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# Nitridation under ammonia of high surface area vanadium aerogels

Odile Merdrignac-Conanec*, Khadija El Badraoui, Paul L'Haridon

*Laboratoire Verres et Céramiques, UMR CNRS 6512, Institut de Chimie de Rennes, Université de Rennes 1, Campus de Beaulieu, F-35042 Rennes Cedex, France*

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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 $V_2O_5$, $1.6H_2O$ 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.


*Keywords:* Aerogel; Vanadium; Nitridation; Oxynitride; VON

## 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 $NH_4VO_3$

*Corresponding author. Fax: +33 2 23 23 56 83.
*E-mail address:* odile.merdrignac@univ-rennes1.fr (O. Merdrignac-Conanec).

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(Fluka, 99.5%)(0.1 mol) in water (1000 $cm^3$). 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 $CO_2$ exchange. Several purge-fill cycles are necessary to remove all the acetone from the gel. A green light powder was obtained after slow $CO_2$ evaporation.

### 2.2. Preparation of the oxynitrides

The vanadium oxide aerogels were treated under $NH_3$ (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 $N_2$ (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 Cu$K\alpha$ 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 $N_2$ by thermal conductivity measurement and as $CO_2$ by infrared detection.

## 3. Results and discussion

### 3.1. Precursors

The vanadium oxide aerogel obtained is a hydrated phase of formula $V_2O_5$, $nH_2O$. TGA results (Fig. 1) 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 $VO_6$ octahedra planes in vanadic oxides [4].

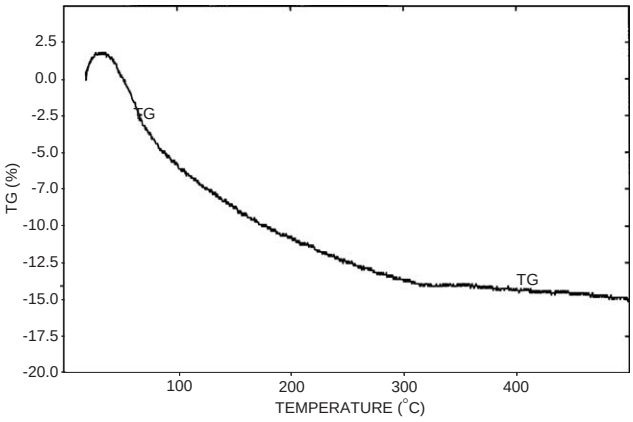


Fig. 1. Thermogravimetric analysis (2 °C $min^{-1}$) in air of the aerogel obtained by solvent exchange in supercritical conditions.

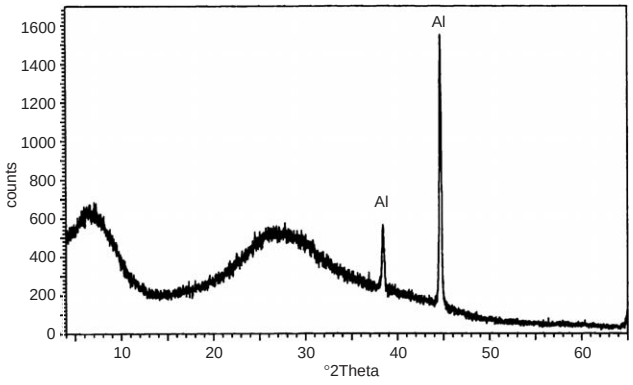


Fig. 2. XRD pattern of the aerogel deposited onto a plate of aluminum.

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 $m^2 g^{-1}$ determined by BET measurements were found for several preparations. Table 1 compares surface area values of $V_2O_5$ gels as a function of the gel preparation method.

A heat treatment at 260 °C in air of the $V_2O_5$, $1.6H_2O$ aerogel gives an X-ray amorphous powder, which crystallizes at 450 °C as orthorhombic $V_2O_5$ shcherbinaite (Fig. 4) with loss of the fibrous structure (Fig. 3c). The BET measurements indicate that the surface area of