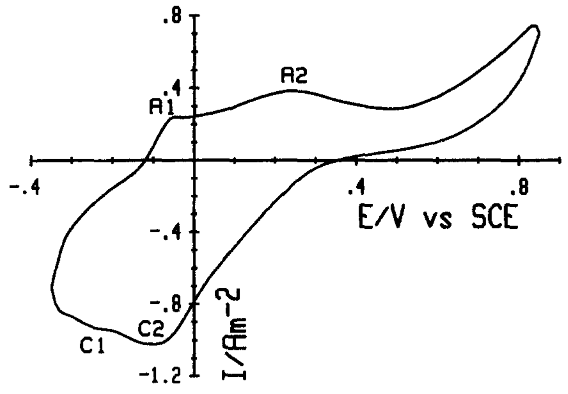

Fig. 1. Cyclic voltammetry curve on an Au electrode in equimolar (0.005 mol/dm^3, pH = 4) solution of NH_4VO_3 and $VOSO_4$ containing 0.5 mol/dm^3 Na_2SO_4 as a base electrolyte. Potential sweep rate 50 mV/s.

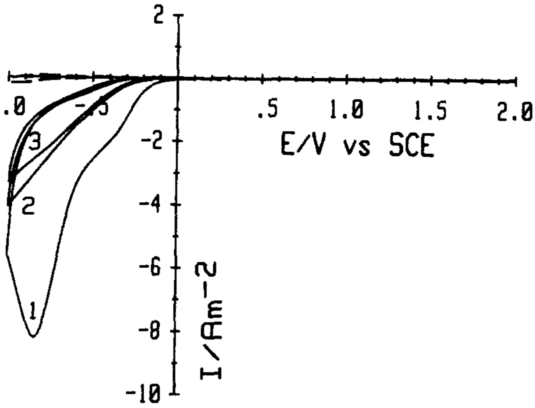

Fig. 2. Cyclic voltammetry curve on the rutile electrode in 0.05 mol/dm^3 solution NH_4VO_3 (pH = 4) containing 0.5 mol/dm^3 Na_2SO_4 as a base electrolyte. Potential sweep rate 20 mV/s.

Fig. 3 shows the cyclic voltammetry curve in 0.5 mol/dm^3 Na_2SO_4 (pH = 4) solution for a rutile electrode annealed with V_2O_5. Two redox systems (A1/C1 and A2/C2) are clearly visible, with the mid-peak positions at −0.155 and +0.150 V, respectively. The system A2/C2 may be identified as the redox couple V^{5+}/V^{4+} and the system A1/C1 as the redox couple V^{4+}/V^{3+}. The difference between the mid-peak positions for these two processes is ~ 0.305 V, which may be compared with

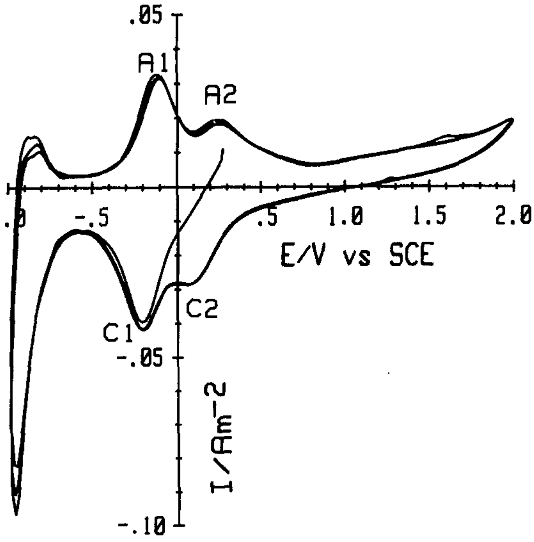

Fig. 3. First three voltammetric cycles on the rutile electrode annealed with V_2O_5 (obtained by thermal decomposition of ammonium metavanadate) in 0.5 mol/dm^3 Na_2SO_4 (pH = 4) solution.

the difference of 0.24 V between the standard redox potentials for the redox systems V^{5+}/V^{4+} and V^{4+}/V^{3+} in aqueous solution. Comparison of figs. 2 and 3 shows that the behavior of the pure rutile electrode and the electrode with deposited vanadium differ dramatically. Electron exchange processes which are difficult or impossible between vanadium ions in solution and pure rutile electrode become fast when vanadium ions are deposited at the surface of rutile. Both redox systems (V^{5+}/V^{4+} and V^{4+}/V^{3+}) seem to behave much more reversible on rutile electrode than on the gold electrode (compare figs. 1 and 3)! It is well known from the literature (see refs. [1,15] and references cited therein) that VO_2, being isostructural with rutile, forms with rutile solid solutions of infinite solubility and rutile structure. So, the only possible explanation for the observed behavior is that vanadium ions have diffused into the crystal lattice of rutile, in the form of tetravalent vanadium, creating a new energy band in the band gap of rutile [15]. This was confirmed in the following experiment. The crystal used in the experiment of fig. 3 was boiled 1 h in 0.5 mol/dm^3 H_2SO_4 and the voltammetric curve performed (fig. 4). It can be seen, that the pair of peaks A2/C2 is no longer visible on the voltammogram, and the total amount of vanadium was significantly lowered. As rutile dissolves to some extent in boiling H_2SO_4, so vanadium left after such treatment must have evidently been present in the crystal lattice of the rutile, below the surface. Thus, the dissolved part of vanadium was present at the surface in the form of monolayer species. The vanadium ions present in the crystal lattice of rutile may be reduced to

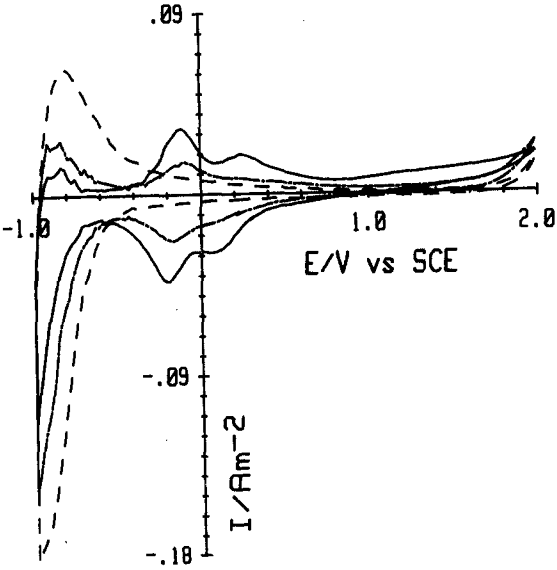

Fig. 4. Cyclic voltammetry curve in 0.5 mol/dm^3 Na_2SO_4 (pH = 4) solution for: pure rutile electrode (dashed line), electrode annealed with V_2O_5 (full line) and the same electrode boiled 1 h in 0.5 mol/dm^3 H_2SO_4 (dotted line).

the 3+ and oxidized to the 4+ oxidation state, but not to the 5+ oxidation state. The overlaying vanadium species undergo both the V^{5+}/V^{4+} and V^{4+}/V^{3+} redox transformation. The quantity of vanadium present in the crystal lattice as tetravalent vanadium was estimated from the charge of the voltammetric peaks to be of the order of half of a monolayer. Polishing of the surface removed vanadium completely, which means that vanadium was placed just below the surface (but not in the outermost layers, as the experiments with boiling H_2SO_4 showed).

Vanadium pentoxide obtained by thermal decomposition of ammonium metavanadate may contain tetravalent vanadium. So, a similar experiment was performed with V_2O_5 obtained by precipitation from aqueous solution. The results were similar, but the shape of the voltammogram suggested that less vanadium diffused into the crystal lattice of rutile.

4. Conclusions

The system V_2O_5/rutile, extensively discussed in the literature, is in fact composed of vanadium oxide supported on the solid solution of V^{4+} ions in rutile. The presence of vanadium in the crystal lattice of rutile changes its band structure, creating a new energy band within the band gap. This band mediates in the electron exchange reactions between rutile and the redox systems at the surface. Similar effects may be expected in the case of heterogeneous catalytic reactions, when the exchange of electrons between the crystal lattice of the catalyst and the surface species is one of the rate determining steps. In such conditions the formation of electrophilic oxygen species at the surface will be enhanced and total oxidation will be favored, resulting in the decrease of selectivity to partial oxidation products. This could explain the inferior catalytic properties observed in the case of rutile-supported vanadium oxide catalyst as compared to anatase. On the other hand, it has been shown that at submonolayer coverage with vanadium, when vanadium atoms are held at the surface of rutile and the solid solution is not formed, both V_2O_5/rutile and V_2O_5/anatase catalyst show the same catalytic properties [16].

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