

Infrared spectra of platinum-impregnated V_2O_5 powders on hydrogen insertion

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Abstract

Infrared spectra were measured in the wavenumber range $400\text{--}4000\text{ cm}^{-1}$ during the heating of platinum-impregnated V_2O_5 powders from room temperature to 250°C in hydrogen gas (0.58 MPa) or on $H_xV_2O_5$ ($x=0\text{--}3.27$) by a Fourier transform IR diffuse reflectance spectrometer. It is found that the O–H stretching vibration mode at 3372 cm^{-1} becomes enlarged as the temperature or hydrogen concentration is increased, whereas the V–O stretching vibration modes tend to disappear, and that a new IR band assigned to the O–H bending mode appears at 920 cm^{-1} ; no clear evidence for the existence of V–H hydride bonds is detected.

These spectral changes suggest a hydrogen-induced amorphization through bond rearrangements. In fact, the Bragg reflection lines due to V_2O_5 tend to be invisible with increasing amount of absorbed hydrogen. The hydrogen-induced amorphization in V_2O_5 is discussed in some detail in the light of information about the structural changes in V_2O_5 on hydrogen insertion and after heat treatment.

1. Introduction

Vanadium pentoxide, V_2O_5 , is a semiconducting material with a band gap of 2.75 eV [1]. The hydrogen spill-over technique [2] allows the insertion of varying amounts of hydrogen in platinum-impregnated V_2O_5 , resulting in vanadium hydrogen bronzes, $H_xV_2O_5$, with a maximum hydrogen concentration $x=3.8$. Structural studies of vanadium hydrogen bronzes have been done [3–6] and their physical and chemical properties have also been measured [3, 7, 8].

Our main concern lies in the fact that at higher hydrogen contents a high degree of structural rearrangement of V_2O_5 occurs, resulting in an amorphous product, $H_xV_2O_5$ ($x>3.0$), as confirmed by both X-ray and neutron diffraction studies [9]. It is considered that the bonding between anions as well as cations and inserted hydrogen is responsible for this hydrogen-induced amorphization in V_2O_5 .

The protons could be located between layers comprising stacks of VO_6 octahedra in V_2O_5 and could be bonded to oxygen in the form of OH or OH_2 groups. In fact IR absorption spectra of $H_{0.33}V_2O_5$ and $D_{0.29}V_2O_5$ [5] exhibit the O–H (D) stretching vibration mode at 3000 cm^{-1} (2500 cm^{-1})

and the O–H (D) bending vibration mode at 925 cm^{-1} (650 cm^{-1}), while the vanadyl stretching vibration modes remain sharp and intense (unchanged); on the other hand, nuclear magnetic resonance (NMR) studies support the existence of V–H hydride bonds with a bond length of about 2 \AA in $\text{H}_x\text{V}_2\text{O}_5$ ($x \geq 3.0$) [3].

To our knowledge, however, no IR spectra have been measured on $\text{H}_x\text{V}_2\text{O}_5$ with x varied systematically. The objective of the present work is to measure the IR spectra of $\text{H}_x\text{V}_2\text{O}_5$ with different values of x in order to get a better understanding of the hydrogen-induced amorphization in V_2O_5 in the light of information about the structural changes in V_2O_5 on hydrogen insertion and after heat treatment.

2. Experimental details

Vanadium hydrogen bronzes, $\text{H}_x\text{V}_2\text{O}_5$, were prepared by the reaction of platinum-impregnated V_2O_5 powders with hydrogen using the so-called hydrogen spill-over technique [2]. The powders of V_2O_5 (about 200 mesh, 99.5% purity) were impregnated with a solution of H_2PtCl_6 so that the surface of the V_2O_5 was catalysed with platinum (4 wt.%). The platinum-impregnated V_2O_5 powders were degassed at $100\text{ }^\circ\text{C}$ for 1 h, then $200\text{ }^\circ\text{C}$ for 30 min and cooled to room temperature, subsequent hydrogenation was performed at $70\text{ }^\circ\text{C}$. The amount of absorbed hydrogen in the platinum-impregnated V_2O_5 powders was controlled by pressure or time and estimated by the pressure drop in the constant-volume system. IR spectra of $\text{H}_x\text{V}_2\text{O}_5$ were measured by a Fourier transform IR (FT-IR) diffuse reflectance spectrometer (JEOL 100) with a resolution of 4 cm^{-1} using a detector of triglycine sulphate (TGS) and KBr as reference; IR spectra were also measured *in situ* during heating of the sample under a hydrogen atmosphere using a micro-reactor attached to the spectrometer.

After hydrogen insertion and/or heat treatment the samples were subjected to X-ray diffractometry, IR spectroscopy and differential scanning calorimetry.

3. Results

Figure 1 shows IR spectra (transmittance) of the platinum-impregnated V_2O_5 powders obtained as the temperature was raised under a hydrogen atmosphere ($P_{\text{H}_2} = 0.58\text{ MPa}$). The following points should be noted: the O–H stretching vibration mode at about 3400 cm^{-1} becomes enlarged with increasing temperature whereas the V–O stretching vibration modes at 1015 and 825 cm^{-1} tend to disappear; a new band assigned to the O–H bending mode [5] appears at 920 cm^{-1} , as indicated by an arrow at 220 and $240\text{ }^\circ\text{C}$, but no clear existence of the V–H stretching vibration modes is confirmed between 1060 and 1200 cm^{-1} , in disagreement with ref. 3. The H–O–H deformation vibration mode at 1612 cm^{-1} also becomes enlarged as the

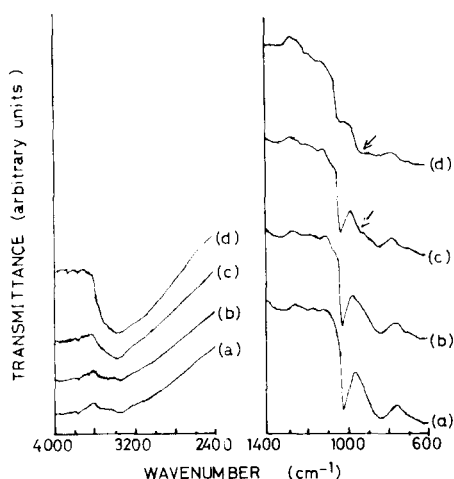


Fig. 1. IR spectra (transmittance) of platinum-impregnated V_2O_5 powders as the temperature was raised under a hydrogen atmosphere ($P_{H_2}=0.58$ MPa): (a) 180, (b) 200, (c) 220 and (d) 240 °C. KBr powders at each temperature were used as reference to obtain these IR spectra.

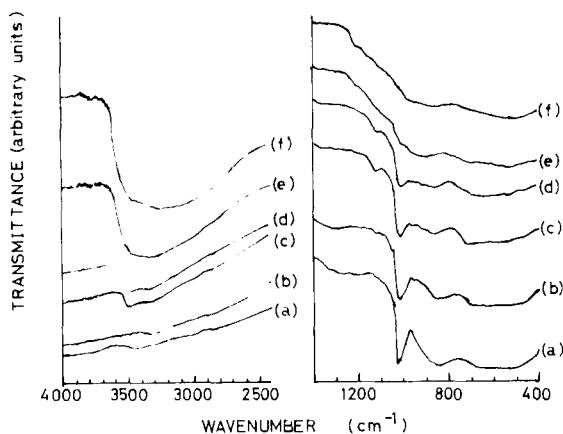


Fig. 2. IR spectra (transmittance) of $H_xV_2O_5$ with definite values of x at room temperature: $x =$ (a) 0, (b) 0.49, (c) 1.03, (d) 1.66, (e) 1.99 and (f) 3.27.

temperature is increased. It can be accepted as being beyond doubt that these spectral changes are associated with an increase in the amount of absorbed hydrogen in V_2O_5 .

IR spectra of $H_xV_2O_5$ with definite values of x were measured at room temperature and are shown in Fig. 2 along with the IR spectra of the platinum-impregnated V_2O_5 powders. The same features as those observed in Fig. 1 are seen, but more prominently, *i.e.* enlargement of the O–H stretching vibration mode at about 3400 cm^{-1} and progressive invisibility of the V–O stretching vibration modes, as if the specimen became glassy as the amount of absorbed hydrogen increased. The O–H bending mode is also observed

at about 920 cm^{-1} , but we find it difficult to assign the small hollow at 1120 cm^{-1} in the spectra of $\text{H}_x\text{V}_2\text{O}_5$ with $x=0.49$, 1.03 and 1.66 to the V-H stretching vibration mode.

X-ray diffraction (XRD) patterns of $\text{H}_x\text{V}_2\text{O}_5$ with different values x and of the platinum-impregnated V_2O_5 powders are presented in Fig. 3. It is evident that the Bragg reflection lines due to V_2O_5 tend to disappear as the amount of absorbed hydrogen is increased and that the XRD pattern becomes almost featureless for $\text{H}_x\text{V}_2\text{O}_5$ with $x=3.27$.

Interplanar spacings and scattering angles of V_2O_5 are in good agreement with those in the ASTM file 9-387 with the lattice parameters $a=11.549\text{ \AA}$, $b=3.569\text{ \AA}$ and $c=4.388\text{ \AA}$. Inserting a small amount of hydrogen contracts rather than expands the lattice of V_2O_5 , which then tends to revert; the lattice parameters of $\text{H}_x\text{V}_2\text{O}_5$ with $x=0.49$ and 1.03 are determined to be $a=11.492\text{ \AA}$, $b=3.559\text{ \AA}$, $c=4.358\text{ \AA}$ and $a=11.550\text{ \AA}$, $b=3.565\text{ \AA}$, $c=4.374\text{ \AA}$ respectively.

In order to find a crystallization peak for the hydrogen-induced glassy sample, differential scanning calorimetry (DSC) was performed. Figure 4 shows the DSC curve for $\text{H}_{3.02}\text{V}_2\text{O}_5$ heated at $10^\circ\text{C min}^{-1}$ in helium ($P_{\text{He}}=0.098\text{ MPa}$). A broad endothermic peak is observed over a temperature range from 50 to 350°C . However, no crystallization peak was observed up to 550°C . This is at variance with the hydrogen-induced amorphization in GdM_2 ($\text{M}\equiv\text{Fe}$, Co , Ni , etc.), where thermoanalysis exhibits a clear crystallization peak(s) after a broad endothermic peak due to partial hydrogen desorption [10, 11].

It should be noted that no appreciable increase in pressure could be detected while the $\text{H}_{3.02}\text{V}_2\text{O}_5$ was being heated to 400°C in the reactor. This is quite different from the situation for hydrogen storage alloys, in which hydrogen absorption-desorption processes are reversible and temperature control can easily produce some pressure decrease or increase in the closed system. Thus we find it difficult to ascribe the endothermic peak in Fig. 4 to hydrogen desorption from $\text{H}_{3.02}\text{V}_2\text{O}_5$. It seems that the mechanism for the

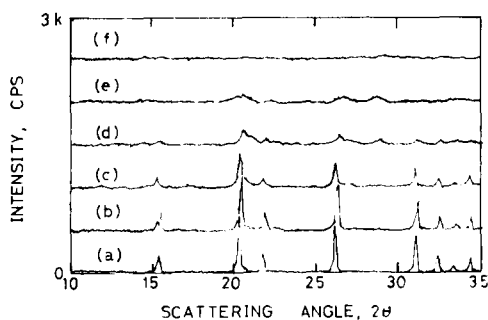


Fig. 3. XRD patterns of $\text{H}_x\text{V}_2\text{O}_5$ and platinum-impregnated V_2O_5 powders ($x=0$): $x=$ (a) 0, (b) 0.49, (c) 1.03, (d) 1.66, (e) 1.99 and (f) 3.27.

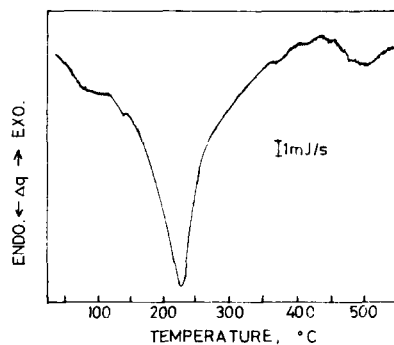


Fig. 4. DSC curve for $\text{H}_{3.02}\text{V}_2\text{O}_5$ (15 mg) heated at $10^\circ\text{C min}^{-1}$ in helium ($P_{\text{He}}=0.098\text{ MPa}$).

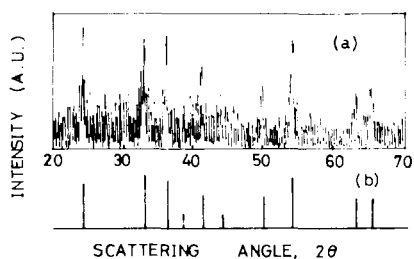


Fig. 5. XRD pattern of $H_{3.02}V_2O_5$ ($x=3.02$) heated under a hydrogen atmosphere ($P_{H_2}=0.027$ MPa) to 400 °C, kept there for 10 min and cooled to room temperature while dynamically pumped, compared with the ASTM file 34-187 (V_2O_3); note that the XRD pattern is expanded with respect to the y axis.

hydrogen-induced amorphization is somewhat different between V_2O_5 and GdM_2 ($M \equiv Fe, Co, Ni, \text{etc.}$). The XRD pattern of $H_{3.02}V_2O_5$ heated under a hydrogen atmosphere ($P_{H_2}=0.027$ MPa) to 400 °C, kept there for 10 min and cooled to room temperature while dynamically pumped is well matched with the ASTM file 34-187 (V_2O_3) as shown in Fig. 5 (note that the XRD pattern is expanded with respect to the y axis).

The XRD pattern of $H_{3.02}V_2O_5$ remains unchanged before and after the heat treatment, except that a few diffuse Bragg reflection lines increase in intensity to some extent. The good match of the XRD patterns as indicated in Fig. 5 suggests that the $H_{3.02}V_2O_5$ has the composition $V_2O_3 \cdot 2(H_{\sim 1.5}O)$ [12] and that the endothermic peak in Fig. 4 corresponds to hydrogen being removed as water vapour. As a matter of fact, the O–H stretching vibration mode at about 3400 cm^{-1} disappeared and the V–O stretching vibration modes increased somewhat in intensity after the heat treatment. However, no original vibration spectrum of V_2O_5 is returned, indicating that hydrogen insertion and its removal as water vapour in the platinum-impregnated V_2O_5 powders are an irreversible process.

4. Discussion

In view of the results obtained here, the hydrogen-induced amorphization in V_2O_5 seems to originate from inserted H atoms bonding with O atoms, resulting in some bond rearrangements [13]. The fact that there is no shift of the V–O stretching vibration modes, which become progressively invisible as the amount of absorbed hydrogen is increased, may be an indication of no excessive bond distortions as well as insignificant changes in V–O distances in the bond rearrangements. The introduction of disorder by this bond rearrangement progressively reduces the structure factor for V_2O_5 and the XRD pattern becomes featureless at a critical hydrogen concentration.

No significant fragmentation of the platinum-activated V_2O_5 powders took place on hydrogen insertion, so it is ruled out that the featureless XRD pattern of $H_xV_2O_5$ ($x \gg 3.0$) is due to a crystalline phase with very small

grain size. The hydrogen-induced amorphization in V_2O_5 seems to be essentially different from that in other materials such as GdM_2 , since no crystallization peak is observed in our thermal analysis with the hydrogen-induced glassy sample.

The hydrogen insertion also causes a change in the valence state of vanadium from V^{5+} in V_2O_5 to $V^{(5-x/2)+}$ in $H_xV_2O_5$ for O^{2-} . The vanadium in $H_xV_2O_5$ is in a state of mixed valence [3, 7]: V^{5+} , V^{4+} and V^{3+} for $1 < x < 2$ and V^{4+} and V^{3+} for $x > 3$. The disorder for amorphization is probably introduced when $x \geq 3.0$ or the valence state of vanadium is V^{3+} or V^{4+} .

Thus we are tempted to measure the core-level spectra of V 2p as well as O 1s for $H_xV_2O_5$, whose IR spectra and XRD patterns were measured, by X-ray photoemission spectroscopy (XPS). It is expected that the formation of O-H bonds causes a splitting in the O 1s line rather than the peak due to OH^- species on the higher binding energy side [3, 14]. We also expect that the V 2p line should exhibit components such as V^{3+} and V^{4+} in addition to V^{5+} . Such XPS studies on $H_xV_2O_5$ are in progress.

Acknowledgments

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