

钒氮共掺杂多孔碳催化剂上苄胺氧化偶联合成亚胺

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摘要: 本工作以生物质壳聚糖作为牺牲模板, 乙酰丙酮钒为金属钒源, ZnCl_2 为造孔剂, 采用高温热解结合酸洗的策略制备出一种钒氮共掺杂多孔碳(V-N-C)催化剂。表征结果表明, V-N-C催化剂的比表面积高达 $1470 \text{ m}^2 \cdot \text{g}^{-1}$, 孔容为 $1.06 \text{ cm}^3 \cdot \text{g}^{-1}$, 质量分数为0.19%的钒物种可能以单原子 VN_x 形式高度分散在载体上。在苄胺氧化偶联合成亚胺的反应中, V-N-C表现出高催化性能, 底物苄胺的转化率和产物亚胺的选择性均为99%, 性能明显优于均相 $\text{VO}(\text{acac})_2$ 和多相 V_2O_5 催化剂。此外 V-N-C 催化剂连续重复使用9次也未出现任何活性衰减的问题, 且对一系列含有不同官能团的底物也具有优良的普适性。机理研究表明, 苄胺和氧气首先分别在催化剂 VN_x 和缺陷位点活化成苄基亚胺和 H_2O_2 中间体, 然后苄基亚胺与苄胺缩合脱 NH_3 生成目标产物亚胺。

关键词: 选择性催化氧化; 多相催化; 钒氮共掺杂多孔碳; 氧化偶联

中图分类号: O614.51; O643.36

文献标识码: A

文章编号: 1001-4861(2022)06-1049-10

DOI: 10.11862/CJIC.2022.112

Synthesis of Amines by Oxidative Coupling of Benzylamine over a Vanadium-Nitrogen Co-doped Porous Carbon Catalyst

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Abstract: Synthesis of imine compounds via benzylamine oxidative coupling has become one of the most ideal methods due to its high atom economy and environmental friendliness. The key is to develop high-performance non-noble metal-based heterogeneous catalysts. In this work, a vanadium-nitrogen co-doped porous carbon (V-N-C) catalyst was prepared via high-temperature pyrolysis (900 °C for 2 h in an inert atmosphere) combined with acid-leaching (1 mol·L⁻¹ HCl solution at 120 °C for 12 h) approach by using biomass chitosan as the sacrificial template, vanadium acetylacetonate as the source of metal vanadium, and ZnCl_2 as the pore-forming agent. Various characterization techniques including a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) investigation were used to analyze the composition, structure, vanadium species size, content, and other physical and chemical properties of the catalyst, and its catalytic performance was evaluated in the oxidative coupling reaction of benzylamine. The characterization results showed that the specific surface area of the V-N-C catalyst was as high as $1470 \text{ m}^2 \cdot \text{g}^{-1}$, the pore volume was $1.06 \text{ cm}^3 \cdot \text{g}^{-1}$, and the mass fraction of the vanadium species was 0.19% that were highly dispersed on the support likely in the form of single atoms (VN_x). In the oxidative self-coupling reaction of benzylamine to the imine (reaction conditions: toluene as solvent, 110 °C, $1.01 \times 10^5 \text{ Pa}$ O_2 , 12 h), the developed V-N-C exhibited excellent activity (99%), exclusive selectivity (99%), outperforming the homogeneous $\text{VO}(\text{acac})_2$ and heterogeneous V_2O_5 catalysts. Moreover, V-N-C was repeatedly used 9 times without any decay

收稿日期: 2022-01-12。收修改稿日期: 2022-04-14。

国家自然科学基金(No.21576243)资助。

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in reactivity and stability. Furthermore, V-N-C presented excellent universality for a series of substrates containing different functional groups. Mechanism studies indicated that the reaction steps were involved in the initial formation of benzylimine and H_2O_2 intermediates by activating benzylamine and oxygen molecules, respectively, on the VN_x and defect sites of V-N-C, then benzylimine and benzylamine condensed to release an NH_3 molecule to generate the target product imine.

Keywords: selective catalytic oxidation; heterogeneous catalysis; vanadium-nitrogen co-doped porous carbon; oxidative coupling

0 引言

亚胺是含有 $\text{C}=\text{N}$ 双键结构的杂环化合物,在环化、氧化还原、加成和缩合等有机反应中作为常见的中间体^[1]。含有杂原子(氧、硫、磷等)的亚胺配体可以与金属离子形成金属配合物,应用于一系列具有生物和药理活性的化合物、杂环或者天然产物的合成^[2-4]。传统亚胺主要是通过均相路易斯酸催化剂的作用下进行伯胺和羰基化合物的缩合反应来获得^[5-6],其缺点是反应过程需要加入脱水剂和使用不稳定的醛基原料来提高反应效率,导致底物利用率低、操作复杂以及对环境造成污染等^[7]。在有氧化剂的条件下,通过胺的氧化偶联合成亚胺是一条绿色的路线。近年来已有许多催化体系被报道,包括贵金属催化剂^[8-11]、光催化剂^[12-14]等,但上述大多数反应存在产率或选择性较低、反应条件相对苛刻、底物适用范围受限等不足。因此,从绿色和可持续的化学观出发,亟待开发一种新型绿色高效的过渡金属催化剂。

过渡金属(M)与杂原子氮共掺杂多孔碳(M-N-C)材料是一类具有广阔应用前景的催化剂,其多孔碳骨架结构有利于反应物和产物的吸附/扩散,从而提高催化活性^[15-18]。而杂原子N的孤对电子可以捕获金属中心,形成稳定的金属活性位点,因而可高效催化多种有机反应^[19-20]。壳聚糖作为可再生生物物质,其结构中含有氨基和羟基功能性基团,具有较强的配位能力,可有效螯合金属离子。壳聚糖-金属配合物衍生材料不仅部分继承载体材料的特点,还有望保留金属中心高度分散的特性,是制备过渡金属基与氮共掺杂碳材料的理想前驱体^[21-23]。此外,在壳聚糖碳化处理过程中,引入造孔剂 ZnCl_2 ,既可有效降低焦油的产生^[10],还可以促进C、H、O间的交联反应,有助于形成多孔结构,增大材料的比表面积^[24],进而提高催化活性和选择性。

以生物物质壳聚糖为牺牲模板, $\text{VO}(\text{acac})_2$ 为金属钒源, ZnCl_2 为活化造孔剂,采用碳热处理结合酸洗

的策略合成出一种高比表面积的钒氮共掺杂多孔碳(V-N-C)催化剂。考察了该催化剂在以 O_2 为氧化剂、甲苯为溶剂的苄胺及其衍生物氧化偶联反应中的催化性能,并初步推测了可能的反应机理。

1 实验部分

1.1 主要试剂

壳聚糖于国药集团化学试剂公司购买;乙酰丙酮钒、氯化锌于上海迈瑞尔化学技术有限公司购买;甲苯、*N,N*-二甲基甲酰胺、苄胺、对甲氧基苄胺、对甲基苄胺、2-甲基苄胺、3-甲基苄胺、对叔丁基苄胺、4-氟苄胺、4-氯苄胺、4-溴苄胺、4-三氟甲基苄胺、苯胺、3-吡啶甲胺、噻吩2-甲胺、糠胺、正己胺、1,2,3,4-四氢喹啉、二苄基胺、环己胺于上海阿拉丁公司购买;邻氨基苯硫酚、2-氨基苯硫酚、对甲氧基苯胺、对氯苯胺、对甲基苯胺购自北京伊诺凯公司。以上试剂均为分析纯,高纯 N_2 (99.999%) 于上海大通气体有限公司购买。

1.2 催化剂表征

采用X射线衍射仪(XRD, D8 Advance型)分析了催化剂的晶体结构,表征条件:工作电压为40 kV,电流40 mA,辐射源为Cu靶 $K\alpha$ 射线,波长为0.154 2 nm, 2θ 范围为 $2^\circ \sim 80^\circ$ 。通过拉曼光谱仪(Renishaw RM 10000, 532 nm)对样品的石墨化程度和缺陷程度进行了分析。采用配有E-1030喷金装置的扫描电子显微镜(SEM, S-4800型, 5 kV)和透射电子显微镜(TEM, JEM-2100F, 200 kV)对样品的形貌进行了表征。利用球差校正的高角度环形暗场扫描透射电子显微镜(HAADF-STEM, FEI Themis Z)探究催化剂中金属物种的尺寸及分散情况。采用物理吸附仪(Micromeritics ASAP 2020型)测定 -196°C 时催化剂的氮气吸附-脱附等温线。使用X射线光电子能谱仪(XPS, Thermo ESCALAB 250XI)获得样品元素价态,表征条件:辐射源为Al $K\alpha$ 射线(1 486.6 eV),系统真空度低于 1.0×10^{-7} Pa。采用电感耦合等离子体

发射光谱仪(ICP-AES, iCAP 7400, Thermo, USA)测定金属含量。

1.3 催化剂制备

V-N-C 催化剂的制备:将 2 g 壳聚糖溶解在 120 mL 0.5% 乙酸溶液中,再加入 6.5 g 氯化锌和 20 mg 乙酰丙酮钒,搅拌混匀,80 ℃水浴条件下回流反应 8 h。然后将样品转入冷冻干燥机中进行干燥处理 12 h。将干燥的样品研磨后置于刚玉舟中,放于管式炉,在 N_2 气氛下,以 $3\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ 升温到 900 ℃,进行碳

化处理 2 h。随后将样品转移到装有 50 mL $1\text{ mol}\cdot\text{L}^{-1}$ HCl 溶液的圆底烧瓶中,120 ℃油浴条件下酸洗 12 h,去除不稳定的金属或者金属氧化物,冷却后抽滤洗涤,放入真空烘箱 120 ℃干燥 12 h,可得黑色固体,将其命名为 V-N-C。制备示意图如图 1 所示。氮共掺杂多孔碳材料(N-C)的制备:采用上述相似的方法,只是在合成中不添加金属钒源,制得黑色固体为 N-C。

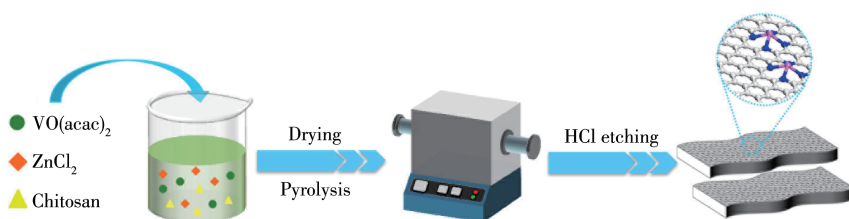


图1 V-N-C催化剂的合成示意图

Fig.1 Schematic illustration of the synthesis process of V-N-C catalyst

1.4 苄胺氧化偶联反应

称取 30 mg V-N-C 催化剂,量取 3 mL 甲苯和 0.5 mmol 苄胺,并依次加入到 10 mL 的 Schlenk 管中并连通氧气袋。在反应前,先用氧气置换试管内的空气(重复 3 次),随后将反应管置于 110 ℃的油浴锅中开始计时进行反应。定时取样,液相混合物在配有火焰离子化检测器和毛细管柱(HP-5, 30 m $\times$ 0.32 mm $\times$ 0.25 μm)的气相色谱(Agilent GC-7890B)上进行定量分析,以联苯为内标物。分析条件:载气为氮气,柱流速为 $1\text{ mL}\cdot\text{min}^{-1}$,进样口和检测器温度均为 280 ℃,进样口分流比是 50:1,柱箱程序升温,初始温度为 60 ℃,以 $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ 的升温速率升至 200 ℃并保持 4 min。转化率、选择性、转换频率(TOF)的计算公式: $\text{Conversion}=(n_0-n_s)/n_0\times 100\%$, $\text{Selectivity}=n_a/(n_a+n_b)\times 100\%$, $\text{TOF}=n_s/(n_c t)$, 其中 n_0 为底物苄胺初始物质的量, n_s 为底物苄胺的物质的量, n_a 为产物亚胺的物质的量, n_b 为副产物的物质的量, n_c 为催化剂的物质的量, t 为反应时间。所得产物经气相色谱-质谱联用仪(GC-MS, Agilent 7890N-5975)确认。

2 结果与讨论

2.1 催化剂表征

图 2a 为 V-N-C 和 N-C 的 XRD 图,在 23.5° 和 43.0° 处均出现 2 个明显的衍射峰,归属于无定型碳的(002)和(101)晶面^[25-26],说明 V-N-C 和 N-C 均属于部

分石墨化 C 基材料。此外,在图中并未发现 V 物种的特征衍射峰,说明催化剂中 V 物种分散度较高且颗粒尺寸较小。如图 2b、2c 所示,样品 V-N-C、N-C 的 N_2 吸附量均较大,且均具有微孔/介孔复合结构,比表面积分别为 $1\,470$ 和 $1\,000\text{ m}^2\cdot\text{g}^{-1}$,总的孔体积分别为 1.06 和 $0.54\text{ cm}^3\cdot\text{g}^{-1}$,较高的比表面积和多孔结构有助于反应物的吸附与扩散。通过 ICP-AES 测定 V-N-C 中金属 V 的质量分数为 0.19%。如图 2d 所示,样品 Raman 光谱中均出现 2 个较强的峰,分别位于 $1\,350\text{ cm}^{-1}$ 处的 D 带以及 $1\,598\text{ cm}^{-1}$ 处的 G 带, I_D/I_G 均为 0.99,表明在高温碳化处理和酸漂洗后不仅使样品表面形成了一定量的石墨碳结构,同时也产生大量的缺陷^[27-29]。图 2e 为 V-N-C 的高分辨率 N1s XPS 谱图,4 个光电子峰分别归属于吡啶氮(398.3 eV)、吡咯氮(399.3 eV)、石墨氮(400.7 eV)和氧化氮(402.7 eV),表明经过高温碳化处理,壳聚糖分子中的 N 原子转化成不同的氮物种分布在碳骨架中。图 2f 为高分辨率 V2p XPS 谱图,其光电子峰很弱,说明样品中 V 含量相对较低,结果与 XRD 及 ICP-AES 相一致。由图 3a 可知,V-N-C 样品呈现不规则块状结构,也没有出现明显的晶格条纹和 V 纳米颗粒(图 3b、3c)。从图 3d 中观察到 0.5 nm 以下的孤立亮点(已用红圈标记)分散在多孔碳网中,因此我们推测 V-N-C 中 V 物种可能以单原子 VN_x 形式高度分散在碳骨架中^[30]。

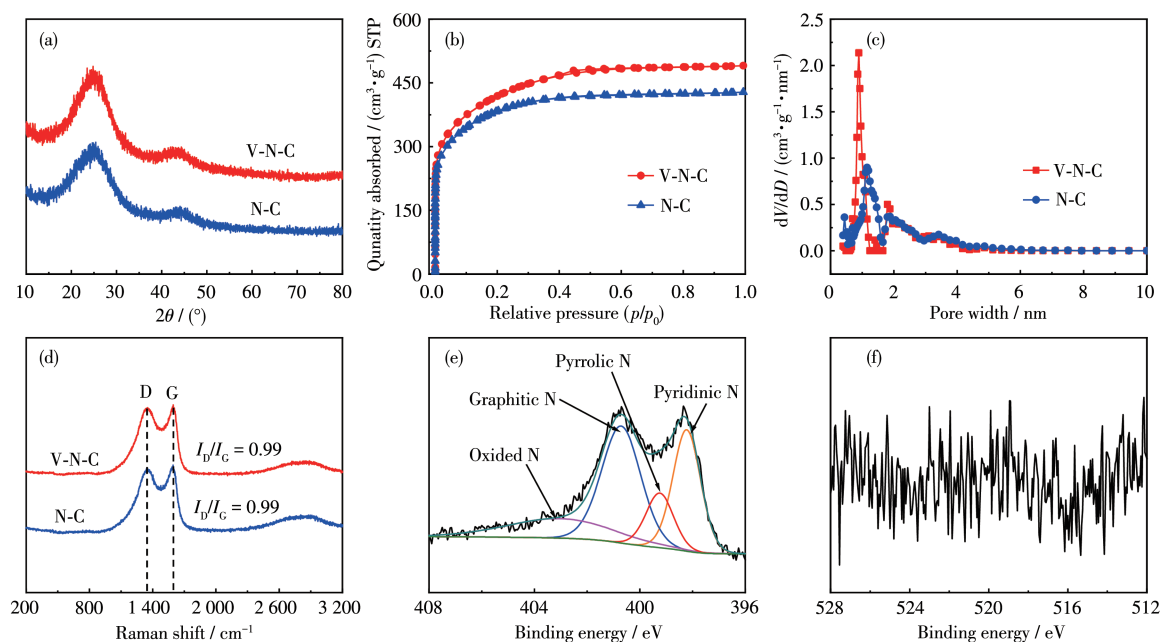


图2 V-N-C和N-C的(a) XRD图、(b) 氮气吸附-脱附等温线、(c) 孔径分布和(d) 拉曼光谱图; V-N-C的(e) N1s和(f) V2p XPS谱图
Fig.2 (a) XRD patterns, (b) N_2 adsorption-desorption isotherms, (c) pore size distributions, (d) Raman spectra of V-N-C and N-C; (e) N1s and (f) V2p XPS spectra of V-N-C

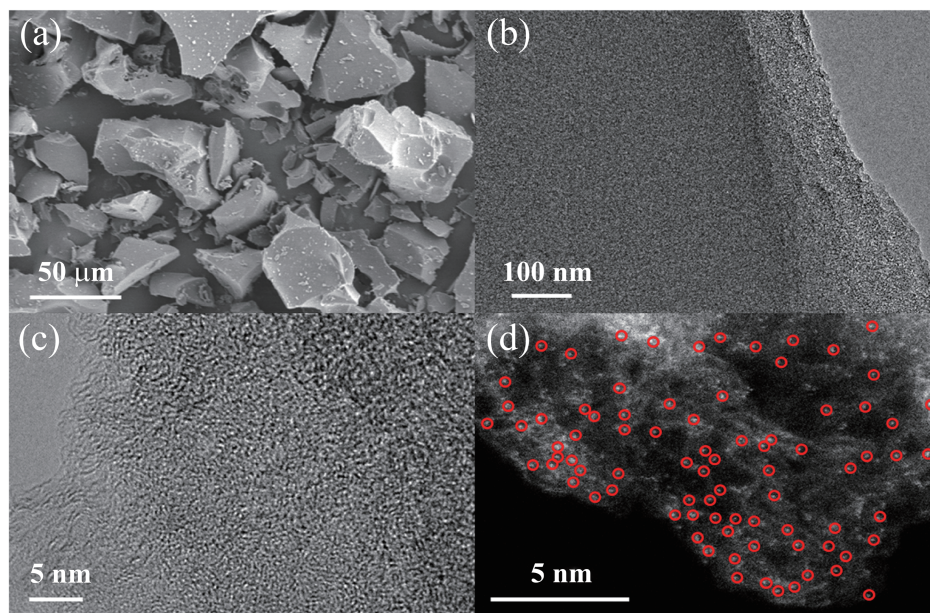


图3 V-N-C的(a) SEM图、(b) TEM图、(c) HRTEM图及(d)球差校正的HAADF-STEM图

Fig.3 (a) SEM image, (b) TEM image, (c) HRTEM image, (d) aberration-corrected HAADF-STEM image of V-N-C

2.2 催化剂反应性能

2.2.1 不同催化剂的催化效果

我们选择以 O_2 为氧化剂的苄胺偶联反应作为探针反应,评价了V-N-C催化剂的催化性能。从表1中可见,在未加催化剂或只有载体N-C的情况下,几乎没有产物的生成(表1, Entry 2、5),说明V基催化剂在反应中不可或缺。与传统催化剂 V_2O_5 和均

相催化剂 $\text{VO}(\text{acac})_2$ 相比(Entry 3、4),V-N-C催化剂的氧化苄胺转化率达99%,目标产物亚胺的选择性高达99%(Entry 1)。此外,我们还考察了V-N-C在无溶剂体系中的反应效果,通过适当延长反应时间,发现苄胺转化率仍可达94%,目标产物亚胺的选择性为99%(Entry 6)。以上结果说明呈单原子分散的V-N-C催化剂在苄胺氧化自偶联反应中具有非常高

的催化活性。而且,与已报道的催化剂(表2, Entry 1~5)相比,V-N-C催化剂展现出最高的TOF值,这可能与其高度分散的 VN_x 中心有关,也进一步说明其具有优异的催化活性。

2.2.2 底物普适性

如表3所示,对V-N-C催化剂的底物适用范围进行了拓展。含有不同官能团的苄胺衍生物均能以较高的转化率和选择性转化为相应的亚胺(表3, Entry 1~9)。对于催化含杂原子胺的氧化偶联反应也具有较高的活性(Entry 10~12)。此外,也可以促进脞性脂肪胺(Entry 13)以及仲胺的氧化偶联(Entry 14)。

2.2.3 苄胺与不同胺的交叉偶联反应

我们也评价了V-N-C在苄胺与不同胺交叉偶联合成不对称亚胺反应中的催化效果。如表4所示,其转化率几乎都达100%,选择性也较高(表4, Entry 1~4)。此外,V-N-C在催化苄胺与环状或直链脂肪胺反应中的活性分别为81%和83%,目标产物的选择性分别为84%和73%(Entry 5、6)。评价结果进一步证明了V-N-C在胺-胺氧化偶联反应中具有良好的普适性。

2.2.4 热过滤实验和重复性能

如图4a所示,采用热过滤实验来判别V-N-C中活性组分的稳定性。当反应进行到90 min时通过

热过滤快速移除V-N-C催化剂,进一步延长反应时间,发现苄胺的转化率不再增加,稳定在49%左右,说明在使用过程中未出现任何活性V物种的溶脱问题,V-N-C催化剂上进行的氧化偶联反应是完全多相催化。另外,如图4b所示,考察了V-N-C的重复使用性,催化剂循环使用9次,催化性能没有任何下降,进一步说明V-N-C具有优良的重复性能。为了进一步验证回收催化剂的稳定性,对使用后的催化剂进行了XRD和HAADF-STEM分析(图5)。发现与新鲜催化剂对比,无论是材料结构还是钒物种尺寸,使用后的V-N-C均未发生明显变化,证实V-N-C催化剂在所考察的催化条件下具有良好的稳定性。

2.2.5 反应机理初探

结合实验结果和文献报道^[35-37],我们推测了V-N-C催化剂上苄胺合成亚胺的可能反应机理,如图6所示。在反应初期,苄胺在 VN_x 位点活化转化为苄基亚胺 $\mathbf{1b}$ ^[30],氧气分子在缺陷位点活化形成中间物 H_2O_2 ^[35]。此时,苄基亚胺 $\mathbf{1b}$ 可通过2条路径得到亚胺 $\mathbf{1c}$ 。路径A: $\mathbf{1b}$ 与另一分子 $\mathbf{1a}$ 缩合脱去 NH_3 生成目标产物 $\mathbf{1c}$;路径B: $\mathbf{1b}$ 与水作用生成苯甲醛,苯甲醛与另一分子 $\mathbf{1a}$ 缩合脱 H_2O 生成目标产物 $\mathbf{1c}$ 。

我们采用比色法^[4]验证反应中产生的中间体 H_2O_2 ,由于 H_2O_2 可将过氧化物酶(POD)氧化,随后N,N-二乙基对苯二胺硫酸盐(DPD)被POD氧化为阳离

表1 不同催化剂在苄胺氧化自偶联中的催化性能

Table 1 Catalytic properties of various catalysts for oxidative self-coupling of benzylamine

Entry	Catalyst	Conversion / %	Selectivity / %	TOF / h^{-1}
1 ^a	V-N-C	99	99	36.51
2 ^a	N-C	2	99	0
3 ^a	$\text{VO}(\text{acac})_2$	68	99	0.33
4 ^a	V_2O_5	45	99	0.06
5 ^a	—	1	99	0
6 ^b	V-N-C	94	99	389.85

^a Reaction conditions: catalyst (30 mg), benzylamine (0.5 mmol), toluene (3 mL), O_2 pressure (1.01×10^5 Pa), 110 $^\circ\text{C}$, 12 h; ^b Catalyst (60 mg), benzylamine (15 mmol), O_2 balloon (1.01×10^5 Pa), 110 $^\circ\text{C}$, 16 h.

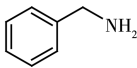
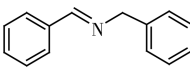
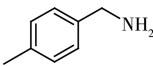
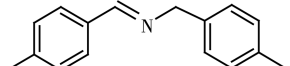
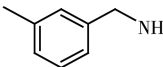
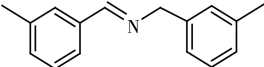
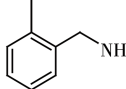
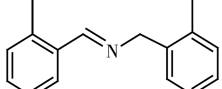
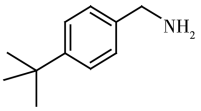
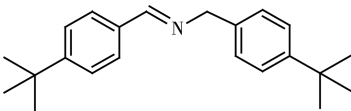
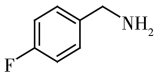
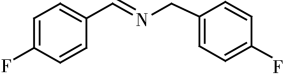
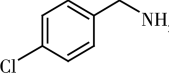
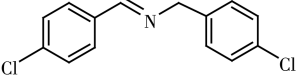
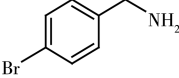
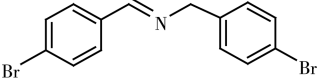
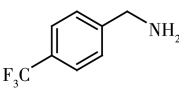
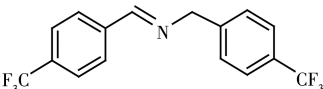
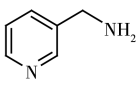
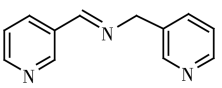
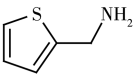
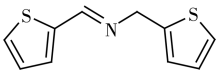
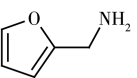
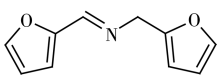
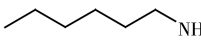
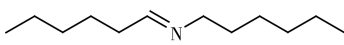
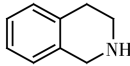
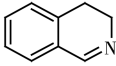
表2 不同催化剂上苄胺氧化自偶联反应活性比较

Table 2 Comparison of the oxidative self-coupling reaction activity of benzylamine over different catalysts

Entry	Catalyst	Time / h	Conversion / %	Selectivity / %	TOF / h^{-1}	Ref.
1	V-N-C	12	99	99	36.51	This work
2	Co-N-C/ SiO_2	24	99	100	0.52	[31]
3	NHPI/ $\text{Fe}(\text{BTC})$	24	98	90	0.24	[32]
4	WOH-D nanosheets	2	69	99	0.85	[33]
5	Cu_{meth} Al_{butox}	15	99	99	0.36	[34]

表3 V-N-C催化多种胺生成亚胺的自偶联反应

Table 3 Self-coupling reaction of various amines to imines catalyzed by V-N-C^a

Entry	Substrate	Product	Conversion / %	Selectivity / %
1			99	100
2			98	99
3			99	99
4			99	99
5			91	93
6			98	98
7			96	98
8			96	99
9			88	84
10			94	97
11			99	91
12			98	99
13			60	67
14			92	98

^a Reaction conditions: amine (0.5 mmol), V-N-C (30 mg), toluene (3 mL), O₂ pressure (1.01×10⁵ Pa), 110 °C, 12 h.

表4 V-N-C催化1a与各种胺的交叉偶联反应

Table 4 Cross-coupling reaction of 1a with various amines catalyzed by V-N-C^a

Entry	Amine 2	Conversion ^b / %	Selectivity ^b / %	
			4	3a
1		99	91	9
2		99	95	5
3		99	90	10
4		99	93	7
5		81	84	16
6		83	73	27

^a Reaction conditions: **1a** (0.125 mmol), amine **2** (0.375 mmol), V-N-C (30 mg), toluene (3 mL), O₂ pressure (1.01×10⁵ Pa), 110 °C, 12 h; ^b Conversion and selectivity were based on **1a** and confirmed by GC-MS.

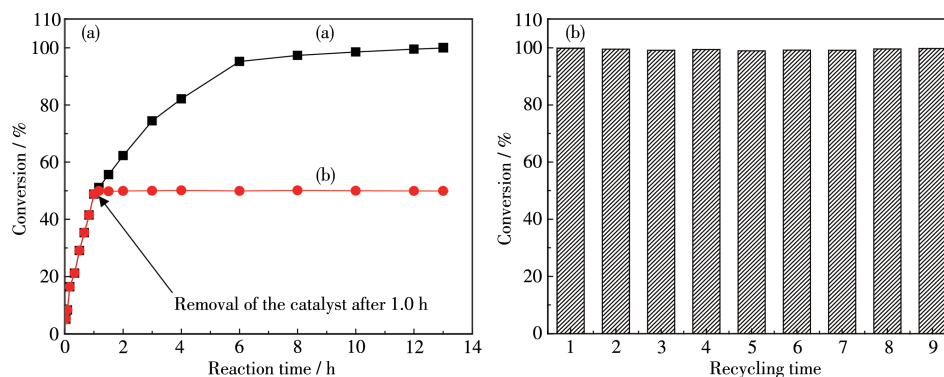


图4 V-N-C催化剂苄胺氧化自偶联中的(a)热过滤实验及(b)重复使用性

Fig.4 (a) Thermal filtration test and (b) reusability for the benzylamine oxidative self-coupling of V-N-C catalyst

子(DPD⁺), DPD⁺在紫外可见(UV-Vis)吸收光谱中510和551 nm处显示2个吸收峰。结果如图7所示,随着反应时间延长,2个吸收峰的强度均明显增加,充

分说明苄胺氧化偶联过程中涉及到了H₂O₂。

为了验证苄基亚胺是反应的中间体,我们以N-苄基甲胺替代苄基亚胺,加入到V-N-C和苄胺中

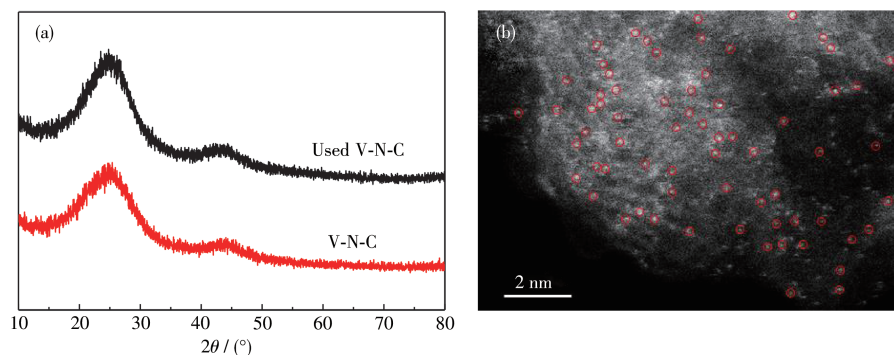


图5 使用后V-N-C催化剂(a) XRD图和(b)球差校正的HAADF-STEM图

Fig.5 (a) XRD pattern and (b) aberration-corrected HAADF-STEM image of spent V-N-C catalyst

进行反应,如图8所示,仅在1 h内就有74%的*N*-亚苄基胺转化为最终产物,进一步说明苄基亚胺是最可能的反应中间体。另外,由于在V-N-C催化苄胺氧化合成亚胺中未检测到任何醛类物质,基本排除了路径B的可能。

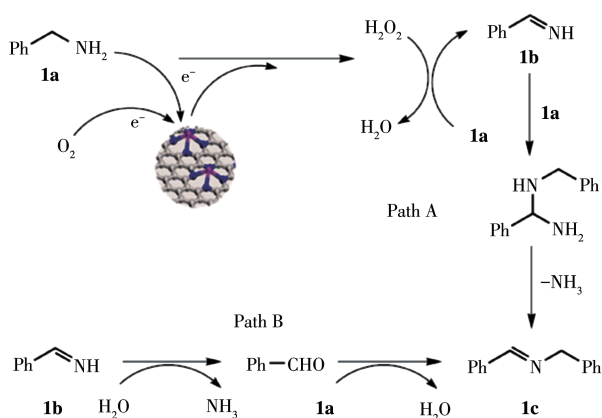
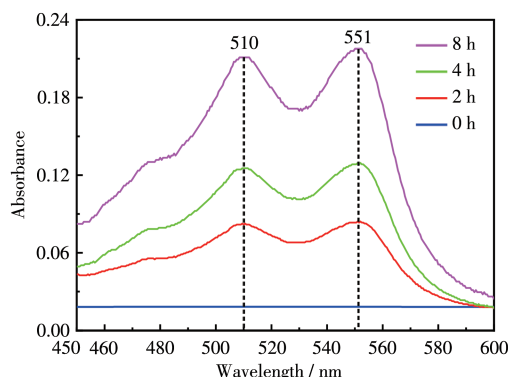
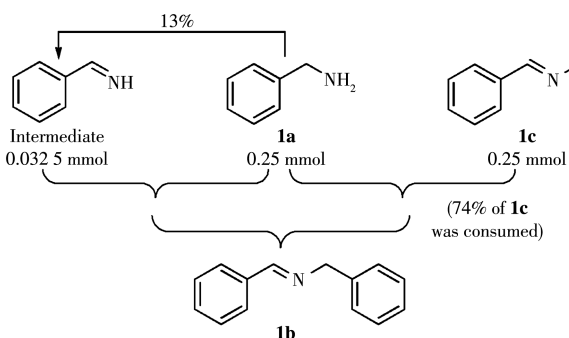


图6 V-N-C催化剂上苄胺合成亚胺可能反应机理

Fig.6 Possible reaction mechanism of benzylamine to imine catalyzed by V-N-C catalyst

图7 V-N-C催化剂上DPD/POD试剂与H₂O₂反应后的UV-Vis吸收谱图Fig.7 UV-Vis absorption spectra of the DPD/POD reagent after reaction with H₂O₂ over V-N-C图8 苄胺和*N*-亚苄基胺在V-N-C催化剂上的氧化偶联反应Fig.8 Oxidative coupling reaction of benzylamine and *N*-benzylidenemethylamine over V-N-C catalyst

3 结论

以壳聚糖为前驱体,乙酰丙酮钒为金属源,氯化锌为造孔剂,采用简单的热处理结合酸洗的方法制备出一种高比表面积钒氮共掺杂多孔碳(V-N-C)催化剂,其在苄胺氧化偶联合成对称亚胺、交叉偶联合成不对称亚胺反应中均表现出优异的反应活性。这可能是由于V-N-C中V物种近乎以单原子形式高度分散在碳载体上,活性中心VN_x充分暴露,使得其催化性能明显优于多相V₂O₅和均相VO(acac)₂催化剂。此外,循环套用9次后,V-N-C的催化性能没有任何降低,说明其具有优良的稳定性,具有潜在应用前景。

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