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# Mesoporous VN prepared by solid–solid phase separation

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ABSTRACT

We recently reported a simple route to prepare mesoporous, conducting nitrides from Zn containing ternary transition metal oxides. Those materials result from the condensation of atomic scale voids created by the loss of Zn by evaporation, the replacement of 3 oxygen anions by 2 nitrogen anions, and in most cases the loss of oxygen to form water on the reduction of the transition metal. In this report, we present a different route to prepare mesoporous VN from K containing vanadium oxides. In this case, ammonolysis results in a multiphase solid product that contains VN, and other water soluble compounds such as KOH or $KNH_2$. On removing the K containing products by washing with degassed water, only mesoporous VN remains. VN materials with different pore sizes (10 nm–20 nm) were synthesized at 600 °C by varying the reaction time, while larger pores are obtained at higher temperatures (50 nm at 800 °C).

## 1. Introduction

While many methods of preparing metal nitrides have been reported [1–5], laboratory scale samples (from a few milligrams to perhaps 10 g) are often synthesized by flowing ammonia over the respective metal oxide or other metal precursors (both coordination compounds and organometallics). The objective of the above syntheses is essentially always to prepare small single crystals or polycrystalline materials with large grains (on the order of microns). Occasionally the object is to deposit or prepare dense thin films [6,7]. In either case the materials generally have few pores or voids and have a low specific surface area. There are many advantages in preparing nano- or meso-structured materials in that the relevant diffusion lengths are very short, significantly decreasing reaction times. However, very few synthetic approaches have been reported in nano-structured VN, including temperature-programmed ammonia reduction of $V_2O_5$ [8] and a two-step ammonolysis reaction of $VCl_4$ in anhydrous chloroform [9]. However, there are no reports of porous nitrides with characteristic pore diameters in the mesoscale regime (10–20 nm). Previously, we reported a synthesis route of metal (oxy)nitride nanomaterials, based on the syntheses of VN, TiN, CrN, $Ta_3N_5$, TaN, NbN, WN, MoN and $Mo_2N$ mesoporous materials via ammonolysis reaction of Zn containing metal oxide (ZMO) precursors at temperatures $>600$ °C. In this investigation, vanadium nitride was synthesized by ammonolysis of potassium containing vanadium oxides to create nano-porous VN with high surface areas and good electrical conductivity.

## 2. Methods

$KVO_3$ was prepared by a solid state reaction of the stoichiometric mixture of powders $K_2CO_3$ (99.6%, Fisher Scientific) and $V_2O_5$ (99.6%, Alfa Aesar). The powders were ground together and heated at 750 °C for 5 h. $K_2V_8O_{21}$ was prepared by a solid state reaction between $K_2CO_3$ (99.6% Fisher Scientific) and $V_2O_5$ (99.6% Alfa Aesar) in a 1:4 M ratio. The powders were ground together and heated at 450 °C for 50 h.

Few grams of these oxides were placed in an alumina boat. The boat was then placed in a stainless steel tube with air tight stainless steel end caps that had welded valves and connections to input and output gas lines. All gases were purified to remove trace amounts of oxygen or water using pellet copper, nickel, palladium and platinum with zeolites as support. The stainless steel tube was then placed in a split tube furnace and the appropriate connections to gas sources made. Argon gas was passed over the sample for 15 min to expel air before establishing a flow of ammonia gas (Anhydrous, Air Gas). The sample was heated to the above reaction temperatures at 150 °C/h. After treatment for a specified period, the furnace power was turned off and the product cooled to room temperature in $\sim$4 h under an ammonia flow. Before the stainless steel tube was taken out of the split tube furnace, argon gas was purged the tube to expel the ammonia gas. The stainless steel tube was left in lab for 24 h with

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one valve open in order to expose the ammonolysis product to air slowly. This latter procedure resulted in the formation of only a very thin oxide on the nitride surface.

Finely ground powders were examined with a Rigaku Ultima VI powder X-ray diffractometer (PXRD) with CuK$_\alpha$ radiation (K$_{\alpha1}$, $\lambda=1.5406$ Å and K$_{\alpha2}$, $\lambda=1.5444$ Å). Crystal structures of the oxides and resultant nitrides were confirmed by PXRD profiles using the GSAS package [10]. The nitride crystalline domain size can be estimated from Lorentzian function from the Rietveld fit as discussed in the Zn paper [11]. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed with a LEO-1550 field emission SEM (FSEM). Nitrogen adsorption/desorption isotherms were measured at −196 °C using a Micromeritics ASAP 2020 system. The samples were degassed at 200 °C for 24 h on a vacuum line.

Elemental analyses of nitrogen and oxygen content of nitride samples were determined with a LECO TC-600 analyzer using the inert gas fusion method. Nitrogen was detected as $N_2$ by thermal conductivity and oxygen as $CO_2$ by infrared detection. The apparatus was calibrated using Leco® standard oxides, and $Si_2N_2O$ and ε-TaN as nitrogen standards [12]. A four point measurement of conductivity of compressed powders a relatively low pressure of 35 bar was used to estimate the conductivity.

## 3. Results and discussion

### 3.1. Ammonolysis of potassium vanadates

$KVO_3$ and $K_2V_8O_{21}$ were synthesized by standard ceramic syntheses, and their purity was confirmed by powder X-ray diffraction (PXRD) as shown in Fig. 1. The patterns matched those expected PDF files of 00-033-1052 and 04-011-9621 for $KVO_3$ and $K_2V_8O_{21}$, respectively. These precursor oxides were prepared at high enough temperatures (750 and 450 °C) to produce large grain sizes, mostly in the 1–20 μm range. Ammonolysis of these oxides was carried out for a range of temperatures between 500 and 800 °C for 8 h at an ammonia flow rate of 200 cm$^3$ min$^{-1}$ through a 1 in. diameter stainless steel flow tube, as summarized in Table 1. The products were handled in an argon filled glove box, to avoid exposure to air. The products were then studied by powder X-ray diffraction using a mylar covered sample holder to prevent exposure to air during that measurement. After these initial X-ray studies, the products were then exposed to air and further processed and characterized.

Above 500 °C and with increasing time or temperature, PXRD showed the formation of VN with the expected rocksalt structure. The refined cell parameters were determined by Rietveld refinement of the PXRD patterns. The VN products from ammonolysis at 600–800 °C show relatively broad diffraction peaks due to the small crystalline domain sizes or the nitride product (10–60 nm). Ammonolysis of $KVO_3$ below 700 °C produces some unknown secondary phase(*s*). Ammonolysis products of $K_2V_8O_{21}$ formed in the temperature range of 600–800 °C also show similar unknown by-product phase(*s*). After washing the products in water, the PXRD shows only single phase VN as shown by the representative PXRD pattern of the ammonolysis product of $KVO_3$ at 600 °C in Fig. 1.

The mass loss due to the sublimation of potassium compounds and the replacement of O by N was also determined. For example, the ammonolysis of 0.1 g of $KVO_3$ at 600, 700 and 800 °C for 8 h, gives approx. a 20% weight loss. However, the expected theoretical mass loss, (loss = (mass $KVO_3$ − mass VN)/mass $KVO_3$) should be 52%. These results suggest that ammonolysis results in a multiphase solid product that contains VN, and water soluble potassium compounds such as KOH or $KNH_2$. Since some mass loss is observed, some of the by-products are apparently volatile. This could include the formation of some water vapor or partial sublimation of potassium compounds. After removing the K containing by-products by washing with degassed water, only mesoporous VN remains.

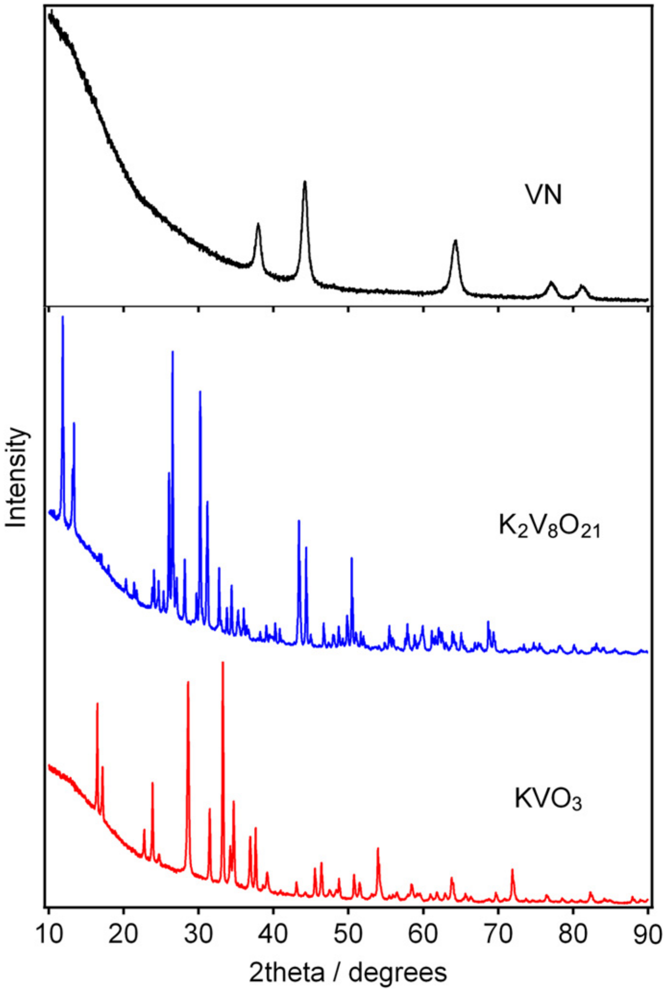

**Fig. 1.** PXRD patterns illustrating the potassium vanadates and the ammonolysis product of $KVO_3$ for 8 h at 600 °C with ammonia flow (200 cm$^3$ min$^{-1}$) washed with $H_2O$.

**Table 1**
Summary of ammonolysis conditions, refined lattice parameters (a) and calculated domain size of pure VN: all reactions are 8 h at an ammonia flow rate of 200 cm$^3$ min$^{-1}$. VN crystallized in space group Fm-3m.

| Precursor | T/°C | XRD phase | a/Å | Domain size/nm |
|---|---|---|---|---|
| $KVO_3$ | 600 | VN, unknown | 4.1231(3) | 10 |
| | 700 | VN, unknown | 4.1262(1) | 26 |
| | 800 | VN, unknown | 4.1341(1) | 46 |
| $K_2V_8O_{21}$ | 600 | VN, $KVO_3$, other | 4.1245(2) | 14 |
| | 700 | VN, $K_2V_8O_6$ | 4.1290(2) | 35 |
| | 800 | VN, unknown | 4.1345(1) | 52 |

### 3.2. Mesoporous VN

Fig. 2 shows the representative SEM images of the oxide precursors and their ammonolysis products. Fig. 2a shows the surface morphology of $KVO_3$ prior to ammonolysis treatment. The ammonolysis product of $KVO_3$ at 600 °C for 8 h is shown in Fig. 2b. The surface of the grains is not as smooth as the surface of starting oxide (Fig. 2a), but no mesoporosity is observed.

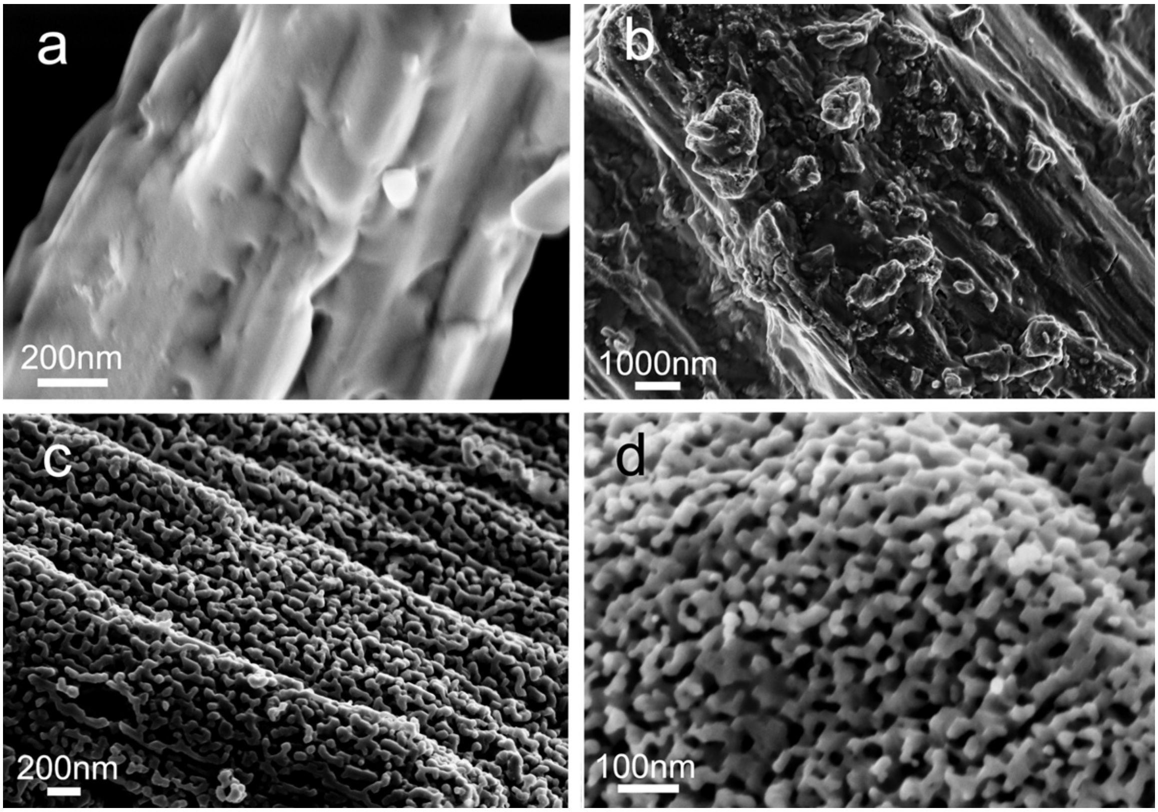

**Fig. 2.** SEM images of $KVO_3$ and its ammonolysis products from 600 to 800 °C, all reactions were 8 h at temperatures with ammonia flow (200 $cm^3$ $min^{-1}$): (a) $KVO_3$, (b) ammonolysis product of $KVO_3$ at 600 °C, (c) water washed ammonolysis product of $KVO_3$ at 800 °C and (d) water washed ammonolysis product of $K_2V_8O_{21}$ at 800 °C.

The PXRD refinement of the product obtained without air exposure shows that VN was formed and that the average nitride crystalline domain size is 10 nm. However PXRD shows the presence of other unidentified solid products. The PXRD refinement of the 700 °C product without air exposure shows that the average VN crystalline domain size has grown to 26 nm.

After washing the products obtained at 800 °C with water, mesoporous surface features are clearly visible. According to the SEM images, the size of the pores range from 30 to 50 nm. The PXRD refinement of the 800 °C product shows that the average VN crystalline domain size is 46 nm. Not surprisingly, larger VN grains and pore sizes are formed at higher temperatures and/or longer reaction times. The ammonolysis products of $K_2V_8O_{21}$ over the same temperature range of 600–800 °C show very similar pore morphologies and sizes as those observed in the products obtained from $KVO_3$. The washed products shown in Fig. 2c and d are also very similar to the mesoporous VN products obtained from the ammonolysis of Zn containing oxides. [11].

The above SEM images show that the pores and particles both have rounded surfaces (see Fig. 2c and d for example). Such rounded surfaces are also found in dealloyed Ag–Au [13], while striking aligned faceting was found in single crystal MnO films produced by reduction of $ZnMn_2O_4$ in forming gas [14]. The shape of the pores is expected to be a function of the surface and bulk diffusion rates and the surface energies of different facets of the product crystalline structure [15] and [16].

### 3.3. Formation mechanisms of mesoporous VN

In contrast to the case of Zn in which $Zn^{2+}$ is reduced to elemental Zn and subsequently sublimes [11], ammonia is not able to reduce $K^+$ to K metal. Thus the mechanism of formation of mesoporous VN in the two cases is different. Under ammonia flow at high temperatures the formation of KOH or $KNH_2$ from potassium oxide is thermodynamically possible [17]. Other compounds such as mixed hydroxides and amides or imides may also be produced. In any case, these by-products are either solids or liquids at the synthesis temperature and apparently sublime slowly if at all. Thus, in the present case, the observed mesoporosity results from phase separation of the nitride from the other by-products. Apparently, the surface energies and diffusion constants of the relevant phases allow such separation to proceed at the mesoscale. As the reaction temperature increases, the scale of phase separation coarsens and the grain size of VN grows. This mechanism is similar to that seen in the formation of porous Vycor, where spinodal decomposition of a borosilicate glass forms two phases that are separated on the nanoscale [18]. The mole fraction of V in $KVO_3$ and $K_2V_8O_{21}$ are 20.0% and 25.8%, respectively. By comparing the SEM images (Fig. 2c and d) of ammonolysis products of $KVO_3$ and $K_2V_8O_{21}$ at 800 °C, the VN from $KVO_3$ (Fig. 2c) shows less open porous feature than from $K_2V_8O_{21}$ (Fig. 2d), consistent with the higher V content of the latter compound.

### 3.4. Chemical, surface area and conductivity properties

The ammonolysis products of single phase VN show $<2$ wt% of oxygen. The BET surface area of a 325 mg sample prepared from $KVO_3$ at 600 °C was $54.4 \pm 0.1$ $m^2/g$. The average pore sizes range from 10 to 20 nm. There is some microporosity (pore diameter $\leq 2$ nm) that accounts for 3.6 $m^2/g$ and a micropore volume of $1.2 \times 10^{-3}$ $cm^3/g$. As we discussed in the report of metal (oxy) nitrides made from Zn contained oxides, the mesoporosity obtained is a feature of the bulk material and not just porosity induced at the surfaces of the original crystalline oxide grains [11]. The conductivity of compressed powders of mesoporous VN at 35 bar is 76 S/cm (VN). This is about two orders of magnitude lower than for the bulk VN, presumably due to both the porosity and weak particle–particle contacts at low pressure.

## 4. Conclusion

A new synthesis method for nano-structured VN from ammonolysis of bulk KMOs has been presented. The proposed mechanism is a balance between loosing internal volume by phase separation of potassium containing products from VN. The sintering rate is slow enough that the porosity is not eliminated during the short heating period, since the diffusion rates in nitrides are so low. The potassium oxide by-products can be washed out with water.

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