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钙钛矿材料在环境催化领域的应用现状及进展

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摘要：日益严重的环境问题和有限的资源促使人们积极探索提高污染物处理效率的途径和方法. 多相催化剂在环境污染高效治理中扮演着重要的角色, 因此, 高活性和高稳定性新型多相催化剂的开发成为一项非常有吸引力和具有挑战性的任务. 钙钛矿材料因其高催化活性和稳定的晶体结构成为环境催化领域的研究热点. 我们综述了钙钛矿材料特性、制备方法、新型钙钛矿材料发展现状和在环境催化领域的应用现状, 并对其面临的挑战及未来发展方向进行了讨论.

关键词：钙钛矿; ABO_3; 环境催化; 进展
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如今全球环境污染形势十分严峻, 已经开始危及人类的生存和发展[1]. 大量的新兴污染物具有高毒性和高稳定性的特点, 这导致传统物理和生化处理方法效率低下, 催化剂的引入可以显著提升传统污染治理方法的效率, 极大程度上降低环境治理成本[2-3]. 由于回收困难和金属污泥问题, 均相催化剂的应用受到限制, 所以多相催化剂成为研究热点[4-5].

作为新型多相催化剂, 钙钛矿材料催化活性高, 结构稳定, 活性组分不易流失, 在环境催化领域具有广阔的应用前景[6-7]. 现综述钙钛矿材料的性质、制备及在环境催化领域的应用现状以及近几年新型钙钛矿材料的研究进展, 并对其未来发展方向进行展望.

1 钙钛矿型氧化物

钙钛矿型氧化物具有天然钙钛矿($CaTiO_3$)晶体结构, 其分子通式为ABO_3, A位离子以稀土或碱土金属为主, B位离子以过渡金属为主, 而在实际制备中元素周期表中绝大多数元素都可以形成钙钛矿结构[8-9]. 钙钛矿型氧化物的结构如图1所示, A位离子处于立方晶胞顶点, 与12个O离子配位, B位离子处于立方晶胞体心, 与6个O离子配位, 形成BO_6的八面体[10-11]. 这种结构使半径相差很大的离子能够共存于晶型中, 同时存在空位或离子半径有一定偏差时, 仍能保持稳定[12-13].

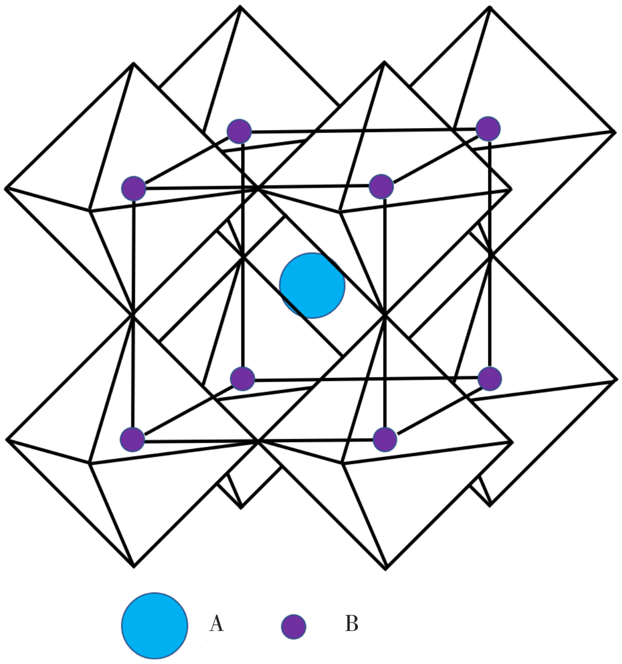

图1 钙钛矿型氧化物的晶体结构

Fig.1 Crystal structure of perovskite oxides

钙钛矿型氧化物的催化活性主要取决于B位元

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素，A位元素调控B位元素的价态和分散状态[14-15]. 通过元素的替换和掺杂可以调控钙钛矿型氧化物的催化性能，A位和B位都可被相同或不同价态离子取代，用$A_{1-x}A'_{x}B_{1-y}B'_{y}O_{3+\delta}$表示[16-17]. 在钙钛矿结构中，O离子也可被非金属离子或卤族元素替换，如：F、Cl、I等[18].

钙钛矿材料具有光、电、磁等物理特性以及氧化还原性、催化活性等化学性质，在催化领域具有广阔的应用前景[19]. 通过掺杂取代和与其他材料的复合，可以改变钙钛矿的物理和化学特性，如能带宽度、离子价态和空位数量等，从而改变离子的配位环境，同时产生多种类型的相变[20-21]. 钙钛矿材料中铁电-顺电(FE-PE)转变、金属-绝缘体(M-I)之间的转变和铁磁-顺磁(FM-PM)转变等前沿课题已成为当今催化化学领域研究的热点[22-23].

2 钙钛矿型氧化物的制备

制备条件对钙钛矿材料的形貌、粒径、比表面积和结晶度具有显著影响，进而影响其催化性能[24-25]. 如今钙钛矿制备已经取得了一定进展. 几种常用制备方法的优缺点列于表1中.

表1 几种常用制备方法的优缺点

Table 1 Advantages and disadvantages of several common preparation methods

Preparation method	Advantages	Shortcomings
Sol-gel method	In the early stage of preparation, the structure, uniformity and chemical state of perovskite can be controlled by controlling the type of complexing agent and calcination temperature. The prepared perovskite material has high purity, uniform particle size and high catalytic activity	The agglomeration and sintering of products result in poor catalysis of perovskite materials
Co-precipitation method	Simple operation, high purity, easy doping and uniform particle size	The low dispersion of precipitant results in high local concentration of product, which leads to particle agglomeration of perovskite and limits its catalytic activity
Hydrothermal synthesis method	The crystallization process occurs directly in the solution without calcination, and the valence state of elements is controllable. Perovskite with complete grain development, uniform particle size distribution and high dispersion can be obtained	High requirements for temperature and air tightness, long preparation period, poor controllability of reaction process and high energy consumption
Mechanical mixing method	Simple operation and low cost	The reaction in the form of physical contact friction is not conducive to the uniform reaction of raw materials, resulting in coarse particles and low purity of the product. The crystal structure reorganization process requires a lot of energy and needs to be carried out at high temperature.
Combustion method	It can be carried out at a low temperature, and the size of the nanoparticles can be controlled by controlling the sintering temperature of the precursor. The product particles are uniform and well dispersed.	Producing a large amount of toxic gases during preparation

发展较为成熟的制备方法仍面临一系列问题，目前也已经研究出一些改进方法. 机械混合法无法满足现阶段研究对钙钛矿纯度和晶粒尺寸的要求，燃烧法制备过程中伴随大量有毒气体的产生，不符合环境保护要求，所以目前钙钛矿材料制备多采用溶胶-凝胶法、共沉淀法和水热合成法[26-27]. 溶胶-凝胶法和共沉淀法制备的钙钛矿团聚和烧结严重，限制了产物的催化活性[28-29]. 与超声或微波联用、对前驱体采取冷冻干燥等手段可以有效限制团聚和烧结[30]. Hosseini等[31]通过超声辅助溶胶-凝胶法合成$LaMnO_3$作为CO选择性还原NO

的催化剂，结果表明超声辅助使钙钛矿晶粒尺寸降低，比表面积增大，氧空位增多，进而显著提升了钙钛矿的催化活性. Yousefi 等[32]分别采用普通共沉淀法，微波辅助共沉淀法和超声波辅助共沉淀法制备 $La_{0.75}Sr_{0.25}MnO_3$，结果表明微波和超声波辅助制备的产物更均匀且反应周期更短，钙钛矿的烧结和团聚也被显著抑制. Huang 等[33]采用冷冻干燥辅助共沉淀法制备 $La_{0.6}Sr_{0.4}MnO_3$，结果表明制备的钙钛矿具有较高的沉淀成分均匀性，这有助于降低结晶温度，从而提高表面积. 一些原料与水反应或遇水分解使水热合成难以实现，以有机溶剂为反应介质可以解决这个问题[34–35]. 杨威[36]以苯甲醇代替水，采用有机溶剂热合成法制备 $LaFeO_3$，结果表明与溶胶-凝胶法相比，制备的样品具有更均匀的晶粒和更高的比表面积.

3 新型钙钛矿材料

钙钛矿材料的应用面临比表面积低，活性位点暴露不足，催化活性受到限制的问题[37]. 针对以上问题，高比表面积新型钙钛矿材料的开发成为研究重点.

3.1 高比表面积单相钙钛矿材料

将钙钛矿材料本身制备成高比表面积的结构是提升其催化活性最直接的办法. 为解决传统钙钛矿材料晶粒聚集程度高，比表面积低的问题，一些研究者制备高比表面积单相钙钛矿材料. 三维有序大孔(Three Dimensional Ordered Microporous, 3DOM)结构孔径和孔隙率可控，联通有序的孔结构也有利于比表面积的提升和反应物的扩散，因此，3DOM 钙钛矿材料在高比表面积单相钙钛矿材料制备中值得关注[38]. Zhang 等[39]制备 3DOM$La_{2-x}K_xNiCoO_6$ 用于烟尘颗粒催化纯化，其比表面积达到溶胶-凝胶法的 8.72 倍，促进催化剂与烟尘颗粒之间的接触，进而显著提升钙钛矿材料的催化活性. Wu 等[40]制备 Pt 修饰的光催化剂 3DOM$SrTiO_3$，结果表明 3DOM 结构的慢光效应提高了入射光的吸收.

3DOM 材料的催化活性与孔径有关，而孔径又由微球模板的直径决定[41]. 在微球制备过程中，单体和引发剂的用量、反应温度、搅拌速度等因素都会影响其直径，由于这些影响因素较为复杂且难以控制，到目前为止很难控制合成不同直径的微球，这也导致 3DOM 钙钛矿材料的制备受到一定限制[42–43]. 此外，粒径在 500 nm 以上的微球很容易聚集，同时孔径过大的 3DOM 钙钛矿材料非常脆弱，难以在催化反应过程中维持结构稳定，以上两个原因导致孔径大于 500 nm 的 3DOM 钙钛矿材料难以制备[44–45]. 因此，孔径大且均匀的 3DOM 钙钛矿材料制备是目前高比表面积单相钙钛矿材料的研究重点.

3.2 负载型钙钛矿材料

将钙钛矿负载在多孔材料表面可以提升颗粒分散性，防止活性金属烧结，提升材料的比表面积，进而显著提升其催化活性[46]. Liu 等[47]制备 $LaFeO_3$/ZSM-5 用于催化高温脱硫，结果表明，$LaFeO_3$/ZSM-5 具有较高的比表面积，其催化活性和稳定性均明显高于溶胶-凝胶法制备的 $LaFeO_3$.

目前负载型钙钛矿材料制备仍以浸渍法为主，传统浸渍法存在活性组分分散性差，与载体结合稳定性不佳等问题[48–49]. 因此，新型高分散性、高稳定性负载方法的开发是一个重要的课题. 在众多新型制备方法中，微波辅助合成法值得关注. 该方法对反应物进行无热梯度加热，提高材料的形成速度和均匀性，同时可以得到高结晶度、高维纳米结构的材料[50–51]. He 等[52]将新石竹生物炭(NAB)和纳米片 Co_3O_4 置于微波反应器中，800 W 反应 60 s，得到 Co_2P-NAB 复合材料，结果表明 Co_2P 结晶度高并均匀分散在 NAB 表面，同时 Co_2P-NAB 在催化降解四环素中表现出较高的稳定性.

载体的类型和性质对负载型钙钛矿材料的催化性能有重要影响，所以新型高比表面积载体的开发也值得关注[53]. 由于钙钛矿材料制备经历高温煅烧过程，所以负载型钙钛矿载体材料应具备较强的热稳定性[54–55]. Pan 等[56]的研究表明由于多孔材料表面晶体生长空间较大，钙钛矿晶粒具有较大的尺寸，在催化反应中呈现更强的稳定性.

3.3 复合型钙钛矿材料

将金属氧化物与钙钛矿复合不仅可以提升材料的比表面积，还可以通过对钙钛矿的改性提升其催化活性[57]. 在众多基体材料中，ZrO_2 和 CeO_2 对钙钛矿的储氧能力和热性能有显著的积极影响，同时能与钙钛矿材料产生积极的相互作用[58]. Song 等[59]制备的 $La_{0.95}Ce_{0.05}Co_{0.7}Cu_{0.3}O_3/ZrO_2$ 催化剂表现出良好的活性和选择性.

目前已知的基体与钙钛矿之间的复合方式有两种，一是通过掺杂过程将金属离子引入钙钛矿晶格，二是通过修饰钙钛矿颗粒表面来获得金属/钙钛矿

复合材料[60-61]. Hammouda等[62]制备CeO_2-$LaMO_3$(M=Cu, Fe)用于非均相芬顿降解双酚A，结果表明部分Ce^{4+}离子进入钙钛矿晶格中，导致Cu和Fe向低价态转化，同时CeO_2中的Ce^{4+}和Ce^{3+}之间的循环反应加快钙钛矿催化剂电子转移速率，两种作用共同提升钙钛矿材料的催化活性和稳定性.

制备方法方面目前的研究主要集中在钙钛矿与金属氧化物的简单复合，主要为简单浸渍或机械混合，其弊端在于钙钛矿在复合材料中的分散性不佳，同时难以达到催化剂的稳定性要求，所以复合型钙钛矿材料的新型制备方法开发也值得关注[63-64].

3.4 钙钛矿型催化剂载体

与普通金属氧化物相比，钙钛矿材料中存在某些元素的异常价态，从而使氧以非化学计量比存在[65]. 这一特性使钙钛矿具有特殊的氧迁移和储存能力，特别适合作为催化剂载体[66]. Zhang等[67]制备$Ni/La_{1-x}Sr_xAlO_{3-y}$，结果表明与Ni/Al_2O_3相比，由于$La_{1-x}Sr_xAlO_{3-y}$中的表面氧的存在，Ni结焦程度显著降低. Kopacč等[68]制备$Cu/SrTiO_3$，结果表明在金属活性组分与载体钙钛矿之间存在电子循环效应，进而实现高催化活性.

目前关于钙钛矿载体的研究较少，主要原因在于其作为载体材料结构稳定性不足，导致负载型催化剂稳定性差[69]. 但由于一系列优良特性的存在，钙钛矿仍是应用前景广阔的载体材料，所以高比表面积高稳定性钙钛矿载体的开发仍是环境催化领域的研究重点.

4 钙钛矿材料在环境催化领域的应用

与过渡金属氧化物相比，钙钛矿材料的热稳定性、化学稳定性和结构稳定性相当高，有利于减少活性组分的流失，延长催化剂寿命，因此，钙钛矿材料可以应用于催化高温下进行的气体或固体反应或低温下发生的液相反应，这使其可以被广泛应用于催化领域[70-73]. 同时元素掺杂的灵活性为新型催化剂的研发提供无限可能[74]. 这些优越特性使钙钛矿材料成为环境催化领域的研究热点.

4.1 废水处理

钙钛矿材料作为水处理固相催化剂具有较高的催化活性，同时其稳定的晶体结构可以有效减少活性组分的浸出和金属污泥的产生，大大减轻二次污染[75-76].

4.1.1 芬顿氧化

传统均相芬顿技术因其存在金属污泥产量大和pH适应范围窄的问题而逐步被非均相芬顿替代，因此非均相催化剂成为芬顿技术领域的研究重点[77]. 由于纯氧化铁或氧化铜在芬顿体系中的催化活性有限，混合金属氧化物催化剂研究越来越受到关注[78].

钙钛矿材料凭借高容差因子，可以同时将多种金属阳离子纳入其晶格中，因此其在非均相芬顿领域具有较大的应用价值[79-80]. 李超等[81]制备$LaFe_xCu_{(1-x)}O_3$并将其用于非均相芬顿降解亚甲基蓝，结果表明pH值在2~10范围内催化剂均具有较高活性，同时Fe和Cu浸出浓度分别在0.1021和0.1110 $mg\cdot L^{-1}$以下，极大程度上减少了金属污泥的产生，避免造成二次污染.

钙钛矿材料表面丰富的氧空位对活化H_2O_2具有重要作用，在芬顿体系中，氧空位都可以作为缺陷位点，促进钙钛矿与H_2O_2之间形成化学键，从而实现自由基的高效产生[82-83]. 同时，氧空位可以影响金属的电子不对称化学状态，提高催化位点的活性[84]. Sun等[85]制备富含氧空位的$LaCu_{0.5}Fe_{0.5}O_{3-\delta}$在催化降解双酚A中表现出优异的稳定性和较高催化活性.

4.1.2 光催化氧化

由于具有较强的氧化能力和稳定性、无毒、生产成本低等优点，TiO_2是目前主要的光催化材料[86-87]. 但TiO_2在光催化中的应用被限制在紫外光区(小于388 nm)，而紫外光只占太阳辐射的4%[88-89]. 因此，开发具有可见光活性的新型光催化剂是一个重要课题.

钙钛矿材料具备适当的电子结构，将带隙能量转移到可见光吸收，同时其晶体结构允许晶格畸变，强烈影响光生电荷载流子的分离并避免复合过程，因此，钙钛矿材料是TiO_2的优良替代材料[90-91]. 金属卤化物钙钛矿具有易于制备、可调谐的带隙和电荷传输特性优良的优势，这使其成为重要的光催化候选材料[92-93]. Huang等[94]制备$FAPbBr_3/TiO_2$用于选择性光催化氧化苯甲醇，结果表明$FAPbBr_3/TiO_2$复合材料中的能带排列促进了苯醇高效、高选择性地光催化氧化成苯甲醛.

金属卤化物钙钛矿作为光催化剂也面临两个主要限制[95-97]：(1) 在极性溶剂中的化学稳定性不佳；(2) 表面易发生化学物质在溶液中的转化；用有机分

子/聚合物或无机氧化物/硫族化合物进行表面改性是保护半导体纳米晶体和修复表面缺陷的有效策略. 因此, 选择合适的表面改性剂对钙钛矿材料进行表面修饰将是改善钙钛矿材料光催化性能和稳定性的重要研究方向.

4.1.3 湿式催化氧化

在湿式催化氧化反应中, 贵金属和过渡金属基催化剂的研究最为广泛, 贵金属催化剂成本高昂, 作为贵金属催化剂的替代品, 过渡金属氧化物在湿式催化氧化技术中应用广泛, 但由于在湿式催化氧化工艺运行过程中催化剂暴露在高温强氧化条件下, 导致了过渡金属离子的浸出, 因此需要额外的工艺来回收有毒的过渡金属离子[98-99].

钙钛矿材料具有优良的氧化还原性能和电子迁移率, 同时稳定的立方晶型结构带来水热稳定性和抗氧化腐蚀能力, 这使其能在湿式催化氧化反应中维持稳定, 大大降低金属离子浸出浓度[100-101]. Palas等[102]将$LaNiO_3$用于湿式空气催化氧化降解活性黑, 催化剂在高温高压的环境中表现出较强的稳定性.

钙钛矿材料在湿式催化氧化技术应用中面临的主要问题仍是金属组分浸出问题, 因此新型高稳定性钙钛矿材料开发是研究重点. 过渡金属催化剂的浸出在一定程度上是不可避免的, 从这个角度讲, 作为唯一的没有生物毒性的过渡金属, 铁系钙钛矿材料应用潜力巨大.

4.1.4 电催化氧化

贵金属是目前最高效的电催化剂, 例如Pt、Ru、Rh和Ir基纳米材料, 但这些材料的高成本使得大规模生产难以实现[103-104]. 为了克服这一问题, 开发新型高活性低成本电催化材料尤为重要.

钙钛矿材料因其优异的热稳定性、离子导电性、电子迁移率和氧化还原行为而成为极具潜力的电催化材料[105-106]. 然而, 传统钙钛矿材料导电性差, 导致大量电能浪费, 元素掺杂是提高钙钛矿综合性能的有效方法[107]. 在保持稳定构型的前提下, 在A位或B位灵活取代, 从而诱导形成复合价态, 可作为氧化还原对, 方便电子的转移过程[108-109]. 此外, 氧空位的形成符合电中性原理, 可以作为新的反应位点捕获激发的自由电子, 延缓e^--h^+对的复合速率, 产生更多的氧化活性物质[110-111]. Chen等[112]将$Sr_xLa_{1-x}Mn_yCo_{1-y}O_{3-\delta}$包裹在钛板上作为阳极用于高效电催化氧化含氨氮有机废水, 5次重复后仍能保持较高的电流效率和催化降解效率. 通过机械混合的方式在电极材料中添加导电剂也可以提高其导电性, 但此类方法制备新型钙钛矿阳极材料的报道仍然较少. 另外, 有效调节钙钛矿氧化物的纳米级形态同时将活性位点与导电支架整合也是一个巨大的挑战.

4.2 有害气体处理

钙钛矿材料表面含有丰富的晶格氧和吸附氧, 通过高效电子转移可以催化气体氧化过程, 进而实现有害气体的净化[113].

4.2.1 CO催化氧化

铂族金属被广泛用作CO氧化反应的催化材料, 但其存在成本高、低温活性低和高温聚集成较大颗粒的缺陷[114].

解决上述问题的一种策略是将贵金属负载到廉价载体上, 提升其分散性以避免聚集, 进而提升其催化活性[115]. 钙钛矿材料具有较强的氧迁移和储存能力以及相对较低的成本, 是贵金属催化剂理想的载体材料[116]. Einaga等[117]制备$LaMO_3$(M=Mn, Fe, Co)并将其用于CO的微波辅助催化氧化, 结果表明催化活性$LaCoO_3>LaMnO_3>LaFeO_3$, 同时Sr对La的部分取代可以显著提升钙钛矿的催化性能.

另一种解决方案是直接用廉价材料取代贵金属成为新型CO氧化催化剂[118]. 钙钛矿材料具有丰富的组成、结构可调性、热稳定性和优良的催化性能, 是贵金属在CO和碳氢基燃料催化氧化中的潜在替代品[119-120]. 然而, 在钙钛矿中活化晶格氧以获得活性氧是一个很大的挑战, 这也导致其催化性能低于预期, 严重制约了高效钙钛矿催化剂的开发[121-122]. 氧的活性和稳定性与固体表面的电子结构和几何结构密切相关, 有研究发现钙钛矿氧化物中金属—O键的共价会严重影响催化活性, 增强B位正离子和O位负离子之间的相互作用, 对晶格氧的活化非常有利[123-124]. Wang等[125]制备$La_{0.4}Sr_{0.6}CoO_{3-\delta}$, 通过调节$Co^{4+}$和$O^{2-}$之间的电荷转移激活催化剂表面的晶格氧, 实现了CO的高效催化氧化.

4.2.2 CH_4催化燃烧

催化燃烧技术一直被认为是一种前景广阔的未燃CH_4完全氧化策略, 而高性能催化剂的开发是其中的关键步骤[126-127]. CH_4催化燃烧目前常用的催化剂包括贵金属材料和单一或杂化的过渡金属氧化物[128]. 贵金属催化剂虽然具有相当高的催化活性, 但存在成本高、热稳定性低、易烧结、易中毒的

缺陷．相比之下，过渡金属氧化物因其较好的热稳定性和较低的成本而被认为是一种合适的候选材料[129]．

在常见的过渡金属氧化物中，钙钛矿材料被广泛用于CH_4的催化燃烧[130]．Poffe等[131]制备高比表面积纳米多孔、高温稳定的$SrTi_{0.65}Fe_{0.35}O_{3-\delta}$，结果表明高孔隙率改善了表面氧的释放和氧的扩散，进而有效改善催化剂在低温环境中的催化性能．复合型钙钛矿材料的设计被认为是开发用于CH_4转化的高性能、可持续催化剂的有效策略[132]．Chen等[133]制备$MnO_x/LaMnO_3$，结果表明由于氧缺陷的产生，Mn^{3+}/Mn^{4+}氧化还原循环和O_2/OL的有效电子转移促进MnO_x和$LaMnO_3$之间的强相互作用，进而保证催化剂在100 h内表现出优异的CH_4催化燃烧活性．

4.2.3 NO_x催化分解

直接催化分解具有工艺简单和不产生二次污染等优点，近年来成为NO_x处理的主流工艺之一[134]．NO_x分解虽然热力学上可行，但需要克服高活化能，因此反应需要在催化剂和一定温度条件下才能进行[135]．目前常用的NO_x直接催化分解催化剂主要包括贵金属、金属氧化物、钙钛矿材料、离子交换ZSM-5分子筛和水滑石型材料等[136]．部分贵金属和金属氧化物催化活性较高，但对SO_2非常敏感，当SO_2存在时易生成硫酸盐，对其产生毒化作用[137]．

钙钛矿材料有良好的热稳定性，同时大量的氧空位或氧过剩有利于NO_x的分解，因此钙钛矿材料成为重要的NO_x催化分解催化剂[138-139]．氧空位的存在和B位离子的氧化还原性质是影响NO_x吸附和活化的两个主要因素，在反应过程中起着重要作用，一方面氧空位为NO_x的吸附提供位点，另一方面结构中产生的电子可以活化NO_x[140-141]．Wang等[142]将$BaBi_{0.05}Co_{0.8}Nb_{0.15}O_{3-\delta}$中空纤维膜与Ni-层状硅酸盐中空球催化剂相结合制备中空纤维膜反应器，用于NO催化分解反应，结果表明，新型催化膜反应器可以克服氧气的抑制作用，在中低温下将NO完全转化为N_2．

4.3 固体废物处理

催化热解将固体废物加热到一定温度获得小分子化合物，进而实现废物无害化和资源化，它具有成本低、易于分离所需产品等优点，引起了人们的广泛关注[143-144]．催化热解通常在无氧或缺氧的气氛中直接对固体废物进行加热，因此需要催化剂适应高温和低氧环境[145-146]．

钙钛矿材料催化活性高、热稳定性强、抗毒性强、氧离子和电子传输性能优良，同时该材料被证明可以在缺氧条件下释放氧气来催化燃料的燃烧或转化[147-148]．基于以上特点，钙钛矿被认为是催化热解反应的理想催化剂．Wang等[149]制备$LaTi_{0.2}Fe_{0.8}O_3$用于催化热解甘蔗渣木质素制备芳基含氧化合物，结果表明催化剂在连续5次氧化还原循环后对甘蔗渣热解具有良好的相稳定性和催化稳定性．催化剂的存在可以控制热解过程中所需产物(如气体、汽油或柴油)的产率，同时可以抑制杂质的产生[150]．钙钛矿材料可以作为高选择性催化剂的基体，提升其催化性能[151]．Li等[152]将$Ni/LaAlO_3$用于大豆秸秆催化热解制合成气，结果表明当Ni添加量为10%时实现H_2、CO产率大幅提高并抑制杂质的产生．

5 结语与展望

总结了钙钛矿材料的特性、制备方法、新型钙钛矿材料发展现状和在环境催化领域的应用现状．阐述了钙钛矿材料作为多相催化材料的优良特性，但其仍然存在着诸多挑战．

(1) 传统钙钛矿材料颗粒聚集度高，比表面积低．低比表面积是限制钙钛矿催化剂活性的主要原因，目前的新型钙钛矿材料往往具有多孔结构和高比表面积，这有利于催化剂活性位点的暴露和催化性能的提升，但新型钙钛矿材料多孔结构的稳定性有待进一步提升．

(2) 对于金属氧化物特别是过渡金属氧化物为基体的钙钛矿复合材料，钙钛矿与载体的相互作用机理尚不明确，基体金属原子是否会进入钙钛矿结构，造成晶体结构畸变是一个值得关注的问题．

(3) 目前常用的复合材料制备方法是浸渍，这限制了负载量，同时造成钙钛矿晶体与载体结合不稳定．所以开发新型钙钛矿复合材料制备方法将成为研究热点之一．

(4) 目前的复合钙钛矿材料多采用外包裹式(即将钙钛矿负载在载体表面)，新型内包裹钙钛矿复合材料(即将改性组分如CeO_2包裹在钙钛矿表面)的催化性能需要进一步研究．

总之，开发新型高活性高稳定性钙钛矿催化剂是多相催化领域中的一个重要课题，值得研究者们的持续关注．

参考文献：

[1] Hao Y, Zheng S, Zhao M, *et al*. Reexamining the relationships among urbanization, industrial structure, and environmental pollution in China-New evidence using the dynamic threshold panel model[J]. *Energy Rep*, 2020, **6**: 28–39.

[2] a. Gu G H, Noh J, Kim S, *et al*. Practical deep-learning representation for fast heterogeneous catalyst screening [J]. *J Phys Chem Lett*, 2020, **11**(9): 3185–3191.

b. Jia Yin-juan(贾银娟), Wang Can(王 灿), Wu Shuang (吴 双), *et al*. Study on catalytic hydrolysis of COS and CS_2 by Al_2O_3-Zn-K(Al_2O_3-Zn-K催化水解COS和CS_2的研究)[J]. *J Mol Catal*(*China*) (分子催化), 2022, **36** (2): 171–179.

c. Zhang Ying(张 迎), Zhu Wen-jie(朱文杰), Fu Te(富 特), *et al*. Research progress of Ce-based catalysts in catalytic combustion control of volatile organic compounds(铈基催化剂在挥发性有机物催化燃烧治理中的研究进展)[J]. *J Mol Catal*(*China*)(分子催化), 2022, **36**(1): 58–70.

[3] a. Durak H, Genel S. Catalytic hydrothermal liquefaction of lactucascariola with a heterogeneous catalyst: The investigation of temperature, reaction time and synergistic effect of catalysts[J]. *Bioresour Technol*, 2020, **309**: 123375.

b. Bai Zhe(白 哲), Dai Fang-fang(代方方), Jia Min-Jie (贾敏杰), *et al*. Suitable oxygen vacancies induce α-MnO_2 catalyst to efficiently eliminate soot(适宜氧空位诱导α-MnO_2高效催化消除碳烟研究)[J]. *J Mol Catal* (*China*)(分子催化), 2021, **35**(6): 529–537.

3c. Zhang Fei(张 飞), Zhu Xin-bo(竺新波), Liu Jin(刘进), *et al*. Effect of preparation method on the catalytic performance of $CuCo_2O_4$ spinel oxides for diesel soot oxidation(制备方法对铜钴尖晶石氧化物催化碳烟燃烧性能的影响)[J]. *J Mol Catal*(*China*) (分子催化), 2021, **35**(6): 549–560 .

[4] Khan H M, Iqbal T, Ali C H, *et al*. Sustainable biodiesel production from waste cooking oil utilizing waste ostrich (Struthio camelus) bones derived heterogeneous catalyst [J]. *Fuel*, 2020, **277**: 118091.

[5] Cen S, Lv X, Jiang Y, *et al*. Synthesis and structure of iron-copper/hollow magnetic/metal-organic framework/coordination sites in a heterogeneous catalyst for a Fentonbased reaction[J]. *Catal Sci Technol*, 2020, **10**(19): 6687–6693.

[6] Kumar Ashish, Kumar Ajay, Krishnan V. Perovskite oxide based materials for energy and environment-oriented photocatalysis[J]. *ACS Catal*, 2020, **10**(17): 10253–10315.

[7] Zhao T, Wang Y, Chen X, *et al*. Vertical growth of porous perovskite nanoarrays on nickel foam for efficient oxygen evolution reaction[J]. *ACS Sustain Chem Eng*, 2020, **8** (12): 4863–4870.

[8] Kim J Y, Lee J W, Jung H S, *et al*. High-efficiency perovskite solar cells[J]. *Chem Rev*, 2020, **120**(15): 7867–7918.

[9] Barcellos D R, Sanders M D, Tong J, *et al*. $BaCe_{0.25}$-$Mn_{0.75}O_{3-\delta}$-a promising perovskite-type oxide for solar thermochemical hydrogen production[J]. *Energy Environ Sci*, 2018, **11**(11): 3256–3265.

[10] Khan A A, Rana M M, Huang G, *et al*. Maximizing piezoelectricity by self-assembled highly porous perovskite-polymer composite films to enable the internet of things[J]. *J Mater Chem A Mater*, 2020, **8**(27): 13619–13629.

[11] May K J, Carlton C E, Stoerzinger K A, *et al*. Influence of oxygen evolution during water oxidation on the surface of perovskite oxide catalysts[J]. *J Phys Chem Lett*, 2012, **3**(22): 3264–3270.

[12] Fang F, Zhao P, Feng N, *et al*. Surface engineering on porous perovskite-type $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ nanotubes for an enhanced performance in diesel soot elimination[J]. *J Hazard Mater*, 2020, **399**: 123014.

[13] Wu T, Gao P. Development of perovskite-type materials for thermoelectric application[J]. *Materials*, 2018, **11**(6): 999.

[14] Liu X, Gong H, Wang T, *et al*. Cobalt-doped perovskite-type oxide $LaMnO_3$ as bifunctional oxygen catalysts for hybrid lithium-oxygen batteries[J]. *Chem-Asian J*, 2018, **13**(5): 528–535.

[15] Yu J, Ran R, Zhong Y, *et al*. Advances in porous perovskites: Synthesis and electrocatalytic performance in fuel cells and metal-air batteries[J]. *Energy Environ Mater*, 2020, **3**(2): 121–145.

[16] Zhao B, Yan B, Yao S, *et al*. $LaFe_{0.9}Ni_{0.1}O_3$ perovskite catalyst with enhanced activity and coke-resistance for dry reforming of ethane[J]. *J Catal*, 2018, **358**: 168–178.

[17] Sun C, Alonso J A, Bian J. Recent advances in perovskite-type oxides for energy conversion and storage applications [J]. *Adv Energy Mater*, 2021, **11**(2): 2000459.

[18] Yang J, Zhu W, Zhang S, *et al*. Role of flue gas

components in HgO oxidation over $La_{0.8}Ce_{0.2}MnO_3$ perovskite catalyst in coal combustion flue gas[J]. *Chem Eng J*, 2019, **360**: 1656–1666.

[19] Wang W, Tadé M O, Shao Z. Research progress of perovskite materials in photocatalysis-and photovoltaics-related energy conversion and environmental treatment [J]. *Chem Soc Rev*, 2015, **44**(15): 5371–5408.

[20] Han N, Wang S, Yao Z, *et al*. Superior three-dimensional perovskite catalyst for catalytic oxidation[J]. *EcoMat*, 2020, **2**(3): e12044.

[21] Li N, Guo J, Ding Y, *et al*. Direct regulation of double cation defects at the A_1A_2 site for a high-performance oxygen evolution reaction perovskite catalyst[J]. *ACS Appl Mater Interfaces*, 2020, **13**(1): 332–340.

[22] Sun Y, Li R, Chen X, *et al*. A-Site management prompts the dynamic reconstructed active phase of perovskite oxide OER catalysts[J]. *Adv Energy Mater*, 2021, **11**(12): 2003755.

[23] Jung J I, Park S, Kim M G, *et al*. Tunable internal and surface structures of the bifunctional oxygen perovskite catalysts[J]. *Adv Energy Mater*, 2015, **5**(24): 1501560.

[24] Lee G, Kim I, Yang I, *et al*. Effects of the preparation method on the crystallinity and catalytic activity of $LaAlO_3$ perovskites for oxidative coupling of methane[J]. *Appl Surf Sci*, 2018, **429**: 55–61.

[25] Ruocco C, De Caprariis B, Palma V, *et al*. Methane dry reforming on Ru perovskites, $AZrRuO_3$: Influence of preparation method and substitution of A cation with alkaline earth metals[J]. *J CO_2 Util*, 2019, **30**: 222–231.

[26] Liu T, Xu Y. Synthesis of nanocrystalline $LaFeO_3$ powders via glucose sol-gel route[J]. *Mater Chem Phys*, 2011, **129**(3): 1047–1050.

[27] Catauro M, Tranquillo E, Dal Poggetto G, *et al*. Influence of the heat treatment on the particles size and on the crystalline phase of TiO_2 synthesized by the sol-gel method[J]. *Materials*, 2018, **11**(12): 2364.

[28] Zong Yan-yao(晏耀宗), Guo Jin-wei(郭谨玮), Chen Ya-zhong(陈亚中), *et al*. $La_{(1-x)}Ca_xMnO_{(3+\delta)}$ Perovskite catalysts preparation and their catalytic performance for methane combustion($La_{(1-x)}Ca_xMnO_{(3+\delta)}$钙钛矿催化剂制备及其甲烷催化燃烧性能研究)[J]. *J Mol Catal (China)*(分子催化), 2015, **29**(1): 82–89.

[29] Ao M, Pham G H, Sage V, *et al*. Structure and activity of strontium substituted $LaCoO_3$ perovskite catalysts for syngas conversion[J]. *J Mol Catal A Chem*, 2016, **416**: 96–104.

[30] Baino F, Fiume E, Miola M, *et al*. Bioactive sol-gel glasses: Processing, properties, and applications[J]. *Int J Appl Ceram Technol*, 2018, **15**(4): 841–860.

[31] Hosseini S A, Mehri B, Niaei A, *et al*. Selective catalytic reduction of NO_x by CO over $LaMnO_3$ nano perovskites prepared by microwave and ultrasound assisted sol-gel method[J]. *J Solgel Sci Technol*, 2018, **85**(3): 647–656.

[32] Yousefi M ,Ranjbar M. Ultrasound and microwave-assisted Co-precipitation synthesis of $La_{0.75}Sr_{0.25}MnO_3$ perovskite nanoparticles from a new Lanthanum(III) coordination polymer precursor[J]. *J Inorg Org Polym Mater*, 2017, **27**(3): 633–640.

[33] Huang Fei, Sun Xiu-cheng, Zheng Yong, *et al*. Facile coprecipitation synthesis of $La_{0.6}Sr_{0.4}MnO_3$ perovskites with high surface area[J]. *Mater Lett*, 2018, **210**: 287–290.

[34] Yao S, Qu F, Wang G, *et al*. Facile hydrothermal synthesis of WO_3 nanorods for photocatalysts and supercapacitors[J]. *J Alloys Compd*, 2017, **724**: 695–702.

[35] Wang B, Zhang C, Zheng W, *et al*. Large-scale synthesis of highly luminescent perovskite nanocrystals by template-assisted solid-state reaction at 800 ℃ [J]. *Chem Mater*, 2019, **32**(1): 308–314.

[36] Yang Wei(杨威). The controlled synthesis of highly active nano-LaFe perovskite and its catalytic mechanism for the removal of small molecule pollution gases(高活性纳米LaFe系钙钛矿的控制合成及其催化脱除小分子污染气体的机制研究)[D]. Beijing(北京): Beijing University of Chemical Technology(北京化工大学), 2013.

[37] Shui Z, Zhao W, Xiao H, *et al*. Controllable porous perovskite with three-dimensional ordered structure as an efficient oxygen reduction reaction electrocatalyst for flexible aluminum-air battery[J]. *J Power Sources*, 2022, **523**: 231028.

[38] Tang R, Sun H, Zhang Z, *et al*. Incorporating plasmonic Au-nanoparticles into three-dimensionally ordered macroporous perovskite frameworks for efficient photocatalytic CO_2 reduction[J]. *Chem Eng J*, 2022, **429**: 132137.

[39] Zhang Peng, Mei Xue-lei, Zhao Xiao-chan, *et al*. Boosting catalytic purification of soot particles over double perovskite-type $La_{2-x}K_xNiCoO_6$ catalysts with an ordered macroporous structure[J]. *Environ Sci Technol*, 2021, **55**(16): 11245–11254.

[40] Wu X, Wang C, Wei Y, *et al*. Multifunctional photocatalysts of Pt-decorated 3DOM perovskite-type $SrTiO_3$ with

enhanced CO_2 adsorption and photoelectron enrichment for selective CO_2 reduction with H_2O to CH_4 [J]. *J Catal*, 2019, **377**: 309–321.

[41] Peng C, Yu D, Zhang C, *et al*. Alkali/alkaline-earth metal-modified MnO_x supported on three-dimensionally ordered macroporous-mesoporous $Ti_xSi_{1-x}O_2$ catalysts: Preparation and catalytic performance for soot combustion [J]. *J Environ Sci*, 2023, **125**: 82–94.

[42] Xu J, Liu J, Zhao Z, *et al*. Three-dimensionally ordered macroporous $LaCo_xFe_{1-x}O_3$ perovskite-type complex oxide catalysts for diesel soot combustion[J]. *Catal Today*, 2010, **153**(3/4): 136–142.

[43] Zheng J, Liu J, Zhao Z, *et al*. The synthesis and catalytic performances of three-dimensionally ordered macroporous perovskite-type $LaMn_{1-x}Fe_xO_3$ complex oxide catalysts with different pore diameters for diesel soot combustion [J]. *Catal Today*, 2012, **191**(1): 146–153.

[44] Feng N, Chen C, Meng J, *et al*. Facile synthesis of three-dimensionally ordered macroporous silicon-doped $La_{0.8}K_{0.2}CoO_3$ perovskite catalysts for soot combustion [J]. *Catal Sci Technol*, 2016, **6**(21): 7718–7728.

[45] Wang Y, Arandiyan H, Scott J, *et al*. High performance Au-Pd supported on 3D hybrid strontium-substituted lanthanum manganite perovskite catalyst for methane combustion[J]. *ACS Catal*, 2016, **6**(10): 6935–6947.

[46] Yadav P K, Das T. Production of syngas from carbon dioxide reforming of methane by using $LaNi_xFe_{1-x}O_3$ perovskite type catalysts[J]. *Int J Hydrogen Energy*, 2019, **44**(3): 1659–1670.

[47] Liu D, Zhou W, Wu J. Texture and structure variation of perovskite $LaFeO_3$/ZSM-5 during high-temperature desulfurization[J]. *Surf Rev Lett*, 2020, **27**(5): 1950151.

[48] Padilla O, Munera J, Gallego J, *et al*. Approach to the characterization of monolithic catalysts based on La perovskite-like oxides and their application for VOC oxidation under simulated indoor environment conditions [J]. *Catalysts*, 2022, **12**(2): 168.

[49] Zhang Z, Ou Z, Qin C, *et al*. Roles of alkali/alkaline earth metals in steam reforming of biomass tar for hydrogen production over perovskite supported Ni catalysts[J]. *Fuel*, 2019, **257**: 116032.

[50] Hoyos L . Ni mesostructured catalysts obtained from rice husk ashes by microwave-assisted synthesis for CO_2 methanation[J]. *J CO_2 Util*, 2020, **42**: 101328.

[51] Xfa B ,Lla B , Xy A , *et al*. High-performance Co_xM_{3-x}-AlO_y (M Ni, Mn) catalysts derived from microwave-assisted synthesis of hydrotalcite precursors for methane catalytic combustion[J]. *Catal Today*, 2020, **347**: 23–30.

[52] He Z, He Y, Chang F, *et al*. Efficient pH-universal degradation of antibiotic tetracycline via Co_2P decorated Neosinocalamusaffinis biochar[J]. *Chemosphere*, 2022, **286**: 131759.

[53] Dz A ,Yy A , Zg A , *et al*. Promoting NO_x reduction via in situ activation of perovskite supported Pd catalysts under alternating lean-burn/fuel-rich operating atmospheres[J]. *Chin J Catal*, 2021, **42**(5): 795–807.

[54] Das S , Bhattar S , Liu L , *et al*. Effect of partial Fe substitution in $La_{0.9}Sr_{0.1}NiO_3$ perovskite-derived catalysts on the reaction mechanism of methane dry reforming[J]. *ACS Catal*, 2020, **10**(21): 12466.

[55] Sellam D, Ikkour K, Dekkar S, *et al*. CO_2 reforming of methane over $LaNiO_3$ perovskite supported catalysts: Influence of silica support[J]. *Bull Chem React Eng*, 2019, **14**(3): 568.

[56] Pan K L , Pan G T , Chong S , *et al*. Removal of VOCs from gas streams with double perovskite-type catalysts[J]. *J Environ Sci*, 2018, **69**: 205–216.

[57] Teixeira G F, Silva Junior E, Vilela R, *et al*. Perovskite structure associated with precious metals: Influence on heterogenous catalytic process[J]. *Catalysts*, 2019, **9**(9): 721.

[58] Wei Zhao, Qi Zhang, Hugang Wang, *et al*. Enhanced catalytic performance of $Ag_2O/BaTiO_3$ heterostructure microspheres by the piezo/pyro-phototronic synergistic effect[J]. *Nano Energy*, 2020, **73**: 104783.

[59] Song Zhao-yu, Shi Xiang-peng, Ning Hong-yan, *et al*. Loading clusters composed of nanoparticles on ZrO_2 support via a perovskite-type oxide of $La_{0.95}Ce_{0.05}$-$Co_{0.7}Cu_{0.3}O_3$ for ethanol synthesis from syngas and its structure variation with reaction time[J]. *Appl Surf Sci*, 2017, **405**: 1–12.

[60] Cao D , Ding H , Luo C , *et al*. Development of a cordierite monolith reactor coated with CeO_2-supported BaSrCo-based perovskite for chemical looping steam methane reforming[J]. *Fuel Process Technol*, 2021, **220**: 106889.

[61] Khaledian H R, Zolfaghari P, Kheyrollahi P, *et al*. Surface modification of $LaMnO_3$ perovskite supported on CeO_2 using argon plasma for high-performance reduction of NO[J]. *J Environ Chem Eng*, 2020, **9**(1): 104581.

[62] Hammouda S B, Zhao F, Safaei Z, *et al*. Reactivity of novel Ceria-Perovskite composites CeO_2-$LaMO_3$ (M=Cu, Fe) in the catalytic wet peroxidative oxidation of the new emergent pollutant ‘Bisphenol F’ : Characterization,

kinetic and mechanism studies[J]. *Appl Catal B*, 2017, **218**: 119–136.

[63] Han S J, Song J H, Bang Y, *et al*. Hydrogen production by steam reforming of ethanol over mesoporous Cu-Ni-Al$_2$O$_3$-ZrO$_2$ xerogel catalysts[J]. *Int J Hydrogen Energy*, 2016, **41**(4): 2554–2563.

[64] Li X, Gao H. Role of ceria in the improvement of NO removal of lanthanum-based perovskite-type catalysts[J]. *RSC Adv*, 2018, **8**(21): 11778–11784.

[65] Wang Y, Yu L, Wang R, *et al*. Microwave catalytic activities of supported perovskite catalysts MO$_x$/LaCo$_{0.5}$Cu$_{0.5}$O$_3$@ CM (M= Mg, Al) for salicylic acid degradation[J]. *J Coll Inter Sci*, 2020, **564**: 392–405.

[66] Cheng X, Kim B J, Fabbri E, *et al*. Co/Fe oxyhydroxides supported on perovskite oxides as oxygen evolution reaction catalyst systems[J]. *ACS Appl Mater Inter*, 2019, **11**(38): 34787–34795.

[67] Zhang Z, Qin C, Ou Z, *et al*. Resistance of Ni/perovskite catalysts to H$_2$S in toluene steam reforming for H$_2$ production[J]. *Int J Hydrogen Energy*, 2020, **45**(51): 26800–26811.

[68] Kopacč D, Likozar B, Hušš M. How size matters: Electronic, cooperative, and geometric effect in perovskite-supported copper catalysts for CO$_2$ reduction[J]. *ACS Catal*, 2020, **10**(7): 4092–4102.

[69] Cao D, Luo C, Wu F, *et al*. Screening loaded perovskite oxygen carriers for chemical looping steam methane reforming[J]. *J Environ Chem Eng*, 2022, **10**(2): 107315.

[70] Hua B, Li M, Zhang Y Q, *et al*. All-in-one perovskite catalyst: smart controls of architecture and composition toward enhanced oxygen/hydrogen evolution reactions[J]. *Adv Energy Mater*, 2017, **7**(20): 1700666.

[71] Moradi G R, Rahmanzadeh M, Khosravian F. The effects of partial substitution of Ni by Zn in LaNiO$_3$ perovskite catalyst for methane dry reforming[J]. *J CO$_2$ Util*, 2014, **6**: 7–11.

[72] Kong J, Yang T, Rui Z, *et al*. Perovskite-based photocatalysts for organic contaminants removal: Current status and future perspectives[J]. *Catal Today*, 2019, **327**: 47–63.

[73] Wang H, Wang X, Meng B, *et al*. Perovskite-based mixed protonic-electronic conducting membranes for hydrogen separation: Recent status and advances[J]. *J Ind Eng Chem*, 2018, **60**: 297–306.

[74] Keav S, Matam S K, Ferri D, *et al*. Structured perovskite-based catalysts and their application as three-way catalytic converters-a review[J]. *Catalysts*, 2014, **4**(3): 226–255.

[75] Xiao H, Liu P, Wang W, *et al*. Ruddlesden-popper perovskite oxides for photocatalysis-based water splitting and wastewater treatment[J]. *Energ Fuel*, 2020, **34**(8): 9208–9221.

[76] Wang Y, Wang R, Lin N, *et al*. Highly efficient microwave-assisted Fenton degradation bisphenol A using iron oxide modified double perovskite intercalated montmorillonite composite nanomaterial as catalyst[J]. *J Coll Inter Sci*, 2021, **594**: 446–459.

[77] Wang H, Zhang L, Hu C, *et al*. Enhanced degradation of organic pollutants over Cu-doped LaAlO$_3$ perovskite through heterogeneous Fenton-like reactions[J]. *Chem Eng J*, 2018, **332**: 572–581.

[78] Hammouda S B, Salazar C, Zhao F, *et al*. Efficient heterogeneous electro-Fenton incineration of a contaminant of emergent concern-cotinine-in aqueous medium using the magnetic double perovskite oxide Sr$_2$FeCuO$_6$ as a highly stable catalayst: Degradation kinetics and oxidation products[J]. *Appl Catal B*, 2019, **240**: 201–214.

[79] Phan T T N, Nikoloski A N, Bahri P A, *et al*. Facile fabrication of perovskite-incorporated hierarchically mesoporous/macroporous silica for efficient photoassisted-Fenton degradation of dye[J]. *Appl Surf Sci*, 2019, **491**: 488–496.

[80] Mao J, Quan X, Wang J, *et al*. Enhanced heterogeneous Fenton-like activity by Cu-doped BiFeO$_3$ perovskite for degradation of organic pollutants[J]. *Front Environ Sci Eng*, 2018, **12**(6): 1–10.

[81] Li Chao(李 超), Chen Xiao-fei(陈晓飞), Yue Xin(岳 欣), *et al*. Preparation of perovskite LaFe$_x$Cu$_{(1-x)}$O$_3$ heterogeneous fenton catalyst and its degradation of methylene blue(钙钛矿型LaFe$_x$Cu$_{(1-x)}$O$_3$固相芬顿催化剂制备及其降解亚甲基蓝性能研究)[J]. *J Mol Catal*(*China*)(分子催化), 2021, **35**(6): 503–517.

[82] Wang Q, Zhou S, Xiao S, *et al*. Novel perovskite-based composites, La$_{1-x}$Nd$_x$FeO$_3$@ activated carbon, as efficient catalysts for the degradation of organic pollutants by heterogeneous electro-Fenton reactions[J]. *RSC Adv*, 2018, **8**(27): 14775–14786.

[83] Li J, Miao J, Duan X, *et al*. Fine-tuning surface properties of perovskites via nanocompositing with inert oxide toward developing superior catalysts for advanced oxidation[J]. *Adv Funct Mater*, 2018, **28**(44): 1804654.

[84] Li L, Feng X, Nie Y, *et al*. Insight into the effect of oxygen

vacancy concentration on the catalytic performance of MnO_2 [J]. *ACS Catal*, 2015, **5**(8): 4825–4832.

[85] Sun W, Wei H, Yang An L, *et al*. Oxygen vacancy mediated $La_{1-x}Ce_xFeO_{3-\delta}$ perovskite oxides as efficient catalysts for CWAO of acrylic acid by A-site Ce doping [J]. *Appl Catal B*, 2019, **245**: 20–28.

[86] Wu Z, Hwang I, Cha G, *et al*. Optimized Pt single atom harvesting on TiO_2 nanotubes-towards a most efficient photocatalyst[J]. *Small*, 2022, **18**(2): 2104892.

[87] Basumatary B, Basumatary R, Ramchiary A, *et al*. Evaluation of Ag@ TiO_2/WO_3 heterojunction photocatalyst for enhanced photocatalytic activity towards methylene blue degradation[J]. *Chemosphere*, 2022, **286**: 131848.

[88] Wang C, Huang H, Weng B, *et al*. Planar heterojunction boosts solar-driven photocatalytic performance and stability of halide perovskite solar photocatalyst cell[J]. *Appl Catal B*, 2022, **301**: 120760.

[89] Yahya N, Aziz F, Jamaludin N A, *et al*. A review of integrated photocatalyst adsorbents for wastewater treatment [J]. *J Environ Chem Eng*, 2018, **6**(6): 7411–7425.

[90] Venkatesh G, Palanisamy G, Srinivasan M, *et al*. Facile fabrication of perovskite type $CaSnO_3$ coupled g-C_3N_4 heterostructure photocatalyst for efficient organic pollutant degradation[J]. *Diam Relat Mater*, 2022, **2022**: 108873.

[91] Djellabi R, Ordonez M F, Conte F, *et al*. A review of advances in multifunctional $XTiO_3$ perovskite-type oxides as piezo-photocatalysts for environmental remediation and energy production[J]. *J Hazard Mater*, 2022, **421**: 126792.

[92] Jiang Z W, Zhao T T, Zhen S J, *et al*. A 2D MOF-based artificial light-harvesting system with chloroplast bionic structure for photochemical catalysis[J]. *J Mater Chem A Mater*, 2021, **9**(14): 9301–9306.

[93] Zhang D, Yu W, Li S, *et al*. Artificial light-harvesting metallacycle system with sequential energy transfer for photochemical catalysis[J]. *J Am Chem Soc*, 2021, **143**(3): 1313–1317.

[94] Huang H, Yuan H, Janssen K P F, *et al*. Efficient and selective photocatalytic oxidation of benzylic alcohols with hybrid organic-inorganic perovskite materials[J]. *ACS Energy Lett*, 2018, **3**(4): 755–759.

[95] Ren K, Yue S, Li C, *et al*. Metal halide perovskites for photocatalysis applications[J]. *J Mater Chem A Mater*, 2022, **10**(2): 407–429.

[96] Zhu Y, Liu Y, Ai Q, *et al*. In situ synthesis of lead-free halide perovskite COF nanocomposites as photocatalysts for photoinduced polymerization in both organic and aqueous phases[J]. *ACS Mater Lett*, 2022, **4**: 464–471.

[97] Wu D, Tao Y, Huang Y, *et al*. High visible-light photocatalytic performance of stable lead-free $Cs_2AgBiBr_6$ double perovskite nanocrystals[J]. *J Catal*, 2021, **397**: 27–35.

[98] Lin N, Gong Y, Wang R, *et al*. Critical review of perovskite-based materials in advanced oxidation system for wastewater treatment: Design, applications and mechanisms[J]. *J Hazard Mater*, 2022, **424**: 127637.

[99] Han P, Li X, Jin C, *et al*. Cation deviated stoichiometry $Ca_{1.1}ZrO_3$ perovskite as an efficient ozonation catalyst for m-cresol wastewater degradation[J]. *Chem Eng J*, 2022, **429**: 132218.

[100] Boczkaj G, Fernandes A. Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review[J]. *Chem Eng J*, 2017, **320**: 608–633.

[101] Sannino D, Vaiano V, Isupova L A, *et al*. Heterogeneous photo-Fenton oxidation of organic pollutants on structured catalysts[J]. *J Adv Oxid Technol*, 2012, **15**(2): 294–300.

[102] Palas B, Ersöz G, Atalay S. Catalytic wet air oxidation of reactive black 5 in the presence of $LaNiO_3$ perovskite catalyst as a green process for azo dye removal[J]. *Chemosphere*, 2018, **209**: 823–830.

[103] Bai J, Liu D, Yang J, *et al*. Nanocatalysts for electrocatalytic oxidation of ethanol[J]. *ChemSusChem*, 2019, **12**(10): 2117–2132.

[104] Mostaghimi A H B, Al-Attas T A, Kibria M G, *et al*. A review on electrocatalytic oxidation of methane to oxygenates[J]. *J Mater Chem A Mater*, 2020, **8**(31): 15575–15590.

[105] Li B, Irvine J T S, Ni J, *et al*. High-performance and durable alcohol-fueled symmetrical solid oxide fuel cell based on ferrite perovskite electrode[J]. *Appl Energy*, 2022, **306**: 118117.

[106] You P, Liu Z, Tai Q, *et al*. Efficient semitransparent perovskite solar cells with graphene electrodes[J]. *Adv Mater*, 2015, **27**(24): 3632–3638.

[107] Shin S S, Yeom E J, Yang W S, *et al*. Colloidally prepared La-doped $BaSnO_3$ electrodes for efficient, photostable perovskite solar cells[J]. *Science*, 2017, **356**(6334): 167–171.

[108] Zhou J , Ren Z , Li S , *et al*. Semi-transparent Cl-doped perovskite solar cells with graphene electrodes for tandem application[J]. *Mater Lett*, 2018, **220**(jun.1): 82–85.

[109] Zhao K, Zou J , Huang F, *et al*. Asymmetric Au

electrodes-induced self-powered organic-inorganic perovskite photodetectors[J]. *IEEE Trans Electron Devices*, 2021, **2021**(99): 1–6.

[110] Zhang L, Li Y, Zhang B, *et al.* (La,Sr) (Ti,Fe)$O_{3-\delta}$ perovskite with in-situ constructed $FeNi_3$ nanoparticles as fuel electrode for reversible solid oxide cell[J]. *Int J Energy Res*, 2021, **45**(15): 21264–21273.

[111] Li B, Irvine J, Ni J, *et al.* High-performance and durable alcohol-fueled symmetrical solid oxide fuel cell based on ferrite perovskite electrode[J]. *Appl Energy*, 2022, **2022**: 306.

[112] Chen Li-jun, Zhang Yu-qing, Ma Cheng-bo. Perovskites $Sr_xLa_{1-x}Mn_yCo_{1-y}O_{3-\delta}$ coated on Ti as stable non-noble anode for efficient electrocatalytic oxidation of organic wastewater containing ammonia nitrogen[J]. *Chem Eng J*, 2020, **393**: 124514.

[113] Mishra A, Prasad R. Preparation and application of perovskite catalysts for diesel soot emissions control: An overview[J]. *Catal Rev*, 2014, **56**(1): 57–81.

[114] Royer S, Duprez D. Catalytic oxidation of carbon monoxide over transition metal oxides[J]. *ChemCatChem*, 2011, **3**(1): 24–65.

[115] Zou X P, Wang L N, Li X N, *et al.* Noble-metal-free single-atom catalysts $CuAl_4O_{7-9}$ for CO oxidation by O_2 [J]. *Angew Chem Int Ed*, 2018, **130**(34): 11155–11159.

[116] Dey S, Dhal G C. Deactivation and regeneration of hopcalite catalyst for carbon monoxide oxidation: A review[J]. *Mater Today Chem*, 2019, **14**: 100180.

[117] Einaga H, Nasu Y, Oda M, *et al.* Catalytic performances of perovskite oxides for CO oxidation under microwave irradiation[J]. *Chem Eng J*, 2016, **283**: 97–104.

[118] Tang S, Xu L, Peng B, *et al.* Ga-doped Pd/CeO_2 model catalysts for CO oxidation reactivity: A density functional theory study[J]. *Appl Surf Sci*, 2022, **575**: 151655.

[119] Wang F, Li Z, Wang H, *et al.* Nano-sized Ag rather than single-atom Ag determines CO oxidation activity and stability[J]. *Nano Res*, 2022, **15**(1): 452–456.

[120] Gonzúlez-Varela D, Araiza D G, Díaz G, *et al.* $LaNiO_3$ perovskite synthesis through the EDTA-citrate complexing method and its application to CO oxidation[J]. *Catalysts*, 2022, **12**(1): 57.

[121] Royer S, Duprez D, Can F, *et al.* Perovskites as substitutes of noble metals for heterogeneous catalysis: Dream or reality[J]. *Chem Rev*, 2014, **114**(20): 10292–10368.

[122] Bian Z, Wang Z, Jiang B, *et al.* A review on perovskite catalysts for reforming of methane to hydrogen production [J]. *Renew Sust Energy Rev*, 2020, **134**: 110291.

[123] Tanaka H, Misono M. Advances in designing perovskite catalysts[J]. *Curr Opin Solid State Mater Sci*, 2001, **5**(5): 381–387.

[124] Yoo J S, Rong X, Liu Y, *et al.* Role of lattice oxygen participation in understanding trends in the oxygen evolution reaction on perovskites[J]. *ACS Catal*, 2018, **8**(5): 4628–4636.

[125] Wang Xi-yang, Huang Ke-ke, Long Yuan, *et al.* Activation of surface oxygen sites in a cobalt-based perovskite model catalyst for CO oxidation[J]. *J Phys Chem Lett*, 2018, **9**(15): 4146–4154.

[126] Losch P, Huang W, Vozniuk O, *et al.* Modular Pd/zeolite composites demonstrating the key role of support hydrophobic/hydrophilic character in methane catalytic combustion[J]. *ACS Catal*, 2019, **9**(6): 4742–4753.

[127] Akbari E, Alavi S M, Rezaei M, *et al.* Barium promoted manganese oxide catalysts in low-temperature methane catalytic combustion[J]. *Int J Hydrogen Energy*, 2021, **46**(7): 5181–5196.

[128] Yan Y, Wu G, Huang W, *et al.* Numerical comparison study of methane catalytic combustion characteristic between newly proposed opposed counter-flow micro-combustor and the conventional ones[J]. *Energy*, 2019, **170**: 403–410.

[129] Huang W, Zha W, Zhao D, *et al.* The effect of active oxygen species in nano-$ZnCr_2O_4$ spinel oxides for methane catalytic combustion[J]. *Solid State Sci*, 2019, **87**: 49–52.

[130] Yang J, Guo Y. Nanostructured perovskite oxides as promising substitutes of noble metals catalysts for catalytic combustion of methane[J]. *Chin Chem Lett*, 2018, **29**(2): 252–260.

[131] Poffe E, Kaper H, Ehrhardt B, *et al.* Understanding oxygen release from nanoporous perovskite oxides and its effect on the catalytic oxidation of CH_4 and CO[J]. *ACS Appl Mater Inter*, 2021, **13**(21): 25483–25492.

[132] Yang X, Gao Q, Zhao Z, *et al.* Surface tuning of noble metal doped perovskite oxide by synergistic effect of thermal treatment and acid etching: A new path to high-performance catalysts for methane combustion[J]. *Appl Catal B*, 2018, **239**: 373–382.

[133] Chen Hua-wei, Li Jin-peng, Cui Wei, *et al.* Precise fabrication of surface-reconstructed $LaMnO_3$ perovskite with enhanced catalytic performance in CH_4 oxidation[J]. *Appl Surf Sci*, 2020, **505**: 144112.

[134] Sun Q, Wang Z, Wang D, *et al*. A review on the catalytic decomposition of NO to N_2 and O_2: Catalysts and processes[J]. *Catal Sci Technol*, 2018, **8**(18): 4563–4575.

[135] Shen Q, Dong S, Li S, *et al*. A review on the catalytic decomposition of NO by perovskite-type oxides[J]. *Catalysts*, 2021, **11**(5): 622.

[136] Jabło ń ska M, Palkovits R. Perovskite-based catalysts for the control of nitrogen oxide emissions from diesel engines[J]. *Catal Sci Technol*, 2019, **9**(9): 2057–2077.

[137] Lima T M, de Macedo V, Silva D S A, *et al*. Molybdenum-promoted cobalt supported on SBA-15: Steam and sulfur dioxide stable catalyst for CO oxidation[J]. *Appl Catal B: Environ*, 2020, **277**: 119248.

[138] Labhasetwar N, Saravanan G, Megarajan S K, *et al*. Perovskite-type catalytic materials for environmental applications[J]. *Sci Technol Adv Mater*, 2015, **16**(3): 036002.

[139] Lim E, Kim Y J, Kim J H, *et al*. NO oxidation activity of Ag-doped perovskite catalysts[J]. *J Catal*, 2014, **319**: 182–193.

[140] Zhong S, Sun Y, Xin H, *et al*. NO oxidation over Ni-Co perovskite catalysts[J]. *Chem Eng J*, 2015, **275**: 351–356.

[141] Zhang Y, Cao G, Yang X. Advances in De-NO_x methods and catalysts for direct catalytic decomposition of NO: A review[J]. *Energ Fuel*, 2021, **35**(8): 6443–6464.

[142] Wang Z, Li Z, Cui Y, *et al*. Highly efficient NO decomposition via dual-functional catalytic perovskite hollow fiber membrane reactor coupled with partial oxidation of methane at medium-low temperature[J]. *Environ Sci Technol*, 2019, **53**(16): 9937–9946.

[143] Peng Y, Wang Y, Ke L, *et al*. A review on catalytic pyrolysis of plastic wastes to high-value products[J]. *Energy Convers Manag*, 2022, **254**: 115243.

[144] Wang Y, Li Y, Wang G, *et al*. Effect of Fe components in red mud on catalytic pyrolysis of low rank coal[J]. *J EenergyIist*, 2022, **100**: 1–9.

[145] Lee T, Jung S, Baek K, *et al*. Functional use of CO_2 to mitigate the formation of bisphenol A in catalytic pyrolysis of polycarbonate[J]. *J Hazard Mater Lett*, 2022, **423**: 126992.

[146] Wang P, Shen Y. Catalytic pyrolysis of cellulose and chitin with calcined dolomite-Pyrolysis kinetics and products analysis[J]. *Fuel*, 2022, **312**: 122875.

[147] Li F, Srivatsa S C, Bhattacharya S. A review on catalytic pyrolysis of microalgae to high-quality bio-oil with low oxygeneous and nitrogenous compounds[J]. *Renew Sustain Energy Rev*, 2019, **108**: 481–497.

[148] Wang P, Yan J, Wang S, *et al*. Synergistic effects of lanthanum ferrite perovskite and hydrogen to promote ammonia production during microalgae catalytic pyrolysis process[J]. *Bioresour Technol*, 2021, **340**: 125641.

[149] Wang H, Han H, Sun E, *et al*. Production of aryl oxygen-containing compounds by catalytic pyrolysis of bagasse lignin over $LaTi_{0.2}Fe_{0.8}O_3$ prepared by different methods[J]. *J Rare Earth*, 2020, **38**(1): 76–83.

[150] Gupta S, Lanjewar R, Mondal P. Enhancement of hydrocarbons and phenols in catalytic pyrolysis bio-oil by employing aluminum hydroxide nanoparticle based spent adsorbent derived catalysts[J]. *Chemosphere*, 2022, **287**: 132220.

[151] Hakimian H, Pyo S, Kim Y M, *et al*. Increased aromatics production by co-feeding waste oil sludge to the catalytic pyrolysis of cellulose[J]. *Energy*, 2022, **239**: 122331.

[152] Li Z, He W, Xiong T, *et al*. Preparation of a $Ni/LaAlO_3$ catalyst and its application in catalytic pyrolysis of soybean straw for syngas production[J]. *Bio Resources*, 2020, **15**(3): 5871–5885.

Application and Progress of the Perovskite Materials in Environmental Catalysis

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Abstract: The increasingly serious environmental problems and limited resources have prompted people to actively explore the improvement of pollutant treatment efficiency. Multiphase catalysts play an important role in the efficient treatment of environmental pollution. Therefore, the development of new multiphase catalysts with high activity and high stability has become a very attractive and challenging task. Due to its high catalytic activity and stable crystal structure, perovskite materials have become a research hotspot in environmental catalysis. The rise of new perovskite materials has also attracted our attention. The material properties, preparation methods, development status of new perovskite materials and their applications in environmental catalysis were reviewed, and the challenges and future development directions were discussed.

Key words: perovskite; ABO_3; environmental catalysis; progress