

Nitridation under ammonia of high surface area vanadium aerogels

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Abstract

Vanadium pentoxide gels have been obtained from decavanadic acid prepared by ion exchange on a resin from ammonium metavanadate solution. The progressive removal of water by solvent exchange in supercritical conditions led to the formation of high surface area $V_2O_5 \cdot 1.6H_2O$ aerogels. Heat treatment under ammonia has been performed on these aerogels in the 450–900 °C temperature range. The oxide precursors and oxynitrides have been characterized by XRD, SEM, TGA, BET. Nitridation leads to divided oxynitride powders in which the fibrous structure of the aerogel is maintained. The use of both very low heating rates and high surface area aerogel precursors allows a higher rate and a lower threshold of nitridation than those reported in previous works. By adjusting the nitridation temperature, it has been possible to prepare oxynitrides with various nitrogen enrichment and vanadium valency states. Whatever the V(O,N) composition, the oxidation of the oxynitrides in air starts between 250 and 300 °C. This determines their potential use as chemical gas sensors at a maximum working temperature of 250 °C.

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1. Introduction

V_2O_5 gels have been known for a long time and can be synthesized by different routes [1]. Among the latter, two types are usually described in the literature depending on whether the precursor is an aqueous solution of an inorganic salt or a metal organic compound. In our work, the inorganic route has been employed consisting in the direct formation of the gel from polyvanadic acid. The direct elimination of the water content of the gels by heating produces low surface area xerogel-type compounds. On the other hand, the progressive removal of water by solvent exchange can lead to the formation of aerogels with high surface areas, which are exploited for catalytic or sensor applications. Such a technique has been used in the present study intended for the preparation of high surface area nitridation precursors.

To our knowledge, the direct nitridation of vanadium aerogels by ammonia has not been reported so far. This process provides a low temperature route for the preparation of oxynitride compounds of which the properties, such as the conductivity, can be controlled as a function of their nitrogen content. For effective use as gas sensor, a substantial exposure of the sensing material to the reactive medium is required, and therefore, it is important to have high specific surface area.

Here we describe the preparation of aerogels via an aqueous route and their subsequent nitridation under ammonia. The oxide precursors and oxynitrides were characterized by XRD, SEM, TGA, BET.

2. Experimental

2.1. Preparation of the oxide precursors

A solution of vanadium V was prepared from dissolution of ammonium metavanadate NH_4VO_3

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(Fluka, 99.5%)(0.1 mol) in water (1000 cm³). Ammonium ions were eliminated by ion exchange using a column filled with a hydrogenated resin DOWEX-50W (Sigma). A yellow decacondensed vanadic acid solution is obtained which turns spontaneously to a gel mixture by addition of a small amount of water [2].

The dark red gel is concentrated by centrifugation and water is thus partially eliminated. The next step consists of replacing the water content by acetone. The wet gels were stirred vigorously in anhydrous acetone and washed several times to ensure complete replacement of water by acetone. The acetone-exchanged gels were then transferred to a Balzers supercritical Point Dryer apparatus for CO₂ exchange. Several purge-fill cycles are necessary to remove all the acetone from the gel. A green light powder was obtained after slow CO₂ evaporation.

2.2. Preparation of the oxynitrides

The vanadium oxide aerogels were treated under NH₃ (Air Liquide, ind.) flow at temperatures ranging from 450 to 900 °C. As previously described [3], the nitridation has been performed in a tubular furnace, controlled by a temperature programmer, using the licked bed technique with a typical ammonia flow of 40 L h⁻¹. Aerogel powders (~200 mg) were placed in an alumina boat and heated under ammonia flow from ambient to 300 °C at a 10 °C min⁻¹ heating rate and then at 1 °C min⁻¹ to the required nitridation temperature and maintained at this temperature for 12 h. Cooling was performed under N₂ (Air Liquide, 99.99%) flow.

2.3. Characterization

X-ray powder diffraction (XRD) data were collected on a Philips apparatus equipped with an Xpert goniometer using CuK α radiation (1.5418 Å). Powder morphology was examined by scanning electron microscopy (SEM) using direct and back-scattered electron techniques. Thermal analysis of powdered samples was carried out under ambient air using a TG-DTA 92 Setaram thermoanalyser. BET measurements were performed on a Micromeritics FlowSorb II 2300 apparatus using a 30% mixture of nitrogen in helium flowing gas. Nitrogen and oxygen contents were determined with an LECO TC-436 analyzer, respectively, as N₂ by thermal conductivity measurement and as CO₂ by infrared detection.

3. Results and discussion

3.1. Precursors

The vanadium oxide aerogel obtained is a hydrated phase of formula V₂O₅·*n*H₂O. TGA results (Fig. 1)

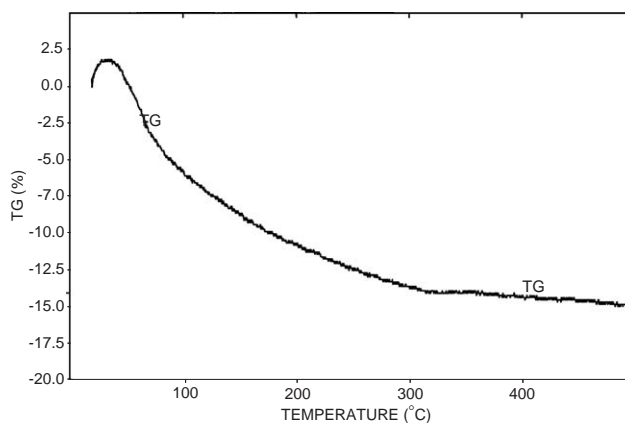


Fig. 1. Thermogravimetric analysis (2 °C min⁻¹) in air of the aerogel obtained by solvent exchange in supercritical conditions.

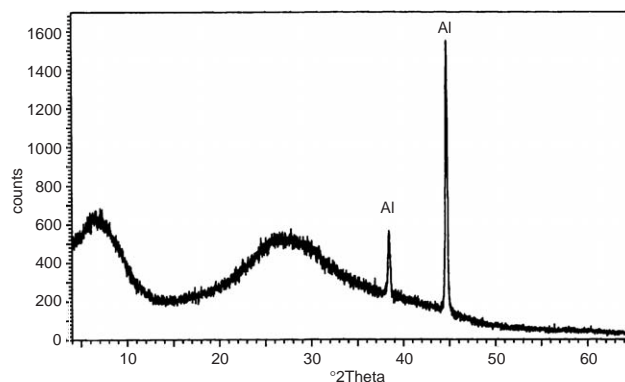


Fig. 2. XRD pattern of the aerogel deposited onto a plate of aluminum.

suggest a value for *n* close to 1.6 in accordance with previous studies reported by Aldebert et al. [4]. The interreticular distance *d* = 12.2 Å observed on the XRD pattern of the aerogel (Fig. 2) is consistent with the water amount lying between the VO₆ octahedra planes in vanadic oxides [4].

The SEM images (Fig. 3) show the fibrous nature of the vanadate aerogel in accordance with ribbon-like structures previously described [5]. The starting aerogel is in the form of threads of ~100 nm diameter and between 1 and 2 μm length. Surface areas of powder samples slightly differed according to the preparation conditions; especially, ageing of the gels before drying as presented in Fig. 3. Typical values close to 150 m² g⁻¹ determined by BET measurements were found for several preparations. Table 1 compares surface area values of V₂O₅ gels as a function of the gel preparation method.

A heat treatment at 260 °C in air of the V₂O₅·1.6H₂O aerogel gives an X-ray amorphous powder, which crystallizes at 450 °C as orthorhombic V₂O₅ scherbi-naite (Fig. 4) with loss of the fibrous structure (Fig. 3c). The BET measurements indicate that the surface area of

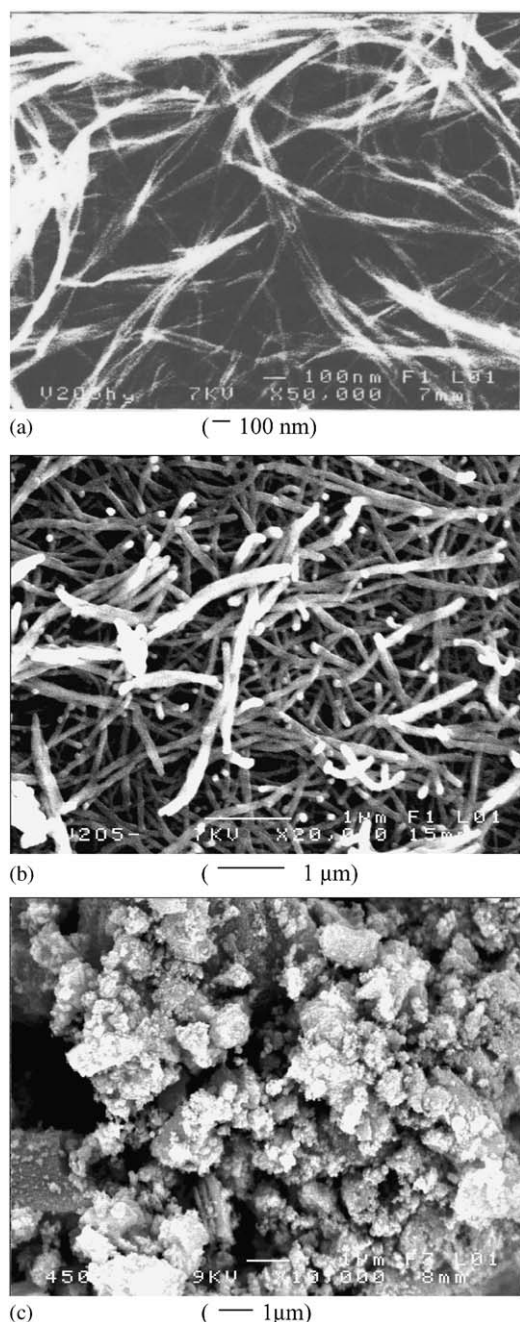


Fig. 3. SEM images of an aerogel obtained by solvent supercritical exchange: (a) fresh hydrated gel; (b) hydrated gel after an ageing of 6 months; (c) aerogel after calcination at 450 °C.

the vanadium oxide decreased from 150 m² g⁻¹ (aerogel) to 16 m² g⁻¹ (crystallized V₂O₅).

3.2. Preparation and characterization of vanadium oxynitride compounds

Transition metal nitrides have been extensively studied because of their catalytic, magnetic or electronic properties. Nevertheless, few studies have actually been published on the preparation of vanadium (oxy)nitrides during the last decade.

Crystals of VON are formed by the thermal decomposition of the metal oxide amide, which can be synthesized from metal oxide trichloride VOCl₃ and liquid ammonia [9]. King et al. have described the preparation of vanadium nitrides containing oxygen by thermal decomposition of ammonium metavanadate in ammonia [10]. More recently, Wang et al. have investigated the structure and physical properties of vanadium oxynitrides obtained by heat-treating commercial crystallized V₂O₅ in anhydrous ammonia [11].

The preparation of cubic VN can be achieved starting from different precursor oxides:

- A conventional method consists of the thermal decomposition of ammonium metavanadate in ammonia at high temperature (1100 °C) [12]. This produces the nitride VN with a low surface area (<1 m² g⁻¹).
- In order to obtain a nitride with a high surface area, the TPR (temperature-programmed reaction) technique can be used [13]. This consists of raising the temperature of the reaction slowly to the required level. Kapoor and Ted Oyama [14] have prepared high surface area (90 m² g⁻¹) cubic VN powders by TPR in which the reactant gas NH₃ flows (72 L h⁻¹) over the precursor V₂O₅ (19 m² g⁻¹). This technique has already been used for the synthesis of compounds such as Mo₂C, WC [15], Mo₂N and W₂N [16].

Two reactions were expected during the nitridation process: the substitution of a part of the oxygen bonded to the vanadium atoms by nitrogen (nitriding reaction) and the decrease of the formal valency of the vanadium (reducing reaction). The first phenomenon involves a change in the oxygen environment of the vanadium to a

Table 1
Surface areas of V₂O₅ gels as a function of the preparation method

Nature of the gel	Starting material	Surface area (m ² g ⁻¹)	Reference
Xerogel	Ammonium metavanadate	0.74	[6]
Aerogel	Ammonium metavanadate	150	[6]
Aerogel	Alkoxides	300–400	[7]
		140–200	[8]

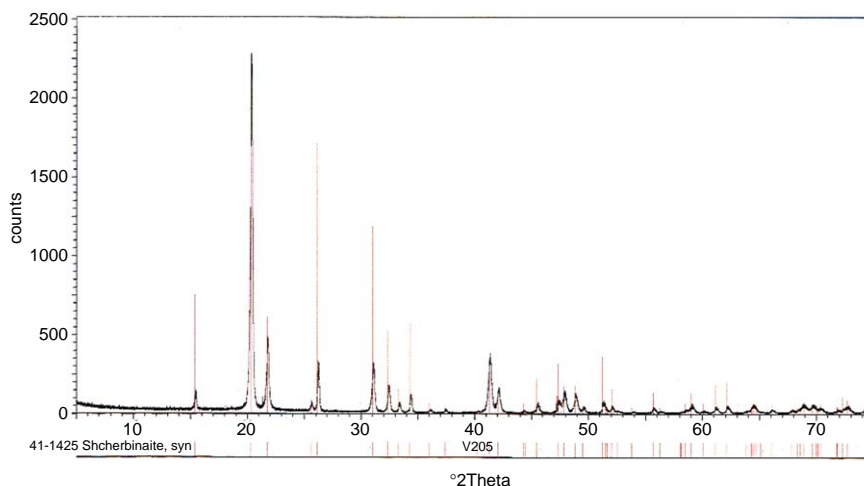


Fig. 4. XRD pattern of V_2O_5 obtained by calcination of the $V_2O_5, 1.6H_2O$ aerogel.

mixed oxygen–nitrogen environment which is accompanied in most cases by a change in structure. In the particular case of vanadium, there is a change from a two-dimensional stacking of octahedra in planes to a face-centered cubic stacking of the NaCl-type. In the second phenomenon, intermediate valency states can exist when the anionic lattice of the cubic stacking is occupied in a statistical manner by oxygen and nitrogen.

The nitridation reaction has been directly carried out on the hydrated amorphous phase of formula $V_2O_5, 1.6H_2O$. In order to avoid possible sintering or melting (V_2O_5 melting point is $690^\circ C$) of the powder, the temperature was raised slowly, in a first stage, at a heating rate of $10^\circ C min^{-1}$ from ambient to $300^\circ C$, and then at $1^\circ C min^{-1}$ to the reaction temperature.

Whatever the reaction temperature, black oxynitride light powders were obtained by nitridation of the aerogel. Their main characteristics and XRD patterns are presented in Table 2 and Fig. 5 respectively.

Crystal structures of the nitrided compounds as a function of the reaction temperature have been studied by XRD analysis. Under $500^\circ C$, the formation of monoclinic VO_2 and the appearance of the cubic phase $V(O,N)$ are observed. The presence of VO_2 indicates that, under $500^\circ C$, the hydrogen produced by the decomposition of ammonia is being consumed in some reducing process with the formation of V^{4+} species as shown previously by Kapoor. In the 550 – $900^\circ C$ temperature range, only the $V(O,N)$ NaCl-type phase is identified (Fig. 5). At the lowest temperatures, the X-ray diffraction patterns show broad peaks characteristic of small crystallites.

Elemental analysis data (Table 2) show that nitridation leads to high nitrogen content $V(O,N)$ oxynitrides from the lowest temperatures. This suggests a nitriding reaction at temperatures lower than those reported in previous works. Indeed, in their studies of the prepara-

Table 2

Analytical data of nitrided aerogels as a function of the nitridation temperature

Compound	Reaction temperature ($^\circ C$)	O (wt%)	N (wt%)	Surface area ($m^2 g^{-1}$)
VON-550	550	14.57	16.61	76
VON-600	600	8.77	17.98	47
VON-700	700	8.60	18.70	42
VON-800	800	7.36	19.50	35
VON-900	900	5.45	19.81	27

tion of high surface area vanadium nitride from crystallized V_2O_5 by TPR reaction, Kapoor et al. observed the nitrogen introduction only at temperatures higher than $600^\circ C$. For Wang et al., who studied the nitridation of crystallized V_2O_5 by thermal treatment under ammonia flow during 24 h, the nitriding reaction was dominant only in the 600 – $700^\circ C$ temperature range. Finally, by direct nitridation of metavanadate, King et al. obtained, after a long time treatment (2×24 h) at $600^\circ C$, 13.7 wt% N vanadium oxynitrides. In the present work, the use of both very low heating rates and high surface area aerogel precursors allows a higher rate of nitridation.

At $600^\circ C$, a drastic decrease in oxygen content conjugated with a low increase of the nitrogen content between VON-550 and VON-600 is observed. In the VON-550 compound, the formal valency of vanadium deduced from the nitrogen and oxygen contents is close to 4 and decreases to a value close to 3.5 in the VON-600. This confirms that ammonia atmosphere is a more reducing agent in this temperature range than under $500^\circ C$.

Results reported in Table 2 also show that the nitrogen content increases with the reaction temperature and, for the highest temperatures, reaches values in

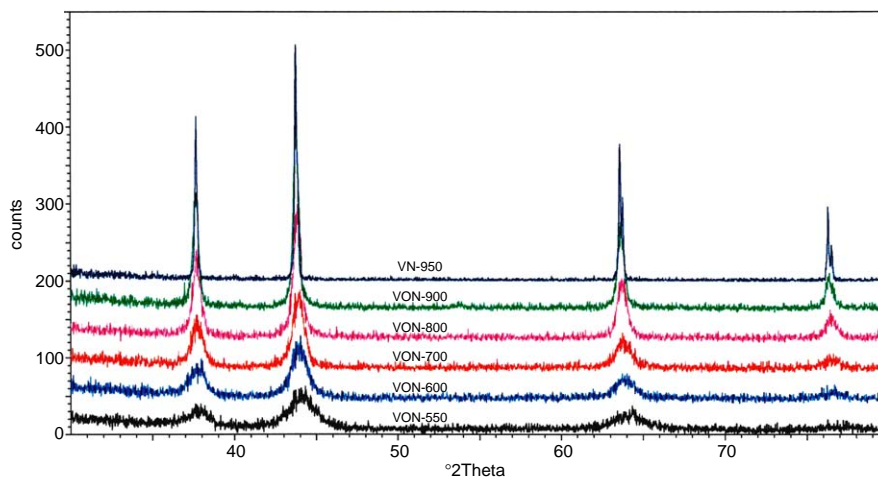


Fig. 5. XRD patterns of vanadium oxynitrides prepared in the 550–900 °C temperature range by nitridation of V_2O_5 , 1.6 H_2O aerogels. The vanadium nitride of the VN-950 pattern is obtained by direct nitridation at 950 °C of commercial ammonium metavanadate.

great accordance with the 19.5 wt% N and 20.2 wt% N found respectively by King and Kapoor. These values are close to the theoretical maximum expected for VN (21.6 wt%). However, oxygen analysis of the specimen prepared at 900 °C indicates that this compound still contains 5.45 wt% oxygen. This result is in fairly good agreement with the results of King et al. who found the presence of low oxygen content (3.8 wt%) in compounds nitrided at 1100 °C. Nitrogen and oxygen contents of VON-900 suggest a formal vanadium valency of 3.34, higher than the valency of 3 expected for the vanadium nitride.

The BET specific surface areas of the oxynitrides (Table 2) developed during synthesis decreased from 76 to 27 m²g⁻¹ with increasing nitridation temperature. Whereas calcination damages the aerogel structure, the thermal treatment under ammonia allows to maintain the fibrous structure of the aerogel despite a certain amount of crumbling of the threads (Fig. 6).

3.3. Thermal stability

In order to determine the temperature range for their possible use as gas sensors, the thermal stability in air of the oxynitrides has been studied. Thermogravimetric analyses (TGA) performed in static air determined the oxidation onset temperature of the different oxynitrides. Fig. 7 presents the TGA curves of the oxynitrides prepared at 600, 800 and 900 °C. The oxidation reaction starts between 250 and 300 °C whatever the nitridation temperature (550–900 °C) of the aerogel. Oxidation into orthorhombic V_2O_5 is complete at a temperature of 500 °C.

The oxidation of the oxynitrides implies two phenomena: the oxygen/nitrogen substitution and the transformation of the reduced valency states of vanadium (V^{3+} and V^{4+}) into V^{5+} . The weight gain measurements

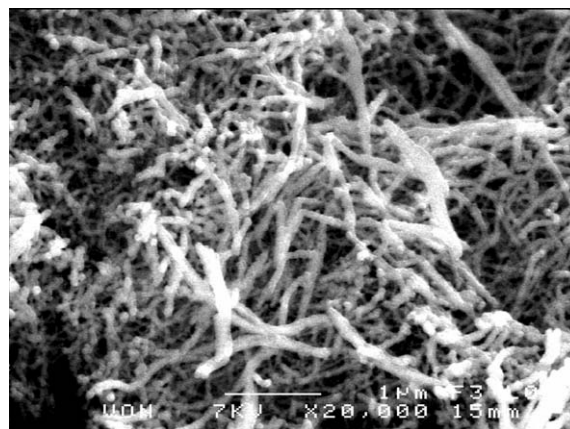


Fig. 6. SEM image of an aerogel derived oxynitride.

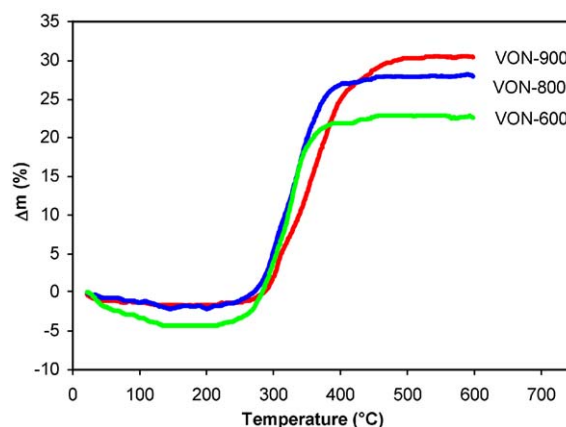


Fig. 7. TGA analyses in static air (2 °C min⁻¹) of V(O,N) oxynitrides prepared by nitridation of V_2O_5 , 1.6 H_2O aerogels at 600, 800 and 900 °C.

confirm the nitrogen contents given in Table 2 and are consistent with the calculated vanadium valency of the vanadium oxynitrides.

The results indicate that the use of these oxynitrides is conditioned by a maximum temperature of 250 °C. Preliminary gas sensing tests regarding this working condition are under investigation.

4. Conclusion

The preparation of amorphous hydrated oxides from vanadic gels using a method of solvent exchange in supercritical conditions allows starting aerogel materials of high specific surface area to be obtained. Nitridation has been carried out using very low heating rates on specimens directly issued from the supercritical exchange. Treatment under ammonia flow at different temperatures produces divided oxynitride powders presenting the fibrous structure of the aerogel precursor.

Both the reduction of V^{5+} and the oxygen/nitrogen substitution take place during the nitridation process. It has been shown that the use of aerogels leads to high nitrogen content vanadium oxynitrides at very low nitridation temperature. By adjusting the reaction temperature, a control over the reducing/nitriding behavior of ammonia is possible. This enables the preparation of vanadium oxynitrides with various oxygen/nitrogen ratios and vanadium valency states.

These materials, for which it is possible to modify the composition in a controlled manner, should be capable of offering interesting surface properties for gas detec-

tion making these compounds potential candidates as chemical gas sensors.

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