

# Low-Temperature Preparation and Mechanism Study of Vanadium Nitride



Yongjie Liu, Qingqing Hu, Donglai Ma, Yue Wang, and Zhixiong You

**Abstract** In this study, VN was successfully prepared in an ammonia atmosphere using  $V_2O_5$  as a raw material at 600 °C. The gas composition of the reaction process was analyzed by Factsage 8.0 software. At the same time, based on the first principles of density functional theory, the adsorption model of  $NH_3$  on the  $V_2O_5$  (001) surface is established. Through the analysis of the structure changes of the adsorption model and the size of the adsorption energy, the mechanism of the adsorption reaction of ammonia and  $V_2O_5$  was revealed. Through thermodynamic calculations and the first-principles calculations method of density functional theory (DFT), the microscopic mechanism of the reaction between ammonia and  $V_2O_5$  is revealed, which is of great significance to the determination of process parameters in the actual reaction.

**Keywords** Vanadium nitride · Ammonia ·  $V_2O_5$  · DFT

## Introduction

In recent years, transition metal nitrides have received extensive attention due to their superior chemical and physical properties, such as high toughness, high-temperature stability, excellent corrosion resistance, extreme hardness, excellent catalytic performance, and electrical conductivity [1–3]. Among transition metal nitrides, vanadium nitride (VN) has attracted much attention due to its excellent physical and chemical properties [4–6]. Thus, it has many applications in the field of structural materials, electrochemistry, and catalysis [7, 8].

Traditionally, the conventional preparation method of vanadium nitride has high temperature (above 1000 °C) and long reaction time due to the diffusion rate of solid–solid reaction related to temperature, such as carbothermal reduction of vanadium

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oxide or direct nitridation of pure metal vanadium [5, 9]. In order to find a method of low temperature, short time, and low cost, ammonia reduction-nitridation is widely studied as a low-cost and efficient method for the preparation of vanadium nitride [10–12]. Mosavati et al. [10] prepared vanadium-based precursor by hydrothermal method for 24 h, and then synthesized VN nanopowders having an average particle diameter of 47 nm under  $\text{NH}_3$  atmosphere at 800 °C. Panda et al. [11] reported that nano-sized vanadium nitride was prepared by sol–gel synthesis of  $\text{V}_2\text{O}_5$  precursor in the atmosphere of ammonia gas. Qin et al. [12] reported using ultra-fast (within 1 min) solution combustion to synthesize vanadium dioxide ( $\text{VO}_2$ ) precursor in an ammonia atmosphere to prepare nano-vanadium nitride powder. The above studies have shown that the nanostructure and high activity of the nanostructure and high activity prepared by the method of hydrothermal method, sol–gel method, and solution combustion synthesis method are used to successfully synthesize the VN nano-powder. During the preparation process of VN, the vanadium-based precursor phase changes to:  $\text{V}_2\text{O}_5 \rightarrow \text{VO}_2 \rightarrow \text{V}_2\text{O}_3 \rightarrow \text{VN}$ . However, there are few theoretical studies on the microscopic mechanism of vanadium nitride formation at the surface of vanadium oxide in ammonia atmosphere.

In this study, VN was successfully prepared by using micron- $\text{V}_2\text{O}_5$  as raw material in ammonia atmosphere at 600 °C. Through thermodynamic calculation, the variation of gas and solid in gas–solid reaction process was analyzed by FactSage 8.0. In order to further analyze the change of the surface microstructure of  $\text{V}_2\text{O}_5$  in the ammonia atmosphere, we use the first-principles calculations method of density functional theory (DFT) to study the structural change of the surface adsorption of  $\text{V}_2\text{O}_5$  (001), providing a deeper theoretical basis for the further study of the ammonia reduction-nitridation of  $\text{V}_2\text{O}_5$ .

## Experimental and Computational Methods

### *Experimental Procedure*

The solid powder raw material for preparing vanadium nitride (VN) is vanadium pentoxide ( $\text{V}_2\text{O}_5$ , >99.9 wt.%). For preparing vanadium nitride,  $\text{V}_2\text{O}_5$  was placed in an alumina crucible and put into the constant-temperature zone of a horizontal resistance furnace. Initially, at the heating stage, a flow of Ar gas (99.999%) was introduced into the furnace tube to get rid of  $\text{O}_2$  and  $\text{H}_2\text{O}$ . The flow rate of Ar gas was kept at about 300 ml/min. When the furnace was heated to the desired temperature (400–600 °C) at the rate of 10 °C  $\text{min}^{-1}$ , the nitridation reaction of the raw materials was performed in a tube furnace at a constant heating temperature of flowing ammonia ( $\text{NH}_3$ , 99.999%) gas at the flow rate of 500 ml/min. After holding at the desired temperature for 1 h, the tube furnace was cooled down under flowing

Ar gas. After reaction and nitridation, the obtained products were examined by X-ray powder diffraction (PANalytical D/max 2500). Scanning electron microscope (Quattro S, ThermoFisher) was carried out to monitor overall morphology.

### Computational Details

All structural optimizations and corresponding total energy calculations were performed using density functional theory (DFT) with the VASP package by the plane wave basis sets [13]. The exchange correlation function used is the generalized gradient approximation of the Perdew–Burke–Ernzerhof (PBE). The plane wave base cutoff energy of 500 eV is used to ensure good accuracy. The structure of vanadium oxide is geometrically optimized by the conjugate gradient method. The maximum force of each atom in the system is less than 0.03 eV/Å and the total energy is less than 10<sup>-5</sup> eV. In order to eliminate the influence of radical-containing systems, we considered spin polarization in our calculations. The V<sub>2</sub>O<sub>5</sub>(001) surface was modeled with the slab supercell approach including a 15 Å vacuum region, as shown in Fig. 1. There are two kinds of vanadium (V<sup>a</sup> and V<sup>b</sup>) and three kinds of lattice oxygen active sites on the surface [14, 15]. Among them, V<sup>a</sup> is vanadium-based oxygen (V<sup>a</sup> = O) located outside the surface and vanadium-based oxygen (V<sup>b</sup> = O) located inside the surface. Lattice oxygen includes single-coordinated terminal oxygen O(1),

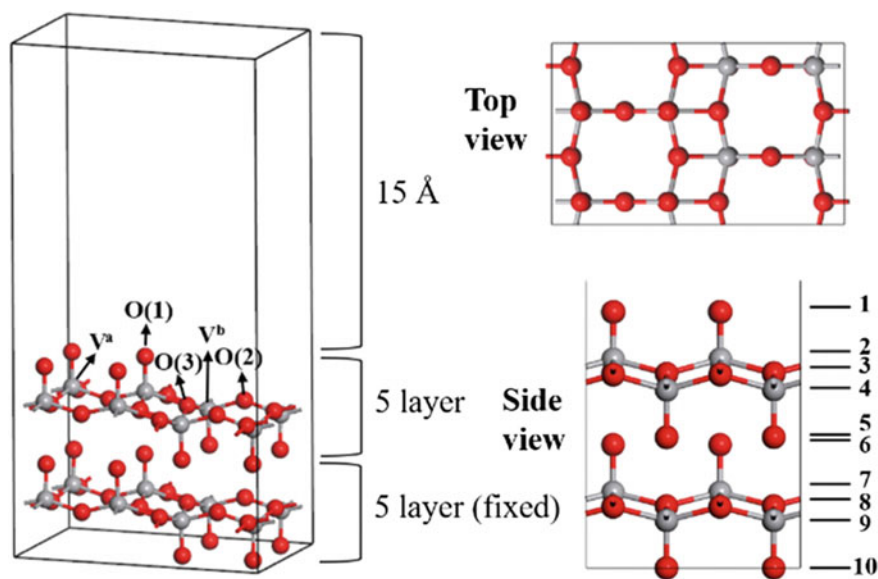


Fig. 1 Configuration of vanadium oxide (V<sub>2</sub>O<sub>5</sub>) slab model

namely, vanadium-based oxygen ( $V = O$ ), double-coordinated oxygen O(2), and tri-coordinated oxygen O(3). It is worth noting that from the structural position of O(1), O(1) is the most prone to adsorption reaction site [16], and O(1) is also the research site of this article. We used a  $(1 \times 2)$  supercell containing a ten-layer slab in which the bottom five layers were fixed and all the other atoms are allowed to relax freely. A  $3 \times 4 \times 1$  k-point grid that has been tested for convergence is used to ensure that the interface has sufficient accuracy. Since the zero-point correction has a small effect on the adsorption energy, the relative energy reported does not include the zero-point energy and thermal correction.

The adsorption energy ( $E_{ad}$ ) is calculated according to Formula (1).

$$E_{ad} = E_{NH_3+V_2O_5} - (E_{NH_3} + E_{V_2O_5}) \quad (1)$$

where  $E_{NH_3+V_2O_5}$  is the surface energy of  $NH_3$  adsorbed on the  $V_2O_5$  surface,  $E_{NH_3}$  is the energy of  $NH_3$ , and  $E_{V_2O_5}$  is the energy of the  $V_2O_5$  clean surface.

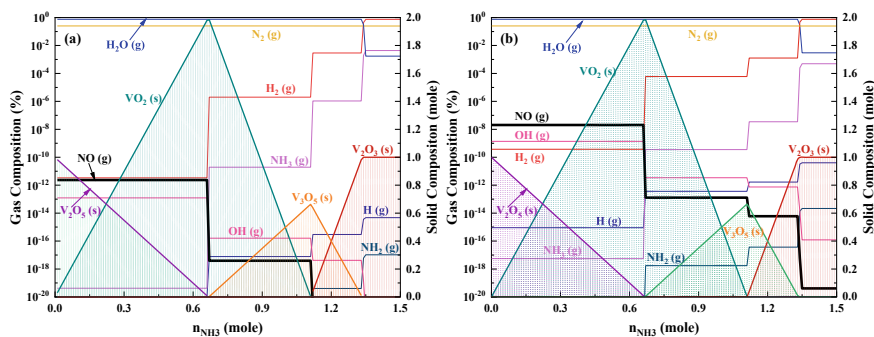
## Results and Discussion

### *Thermodynamic Analysis*

As shown in Table 1, the main reactions and their standard Gibbs free energies during reduction-nitridation process were calculated by FactSage 8.0. From the products of Eqs. 3 and 4, it can be seen that there are two possible ways for  $V_2O_5$  to react with  $NH_3$ . The products of the two different pathways are  $N_2$  and  $NO$ , respectively. It can be seen from Eq. 2 that  $NO$  easily reacts with  $NH_3$ , indicating that it is difficult

**Table 1** Main reactions and their standard Gibbs free energies

Eq.	Chemical equation	$\Delta_r G^\ominus$ (J/mol)	Starting reaction temperature ( $^\circ C$ )
1	$NH_3 = 1/2N_2 + 1/3H_2$	21,562.34–114.50 T	188
2	$NH_3 + 3/2NO = 5/4N_2 + 3/2H_2O$	–455,952.62–15.85 T	–
3	$V_2O_5 + 2/3NH_3 = 2VO_2 + 1/3N_2 + H_2O$	–112,843.32–123.41 T	–
4	$V_2O_5 + 2/5NH_3 = 2VO_2 + 2/5NO + 3/5H_2O$	8719.67–119.12 T	73
5	$VO_2 + 1/3NH_3 = 1/2V_2O_3 + 1/6N_2 + 1/2H_2O$	–18,870.21–45.52 T	–
6	$VO_2 + 1/5NH_3 = 1/2V_2O_3 + 1/5NO + 3/10H_2O$	41,922.70–43.41 T	966
7	$V_2O_3 + 2NH_3 = 2VN + 3H_2O$	105,711.36–149.15 T	709
8	$V_2O_5 + H_2 = 2VO_2 + H_2O$	–127,002.18–47.65 T	–
9	$VO_2 + H_2 = V_2O_3 + H_2O$	–26,057.75–7.35 T	–



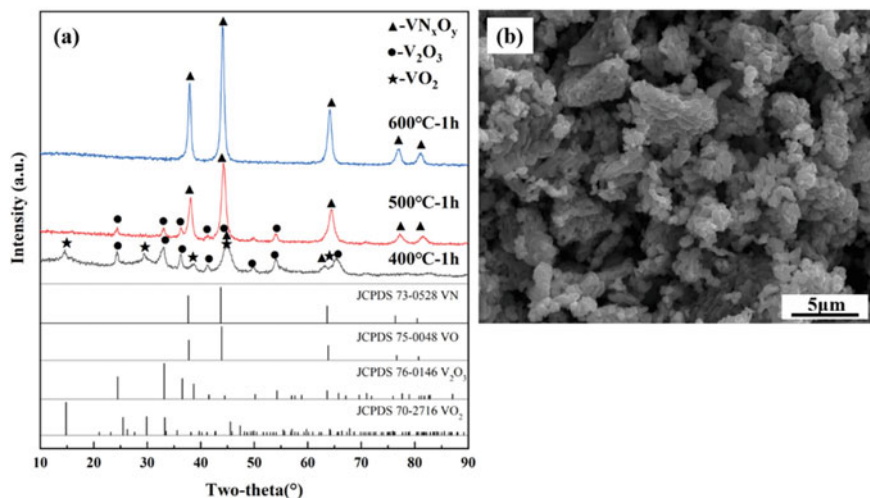
**Fig. 2** Equilibrium composition of solid and gas products in the  $\text{NH}_3\text{-V}_2\text{O}_5$  (1.0 mol  $\text{V}_2\text{O}_5$ ) system at different temperatures: **a** 400 °C **b** 600 °C

to detect the formation of NO during the actual reaction process. Meanwhile, the reaction pathway of  $\text{VO}_2$  is similar to that of  $\text{V}_2\text{O}_5$ . However, it can be seen from Eq. 6 that the initial temperature of NO generation is 966 °C under standard condition, indicating that the reaction between  $\text{VO}_2$  and  $\text{NH}_3$  is dominated by Eq. 5. In addition, the temperature required to generate VN under standard conditions is 703 °C, under standard condition by Eq. 7. Equations 8 and 9 show that  $\text{H}_2$  can reduce  $\text{V}_2\text{O}_5$  to  $\text{V}_2\text{O}_3$ . This indicates that  $\text{H}_2$  decomposed from ammonia gas also participates in the reaction.

In order to further illustrate the  $\text{NH}_3\text{-V}_2\text{O}_5$  system changes during the reaction, the solid and gas phase composition was calculated as a function of input  $\text{NH}_3$  under standard condition. Figure 2 shows the equilibrium of the gas–solid composition of the product with the increase of ammonia at 400 and 600 °C. As shown in Fig. 2, the solid phase changes to:  $\text{V}_2\text{O}_5 \rightarrow \text{VO}_2 \rightarrow \text{V}_3\text{O}_5 \rightarrow \text{V}_2\text{O}_3$ . In our previous study, with the further increase of ammonia,  $\text{V}_2\text{O}_3$  would eventually change to VN [17]. In the gas product, its main components are  $\text{H}_2\text{O}$  and  $\text{N}_2$ . As the reaction progresses, the content of  $\text{H}_2$  and  $\text{NH}_3$  will gradually increase. It is worth mentioning that the black line is the change of NO gas. When  $\text{V}_2\text{O}_5$  is gradually transformed into  $\text{V}_2\text{O}_3$ , the NO gas content also drops by orders of magnitudes. Meanwhile, when the temperature increases from 400° to 600° °C, the content of NO gas increases by several orders of magnitude, while the content of ammonia decreases by several orders of magnitude, indicating that the increase of temperature is beneficial to the reaction. In addition, it can be seen from Eq. 2 that NO and  $\text{NH}_3$  will react, resulting in a small amount of NO compared to the content of  $\text{N}_2$ .

### Phase Transformation Analysis

The phase transformation during the preparation of VN was shown in Fig. 3a. As shown in Fig. 3a, after reacting at 400 °C for 1 h, the sample consisted of  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ ,

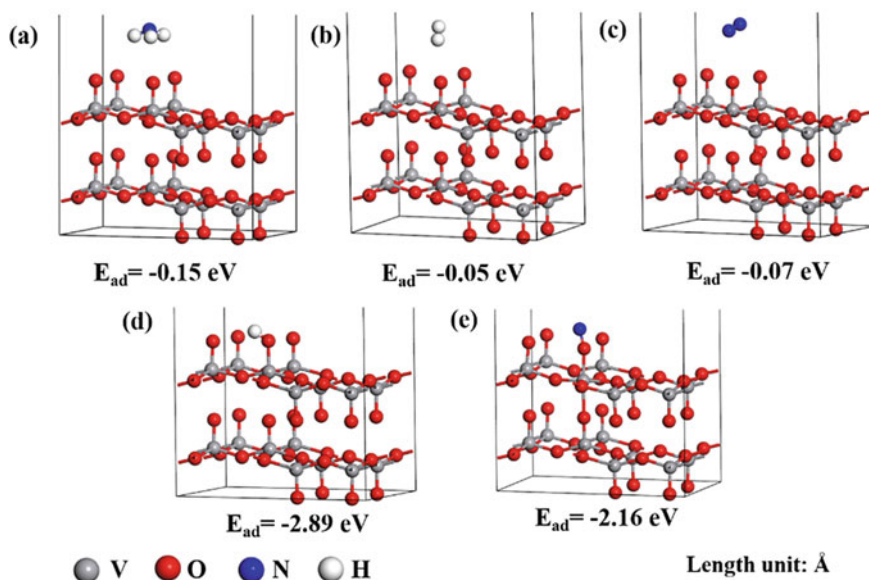


**Fig. 3** The phase and SEM images of the reaction products: **a** XRD patterns of the products; **b** SEM image of the  $V_2O_5$  at 600 °C after reacting for 1 h

and VN. It can be concluded that, in this case, the reaction time was not sufficient to completely reduce vanadium oxides. With the increase of temperature to 500 °C, the diffraction peak of  $VO_2$  disappeared leaving only the diffraction peaks of  $V_2O_3$  and VN. When the temperature was 600 °C, all diffraction peaks were assigned to VN. In addition, the lattice parameters and structure of VO and VN are similar. Therefore, the VN produced by the reaction is a solid solution of  $VN_xO_y$  ( $x < 1$ ,  $y < 1$ ). It is worth noting that the above thermodynamic calculation shows that the initial temperature of VN generation in the standard state is 709 °C, while the actual experimental reaction temperature is lower than the theoretical temperature, which is due to dynamics and other factors. Figure 3b shows a scanning electron micrograph (SEM) of the product reacted at 600 °C for 1 h. The product is micron-sized particles composed of many small cubes.

### DFT Analysis

In order to further study the reaction of adsorbed gas on the microscopic surface of  $V_2O_5$  under ammonia atmosphere, we used DFT to calculate the structural changes and adsorption energy of  $NH_3$ ,  $H_2$ ,  $N_2$ , H, and N adsorbed on the surface of  $V_2O_5$  (001), as shown in Fig. 4. On the surface of  $V_2O_5$ , the structural position of O(1) site shows that O(1) is most likely to adsorb gas. Meanwhile, Fu et al. [16] also found that O(1) and H combined to form  $H_2O$  would leave the solid surface, thus changing the structure of  $V_2O_5$ . From Fig. 4a–c, it can be seen that the adsorption energy ( $E_{ad} = -0.15$  eV) of  $NH_3$  adsorbed on the surface of  $V_2O_5$  (001) is



**Fig. 4** Adsorption structures of **a**  $NH_3$ , **b**  $H_2$ , **c**  $N_2$ , **d** H, **e** N on the surface of  $V_2O_5$  (001)

the largest, indicating that in the actual reaction process, ammonia is most easily adsorbed on the surface of the reactant and reacts with  $V_2O_5$ . In addition,  $NH_3$  and  $H_2$  are easily decomposed to obtain active N atoms and H atoms. In the actual reaction process, there are active N atoms and H atoms in the ammonia atmosphere. Therefore, we calculate the adsorption of H and N atom on the  $V_2O_5$  (001) surface, as shown in Fig. 4d, e. The adsorption energies of the H and N atom are  $-2.89$  eV and  $-2.16$  eV, respectively, indicating that H and N atoms can react spontaneously with O(1). Meanwhile, the bond length between O(1) and V atom becomes longer, and O(1) has a tendency to desorb on the  $V_2O_5$  (001) surface.

## Conclusions

VN was successfully prepared in ammonia atmosphere using  $V_2O_5$  as a raw material at  $600$  °C for 1 h. Through thermodynamic calculation, the gas–solid change in the reaction process was analyzed. The formation of NO gas was found at the initial stage of the reaction. NO gas will react with  $NH_3$ , resulting in a very low NO content in the product gas. Meanwhile, through DFT study, it was found that  $NH_3$  was easily adsorbed on  $V_2O_5$  (001) surface compared with  $N_2$  and  $H_2$ . The active N and H atoms obtained from the decomposition of  $NH_3$  and  $H_2$  are easily adsorbed on the surface of  $V_2O_5$  (001) and bind to O(1). Meanwhile, O(1) has a tendency to detach

from the  $V_2O_5$  (001) surface, which shows the change process of the microscopic reaction process.

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