Preparation of a novel V₂C mxene/g-C₃N₄ and its performance in plasma catalytic denitrification

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ABSTRACT. In this work, the g-C₃N₄/V₂C MXene composite catalyst was prepared by solvothermal method, and its denitration performance under synergistic plasma (NTP) was investigated. The results showed that when the mass ratio of V₂C is 3%, the denitration performance of V-CN-3-NTP is as high as 83.3%, which is 1.2 and 2.1 times that of the V₂C-NTP and g-C₃N₄-NTP systems alone. The apparent morphology, phase structure, and catalytic mechanism of the catalyst were studied by SEM, TEM, XRD, FTIR, XPS, etc. The results showed that g-C₃N₄ grows well on V₂C mxene. V₂C is not only an electron acceptor but also an active site for NO adsorption. The electrons and holes generated by V₂C could be effectively separated by the high-voltage electric field, which improves the denitration performance and shows a good synergistic effect.

1 INTRODUCTION

The exhaust gas emitted from human production and life has caused a lot of irreversible harm to the environment, and nitrogen oxides (NO_x), as the most difficult part of exhaust gas treatment, has seriously affected people's daily life¹. As a new type of gas pollutant treatment technology, plasma denitration technology improves the technical defects of traditional denitration process such as high energy consumption and high cost, and avoids the reducing agent required in SCR (selective catalytic reduction), and does not produce secondary pollution², which is one of the most promising and effective technologies in the treatment of air pollution. During the discharge process, the breakdown gas generates high-energy electrons to provide energy for the reaction, thereby generating a series of reactive groups (such as N⁺ and O⁺), and these reactive groups react with NO gas molecules to form harmless substances. So far, plasma denitration technology still has some drawbacks (large power consumption, relatively low denitration efficiency, etc.). Therefore, in order to solve these problems, the denitration reaction with the catalysts-NTP synergistic method has become a hot research topic. Wang³ et al. reported a new type of 12Mn-12Cu/ZSM5 catalyst in the plasma-catalyst system. The results showed that the combination of plasma and the catalyst improved the removal efficiency of NO, and the introduction of Mn improved the performance of the Cu/ZSM5 catalyst. Yu⁴ et al. divided the catalytic process of the plasma-assisted catalyst into two stages: in the first stage, NO_x were adsorbed by the catalyst (not discharged); in the second stage, using N₂ and Ar as carrier gas, the adsorbed NO_x were decomposed into N₂ and O₂. The instantaneous

increase of active oxygen groups was the main reason for improving the conversion of NO_x, and solid carbon was added as a trapping agent for active oxygen groups to increase the conversion rate of NO_x in the N₂ plasma. However, in order to improve the denitration efficiency, many researchers used metals as catalysts, which were too costly and may cause metal pollution. Most of the relative studies require the addition of reducing agents (such as CH₄ and NH₃) to the reaction system, which did not exert the synergistic effect of this kind of system. This work aimed to construct a cheap new plasma synergistic catalytic system to overcome these problems.

g-C₃N₄ (graphite phase carbon nitride), as a non-metallic material, has attracted attention in the field of catalysis due to its suitable band gap, easy synthesis, low cost, and good physical and chemical properties⁵. However, its lower carrier separation efficiency and smaller specific surface area limited its practical application in the field of catalysis. Therefore, researchers have made efforts to improve its performance defects, and through a series of methods (such as surface control⁶, doping⁷ and formation of heterojunctions with semiconductors⁸), the separation efficiency and specific surface area of electrons and holes have been increased, and the specific surface area has been increased. The active sites on the surface further increased the activity of the catalyst⁹. The electrons of g-C₃N₄ was migrated by the high-voltage electric field, which improved its reduction performance and facilitated the reduction of NO¹⁰. In this work, a one-dimensional tubular g-C₃N₄ was prepared, which exposed more active sites under the support of a large specific surface area, thereby improving its denitration performance.

Transition metal carbides and nitrides (called MXenes)

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are one of the latest 2D materials. Since Naguib et al¹¹ first developed Ti_3C_2 , they have promoted a lot of research, are widely used, and show excellent performance. In addition, the large specific surface area and abundant surface functions made MXenes effective adsorbents for various molecular and ionic species, expanding their applications in ion screening, catalysts and sensors¹²⁻¹⁴. Vanadium carbide (V_2C) is a typical MXene material, which has similar properties to titanium carbide (Ti_3C_2), has metal conductivity and hydrophilicity, and has excellent chemical stability and light stability¹⁵. Among them, good thermal stability is an important prerequisite for maintaining good properties in plasma¹⁶. V_2C was mostly used in energy storage and conversion, such as batteries, capacitors, etc¹⁷⁻¹⁹. But due to its excellent performance, it had a very broad prospect in catalysis. This article applies V_2C to the field of catalysis for the first time, and uses it with $\text{g-C}_3\text{N}_4$ for denitration in the plasma-catalysts system.

In this work, the solvothermal method was used to grow V_2C etched by HF on the dicyandiamide supramolecular precursor, and then calcined at high temperature to generate $\text{V}_2\text{C}/\text{CN}$ composite. Under the action of the low-temperature plasma synergistic catalyst, the denitration performance of the $\text{V}_2\text{C}/\text{CN}$ composite reaches up to 83.3%, which is 2.1 and 1.2 times that of the CN-NTP system and the $\text{V}_2\text{C-NTP}$ system alone. In addition, characterization techniques were used to study the properties of the catalyst, and the synergistic mechanism of $\text{V}_2\text{C}/\text{CN}$ and NTP was studied.

2 EXPERIMENTAL SECTION

Scheme 1. Schematic Diagram of the Synthesis Process of the $\text{V}_2\text{C}/\text{g-C}_3\text{N}_4$ catalyst

2.3 Characterization

The crystal phase was determined by X-ray diffraction (XRD, Bruker D8 Advance, Germany, $\text{Cu K}\alpha$). The X-ray photoelectron spectra (XPS) of samples were collected by a spectrometer (Thermo Fischer, ESCALABXi+, $\text{Al-K}\alpha$). The morphologies of materials were characterized on a scanning electron microscope (SEM, JSM-IT300A). The Brunauer Emmett Teller surface area (BET) was obtained by N_2 adsorption-desorption isotherms measured at 77 K on a surface area analyzer (Micromeritics, ASAP2460), and pore structural parameters were determined by the

2.1 Synthesis of V_2C

In an ice bath, V_2AlC (1 g) powder was slowly added to 20 mL of hydrofluoric acid (48%) within 5 minutes and stirred the above mixture vigorously at 35°C for 24 hours, then increased the temperature to 50°C and continue stirring for 48 hours. The as-prepared suspension was then centrifuged, and the obtained solids were washed repeatedly with deionized water until the pH value is close to neutral (>6), and then freeze-dry to obtain V_2C MXene powder¹⁵.

2.2 Synthesis of $\text{V}_2\text{C}/\text{g-C}_3\text{N}_4$

3 g of dicyandiamide (DCDA) was added to a mixed solvent consisting of deionized water and isopropanol (water/isopropanol volume ratio=1:2), and stirred for 30 min. Then a certain amount of V_2C was added to the mixed solution and stirred, and then the obtained solution was transferred to a 25mL autoclave and kept at 180°C for 10 hours. After the reaction was completed, the product was centrifuged to obtain a supramolecular precursor. Then, washed three times with water and ethanol to remove the remaining solvent, and then dried in a vacuum at 80°C overnight. Finally, the supramolecular precursor was heated to 550°C at a heating rate of $10^\circ\text{C}/\text{min}$, and stored in the air for 2 hours to generate a $\text{g-C}_3\text{N}_4(\text{CN})/\text{V}_2\text{C}$ sample. The final products were designated as C/V-1, C/V-2, C/V-3, and C/V-4, corresponding to the weight of V_2C MXene to dicyandiamide (1, 2, 3, and 4 wt %)²⁰.

Barrett–Joyner–Halenda (BJH) method. Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 449F3 instrument under a nitrogen atmosphere.

2.4 Experimental procedure and apparatus

Fig. 1 Schematics of experimental apparatus.

The NO denitrification device consists of a gas generator, a dielectric barrier discharge (DBD) reactor, and a gas detection device (as shown in the Fig. 1). The simulated flue gas is composed of 500ppm NO, 8% O₂ and N₂ balance gas. Use a flow controller (MFC) to control the gas flow at 500 mL/min. The experimental sample is 0.5g. The inlet and outlet NO and NO₂ concentrations are analyzed online with KM950 flue gas analyzer. All tests are performed at atmospheric pressure and room

temperature. The denitration efficiency is calculated as follows:

$$\eta = (1 - C/C_0) \times 100\%$$

where η is the denitration rate (%), C_0 is the inlet NO concentration (ppm) and C is the outlet NO concentration (ppm).

The two stainless steel electrodes ($\phi 50 \times 15$ mm) are high voltage electrodes and ground electrodes. The distance between the two electrodes is 10 mm. The DBD ($\phi 60 \times 8$ mm, DBD-100B, Nanjing Suman Electronics Co., Ltd., China) reactor made of quartz glass is placed between the two electrodes.

3 RESULTS AND DISCUSSION

3.1. SEM

Fig. 2 SEM images of (a) V₂C; (b) g-C₃N₄

The morphology and microstructure of the prepared catalyst were analyzed by SEM. As shown in Fig. 2(a), the V₂AlC precursor was etched in HF and freeze-dried in a liquid environment to obtain a good two-dimensional layered structure, and clearly depicted very thin two-dimensional flakes. Obviously, hydrothermal treatment transformed DCDA12-180 into a 1D hexagon. It's important to note that subsequent calcination of DCDA12-180 at 550°C produced 1D mesoporous g-C₃N₄ microtubes, retaining the 1D hexagonal microtubular morphology (Fig. 2b). Volume shrinkage occurred during high-temperature calcination, which could be attributed to the formation of a denser structure with a higher degree of polymerization.

3.2 XRD

Fig. 3 XRD patterns of as-obtained catalysts

X-ray diffraction technology was used to analyze the phase and crystal structure of the catalyst. The analysis results are shown in Fig. 3, and the results confirmed the successful synthesis of CN, V₂C and V₂C/CN composite. Two main XRD peaks can be clearly found in the V₂C spectrum, corresponding to approximately 13.6° and 41.2° respectively. And after HF etching, a new XRD peak appeared at about 7.1°, corresponding to the (0002) crystal plane of V₂C, indicating the successful synthesis of V₂C¹⁵. There are two typical XRD peaks of graphite phase carbon nitride in the CN spectrum, at about 13.0° and 27.8°, corresponding to the in-plane tri-s-triazine motifs packing of CN and the interlayer of conjugated aromatic segments, respectively²⁰. Due to the weak strength and low V₂C content, the (0002) crystal plane of V₂C is not observed in the V₂C/CN composite, but other

characteristic peaks of V₂C and CN can be clearly found on the spectrum. It shows the successful synthesis of V₂C/CN.

3.3 TG

As shown in Fig. 4, the thermogravimetric curves of V₂C, CN, and CV-3 from 25°C to 800°C in a nitrogen atmosphere were characterized. The results showed that the weight loss rate of the catalyst decreases in

Fig. 4 TGA curves of V₂C, CN, and CV-3 composite the following sequence: CN (100%)>V₂C (15.97%)>CV-3 (8.85%). It can be seen that the thermal stability of CV-3 is much higher than that of CN and V₂C. The thermal decomposition process of V₂C is divided into two stages. The first stage occurred at 280°C. Most of the decomposition is attributed to the loss of crystalline water and water adsorbed by the stream. The second stage is from about 300°C to 800°C. °C, due to the loss of OH/O/F functional groups, in this process, OH/O/F is released in the form of H₂O, O₂, HF¹⁶. CN was decomposed once at about 550°C to 750°C. At this time, the structure of CN was completely destroyed and CN was completely decomposed²¹. The thermal decomposition

process of CV-3 can be divided into three stages, including the decomposition of oxygen-containing functional groups produced by the mutual bonding of V₂C and CN (430°C to 530°C), the decomposition of functional groups in V₂C and the collapse of CN structure (530°C to 630°C) and the decomposition of CN (630°C to 700°C). It can be concluded that the addition of V₂C greatly improves the thermal stability of CN, enabling it to maintain a relatively stable structure at high temperatures.

3.4 XPS

XPS was used to analyze the surface atomic composition and valence of C/V-3. The measured energy spectrum of C/V-3 clearly shows that the synthesized composite material contains V, N, O and C elements (Fig. 5(a)), indicating the formation of V₂C/CN phase. By analyzing the N 1s peak (Fig. 5(c)), it was determined that the binding energies of N 1s were 398.67 eV and 400.20 eV, 401.30 eV, respectively, which can be attributed to C-N=C, N-(C)₃, C-N-H²⁰. For O 1s (Fig5. (b)), the observed peak can be decomposed into four components, including C-V-OH_x(532.01 eV), C-V-O_x (532.40 eV), C=O(533.66 eV) and VO_x (530.15 eV)²¹. The deconvoluted V 2p (Fig5. (d)) shows V 2p_{1/2} at 513.51 eV and V 2p_{3/2} at 521.41 eV, indicating the presence of V²⁺, which can be attributed to the remaining unreacted MAX phase in the prepared MXene and the same binding energy the overlap of the lower V-C peak. V 2p_{1/2} at 516.62 eV and V 2p_{3/2} at 524.86 eV correspond to V⁴⁺ and VO₂(P) of V₂C, respectively¹⁹. The C 1s area (Fig5. (e)) shows the existence of V-C (284.89 eV), C-C (288.47 eV), C-OH (286.60 eV) and C=O (293.43 eV). XPS analysis results further prove that V₂C has been successfully compounded on the CN substrate.

Fig. 5 (a) XPS survey spectra and high-resolution XPS spectra of (b) O 1s; (c) N 1s; (d) V 2p; (e) C 1s

3.5 Denitration experiment

The denitration effect of all samples is significant, and reaches the maximum value quickly within the first 6 minutes. Then, with the reduction of NO and the

formation of by-products, the by-products gradually blocked the reaction sites of the catalyst, and the denitration performance began to slowly decrease and finally reached an equilibrium value. The results show that the V₂C/CN-NTP system has better denitration performance than the single NTP system (28.1%), the

CN-NTP system (35.2%) and the V₂C-NTP system (60.6%). Among them, the V₂C/CN-NTP system showed the best denitration performance, which was 2.1 and 1.2 times that of the CN-NTP system and the V₂C-NTP system, respectively. Therefore, it also proved that there is a synergistic effect between V₂C/CN and NTP (as shown in the Fig. 6).

Fig. 6(a)Removal of NO with different treatment process. Conditions: simulated flue gasN₂/O₂/NO=72%/8%/20%
(b) Comparison of V₂C、CN and CV-3 coupled NTP removal NO efficiency

3.6 BET

As shown in the Fig. 7, the specific surface area and pore structure of g-C₃N₄, V₂C and C/V-3 composite materials were studied by the N₂ adsorption-desorption analysis method. Although the three samples have type IV isotherms with H3 hysteresis loops, verifying the existence of the mesoporous structure, their specific surface area and pore volume are relatively low (as shown in the table. 1). A sharp peak from 2 to 20 nm is observed in the pore size distribution curve (as shown in

Fig. 7 N₂ adsorption-desorption isotherm of (a)g-C₃N₄; (b) C/V-3; and (c) V₂C and corresponding BJH PSD curves(inset)

the figure 7(a)).This indicates that g-C₃N₄ has a relatively uniform pore distribution and mesoporous characteristics²⁰. Interestingly, the specific surface area of the binary C/V-3 composite material and the pore volume is higher than that of a single CN and V₂C. This may be due to the formation of CN between the V₂C layers that will expand the V₂C layers and increase the BET specific surface area and pore volume. The high specific surface area can provide abundant active reaction sites. And promote more NO molecules to be adsorbed on its surface²². Therefore, it can be concluded that compared with a single sample, the specific surface area helps to improve the photocatalytic activity, but it is not the key to improving the photocatalytic efficiency of the system Factors. As shown in the table.1,

Table. 1 Textural Properties of V₂C, g-C₃N₄, and C/V-3

sample	S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)
V ₂ C	5.1890	0.04
g-C ₃ N ₄	34.2663	0.087
C/V-3	44.6565	0.25

Compared with the pure CN sample, the SBET of C/V-3 increased by 39.4675m²g⁻¹and V_{total} increased by 0.21cm³g⁻¹, which indicates that the large S_{BET} and excellent adsorption performance of the composite are due to g-C₃N₄. In general, the adsorption capacity of the catalyst is significantly improved. The improved NO adsorption function can promote the photocatalytic oxidation process²³.

4 Mechanism analysis

As shown in the fig.8, the mechanism of the V₂C/g-C₃N₄-NTP synergistic effect was studied. The high-energy electrons generated by the plasma convert N₂ into N* and adsorbed N₂(eq 2). In addition, due to the active groups generated during the discharge process, g-C₃N₄ is excited, and the electrons in the valence band position of g-C₃N₄ are excited to conduction. The electrons in the conduction band of g-C₃N₄ are transferred to the valence band of V₂C due to the built-in electric field, and the holes are formed in the valence band, which significantly enhances the separation of electrons and holes²⁴. Part of the high-energy electrons

can also be injected into the conduction band of g-C₃N₄ by hitting its surface. The electrons and injected electrons participate in the conversion process of NO adsorbed on the surface of the g-C₃N₄ catalyst. Finally, NO is reduced to produce N₂ and O₂(eqs 3-5). At the same time, the O* and O₃ produced during the reaction oxidize NO to intermediate product NO₂(eq 6), and then NO₂ reacts with N* to be reduced to N₂ and O₂(eqs 7-11). Therefore, the high-energy electric field generated by the plasma can also effectively separate electrons and holes. In return, the g-C₃N₄ catalyst changed the discharge method and made the discharge more uniform. This synergistic effect improved the NO conversion rate and energy efficiency¹⁰.

Fig. 8 Reaction mechanism

5 Conclusions

In this work, a new g-C₃N₄/V₂C MXene catalyst has been successfully synthesized, and used for plasma denitration technology for the first time. The optimized

composite C/V-3 showed an improved NO removal of 83.3% in the high-energy electric field, which is 1.2 and 2.1 times higher than V₂C-NTP and g-C₃N₄-NTP systems alone, respectively. The electrons transferred to V₂C and the injected electrons react with the generated active

groups to reduce NO to N₂ and O₂. G-C₃N₄ can be excited by high-energy electric field and then can transfer electrons to V₂C MXene which facilitates the separation of electron-hole pairs. The synergistic effects of catalysts-plasma system promoted the transfer of electrons. The results of this study reveal the significant potential of V₂C MXene for application in the denitration technology field.

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