

## 活性炭原料选择、活化方法及改性技术的研究进展

张 乾<sup>1</sup>, 张雯澜<sup>2</sup>, 庄 柯<sup>1</sup>, 张博雅<sup>2</sup>, 许 芸<sup>1</sup>, 李晓曼<sup>2</sup>, 张亚平<sup>2</sup>, 沈 凯<sup>2</sup>

(1. 国家能源集团科学技术研究院有限公司 低碳智能燃煤发电与超净排放全国重点实验室, 江苏 南京 210023;  
2. 东南大学 a. 能源与环境学院; b. 能源热转换及其过程测控教育部重点实验室, 江苏 南京 210096)

**摘要:** 活性炭因其优异的吸附性能和经济效益, 被视为一种有效的脱硫脱硝材料。本文从活性炭的原料选择、活化方法和改性技术三个方向, 系统地综述改性活性炭用于工业废气中脱除 SO<sub>2</sub> 和 NO<sub>x</sub> 的研究进展; 详细讨论不同原料制备活性炭的特点, 以及活化方式对活性炭性能的影响, 探讨采用酸碱改性、金属氧化物负载、氨改性、紫外改性、微波改性、纳米材料复合改性等方式来进一步增强活性炭的功能性。结果表明: 对比煤基、生物质等多种原料, 低阶煤、高木质素和富氮生物质是制备高性能活性炭的优选原料。物理与化学活化方式通过调控孔结构和比表面积, 显著影响其吸附性能。多种改性方法进一步提升了功能性; 金属氧化物负载利用氧化还原循环增强催化性能; 氨改性引入含氮官能团, 提高表面碱性和气体亲和力; 矿石负载则实现性能与成本的平衡。此外, 紫外辐照、微波加热及纳米材料复合等新型改性手段有望进一步强化反应位点与结构稳定性, 但其在工艺复杂性、成本控制及规模化应用方面仍面临挑战。总之, 活性炭通过结构优化与功能改性展现出高效协同脱硫脱硝的潜力, 是实现工业清洁排放的重要材料基础。

**关键词:** 活性炭; 脱硫; 脱硝; SO<sub>2</sub>; NO<sub>x</sub>

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## Research progress on selection, activation method and modification technology of activated carbon raw materials

ZHANG Qian<sup>1</sup>, ZHANG Wenlan<sup>2</sup>, ZHUANG Ke<sup>1</sup>, ZHANG Boya<sup>2</sup>, XU Yun<sup>1</sup>,  
LI Xiaoman<sup>2</sup>, ZHANG Yaping<sup>2</sup>, SHEN Kai<sup>2</sup>

(1. State Key Laboratory of Low-carbon Smart Coal-fired Power Generation and Ultra-clean Emission, China Energy Science and Technology Research Institute Co., Ltd., Nanjing 210023, Jiangsu, China; 2. Southeast University a. School of Energy and Environment; b. Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Nanjing 210096, Jiangsu, China)

**Abstract:** Activated carbon is regarded as an effective desulfurization and denitrification material due to its excellent adsorption performance and economic benefits. This paper systematically reviews the research progress of modified activated carbon for the removal of SO<sub>2</sub> and NO<sub>x</sub> from industrial waste gas from three directions: raw material selection, activation method and modification technology. The characteristics of activated carbon prepared from different raw materials and the influence of activation methods on the performance of activated carbon are discussed in detail, and the functions of activated carbon are further enhanced by acid-base modification, metal oxide loading, ammonia modification, ultraviolet modification, microwave modification, and nanomaterial composite modification. The results show that compared with coal-based,

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**作者简介:** 张 乾(1986—), 男, 高级工程师, 从事烟气污染物治理工艺与装备开发的研究工作。

**通信作者:** 庄 柯(1980—), 男, 博士, 正高级工程师, 从事火电机组污染物排放控制技术的研究工作。

biomass, and other raw materials, low-rank coal, high lignin and nitrogen-rich biomass are the preferred raw materials for the preparation of high-performance activated carbon. Physical and chemical activation methods significantly affect the adsorption performance by regulating pore structure and specific surface area. A variety of modification methods further improve the functionality: metal oxide loading uses redox cycling to enhance catalytic performance; ammonia modification introduces nitrogen-containing functional groups to improve surface alkalinity and gas affinity; ore loading balances performance and cost. In addition, new modification methods such as ultraviolet irradiation, microwave heating, and nanomaterial composite are expected to further strengthen the reaction site and structural stability, but they still face challenges in process complexity, cost control, and large-scale application. In conclusion, activated carbon demonstrates the potential of efficient and collaborative desulfurization and denitrification through structural optimization and functional modification, and is an important material basis for achieving clean industrial emissions.

**Key words:** activated carbon; desulfurization; denitrification;  $\text{SO}_2$ ;  $\text{NO}_x$

工业废气中二氧化硫( $\text{SO}_2$ )和氮氧化物( $\text{NO}_x$ )排放是当前环境保护领域关注的焦点问题之一。根据《2022年生态环境统计年报》,全国 $\text{SO}_2$ 工业源排放183.5万吨,占比为75.36%; $\text{NO}_x$ 工业源排放333.3万吨,占比为37.21%。《关于推进实施钢铁行业超低排放的意见》指出,烧结机机头、球团焙烧烟气中 $\text{SO}_2$ 、 $\text{NO}_x$ 排放质量浓度小时均值不高于35、50  $\text{mg}/\text{m}^3$ 。随着排放标准的日渐严格,去除工业废气中 $\text{SO}_2$ 与 $\text{NO}_x$ 的需求日益增长。

现行的 $\text{SO}_2$ 和 $\text{NO}_x$ 脱除技术主要包括湿法脱硫、干法脱硫、SCR脱硝和SNCR脱硝等<sup>[1]</sup>。在脱硫领域,湿法脱硫效率高,但设备投资大、运行成本高、副产物生成量大、水资源消耗量大;干法和半干法脱硫技术具备占地面积小、无废水排放等优点。在脱硝领域,选择性催化还原(SCR)是目前的主流技术,其通过氨气在催化剂的作用下与 $\text{NO}_x$ 反应生成氮气和水,具有高效稳定性。随着环保要求的日益提高,脱硫脱硝的协同控制技术逐渐受到重视,如湿法脱硫协同SCR脱硝技术,具有高效协同处理潜力,但也存在投资高、工艺复杂等特点。相比之下,活性炭吸附法凭借多功能性、高吸附性能、良好再生性、较低成本及操作简便等优势引起广泛关注<sup>[2]</sup>。该技术已在工业中应用,如河钢邯钢与武钢焦化厂采用逆流式活性炭工艺,有效提升了烟气净化效率,实现了稳定达标排放<sup>[3-4]</sup>。

活性炭作为活性炭吸附法中重要的吸附剂和催化剂载体,其性能优劣直接影响治理效率。近年来,研究聚焦于原材料选择、活化与改性方式的优化,以调控其表面化学性质与孔结构,从而提高其

对 $\text{SO}_2$ 和 $\text{NO}_x$ 的去除效果。基于此,本文综述近年来的相关文献,从原料选择、活化方式和改性方式三个方面系统介绍目前新型改性活性炭脱硫脱硝材料的研究进展,以为同行提供借鉴或参考。

## 1 活性炭材料的原料选择

活性炭的原料选择直接影响着其孔结构、表面化学性质以及吸附性能。不同原料在活性炭制备中具有独特的优势和适用性,对最终产品的性能产生重要影响。

### 1.1 煤基活性炭

煤炭资源储量丰富,可提供稳定的原料供应,其制备的活性炭具有较发达的孔结构和丰富的含氧官能团,能够高效吸附 $\text{SO}_2$ 和 $\text{NO}_x$ 等有害气体<sup>[5]</sup>,且在高温下具有良好的稳定性,能在工业生产环境中长期稳定运行<sup>[6]</sup>。

不同煤种制备的活性炭性能差异显著。ZHOU等<sup>[7]</sup>以褐煤、烟煤、无烟煤和焦煤等不同阶数的煤为原料制备活性炭,结果表明:低阶煤制备的活性炭孔隙结构发达,含氧官能团更多, $\text{SO}_2$ 吸附性能更优;而高阶煤(如焦煤)结块性强,不利于微孔形成。WANG等<sup>[8]</sup>对褐煤和烟煤进行比较,发现烟煤产率较高,褐煤则具有更丰富的孔隙结构和更强的 $\text{SO}_2$ 吸附能力。NIU等<sup>[9]</sup>提出矿物催化指数可用于评估煤中矿物成分的活性和应用潜力,认为矿物成分可促进微孔的产生以及微孔向中孔/宏孔的转化,从而优化孔隙结构,改善表面化学性质,促进 $\text{NO}$ 和 $\text{NH}_3$ 的吸附并催化 $\text{NH}_3$ -SCR反应,提高 $\text{NO}$ 的去除率。不同煤种的性能对比如表1所示。

表 1 不同种类煤基活性炭

Table 1 Different types of coal-based activated carbon

原材料名称	比表面积/ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	测试条件	去除能力	
			$\text{SO}_2/(\text{mg} \cdot \text{g}^{-1})$	$\text{NO}_x$
印尼褐煤 <sup>[8]</sup>	529.00	75 °C, 0.150% $\text{SO}_2$	122.850	—
新疆哈密煤 <sup>[10]</sup>	671.70	(120 ± 5) °C, 0.102% $\text{SO}_2$	31.240	—
准东煤 <sup>[11]</sup>	531.00	室温, 0.100% $\text{SO}_2$	43.600	—
准东煤 <sup>[12]</sup>	541.00	298 K, 0.050% $\text{SO}_2$	33.000	—
准东煤 <sup>[13]</sup>	556.10	77 K, 0.080% $\text{NO}$	—	43.160 mg/g
胜利褐煤 <sup>[7]</sup>	504.00	75 °C, 0.150% $\text{SO}_2$	116.580	—
胜利褐煤 <sup>[14]</sup>	443.00	75 °C, 0.150% $\text{SO}_2$	108.120	—
胜利褐煤 <sup>[15]</sup>	347.26	75 °C, 0.170% $\text{SO}_2$	80.100	—
蒙东褐煤 <sup>[16]</sup>	467.29	75 °C, 0.170% $\text{SO}_2$	89.610	—
贫煤 <sup>[17]</sup>	—	75 °C, 0.020% $\text{SO}_2$	45.850	—
君庙煤和红沙泉煤 <sup>[18]</sup>	640.00	393 K, 0.050% $\text{NO}$ , 0.050% $\text{NH}_3$ , 0.150% $\text{SO}_2$	25.700 ~ 34.400	27.7%
山西低阶煤 <sup>[19]</sup>	370.42	80 °C, 0.018%~0.020% $\text{NO}$ , 0.055%~0.060% $\text{SO}_2$	5.463	1.935 mg/g

除了选用不同煤种外, 还可以通过配煤拓宽孔径分布, 优化炭化工艺并提升煤炭利用率<sup>[20]</sup>; 同时加入其他组分可以有效降低成本, 兼顾经济性与性能。NIU 等<sup>[21]</sup>用赤泥作部分替代煤炭制备活性炭, 发现赤泥中 Fe、Ca、Na 等矿物促进热解反应, 形成分级孔结构, 使微孔面积、总比表面积与总孔容分别提高 11%、49% 和 88%。此外, 他们还通过改变焦炭粉和苯渣的添加量, 调节活性炭的理化结构和性能<sup>[22]</sup>。研究表明, 配入焦炭粉使硫容量下降、苯渣略有提升; 添加 20% 副产物和废弃物即可获得与未改性活性焦(51.2 mg/g) 相当的性能, 同时可降低生产成本。

## 1.2 生物质活性炭

废弃生物质来源广泛, 其资源化利用可减少污染。其制备的活性炭孔结构优良、吸附性能强且成本低, 具有显著优势。

### 1.2.1 木质活性炭

具有较高木质素含量的原料富含碳源、灰分低, 制备的活性炭具有高孔隙率和比表面积<sup>[23]</sup>。不同种类木质活性炭的测试条件及去除能力如表 2 所示。由表 2 可以看出, 多种木质材料经活化后比表面积可超过 1 000  $\text{m}^2/\text{g}$ , 具有优异的  $\text{SO}_2$  与  $\text{NO}_x$  吸附性能。BRAGHIROLI 等<sup>[24]</sup>以桦木生物炭为例, 在 KOH、 $\text{CO}_2$  和蒸汽活化下比表面积分别达到 1 700、881 和 590  $\text{m}^2/\text{g}$ 。ROSAS 等<sup>[25]</sup>以硫酸

盐木质素制备活性炭, 比表面积达到了 930  $\text{m}^2/\text{g}$ 。LIU 等<sup>[36]</sup>用椰壳制备活性炭, 最大比表面积为 971  $\text{m}^2/\text{g}$ 。LIU 等<sup>[37]</sup>指出果壳活性炭具有较大的比表面积、较多的微孔分布以及较多的羟基和羧基基团, 比其他活性炭更适合作为载体。CHEN 等<sup>[26]</sup>将锯末转化为有价值的富钙活性炭块, 其比表面积达到 1 133  $\text{m}^2/\text{g}$ , 具有 18 MPa 的抗压强度和超过 60 d 的优异耐水性,  $\text{SO}_2$  吸附能力为 57.1 mg/g。QIN 等<sup>[32]</sup>制备核桃壳基催化剂, 比表面积高达 1 425.84  $\text{m}^2/\text{g}$ , 协同脱除效率超过 80%。ZHANG 等<sup>[28]</sup>采用沸石咪唑酸盐骨架(ZIF-8)辅助竹子热解制备生物炭,  $\text{SO}_2$  吸附量达 166 mg/g, 循环 8 次后吸附效率仍超 93%。

### 1.2.2 秸秆和污泥活性炭

秸秆中含有丰富的含氮官能团, 这些官能团对  $\text{SO}_2$  的脱除有着天然的优势<sup>[38]</sup>。不同种类秸秆活性炭的测试条件及去除能力如表 3 所示。ZHANG 等<sup>[39]</sup>采用花生壳、玉米秸秆和玉米芯制备富氮活性炭, 发现原料显著影响含氮量和吸附性能, 其中玉米芯制备活性炭的含氮量最高, 吸附效果最好, 其比表面积为 654  $\text{m}^2/\text{g}$ , 微孔比表面积高达 570.69  $\text{m}^2/\text{g}$ , 吸附容量达到 182.47 mg/g。CHEN 等<sup>[41]</sup>发现, 大豆秸秆在我国储量丰富, 其高含氮量和分子结构中活性基团的存在可有效提高气态污染物的吸附速率, 是优质碳源材料。大

表2 不同种类木质活性炭

Table 2 Different types of wooden activated carbon

原材料名称	比表面积/ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	测试条件	去除能力	
			SO <sub>2</sub>	NO <sub>x</sub>
黑云杉和白桦树 <sup>[24]</sup>	590.00	20 °C, 0.005% SO <sub>2</sub>	76.90 mg/g	—
桉树硫酸盐木质素 <sup>[25]</sup>	1 321.00	20 °C, 0.250% SO <sub>2</sub>	94.82 mg/g	—
杉木木屑 <sup>[26]</sup>	1 133.00	70 °C, 0.440% SO <sub>2</sub>	57.10 mg/g	—
棕榈油果壳纤维 <sup>[27]</sup>	2 70.60	70 °C, 0.200% SO <sub>2</sub>	73.89 mg/g	—
竹子 <sup>[28]</sup>	5 57.40	90 °C, 0.100% SO <sub>2</sub>	166.00 mg/g	—
椰壳 <sup>[29]</sup>	947.56	60 °C, 0.0300% SO <sub>2</sub>	24.06 mg/g	—
椰壳 <sup>[30]</sup>	1 114.00	25 °C, 0.000 2%~0.001 0% SO <sub>2</sub>	47.00 mg/g	—
椰壳 <sup>[31]</sup>	1 314.50	-20 ~ 80 °C, 0.100% SO <sub>2</sub> , 0.020% NO	123.11 mg/g	13.24 mg/g
核桃壳 <sup>[32]</sup>	1 425.84	300 ~ 350 °C, 0.020% SO <sub>2</sub> , 0.030% NO <sub>x</sub>	80% 以上	>80%
花生壳 <sup>[33]</sup>	385.99	100 ~ 250 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	87.6%
废竹 <sup>[34]</sup>	973.00	200 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	>92%
猕猴桃树枝 <sup>[35]</sup>	119.74	125 ~ 225 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	>90%

表3 不同种类秸秆活性炭

Table 3 Different types of straw activated carbon

原材料名称	比表面积/ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	测试条件	去除能力	
			SO <sub>2</sub> /( $\text{mg} \cdot \text{g}^{-1}$ )	NO <sub>x</sub>
玉米芯 <sup>[39]</sup>	654.00	120 °C, 0.100% SO <sub>2</sub>	182.47	—
玉米芯 <sup>[40]</sup>	25.54	120 °C, 0.200% SO <sub>2</sub>	156.20	—
大豆秸秆 <sup>[41]</sup>	347.28	70 °C, 0.100% SO <sub>2</sub>	84.57	—
大豆秸秆 <sup>[42]</sup>	355.60	(75 ± 1) °C, 0.150% SO <sub>2</sub>	146.31	—
大豆秸秆 <sup>[43]</sup>	371.11	30/120 °C, 1% SO <sub>2</sub> /N <sub>2</sub>	115.40	—
大豆秸秆 <sup>[44]</sup>	500.21	30/120 °C, 1% SO <sub>2</sub> /N <sub>2</sub>	201.90	—
水稻秸秆 <sup>[45]</sup>	138.10	25 °C, 0.3% SO <sub>2</sub> /N <sub>2</sub>	260.00	—
荷叶 <sup>[46]</sup>	377.50	100 ~ 300 °C, 0.060% NO, 0.060% NH <sub>3</sub>	—	>95%

量研究发现, 经过金属氧化物改性<sup>[42]</sup>、氨改性<sup>[40,43]</sup>等方式制备的大豆秸秆活性炭能够获得较高的脱硫效率。

污水处理行业的发展使活性污泥产量剧增, 该污泥需被合理利用<sup>[47]</sup>。污泥中含有大量有机物, 可用于制备吸附材料<sup>[48]</sup>。IBERAHIM 等<sup>[49]</sup>采用棕榈油污泥热解制备生物炭, 产率为 54.25 g, SO<sub>2</sub> 吸附量 9.75 mg/g。随后其表面被进一步研究, 经 CO<sub>2</sub> 活化后, 活性炭的吸附容量提升至 16.65 mg/g<sup>[50]</sup>。与其他活性生物质材料相比, 污泥活性炭的吸附效果普遍偏低, 仍需要进一步探究。

总体而言, 虽然生物质材料能表现出一定的成效, 但由其制成的活性炭在机械强度上存在不

足, 有些产品甚至无法达到现行的国家标准。然而, 目前将生物质用作脱硫脱硝活性炭的原料仍然具有发展潜力<sup>[20]</sup>。

## 2 活性炭材料的活化方式

活性炭的制备包括碳化和活化两阶段。前驱体在 300 ~ 600 °C 下碳化形成初步多孔结构, 但碳化过程中产生的焦油产物会堵塞孔隙, 需通过进一步活化来改善孔结构和比表面积<sup>[51]</sup>。

### 2.1 物理活化

物理活化可在水蒸气、CO<sub>2</sub> 或 O<sub>2</sub> 等气氛下进行热处理 (700 ~ 900 °C) 实现<sup>[52]</sup>, 该方法通过碳素溶解损失反应 ( $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ , Boudouard 反应)

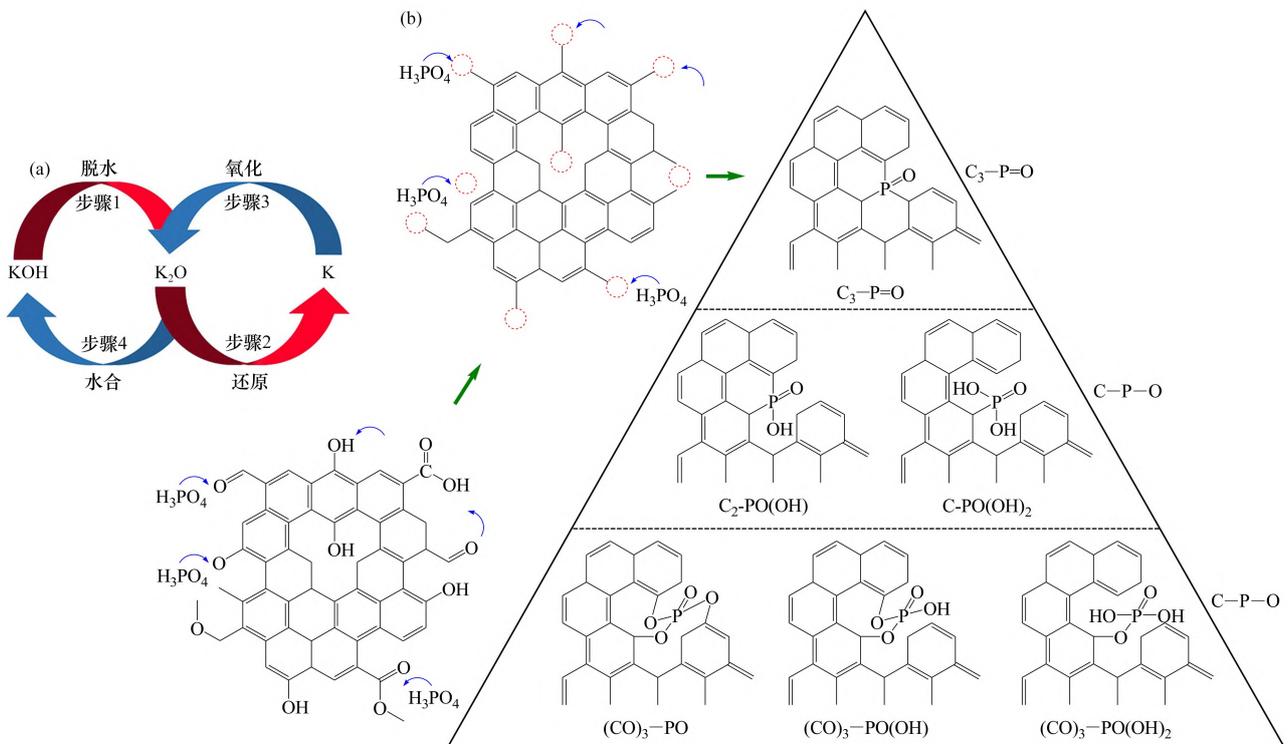
或气化反应( $C + H_2O \rightarrow CO + H_2$ )消除反应活性高的碳原子,减少碳孔隙中的焦油产物,同时扩大孔径,增加孔隙率<sup>[53]</sup>。

物理活化法的优点在于过程相对简单,能够在不引入外来杂质的情况下,有效调控活性炭的孔结构。朱圣林<sup>[54]</sup>对比了水蒸气和  $CO_2$  活化,发现前者制得的样品比表面积与吸附量更高,且微孔比表面积与总比表面积的比值可作为初步评估活性炭脱硫性能的指标之一。BRAGHIROLI 等<sup>[24]</sup>发现,虽然 KOH 活化后活性炭的多孔性最强,孔隙更发达,但其吸附性能却比水蒸气活化的低。周健生等<sup>[55]</sup>以新疆哈密煤为原料,采用碳酸钾、水蒸气、 $CO_2$ 、碳酸钾/水蒸气联合活化制备活性炭,发现水蒸气的引入促进了碳酸钾活化,使联合活化活性炭形成发达的微孔结构;而碳酸钾对水蒸气活化产生中孔的能力有一定的抑制作用,导致联合活化活性炭的中孔和总孔体积比单一水蒸气活化低。

## 2.2 化学活化

化学活化是将原材料与化学活化剂混合加热,

在活性炭的生成过程中起到脱水 and 脱气的作用,从而增加产物的比表面积和孔隙率。KOH 和  $H_3PO_4$  的活化机理如图 1 所示。由图 1(a)可见:KOH 在脱水过程转化为  $K_2O$ ,接着被还原为 K,游离钾渗入石墨层导致其结构膨胀,经过氧化和水合等一系列反应后,石墨层中存在 K、 $K_2O$ 、 $K_2CO_3$  和 KOH,从而在活性炭样品表面形成多孔表面,比表面积得到提高。由图 1(b)可见:在生物质热解过程中, $H_3PO_4$  优先将原有的含氧基团释放出来,随后进入氧空位产生丰富的含磷基团并带来大量的氧。随着  $H_3PO_4$  含量的增加, $H_3PO_4$  与碳进行反应,在碳上生成空位,增加了活性炭的孔隙率。HUANG 等<sup>[58]</sup>发现  $ZnCl_2$ 、 $H_2PO_4$  和 KOH 活化都能增加活性炭的比表面积,但高浓度的  $ZnCl_2$  和  $H_3PO_4$  会堵塞微孔并破坏其原有结构;而 KOH 活化可以优化活性炭的孔隙结构,生成一定含氧官能团,有利于提高吸附性能。JACOBS 等<sup>[59]</sup>使用 KOH、NaOH 和 KOH/ $K_2CO_3$  混合物作为活化剂制备活性炭,发现活化过程有效开发了活性炭的孔隙结构,增加了更多的微孔,



(a) KOH 活化<sup>[56]</sup>; (b)  $H_3PO_4$  活化<sup>[57]</sup>

图 1 KOH 和  $H_3PO_4$  的活化机理

Fig. 1 Activation mechanism of KOH and  $H_3PO_4$

提高吸附能力。SUN 等<sup>[60]</sup>认为酸能更有效地侵蚀原料半焦的表面,导致孔隙结构更发达、官能团更多,而碱活化法可能改变半焦表面的孔隙结构。

基于这些活化方式,ZHU 等<sup>[61]</sup>提出了定向调节活性炭孔结构的系统制备机制。此研究以椰子壳为原料,结合多种碳化和活化方式(如水热、CaCl<sub>2</sub> 浸渍等),得到了一系列具有不同典型孔隙层次和相似比表面积的活性炭,以及具有相似孔隙层次和不同比表面积的样品,证明调节孔径结构和比表面积的策略可定向制备不同应用的高效活性炭。综上所述,物理与化学活化均可有效改善活性炭的孔结构,实际应用应根据目标合理选择,并综合考虑成本与环境影响。

### 3 活性炭材料的改性方式

活性炭的改性是指在活性炭表面建立位点和官能团来修饰活性炭的化学性质,生成固定化官能团的带电表面,并破坏抑制这些目标气体吸附的官能团。常见的活性炭改性方式有酸碱改性、

氨改性、金属氧化物负载等<sup>[20]</sup>。

#### 3.1 酸碱改性

酸碱改性与化学活化类似,但侧重点不同。化学活化注重活性炭的孔隙结构变化,酸碱改性侧重活性炭表面官能团的变化,但在大多数情况下这两个步骤可以合并成一步进行。

碱性改性可引入羟基、羧基等官能团,增强与SO<sub>2</sub>、NO<sub>x</sub>的相互作用。ZHANG 等<sup>[62]</sup>通过NaOH改性合成富含羟基的活性炭来探索羟基官能团的作用,结果表明:在物理吸附方面,羟基能与SO<sub>2</sub>形成偶极之间的相互作用,而在化学吸附方面,虽然羟基官能团能降低反应能垒,但通过反应平衡常数分析,化学吸附几乎不会发生。KIM 等<sup>[63]</sup>采用苹果酸处理粉煤灰和石油沥青,提升羧基含量并产生微孔结构。FU 等<sup>[64]</sup>采用KOH活化煤基活性炭的方法来实现无氨还原NO<sub>x</sub>,如图2(a)所示。由图2(a)可见,KOH活化可增加活性炭中的无定形碳、孔隙结构和碳氧官能团,这对脱硝性能有积极影响。

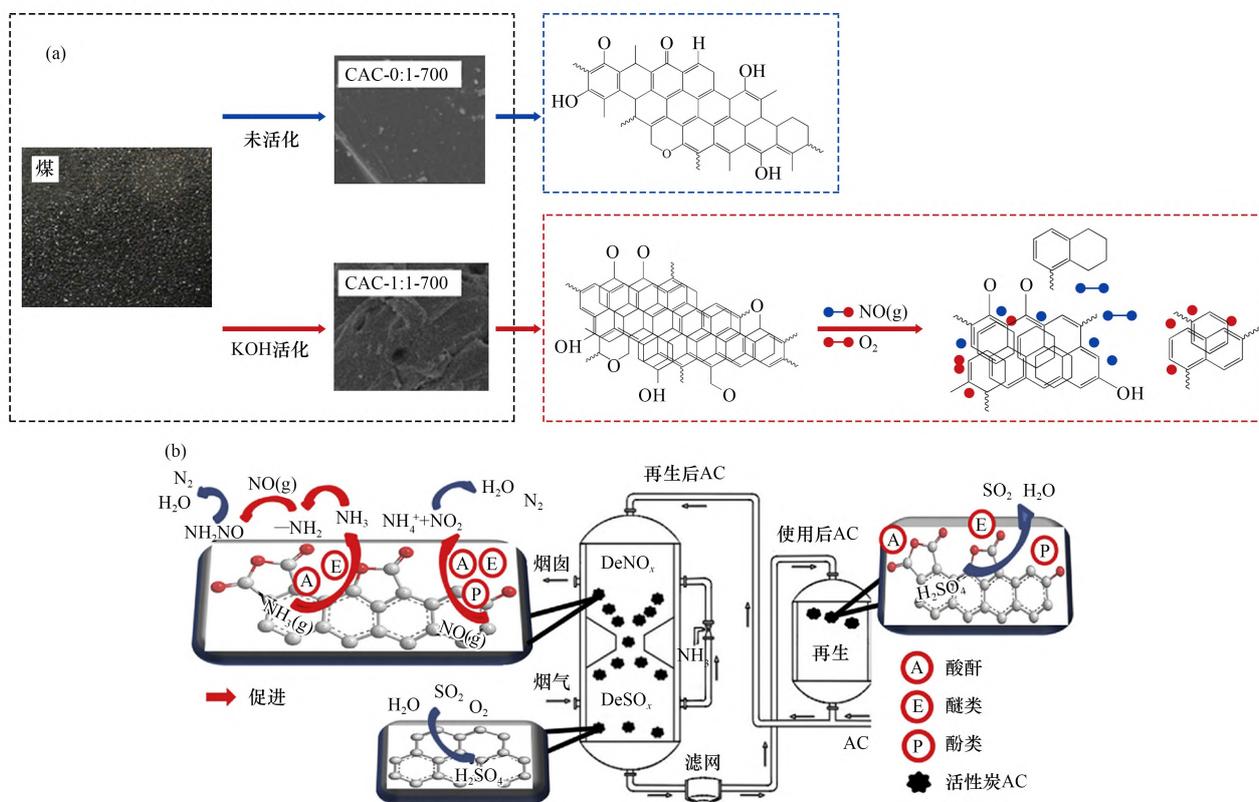


Fig. 2 The mechanism of sulfur and nitrogen removal from activated carbon under acid-base modification conditions

与碱性改性相比,对于酸性改性的研究较少,该方法一般用于增强催化剂的酸性、提高脱硝效率。如图 2(b)所示,LI 等<sup>[65]</sup>采用 HCl 和 HF 处理煤基活性炭,进行活性炭的循环脱硫—再生—脱硝,发现酸酐、酯和酚基的形成提升了 NO 氧化为 NO<sub>2</sub> 的能力,并最终促进 SCR 快速反应。YE 等<sup>[66]</sup>详细探讨了硝酸、硫酸、过氧化氢、草酸和磷酸对活性炭表面改性的影响,认为酸改性可增强物理结构与官能团种类,提高 SO<sub>2</sub> 饱和和吸附时间与脱硝性能;其中硝酸处理显著增加了表面吸附氧和含氮基团数量,有助于脱硫脱硝性能的提升。

### 3.2 氨改性

氨在高温下分解为 NH<sub>2</sub>·、NH·等自由基,与水蒸气和碳反应形成含氮官能团,增加活性炭表面的碱性和亲和力,有利于 SO<sub>2</sub> 的脱除并提高 NO<sub>x</sub> 的吸附效率<sup>[41]</sup>。

WANG 等<sup>[67]</sup>发现氨化作用改变了活性炭的化学性质,氮原子的掺杂导致静电势分布不均匀和表面极性变化,使 SO<sub>2</sub>、H<sub>2</sub>O 和 O<sub>2</sub> 通过氢键和范德华力吸附在含有吡咯官能团的石墨烯上,以吡咯官能团相对强的氢键来吸附 SO<sub>2</sub>。YANG 等<sup>[57]</sup>采用 H<sub>3</sub>PO<sub>4</sub> 活化和 NH<sub>3</sub> 改性制备 N、P 共掺介孔生物炭,发现 NH<sub>3</sub> 优先与 P—O 基团反应形成胺类,进一步转化为吡啶、吡咯或 N—P 和季铵盐,从而引入丰富的含氮结构并产生更多的介孔。LI 等<sup>[68]</sup>用氨水或硝酸溶液处理活性炭,增加含氮官能团的含量和种类。如图 3 所示,改性后含氧官能团的含量增加,表面含氮官能团的类型和含量发生变化,具有吡咯或吡啶结构的活性基团可促进 NO 吸附,但也可能会被 NH<sub>3</sub> 还原或被 O<sub>2</sub> 氧化生成硝基、硝酸盐、胺和亚胺等非活性基团。SHAO 等<sup>[40]</sup>和 ZHANG 等<sup>[43]</sup>分别采用甲基二乙醇胺浸渍和高温氨化结合 CO<sub>2</sub> 活化改善炭的理化特性,发现改性虽降低了比表面积,但显著提高了表面氮含量,使得 120 °C 时氮官能团对 SO<sub>2</sub> 的吸附作用强于孔隙结构。ZHANG 等<sup>[44]</sup>采用一步高温 CO<sub>2</sub>-NH<sub>3</sub> 改性方法制备活性生物炭,发现两者协同可实现热活化和氮掺杂,使自由基进入微孔并通过热蚀刻扩大孔径。

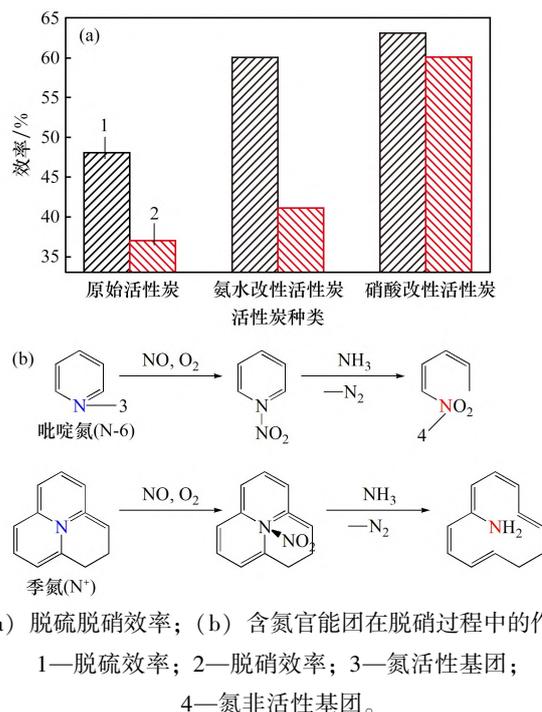


图 3 氨改性活性炭与未改性活性炭脱硫脱硝效率及机理比较

Fig. 3 Comparison of desulfurization and denitrification efficiency and mechanism between ammonia-modified activated carbon and unmodified activated carbon

### 3.3 金属氧化物负载

金属氧化物可作为催化剂促进 SO<sub>2</sub> 氧化生成 SO<sub>3</sub> 并形成硫酸盐,或催化 NO 与 NH<sub>3</sub> 等还原剂反应,从而提高脱硫脱硝效率。目前采用的金属包括 Cu、Co、Ti、Ni、Mn、Fe、V 等。常见金属负载活性炭如表 4 所示。由表 4 可以看出,金属负载改性活性炭大多数用于脱硝过程。对于一元负载,主要采用 V、Cu、Mn 等金属,如 GUO 等<sup>[70]</sup>发现 V<sub>2</sub>O<sub>5</sub> 与 SO<sub>2</sub> 反应生成 V<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>,其不会使催化剂失活,而是作为催化 SO<sub>2</sub> 氧化为 H<sub>2</sub>SO<sub>4</sub> 的活性组分,因此 V<sub>2</sub>O<sub>5</sub>/AC 的硫容量由 V<sub>2</sub>O<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub> 和 H<sub>2</sub>SO<sub>4</sub> 的生成量决定。XIE 等<sup>[73]</sup>通过预氧化提高 V<sup>4+</sup> 转化为 V<sup>5+</sup> 的比例及表面活性氧的含量,促进 SCR 快速反应。KONG 等<sup>[75]</sup>将 V<sub>2</sub>O<sub>5</sub>、MnO 和 CuO 分别负载到松木炭上,研究表明:在 160 °C 下 CuO 表现出最高 NO<sub>x</sub> 还原活性,孔结构则因 Mn 与 V 的加入而略有减小。

二元负载多以 Mn 为基础,Mn 具有极高的表面活性,在低温条件下具有较高的转化能力<sup>[104]</sup>。

表4 常见负载金属及其去除SO<sub>2</sub>和NO<sub>x</sub>的能力Table 4 Common loaded metals and their ability to remove SO<sub>2</sub> and NO<sub>x</sub>

负载金属	测试条件	去除能力	
		SO <sub>2</sub>	NO <sub>x</sub>
Cu <sup>[69]</sup>	(18 ± 2) °C, 0.150% SO <sub>2</sub>	20.50 mg/g	—
V <sup>[70]</sup>	120 °C, 0.150% SO <sub>2</sub>	42.40 mg/g	—
Zn-Fe <sup>[71]</sup>	35 °C, 0.100% SO <sub>2</sub>	277.80 mg/g	—
Co-Ti-Mn <sup>[72]</sup>	80 °C, 0.300% SO <sub>2</sub>	174.40 mg/g	—
V <sup>[73-74]</sup>	120 ~ 240 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	97.70%
	120 ~ 250 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	100.00%
Cu <sup>[75-76]</sup>	440 °C, 0.100% NO	—	100.00%
	160 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	20.20%
Mn <sup>[77]</sup>	150 °C, 0.040% NO, 0.040% NH <sub>3</sub>	—	97.00%
Ce <sup>[78]</sup>	230 °C, 0.100% NO <sub>x</sub> , 0.100% NH <sub>3</sub>	—	93.44%
Fe <sup>[79]</sup>	350 °C, 0.100% NO	—	95.00%
Cr-Fe <sup>[80]</sup>	180 °C, 0.040% NO, 0.040% NH <sub>3</sub>	—	100.00%
Mn-Fe <sup>[81-85]</sup>	120 ~ 240 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	100.00%
	120 ~ 240 °C, 0.040% NO, 0.040% NH <sub>3</sub>	—	94.70%
	200 ~ 300 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	90.00%
	125 ~ 200 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	>90.00%
	150 °C, 0.040% NO, 0.040% NH <sub>3</sub>	—	91.30%
Mn-Ni <sup>[86]</sup>	200 ~ 250 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	80.00% ~ 97.00%
Mn-Zr <sup>[87]</sup>	200 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	86.00%
Mn-Sm <sup>[88]</sup>	200 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	85.00%
Mn-Cu <sup>[89]</sup>	225 °C, 0.050% NO	—	99.00%
Mn-Ti <sup>[90]</sup>	300 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	92.00%
Mn-Ce <sup>[91]</sup>	175 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	99.20%
Mn-Ce <sup>[92]</sup>	240 °C, 0.100% NO, 0.100% NH <sub>3</sub>	—	≈100.00%
Ce-V <sup>[93]</sup>	180 ~ 200 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	>90.00%
Ce-Co-Fe <sup>[94]</sup>	250 ~ 350 °C, 0.100% NO, 0.100% NH <sub>3</sub>	—	90.00%
Ce-Mn-V <sup>[95]</sup>	100 ~ 150 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	98.00%
Ce-Mn-Zr <sup>[96]</sup>	200 °C, 0.050% NO	—	97.00%
Ce-Mn-Fe <sup>[97]</sup>	125 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	>90.00%
Cu-Mn-Fe <sup>[98]</sup>	100 °C, 0.050% NO, 0.050% NH <sub>3</sub>	—	74.00%
Co <sup>[99]</sup>	150 °C, 无明确浓度条件	94.20%	92.70%
Co <sup>[100]</sup>	100 °C, 0.005% ~ 0.030% NO <sub>x</sub> /SO <sub>2</sub>	123.10 mg/g	130.20 mg/g
Cu <sup>[101]</sup>	23 °C, 0.009% SO <sub>2</sub> , 0.009% NH <sub>3</sub>	1.03 mmol/g	1.45 mmol/g
Fe <sup>[102]</sup>	200 ~ 500 °C, 0.100% SO <sub>2</sub> , 0.050% NO	100.00%	95.00%
Mn-Ce <sup>[103]</sup>	150 °C, 0.050% NO, 0.050% NH <sub>3</sub> , 0.005% SO <sub>2</sub>	10.20 mg/g	5.40 mg/g

YIN 等<sup>[82]</sup>发现添加 Mn 后 Fe<sub>2</sub>O<sub>3</sub>/AC 催化剂可在低温下展现出优异的 NO<sub>x</sub> 转化性能, 在 180 ~ 240 °C 范围内, NO<sub>x</sub> 转化率超过 94.7%。CHEN 等<sup>[87]</sup>制备了 Zr-Mn/BC 催化剂, 发现此催化剂上有更多的

布氏酸位点和路易斯酸位点。如图 4(a) 所示, 配位的 NH<sub>3</sub> 会被氧化成—NH<sub>2</sub> 中间产物, NO<sub>2</sub> 被氧化成 NO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> 物种与 NH<sub>4</sub><sup>+</sup> 生成 NH<sub>4</sub>NO<sub>3</sub>。在较低温度下, NH<sub>4</sub>NO<sub>3</sub> 可与吸收的 NO<sub>2</sub> 反应生成

$N_2$  和  $H_2O$ , 但在较高温度下,  $NH_4NO_3$  物种会分解成  $N_2O$  和  $H_2O$ , 添加 Zr 可以避免  $NH_4NO_3$  的分解。YANG 等<sup>[91]</sup> 制备 MnCe 负载生物炭催化剂, 如图 4(b) 所示。由图 4(b) 可见, Mn 起主要催化作用, Ce 起辅助催化作用, 氧从  $CeO_2$  转移到  $Mn_2O_3$ , 促进了循环催化反应的速率, 从而显著提高了 NO 转化率。

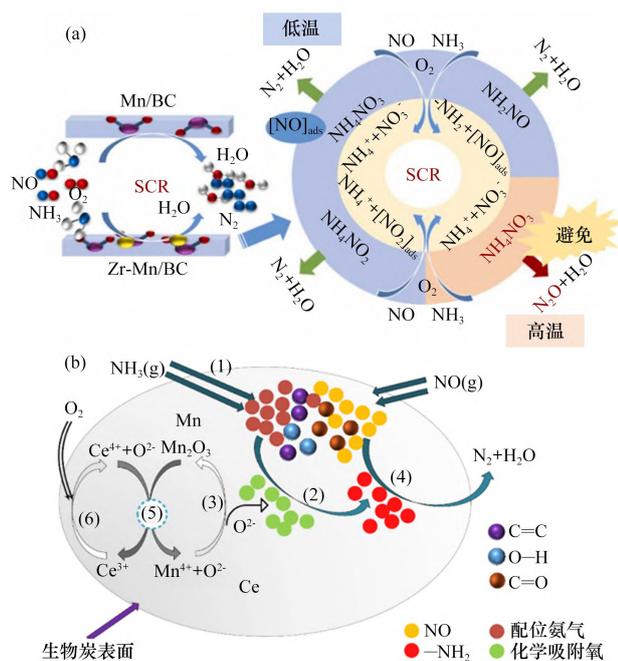


Fig. 4 Mechanism of synergistic removal of  $NO_x$  by binary loading

为了提高催化效率, 研究者<sup>[105]</sup> 在二元负载的基础上引入第三种元素。如图 5(a) 所示, 三元金属氧化物催化剂可以在三种不同价位的金属氧化物之间产生双重氧化还原循环, 显著改善电子传递并促进 NO/ $NH_3$  的吸附/活化。LU 等<sup>[94]</sup> 制备了  $Fe_xCo_yCe_zO_m$  改性活性炭, 研究表明: NO 可被表面吸附氧化, 气相  $O_2$  被  $Fe_3O_4$  和  $Co_3O_4$  捕获, 铈氧化物将吸附氧转变为晶格氧来储存氧, 并促进  $Ce^{3+}$  氧化为  $Ce^{4+}$ 。金属氧化物在不同价态之间的转化可以释放出晶格氧, 同时吸附的 NO 还可能被氧化成  $NO_2$ 。如图 5(b) 所示, PENG 等<sup>[98]</sup> 采用一步混合法制备了  $CuO$ 、 $MnO_2$  和  $Fe_2O_3$  改性活性炭, 结果表明: 混合金属氧化物增加了活性炭

的介孔结构, 其酸性官能团、表面化学吸附氧和晶格氧的数量得到了极大改善, 从而促进了通过 E-R 机理进行的 SCR 反应。这些金属存在多种价态, 发生了  $Mn^{3+} + Fe^{3+} \leftrightarrow Mn^{4+} + Fe^{2+}$ 、 $Mn^{3+} + Cu^{2+} \leftrightarrow Mn^{4+} + Cu^+$ 、 $Cu^+ + Fe^{3+} \leftrightarrow Cu^{2+} + Fe^{2+}$  循环, 催化反应通过这些金属之间的电子转移实现。同时, 样品中存在的  $MnFe_2O_4$ 、 $CuFe_2O_4$  和  $CuMn_2O_4$  等尖晶石, 不仅增强了 SCR 的催化效果, 还有利于抑制  $N_2O$  的生成, 提高抗硫性能。

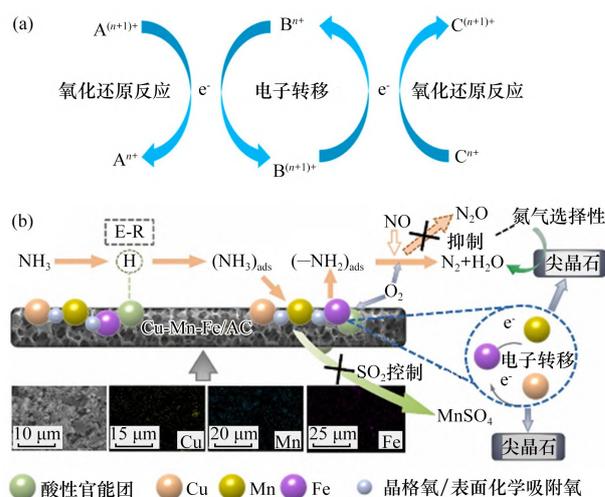


图 5 三元负载协同脱除  $NO_x$  机理

Fig. 5 Mechanism of Synergistic Removal of  $NO_x$  by Ternary Loading

总体而言, 研究中引入的绝大多数是过渡金属, 其氧化物参与了 NO 与  $NH_3$  的反应, 可将 NO 氧化成  $NO_2$ , 从而提高脱硝效率。然而, 常用的金属负载方法成本较高, 且采用常用浸渍方法后的处理步骤复杂。活性金属组分仅支撑在材料表面, 其在热再生过程中容易从基体中流失, 难以再生<sup>[106]</sup>。因此, 制备一种成本低、工艺简单的新型高效改性活性炭具有重要意义。

### 3.4 矿石负载

矿石分布广泛, 含有大量的过渡金属。采用矿石代替化学药剂改性活性炭可以显著降低生产成本, 且共混法简单高效, 能够在较低的成本下得到较高的性能<sup>[107]</sup>。

常用的矿石成分有 Mn、Fe、Ca、Cu 等, 如表 5 所示。朱圣林<sup>[54]</sup> 研究结果表明, 矿石成分会

表5 矿石负载活性炭  
Table 5 Activated carbon loaded on ores

金属元素	添加物	比表面积/ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	测试条件	去除能力	
				$\text{SO}_2 / (\text{mg} \cdot \text{g}^{-1})$	$\text{NO}_x / \%$
Mn、Fe <sup>[54]</sup>	锰铁矿石	645	120 °C ,0. 102% $\text{SO}_2$	38. 50	—
Mn <sup>[108]</sup>	软锰矿	—	80 °C ,0. 300% $\text{SO}_2$	205. 00	—
Ca、Mg <sup>[109]</sup>	固有矿物	933	25 °C ,0. 250% $\text{SO}_2$	73. 40	—
Cu、Fe <sup>[106]</sup>	铜矿石	419	80 °C ,0. 300% $\text{SO}_2$	174. 80	—
Ca <sup>[110]</sup>	方解石	671	120 °C ,0. 250% $\text{SO}_2$	54. 70	—
Ca、Fe <sup>[111]</sup>	黄铁矿 方解石	489	120 °C ,0. 300% $\text{SO}_2$ ,0. 030% $\text{NO}$	112. 60	6. 90 ~ 14. 00
Ca、Fe <sup>[112]</sup>	黄铁矿 方解石	808	393 K,0. 150% $\text{SO}_2$ ,0. 050% $\text{NO}$ ,0. 050% $\text{NH}_3$	38. 10	22. 70
Mn、Fe <sup>[113]</sup>	锰矿石	590	150 °C ,0. 300% $\text{SO}_2$ ,0. 050% $\text{NO}$ ,0. 055% $\text{NH}_3$	138. 50	98. 60
Mn、Fe <sup>[114]</sup>	软锰矿	479	150 °C ,0. 050% $\text{NO}$ ,0. 050% $\text{NH}_3$	—	74. 20
Ti <sup>[115]</sup>	辉绿岩 钛矿石	364	150 °C ,0. 050% $\text{NO}$ ,0. 050% $\text{NH}_3$	—	66. 40
Fe <sup>[116]</sup>	黄铁矿	836	120 °C ,0. 110% $\text{SO}_2$	65. 20	—
Mn、Fe <sup>[117]</sup>	锰铁矿	—	120 °C ,0. 045% $\text{NO}$ ,0. 045% $\text{NH}_3$	—	95. 10

在活性炭表面形成含氧酸性基团,含 Mn 和 Fe 的矿石表现出优异的脱硝性能,这可能是由于多种价态的金属阳离子在脱硝过程中相互转换,迅速传递电子,易使气相氧进入空穴通过捕获电子后形成晶格氧。YUAN 等<sup>[106]</sup>以铜矿石和煤为原料制备活性炭,引入了更多的  $\text{CuO}$ 、 $\text{Fe}_2\text{O}_3$ 、 $\text{Fe}_3\text{O}_4$  和  $\text{C}=\text{O}$  基团,促进了  $\text{SO}_2$  的吸附和氧化。WANG 等<sup>[109]</sup>通过调整煤炭矿物分布,获得了各种孔隙结构的活性炭。矿物中的钙和镁成分显著促进了中孔和大孔的发展,表现出优异的  $\text{SO}_2$  吸附能力。ZHANG 等<sup>[110]</sup>认为方解石( $\text{CaCO}_3$ )是煤中主要的含钙矿物,不仅可以蚀刻碳表面,还使  $\text{CaO}$  参与脱硫过程,最终形成  $\text{CaSO}_4$ ,进一步促进脱硫。ZHANG 等<sup>[111]</sup>利用方解石和黄铁矿生产高性能活性炭,结果表明:方解石和黄铁矿在活性炭制备过程中被转化为赤铁矿、氧化钙、钛硼钛矿等,对活性炭中  $\text{SO}_2$  和  $\text{NO}$  的去除能力有明显的促进作用。

### 3.5 新型改性方式

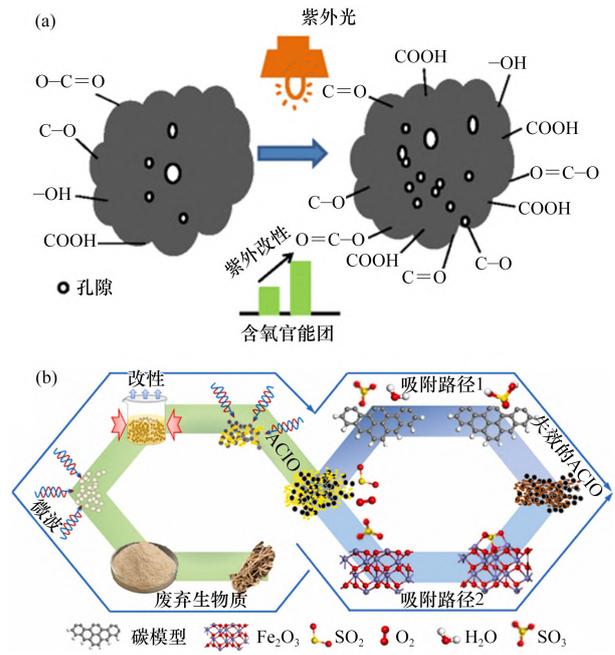
近年来,研究者们开发了一些新型改性方法,如微波辅助改性、纳米材料复合改性、紫外辐照改性等。

紫外辐照改性利用 UV 引发的单体在聚合物表面进行接枝聚合,可以增加活性炭表面官能团的数量,而不会造成二次污染。具体机理<sup>[118]</sup>如图 6(a)所示。由图 6(a)可见,随着辐照时间的延长和辐照距离的缩短,表面的羟基、羧基等官能团的强度增加,而脂肪族链的减少,使活性炭表面的极性提高;同时,芳香结构的形成随着时间的延长而逐渐显现,从而使去除效果得到提升。CHEN 等<sup>[41]</sup>采用  $\text{CO}_2$  与紫外改性相结合的方法,发现在 UV 照射下,材料表面的一些内酯和羟基被氧化为羧基;而  $\text{CO}_2$  与材料表面基团相互作用形成酯基,再加上酸性挥发组分在高温下完全挥发,形成无机盐或无机碱,使得活性炭材料的总碱度增加,增强了活性炭的吸附能力。

微波辅助改性利用微波的热效应和非热效应,可以在几分钟内实现活性炭表面官能团的引入或调整,并改变其孔隙结构。ZAMIRI 等<sup>[119]</sup>通过微波诱导活化,以新型前驱体芦苇草制备活性炭。活性炭的比表面积可达到  $(699 \pm 7) \text{ m}^2/\text{g}$ ,产率为  $44.8\% \pm 1.2\%$ 。IZGI 等<sup>[120]</sup>采用常规加热和微波加热相结合的方法,用磷酸活化剂制备比表面积为  $1\ 128 \text{ m}^2/\text{g}$  的杏仁壳活性炭。TIAN 等<sup>[42]</sup>采用

微波加热法制备氧化铁改性材料，如图 6 (b) 所示，研究表明：氧化铁的加入可以提供更多的活性催化氧化位点，其在催化氧化后与 SO<sub>2</sub> 反应生成硫酸盐，这些硫酸盐储存在材料孔隙中，从而释放表面的活性位点，加速 SO<sub>2</sub> 的催化氧化。GUO 等<sup>[121]</sup>提出了一种以微波辅助粉煤灰和电石渣为吸附剂、活性炭为催化吸附介质的高效低成本脱硫脱硝技术，其最大比表面积和总孔容积分别为 54.43 m<sup>2</sup>/g 和 0.136 cm<sup>3</sup>/g，脱硫的 t<sub>90%</sub> 值（脱除效率达到 90% 所耗费的时间，t<sub>80%</sub> 亦同）和脱硝的 t<sub>80%</sub> 值分别为 86、30 min。

纳米材料因具有高度稳定和独特的纳米结构、高催化活性和大比表面积等物理化学特性受到广泛关注。纳米材料复合改性是通过将如纳米铁、纳米铜等纳米材料均匀分散在活性炭表面，以提高其催化活性和稳定性。DUAN 等<sup>[122]</sup>将牺牲型铜基金属有机骨架 (MOF) 模板加载到低成本的活性半焦炭上，使氧化铜纳米粒子 (Cu<sub>2</sub>O/CuO) 作为活性位点分布在 MOF 衍生的碳八面体和活化的半焦上。如图 7 所示，优化后的样品具有超低表面负载和较高的 Cu 离子含量，突破时间为 822 min，SO<sub>2</sub> 吸附量为 233.11 mg/g，性能最好的样品在 10 次脱硫 - 再生循环中表现出稳定性和可逆性。ZHU 等<sup>[123]</sup>使用负载纳米 MnO<sub>x</sub>-Cu 的活性炭制备

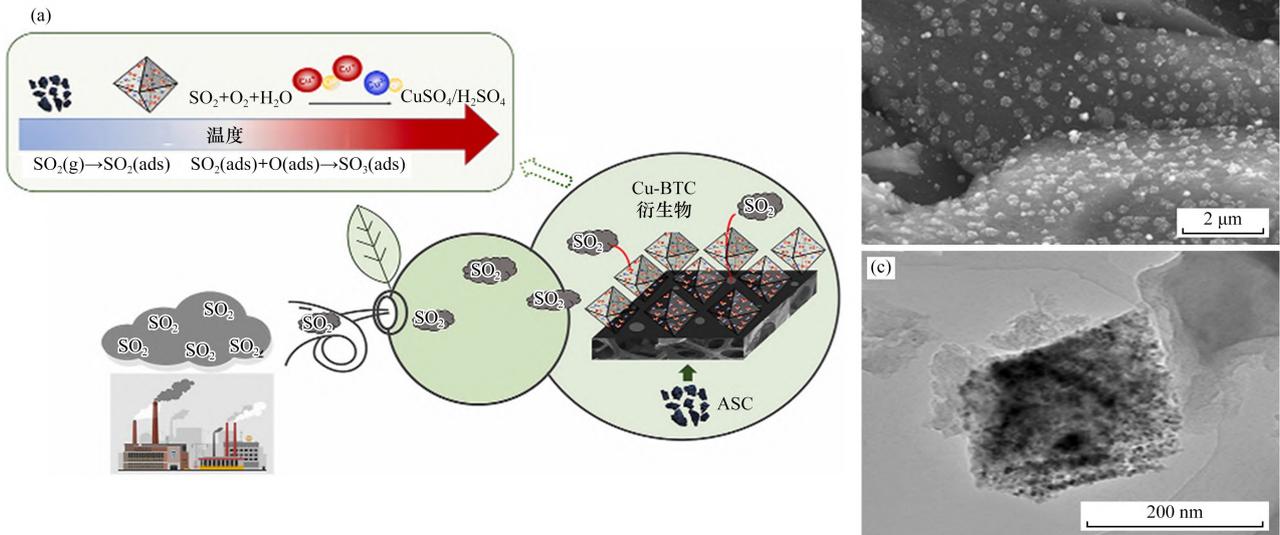


(a) 紫外线改性活性炭制备；  
(b) 氧化铁微波改性活性炭制备及机理  
图 6 紫外和微波改性方式制备活性炭及机理

Fig. 6 Preparation and mechanism of activated carbon by ultraviolet and microwave modification methods

了低温 SCR 催化剂，试验结果表明，当反应温度为 200 °C 时，NO 转化率达到 96.82%，对 N<sub>2</sub> 的选择性几乎达到 99%。

但这些方法都有着成本高且制备复杂的缺点，



Cu<sub>x</sub>O 纳米材料复合改性活性炭：(a) 吸附原理；(b) 扫描电镜结果；(c) 透射电镜结果

图 7 纳米材料复合改性方式制备活性炭形态及机理

Fig. 7 Morphology and mechanism of activated carbon prepared by nanomaterial-compliant modification methods

如微波设备成本较高且加热过程需要严格控制,以避免过热或不均匀;纳米材料的制备过程较为复杂,需要控制粒度、分散性等参数;紫外辐射需要添加光敏剂,且部分活性炭结构可能对紫外辐射不敏感,改性效果受限。新型改性方式仍有发展空间,合适的改性方法应根据具体需求、试验条件和成本等因素综合考虑。

#### 4 结语

(1) 原材料的选择直接影响活性炭的孔结构、表面官能团以及吸附性能。通过比较煤基和生物质等多种原料制备活性炭的结构特性与吸附性能,发现低阶煤因其结构松散、含碳量高且矿物分布合理,是高比表面积活性炭的优良煤源;高木质素生物炭具有大比表面积以及富氮生物质具备富含氮官能团,可提高脱硫脱硝选择性,是实现高效、可持续吸附材料开发的重要方向;污泥活性炭具有一定利用价值,但其比表面积低、机械强度差,尚需进一步改进;同时合理进行原料混配可在保证性能的同时降低制备成本。

(2) 活化是制备高效活性炭的关键步骤。活化剂种类与投加比例对孔结构调控起关键作用,需根据目标污染物种类进行定向设计。物理活化能够在较高温下去除气体分子,形成孔隙结构,尤其在调控中孔结构时具有优势,其局限性在于活化过程较为缓慢,且能效较低;化学活化通过化学反应破坏原料的碳结构,显著提高比表面积和微孔体积;物理与化学活化的联合应用能实现更优化的孔结构设计,调控孔径分布,并提高材料对不同气体污染物的吸附性能,尤其适合复杂废气的治理。

(3) 改性技术能够增强活性炭的表面反应活性和催化能力。金属氧化物负载能引入氧化还原循环反应路径,显著提高脱硝/脱硫效率;氮改性可引入含氮官能团,提高活性炭表面碱性与极性,增强  $\text{SO}_2/\text{NO}_x$  分子吸附亲和力;矿石负载方法简便、成本低,能有效提升表面活性,是工业推广的潜在方向;紫外辐照、微波加热、纳米材料复合等新型改性手段可进一步提升表面能级与结构稳定性,但目前工程化应用中仍存在设备要求

高、成本偏高、再生困难等问题。

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