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Short communication

Vanadium oxides anchored on nitrogen-incorporated carbon: An efficient heterogeneous catalyst for the selective oxidation of sulfide to sulfoxide



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A B S T R A C T
A highly efficient and durable metal catalyst stabilized by proper support is vital for organic catalytic trans- formations. In this study, a sequential pyrolysis–acid etching strategy was reported to prepare a nitrogen-rich nanocarbon inlaid with vanadium oxide catalyst (V@CN-750), which was evolved from the preassembly of a chitin – V precursor. V@CN-750 exhibited excellent activity and selectivity of 96% and 98%, respectively, for catalytic oxidation of thioanisole to sulfoxide at 40 °C for 8 h, which is considerably superior to that of V ₂ O ₂ paparenticles and homogeneous VO(acco). Moreover, V@CN-750 can be recycled at least eight times without

1. Introduction

Vanadyl acetylacetonate, [VO(acac)₂], has often been used as a homogeneous catalyst for several organic oxidation reactions, including hydroxylation of benzene [1,2], epoxidation of olefins [3], oxidative dehvdrogenation of amines and aldehvdes [4], and selective oxidation of thioanisole and styrene [5]. Although it usually exhibits high activity and selectivity during these transformations, $VO(acac)_2$ itself is entirely dissolved in the reaction medium, resulting in a difficult catalyst recovery and repeated use [6-8]. To overcome these problems, immobilization of VO(acac)₂ molecules onto porous supports, such as activated carbon, clay, and periodic mesoporous organosilica, via the reaction between the carbonyl group of the acetylacetonate ligand and amino group pre-grafted onto the material surfaces, has been widely investigated [9-15]. However, the procedure for preparing most of these functionalized supports is complicated. Further, in many cases, the pre-pendant amino groups may block the pore channel of the prepared porous catalyst, which compromises the catalytic activity. Therefore, finding other supports that tether with abundant anchoring sites and can be used to stabilize the catalytically active species, such as vanadium oxide sites derived from VO(acac)₂, and fabricating highperformance heterogeneous catalysts with leaching-resistant properties are still challenging.

Chitin, a long-chain polymer of *N*-acetylglucosamine, is a derivative of glucose [16]. Owing to its attractive physiochemical properties, such as its low cost, eco-friendliness, and abundance, it has vast potential for

a myriad of applications [17,18]. Notably, there are several amino and hydroxyl groups in its structure that can help trap metal ions owing to their strong binding affinity. Therefore, chitin has great potential as both carbon and nitrogen precursors for the derivation of N-incorporated carbon inlaid with metal catalysts by taking full advantage of its high coordination ability with metal ions and carbon metabolism, and thereby achieving high activity and stability. However, for organic catalysis, application of chitin as precursors for deriving N-incorporated carbon implanted with metal active sites as heterogeneous catalysts has not been sufficiently investigated [19].

Selective oxidation of sulfide to sulfoxide is an important organic reaction that plays an indispensable role in the production of medical intermediates and fine chemicals [20]. Till date, many metal-based catalysts have been studied for sulfide selective oxidation, such as Nb, Mo, W, Fe, Ti, and V, in the presence of a suitable oxidant [21-26]. Despite this considerable progress, sulfoxide synthesis with high selectivity still encounter a major challenge owing to the unavoidable over oxidation (see Scheme S1 in the Supporting Information) [21]. Herein, a novel method to prepare N-incorporated carbon-supported V catalyst (V@CN-750) is reported via in situ pyrolysis of chitin and the VO(acac)₂ complex at 750 °C followed with dilute HCl etching. Furthermore, V@CN-750 was used for selective oxidation of sulfide to sulfoxide to investigate the active phase and stability. Results indicate that the V@CN-750 catalyst exhibits superior activity, selectivity, and recyclability for the conversion of sulfide to the corresponding sulfoxide with tert-butyl hydroperoxide (TBHP) as an oxidant. It is believed that

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Fig. 1. (a) UV Raman spectra of CN and V@CN-750, (b) TEM image and high-resolution XPS spectra of (c) N 1 s and (d) V 2p for V@CN-750.

the strong interaction between the highly dispersed vanadium sites and nitrogen dopant are responsible for the good catalytic properties of the prepared V@CN-750.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of the V@CN material

In a typical experiment, chitosan (2.0 g) and VO $(acac)_2$ (0.3 g) was added in sequence to 2-wt% acetic acid solution (120 mL). After the solids were thoroughly dissolved, the solution was continuously stirred at 80 °C for 6 h to form a gel-like mixture. Then, it was dried in an oven at 120 °C for 12 h. Subsequently, pyrolysis process was conducted in a tube furnace under N2 atmosphere (80 mL/min) at a heating rate of 2.3 °C/min from room temperature to 750 °C and kept at this temperature for 4 h. After the system was naturally cooled down to room temperature, the obtained solid was transferred to a 1-M HCl solution and refluxed at 60 °C for 6 h. Finally, the product was collected by filtration, washed several times with distilled water and absolute ethanol, and dried overnight in an oven at 120 °C; V@CN-750 was obtained as the resulting black solid. The products obtained at different pyrolysis temperatures, i.e., 650 °C and 850 °C, were prepared and denoted as V@CN-650 and V@CN-850, respectively. The N-incorporated carbon (CN) support was synthesized by annealing pure chitosan at 750 °C using the same method used for the preparation of V@CN.

2.2. General procedure for the activity test

Catalytic oxidation of sulfide was conducted in a 10 mL tube.

Typically, 1 mmol of sulfide, 3 mL of CH₃CN (solvent), and 20 mg of V@CN-750 were added to the tube. The reaction was set to start upon the addition of 1.5 mmol of TBHP as the oxidant at 40 °C under magnetic stirring (1000 rpm). To monitor the reaction kinetics, a set of parallel experiments were conducted simultaneously, and sampled at regular intervals. The liquid mixtures were analyzed on a gas chromatograph (Agilent GC-7890B) equipped with a flame ionization detector and a capillary column (DB-5, 30 m \times 0.45 mm \times 0.42 µm) at certain reaction intervals using toluene as the internal standard.

General procedure for the recyclability test: After each reaction, the catalyst was collected from the reaction system via filtration. Then, the recovered catalyst was rinsed with acetone six times, dried at 120 $^{\circ}$ C for 12 h, and then subjected to the next reaction cycle.

3. Results and discussion

3.1. Catalyst characterization

Catalyst was prepared based on the utilization of amino and hydroxyl group-rich chemistry to trap the vanadium oxides and simultaneously derive the N-incorporated carbon amorphous structure. To achieve this goal, three steps are involved in the current strategy: (i) forming a chitosan – V precursor, (ii) carbonizing the chitosan–V precursor at high temperature under an inert atmosphere, and (iii) removing unstable species by diluted HCl etching. The X-ray diffraction (XRD) pattern of the prepared V@CN-750 showed only two broad peaks at 24° and 43° (Fig. S1), corresponding to the (002) and (004) planes of graphitized carbon, respectively [27]. The carbon support was formed due to the annealing of chitosan, which was used to chelate with vanadium oxides [17]. Moreover, no other crystalline V-based diffraction peaks were observed, probably due to the formation of noncrystalline phases. In accordance with the XRD result, the visible Raman spectrum of V@CN-750 showed only two characteristic bands at approximately 1352 and 1595 cm⁻¹ (Fig. S2), which were attributed to the disordered/defected carbon (D band) and graphitic carbon (G band), respectively [28]. These defects can serve as anchor sites to bind and highly disperse the metal species, which are beneficial for enhancing the catalytic performance of derived V@CN-750 [26].

Fig. 1a shows the ultraviolet (UV) Raman spectra of CN and V@CN-750. The CN support did not show any Raman signals, whereas V@CN-750 displayed two broad bands at 896 and 1003 cm^{-1} , which were attributed to V-O-V and V=O stretching modes of the vanadate species, respectively [29]. As shown in Fig. S3, the scanning electron microscopy (SEM) image of V@CN-750 clearly displayed an irregular sheet structure and energy-dispersive X-ray (EDX) spectroscopy elemental mapping revealed the uniform distribution of C, N, and V over the entire carbon skeleton. No apparent nanoparticles were observed via transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis (Fig. 1b and Fig. S4), implying that the vanadium oxide species were highly distributed on the CN support. The particle size of the catalyst was within 75 to 100 µm determined by using a laboratory standard vibrating screen. Based on the ICP-AES analysis, the actual vanadium content in V@CN-750 was 7.1 wt% (Table S1), slightly lower than the result obtained by TGA (Fig. S5). The specific surface area of V@CN-750 was calculated to be 23.1 m²/g (Table S1).

Then, we analyzed the high-resolution N 1 s, V 2p, and O 1 s X-ray photoelectron spectroscopy (XPS) spectra of V@CN-750 to reveal the N, V, and O chemical environments. The N 1 s spectra could be deconvoluted into four peaks assignable to the pyridinic N (398.9 eV), pyrrolic N (399.9 eV), graphitic N (401.2 eV), and oxidized N (403.1 eV) [30,31], indicating that N was structurally integrated into the carbon matrix (Fig. 1c). The XPS percentages showed that the nitrogen content in V@CN-750 was approximately 6.9 atom% (Table S1). The high N content provided good wettability, which promoted the full contact between the catalyst and substrate, thereby boosting the catalytic performance [32-34]. The XPS spectrum of the V 2p region in V@CN-750 showed binding energies of V 2p1/2 and V 2p3/2 at 524.3 and 516.5 eV (Fig. 1d), respectively, which indicated the presence of V(IV) in the derived carbon networks [30,31]. This was essentially similar to the V 2p band profile of [VO(acac)₂] [13]. Furthermore, O 1 s XPS spectra in Fig. S6c can be fitted into three main peaks centered at 531.1, 532.4, and 533.2 eV, which are corresponding to V-O-N, O-C=O, and C-O bonds, respectively [30-32]. The peaks at 531.1 eV for V-O-N bond shows the formation of vanadium oxide on CN surface (Fig. S6 and Tables S3 and S4), which agrees with the analysis of V 2p3/2 XPS spectra.

Then, catalytic oxidation of thioanisole to sulfoxide was exploited as a model reaction to investigate the catalytic performance of V@CN-750. The kinetic profile was recorded and is shown in Fig. 2. The conversion of thioanisole increased rapidly during the first 4 h, whereas the selectivity was kept as 99% to that of sulfoxide. For V@CN-750, a high thioanisole conversion of 96% with a sulfoxide selectivity of 98% was achieved at 40 °C for 8 h. Notably, a limited amount of the deep oxidation product, methyl phenyl sulfone, was detected as the only byproduct during the oxidation process.

The catalytic oxidation performances of various catalysts are compared in Table 1. Almost no reaction occurred in a blank experiment (without catalyst), in the presence of the pure CN support, and in the absence of TBHP (entries 1, 2, and 8), showing that a suitable catalyst and oxidant are essential for sulfoxidation. For comparison, V@CN-650 and V@CN-850 were also prepared and characterized. The corresponding results are shown in Figs. S7–S15 and Tables S1–S4. These results suggest that the control catalysts have similar V contents and morphological features to those of V@CN-750. When applied to this reaction, these two catalysts exhibited slightly lower performances than V@CN-750 (entries 3 and 5). The higher activity of V@CN-750 is likely



Fig. 2. Conversion and selectivity of thioanisole for sulfoxide as a function of reaction time over V@CN-750.

Table 1	
Selective oxidation of thioanisole to sulfoxide with TBHP on various ca	atalysts

Catalyst	Time (h)	Conversion (%)	Selectivity (%)
Blank	8	1	100
CNs	8	2	100
V@CN-650	8	90	97
V@CN-750	8	96	98
V@CN-850	8	92	97
V_2O_5	4	93	70
VO(acac) ₂	4	92	61
V@CN-750	8	1	100
	Catalyst Blank CNs V@CN-650 V@CN-750 V@CN-850 V ₂ O ₅ VO(acac) ₂ V@CN-750	Catalyst Time (h) Blank 8 CNs 8 V@CN-650 8 V@CN-750 8 V@CN-850 8 V2O5 4 VO(acac)2 4 V@CN-750 8	Catalyst Time (h) Conversion (%) Blank 8 1 CNs 8 2 V@CN-650 8 90 V@CN-750 8 96 V@CN-850 8 92 V_2O_5 4 93 VO(acac)_2 4 92 V@CN-750 8 1

^a In the absence of TBHP.

associated with its relatively higher content of N species (Table S2) [25,26]. The catalytic performance of V_2O_5 was also tested. It showed 93% conversion after 4 h with 70% conversion to sulfoxide (entry 6). Furthermore, VO(acac)₂ also showed a relative lower catalytic activity and selectivity (entry 7). Herein, V@CN-750 could achieve this transformation with a high activity and selectivity under mild conditions, thereby promoting the development of selective oxidation of sulfides to sulfoxides. The excellent catalytic properties of V@CN-750 are likely owing to the combination of abundant nitrogen dopant and well-dispersed vanadium sites encapsulated in the carbon skeletons [13].

Based on the above results and previous work [15], a possible reaction mechanism for the selective oxidation of sulfide is briefly described as follows: initially, in V@CN-750, the vanadium sites that coordinated with the adjacent nitrogen functionalities interacts with the active oxygen atom of TBHP to obtain oxygenated intermediate. Subsequently, the intermediate species experience nucleophilic attack by sulfur molecules, followed by concerted oxygen intermolecular transfer. Finally, it results in the formation of sulfoxide simultaneously with the regeneration of V@CN-750.

The durability of V@CN-750 was also tested. As shown in Fig. S16, the catalytic activity and selectivity remained almost unchanged for at least up to eight reaction cycles, confirming the excellent recyclability of the developed catalyst. A hot filtration experiment was also conducted and distinctly excluded the potential leaching problem of the active V-species from the V@CN-750 catalyst (Fig. S17). Moreover, XRD, SEM, TEM, and XPS measurements of the catalyst after the reaction were also performed (Figs. S18–S21). No obvious changes were observed compared with the fresh one, thereby confirming that V@CN-750 exhibited excellent stability under the investigated catalytic conditions.

We subsequently explored the generality of V@CN-750 in the

Table 2

Scope of substrates in the catalytic oxidation of sulfides in the presence of TBHP catalyzed by V@CN-750.

Entry	Sulfide	Time (h)	Conversion (%)	Selectivity (%)
1	S S	8	96	97
2	S S	8	95	96
3	S S	8	99	96
4	F S	8	97	96
5	Cl ² S	8	97	96
6	Br	9	98	99
7	S CI	10	92	97
8	S S	15	96	96
9	0 S	24	89	98
10	HO ~ S	24	68	94
11		24	73	92

Reaction conditions: sulfide (1 mmol), TBHP (1.5 mmol), catalyst (20 mg), MeCN (3 mL), and temperature (40 °C).

selective oxidation of diverse aromatic sulfides at the same temperature. As listed in Table 2, in general, various aromatic sulfides bearing electron-donating and withdrawing groups, regardless of the *ortho-* or *para-*positions, could be efficiently converted to their corresponding sulfoxide with high yields. Halogen-substituted sulfide, such as those with -F, -Cl, and -Br were tolerated under the present conditions, yielding the desired sulfoxide with a 96% selectivity. Notably, even for benzyl phenyl sulfide (a bulky substitution), a high 73% conversion with 92% sulfoxide still could be achieved by prolonging the reaction time to 24 h.

4. Conclusions

We developed a reusable heterogeneous non-noble metal catalyst comprising vanadium oxides entrapped within N-incorporated carbon via a facile and cost-effective strategy. The resulting V@CN-750

demonstrated excellent catalytic activity, chemoselectivity, and stability for catalytic oxidation of sulfides to sulfoxides, which was significantly better than those of V_2O_5 nanoparticles and homogeneous VO (acac)₂, likely originating from the abundant nitrogen dopant and highly dispersed vanadium oxide species within the carbon networks.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106101.

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