科学通报 2025 年 第 70 卷 第 14 期: 2117 ~ 2124

环境催化专题 论 文

《中国科学》杂志社
SCIENCE CHINA PRESS

非金属碳基催化剂氨选择性催化氧化反应性能研究

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2024-06-27 收稿, 2024-08-05 修回, 2024-09-02 接受, 2024-09-06 网络版发表
国家重点研发计划(2023YFC3707303)、国家自然科学基金(22276202)和中国科学院青年创新促进会(Y2023011)资助

摘要 氨气(NH_3)是大气颗粒物的重要前体物之一, 对NH_3的高效净化是应对颗粒物污染的重要手段. 本文研究了碳基催化剂的氨选择性催化氧化(NH_3-SCO)反应性能, 并探究了影响碳基催化剂NH_3-SCO反应性能的关键官能团物种. 研究结果表明, C-OH和C-O-C物种与催化活性密切相关. 此外, 本研究提出了一种高效生成表面C-OH和C-O-C含氧官能团的调控方法, 可以有效提升催化剂对NH_3的催化氧化能力, 并保持良好的N_2选择性. 本研究揭示了碳基催化剂在NH_3-SCO反应中的活性位点, 为发展非金属碳基NH_3-SCO催化剂提供了新的思路.

关键词 氨气, 选择性催化氧化, 碳基催化剂, 含氧官能团

氨气(NH_3)是重要的大气污染物之一, 可以与大气中的NO_x、SO_x等酸性气体结合形成铵盐, 铵盐是大气中$PM_{2.5}$的重要组成部分[1~3]. 大气中的NH_3主要来源于农业源和非农业源, 农业源污染可以通过相应的管理手段得到有效控制[4]. 非农业源排放的NH_3主要来源于固定源(如水泥厂和火电厂)烟气和机动车尾气脱硝过程中使用的还原剂氨未完全反应发生的"逃逸"[5~8]. 研究发现, 非农业源排放对夏季北京城区大气NH_3的贡献率约为63%[9]. 因此, 非农业源的NH_3排放与城市大气颗粒物污染密切相关[10~12].

氨气的处理方法包括吸收法、热分解法、生物降解法和催化氧化法, 其中氨选择性催化氧化技术(selective catalytic oxidation of NH_3, NH_3-SCO)是一种高效节能的NH_3净化方法[13,14], 是处理固定源(如火电厂和水泥厂)和移动源脱硝过程中未完全反应NH_3的最有前景的技术之一[15,16]. 贵金属催化剂具有优异的NH_3-SCO活性, 但仍存在高温选择性差和价格昂贵等问题[17~19]. 因此, 亟需发展具有良好NH_3-SCO活性、高N_2选择性且价格低廉的NH_3-SCO催化剂.

碳材料以其较大的比表面积通常作为吸附材料被应用[20~22]. 近年来, 非金属碳基催化剂在NH_3选择性催化还原NO_x反应(NH_3-SCR)中的应用逐渐受到关注[23~25], 但对于非金属碳基催化剂在NH_3-SCO反应中的研究尚未见报道. 本文通过硝酸氧化、水热处理和惰性气氛处理等手段对碳材料表面官能团进行调控, 制备出具有良好NH_3-SCO性能的碳基催化剂, 结合扫描电子显微镜、程序升温分解-质谱、红外光谱、氨程序升温脱附和X射线光电子能谱等表征手段探究了影响碳基催化剂NH_3-SCO性能的关键因素. 研究结果表明, 经过水热处理后的催化剂不仅表现出较高的NH_3-SCO活性, 还保持了良好的N_2选择性, 这为设计用于处理固定源含NH_3烟气的非金属碳基催化剂提供了

引用格式: 段汝丞, 符瑜, 何广智, 等. 非金属碳基催化剂氨选择性催化氧化反应性能研究. 科学通报, 2025, 70: 2117–2124
Duan R, Fu Y, He G, et al. Study of selective catalytic oxidation of ammonia over metal-free carbon-based catalysts (in Chinese). Chin Sci Bull, 2025, 70: 2117–2124, doi: 10.1360/TB-2024-0690

可行方案.

1 实验

1.1 催化剂制备

首先，将活性炭(购买自山西新华化工有限责任公司)在浓盐酸中浸泡12 h，以去除可能存在的各种杂质并用去离子水洗涤烘干．然后在N_2气氛中900°C处理2 h以去除原本可能存在的含氧官能团，得到的新鲜活性炭催化剂命名为AC. AC在浓硝酸中氧化3 h, 洗涤烘干后在N_2气氛下400°C处理2 h以去除催化剂孔道中残存的硝酸, 得到OAC催化剂. 对OAC催化剂进行水热处理, 即在含5% H_2O的空气气氛中400°C处理3 h, 得到的催化剂命名为OAC-HT. 将OAC-HT催化剂在N_2气氛下700°C处理2 h使C-OH和C-O-C官能团分解，得到OAC-HT-700催化剂.

1.2 催化剂评价与表征

1.2.1 催化剂活性测试

催化剂活性评价实验在自制的固定床反应器上进行，活性评价装置由进气系统、温控系统和气体检测系统组成．将500 mg催化剂(40~60目)置于10 mm内径的石英反应管中，并在催化剂两端放置石英棉对催化剂进行固定．反应气体由500 ppm(348 mg/m^3)NH_3、5 vol% O_2和N_2组成，进气和尾气的浓度均由Nicolet iS50红外光谱仪进行检测.

氨气转化率和氮气选择性根据下面的公式进行计算:

$$\text{氨气转化率}=\left(1-\frac{(NH_3)_{\text{出口}}}{(NH_3)_{\text{进口}}}\right)\times 100\%, \tag{1}$$

$$\text{氮气选择性}=\left(1-\frac{(NO_x)_{\text{出口}}+2(N_2O)_{\text{出口}}}{(NH_3)_{\text{进口}}-(NH_3)_{\text{出口}}}\right)\times 100\%. \tag{2}$$

1.2.2 催化剂表征方法

使用日本Hitachi公司生产的SU8000场发射扫描电子显微镜(field-emission scanning electron microscope, FE-SEM)在3 kV加速电压下对催化剂的形貌结构进行观测. 使用德国Bruker公司生产的VERTEX 80v傅里叶变换红外光谱仪(Fourier transform infrared spectrometer, FTIR)在真空条件下对催化剂的红外吸收光谱进行测试. 使用美国Thermo Fisher Scientific公司生产的ESCALAB250Xi型号的X射线光电子能谱仪(X-ray photoelectron spectrometer, XPS)对催化剂表面元素(C 1s和O 1s)进行测试, 利用C 1s(BE=284.8 eV)对所得谱图进行校正. 使用Mettler-Toledo TGA/DSC1-1100LF系统进行热重分析(thermogravimetric analysis, TGA), 实验气氛由N_2和5 vol% O_2组成, 升温速率为10°C/min. 在程序升温分解实验中，将100 mg催化剂置于4 mm内径的石英反应管中，并在催化剂两端放置石英棉对催化剂进行固定，载气为50 mL/min He，升温速率为10°C/min, 催化剂分解产物(CO和CO_2)使用移动式质谱仪(GSD 350-OmniStar)进行检测.

使用与固定床流动反应器相连的美国Thermo Fisher Scientific公司生产的Nicolet Antaris IGS气体分析仪进行氨程序升温脱附(ammonia temperature-programmed desorption, NH_3-TPD)测试. 将250 mg催化剂置于6 mm内径的石英反应管中，并在催化剂两端放置石英棉对催化剂进行固定．催化剂首先在200 mL/min N_2气氛中400°C预处理以去除表面吸附杂质，随后在500 ppm NH_3气氛50°C下吸附至饱和，并使用N_2气氛吹扫，最后以10°C/min的速率升温至400°C.

2 结果与讨论

2.1 活性评价结果

如图1(a)所示，未经任何氧化处理的新鲜AC催化剂在250°C以下基本没有NH_3-SCO活性. 经过硝酸氧化得到的OAC催化剂的NH_3催化氧化性能有了略微提升, 对OAC催化剂进行水热处理后的OAC-HT催化剂的催化性能显著提高．OAC和OAC-HT催化剂的T50分别为360和310°C，与AC催化剂的T50(380°C)相比分别降低了20和70°C．OAC-HT催化剂在经过700°C N_2气氛处理(OAC-HT-700)后催化活性明显降低．所有催化剂在整个温度区间内(100~400°C)都保持了95%以上的N_2选择性(图1(b)).

2.2 催化剂表征结果

图2展示了碳基催化剂的形貌信息，所有催化剂均为不规则的块状结构，大小在1~50 μm，并且OAC-HT催化剂表面具有更多孔道结构. 在经过不同处理后, 各个催化剂的孔径基本没有发生改变，与AC和OAC催化剂相比，OAC-HT催化剂的比表面积和孔容显著增加(表1)，以上结果均表明水热处理有助于催化剂孔道的形成, 进而增加反应物与催化剂之间的接触面积.

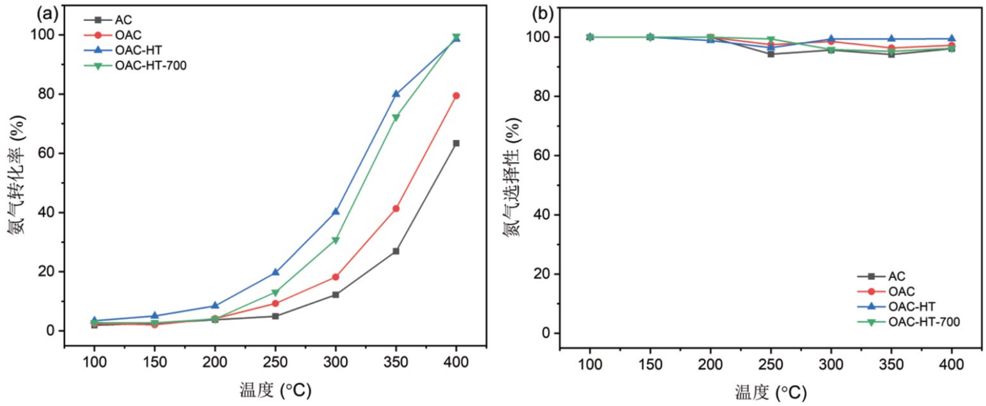

图 1 不同碳基催化剂活性评价结果. (a) 氨气转化率; (b) 氮气选择性. 反应条件: 500 ppm氨气, 5 vol%氧气, 氮气为平衡气, 12000 h^{-1}的反应空速

Figure 1 Activity test of various carbon-based catalysts. (a) NH_3 conversion; (b) N_2 selectivity. The reaction condition: 500 ppm NH_3, 5 vol% O_2, N_2 as balance gas, and gas hourly space velocity (GHSV) = 12000 h^{-1}

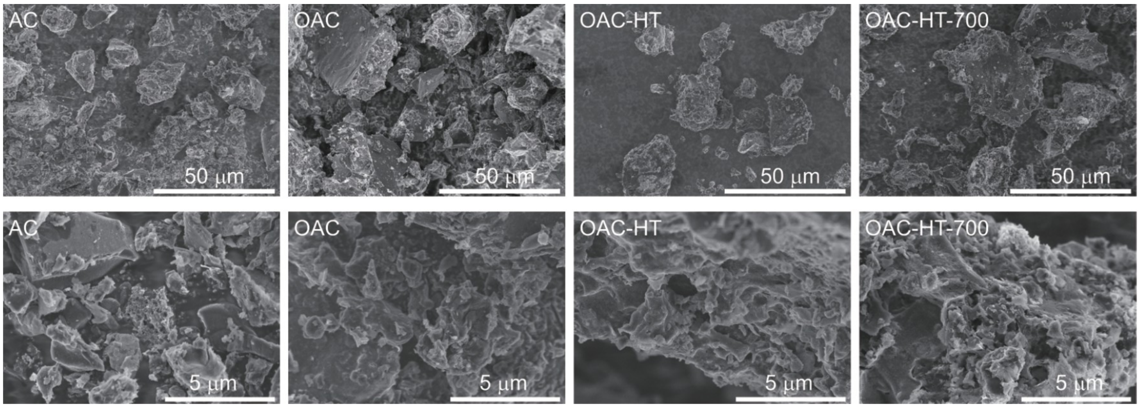

图 2 不同碳基催化剂的SEM图像

Figure 2 SEM images of various carbon-based catalysts

表 1 **不同催化剂的N_2吸/脱附分析结果**

Table 1 N_2 adsorption-desorption analysis results of various catalysts

催化剂	比表面积(m^2/g)	孔容(cm^3/g)	孔径(nm)
AC	288	0.15	2.1
OAC	293	0.15	2.0
OAC-HT	533	0.28	2.1
OAC-HT-700	630	0.33	2.1

碳基催化剂的FTIR谱图(图3(a))表明, 相较于AC催化剂, OAC和OAC-HT催化剂表面的C-OH和C-O-C吸收峰强度明显增强[26,27]. 经过700°C N_2处理后, OAC-HT-700催化剂表面C-OH吸收峰强度降低, 但C-O-C峰强度基本不变. NH_3-TPD结果(图3(b))显示, NH_3吸附量从高到低排序为: OAC-HT > OAC > OAC-HT-700 > AC, 这与催化剂表面C-OH特征峰的变化一致, 表明C-OH是碳基催化剂上NH_3的重要吸附位点.

催化剂的O 1s谱图如图4(a)~(d)所示, 结合能在531.1、532.1、533.3、534和535.8 eV附近的峰分别归属为羰基(C=O)、羟基和醚(C-OH/C-O-C)、内酯(-COO-)、羧基(-COOH)和吸附H_2O的特征峰[23,28,29]. 结果表明, 硝酸氧化(OAC催化剂)和水热处理(OAC-HT催化剂)提高了催化剂的C-OH和C-O-C含量, 700°C N_2处理(OAC-HT-700催化剂)使催化剂表面C-OH和C-O-C相对含量显著降低(图4(e)), 这与FTIR和NH_3-TPD的结论一致.

碳材料表面存在丰富的含氧官能团, 例如羧基(-COOH)、内酯(-COOC-)、酸酐(-COOOC-)、羟基(C-OH)、醚(C-O-C)和羰基(C=O)等. 这些含氧官能团在催化反应中发挥重要作用[30,31], 因此, 对碳材料表面含氧官能团的表征是探究碳基催化剂NH_3-SCO反应机制的

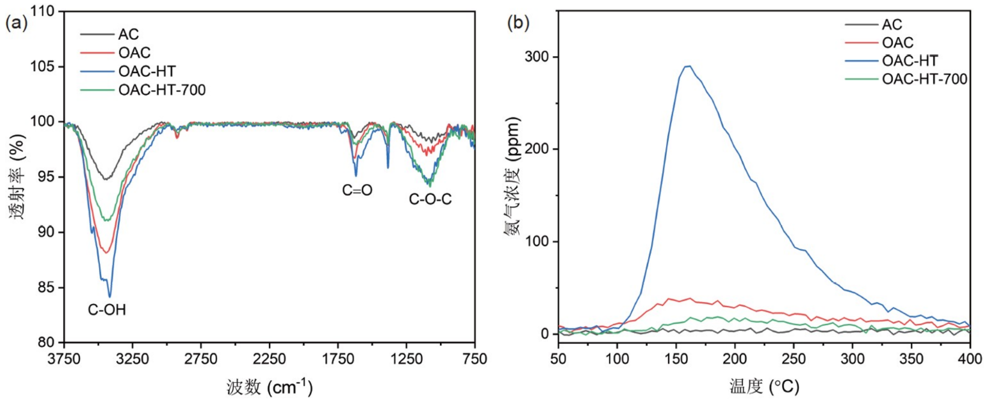

图 3 红外光谱和NH_3-TPD实验. (a) 不同碳基催化剂的红外谱图; (b) 不同碳基催化剂的NH_3-TPD曲线
Figure 3 FTIR and NH_3-TPD experiments. (a) FTIR spectra of various carbon-based catalysts; (b) NH_3-TPD curves of various carbon-based catalysts

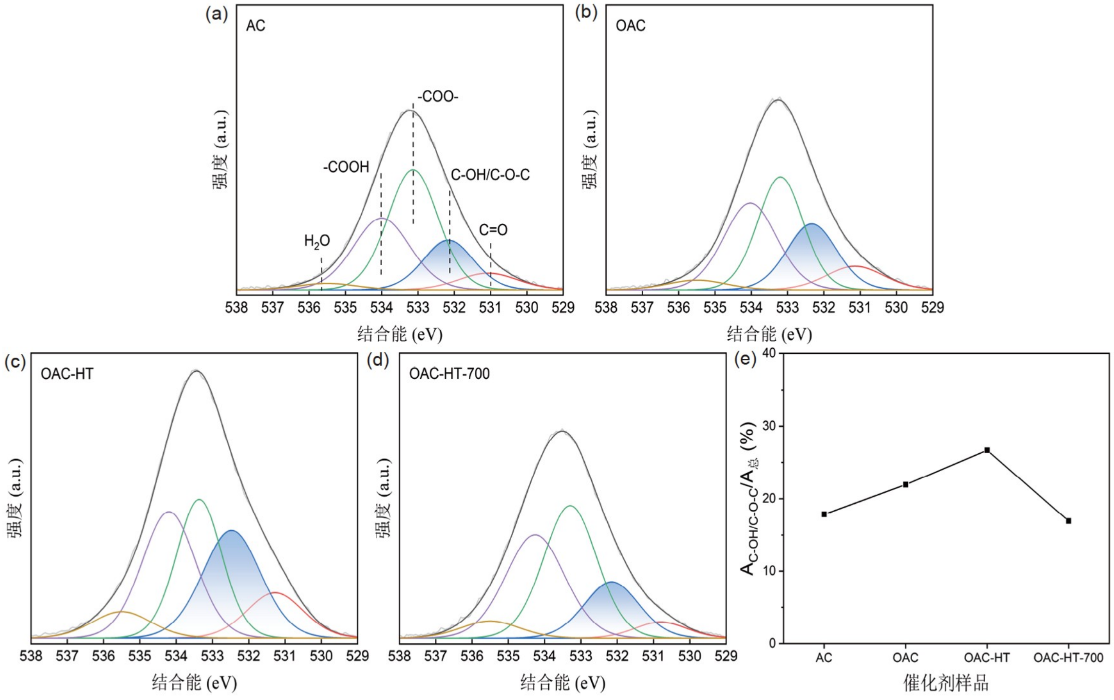

图 4 不同碳基催化剂的XPS分析. (a)~(d) O 1s谱图; (e) C-OH/C-O-C特征峰面积占总面积的百分比
Figure 4 XPS analysis of various carbon-based catalysts. (a)–(d) O 1s spectra; (e) percentage of C-OH/C-O-C characteristic peak area

关键手段. 已有研究表明, 不同含氧官能团在惰性气氛中的分解温度不同, 并且不同含氧官能团分解会释放对应的CO和CO_2分子[32~34], 因此可以通过设置不同的前处理温度来去除不同的官能团. 图5(a)展示了OAC-HT催化剂程序升温分解产生的CO_2(红线)和CO(蓝线)信号, 180°C附近的CO_2信号来源于-COOH的分解; -COOOC-在430°C附近分解会产生CO_2和CO; -COOC-在460~580°C分解并形成一个大而宽的CO_2峰; C-OH和C-O-C在550~780°C处分解形成一个明显的CO峰; C=O在850°C处分解产生CO_2和CO. 图5(b)展示了不同碳基催化剂程序升温分解释放的CO信号, 结果表明, 水热处理(OAC-HT催化剂)明显增加了C-OH和C-O-C官能团的含量, 而OAC-HT-700催化剂的C-OH和C-O-C含量显著下降. 以上表征结果都表明C-OH和C-O-C官能团对催化剂的NH_3-SCO性能具有重要作用.

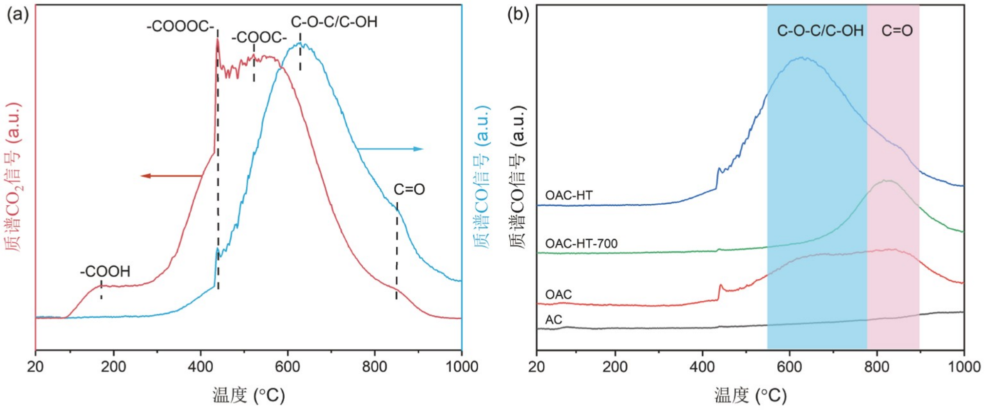

图 5 程序升温分解实验. (a) OAC-HT催化剂分解产生的CO(蓝线)和CO_2(红线)信号; (b) 不同碳基催化剂分解产生的CO信号

Figure 5 Temperature-programmed decomposition experiments. (a) CO and CO_2 signals from the OAC-HT catalyst decomposition; (b) CO signals from various carbon-based catalysts decomposition

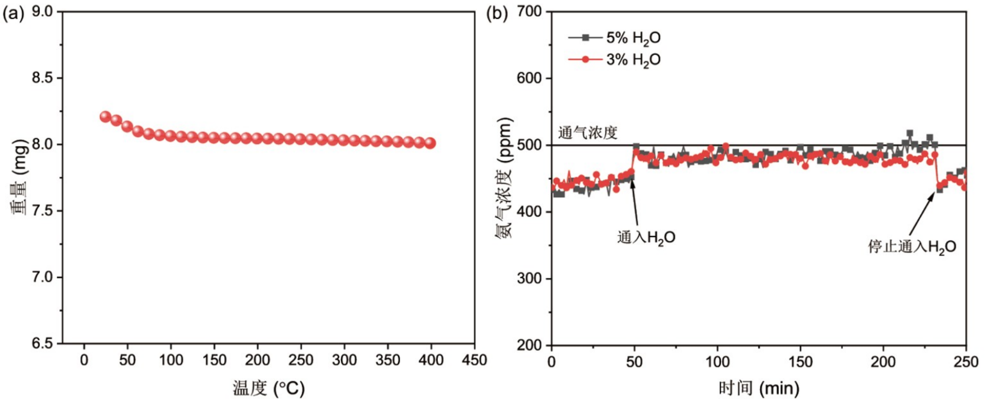

图 6 OAC-HT催化剂的热稳定性和抗水性能测试. (a) 在5 vol% O_2气氛中的热重曲线; (b) 在250°C下的抗水性能测试

Figure 6 Thermal stability and water resistance testing of OAC-HT catalysts. (a) TGA curve of OAC-HT catalyst at a heating rate of 10°C/min in an atmosphere containing 5 vol% O_2 and N_2 as balance gas; (b) H_2O resistance of the OAC-HT catalyst at 250°C

图6(a)和(b)分别展示了OAC-HT催化剂的热稳定性和其在250°C下的抗水性能. 结果表明, 催化剂质量在活性测试温度范围(100~400°C)内基本没有变化, 具有良好的热稳定性(图6(a)). 抗水性能测试结果(图6(b))显示, 3%和5% H_2O的通入均抑制了催化剂对NH_3的催化氧化能力, 停止通入H_2O后催化剂的活性恢复到初始状态, 表明H_2O可能与NH_3发生对活性位点的竞争吸附, 从而抑制催化剂的NH_3-SCO活性. 该抑制效应具有可逆性, 即停止通入H_2O后, 催化活性恢复.

3 结论

本研究通过水热处理法对碳材料表面官能团进行调控, 在保持良好N_2选择性的同时, 提高了碳基催化剂的NH_3-SCO性能. 通过FTIR、TPD-MS和XPS等表征手段, 揭示了C-OH和C-O-C官能团在NH_3-SCO反应中发挥了重要作用. 本研究为制备具有优异NH_3-SCO活性和N_2选择性的碳基催化剂提供了有效策略, 并为发展非贵金属NH_3-SCO催化剂提供了思路.

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Summary for “非金属碳基催化剂氨选择性催化氧化反应性能研究”

Study of selective catalytic oxidation of ammonia over metal-free carbon-based catalysts

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Ammonia (NH_3) is a significant atmospheric pollutant that leads to severe environmental and health risks. NH_3 can irritate the respiratory tract, leading to symptoms such as coughing and wheezing. In the atmosphere, NH_3 is the only alkaline gas and serves as an important precursor pollutant, combining with acidic gases to form secondary pollutants like nitrate and sulfate aerosols, which are key components of the fine particulate matter ($PM_{2.5}$). $PM_{2.5}$ is associated with severe health hazards, including the respiratory and cardiovascular diseases, and can also impact the growth and reproduction of plants and animals. Therefore, it is essential to eliminate NH_3 and its secondary contamination.

NH_3 emissions arise from various sources. In agricultural production, the ammonia fertilizer and the animal husbandry contribute significantly to atmospheric NH_3, which are the main sources of NH_3 emissions in the atmosphere. This portion of NH_3 emissions can be limited through appropriate management practices and policy measures. For non-agricultural sources, such as stationary sources and vehicles, NH_3 emissions mainly result from the incomplete reaction of ammonia as a reductant in the de-NO_x process. Methods for treating NH_3 from non-agricultural sources include absorption, thermal decomposition, biodegradation, and catalytic oxidation, among which selective catalytic oxidation of ammonia (NH_3-SCO) is an efficient and energy-saving purification method. The development of effective catalysts is crucial for the NH_3-SCO technology. Noble metal catalysts are commonly used in the NH_3-SCO reaction due to their high catalytic activity. However, high cost and poor N_2 selectivity at high temperatures limit the use of noble metal catalysts. Therefore, there is a growing need to develop the NH_3-SCO catalysts with a low-content or even no noble metal.

Carbon materials possess a large specific surface area and are often used as adsorbent materials to treat wastewaters or exhaust gases. Additionally, the surface of carbon materials contains abundant oxygen-containing functional groups, such as carboxyl (COOH), hydroxyl (C-OH), ether (C-O-C), and carbonyl (C=O), which can serve as the active sites for catalytic reactions. These properties make carbon-based catalysts potential substitutes for the noble metal catalysts. Currently, the main methods for modifying the functional groups of carbon-based catalysts involve acid oxidation and alkali treatment. These methods primarily aim to increase the overall content of surface functional groups or to significantly enhance the specific functional groups. In this study, we modified the surface functional groups of carbon-based catalysts through nitric acid oxidation, hydrothermal treatment, and inert atmosphere heat treatment. We then investigated the performance of these metal-free carbon-based catalysts in the NH_3-SCO reaction.

The physicochemical properties of the catalysts, especially the effects of the oxygen-containing functional groups on the NH_3-SCO reaction, were analyzed using various characterization techniques, including scanning electron microscopy (SEM), temperature-programmed decomposition-mass spectrometry (TPD-MS), Fourier transform infrared spectroscopy (FTIR), ammonia temperature-programmed desorption (NH_3-TPD), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). The results indicated that the methods of modifying the surface oxygen-containing functional groups significantly increased the content of C-OH and C-O-C groups, and these species were closely related to the NH_3-SCO activity. Those methods markedly improved the NH_3-SCO activity of carbon-based catalysts while maintaining good N_2 selectivity. Furthermore, the modified carbon-based catalysts also maintained good thermal stability.

This study reveals the active sites of carbon-based catalysts in the NH_3-SCO reaction and proposes feasible methods to design the metal-free carbon-based catalysts for the treatment of NH_3-containing flue gas from stationary sources. This study also provides a valuable idea for developing efficient and cost-effective substitutes to the noble metal catalysts for NH_3 elimination.

ammonia, selective catalytic oxidation, carbon-based catalysts, oxygen-containing functional groups

doi: 10.1360/TB-2024-0690